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Thermodynamic Properties of Iron and Silicon

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This work reviews and discusses the data on the various thermodynamic properties of iron and silicon available through March 1984. These include heat capacity, enthalpy, enthalpies of transition and melting, vapor pressure, and enthalpy of vaporization. The recommended values for heat capacity, enthalpy, entropy, and Gibbs energy function cover the temperature range from 1 to 3200 K for iron and 1 to 3600 K for silicon. The recommended values for vapor pressure cover the temperature range from 298.15 to 3200 K for iron and from 298.15 to 3600 K for silicon. These values are referred to temperatures based on the International Practical Temperature Scale of 1968. The energy units used are joules per mol (J mol^{-1}). The uncertainties in the recommended values of the heat capacity range from $\pm 1.5\%$ to $\pm 5\%$.

Key words: critical evaluation; data analysis; enthalpy; enthalpy of melting; enthalpy of transition; enthalpy of vaporization; Gibbs energy function; heat capacity; iron; recommended values; silicon; vapor pressure.

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1. Introduction

The principal objective of this work is to critically evaluate and analyze all the available data on the heat capacity, enthalpy, and vapor pressure of iron and silicon 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 Sec. 2 for iron and in Sec. 3 for silicon. The recommended values cover the temperature range from 1 to 3200 K for iron and from 1 to 3600 K for silicon.

The temperature dependence of the following thermo-

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dynamic properties are covered:

(1) Low-temperature ($T < 298.15$ K) heat capacity, C_p°,

(2) High-temperature ($T > 298.15$ K) heat capacity, C_p°,

(3) High-temperature enthalpies, $H^\circ(T) - H^\circ$ (298.15 K), and

(4) Vapor pressure, P.

The details of the data analysis have been discussed elsewhere.[1]

2. Thermodynamic Properties of Iron

2.1. Phase and Structure

Alpha-iron has a bcc structure isotypic with W below 1185 K, fcc (γ-Fe) structure isotypic with Cu between 1185 and 1667 K, and bcc (δ-Fe) structure isotypic with W above 1667 K. These transition temperatures are based on the studies of Sale and Normanton.[2] Its atomic weight is 55.847. It is ferromagnetic at temperatures below 1043 K and paramagnetic above that temperature. Its melting point of 1811 ± 3 K is based on the measurements of Treverton and Margrave,[3] Cezairliyan and McClure,[4] and of Boulanger.[5] These temperatures and thermodynamic properties reported here are based on the International Practical Temperature Scale of 1968 (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. Some of them from which the recommended value is derived are listed below:

Source	γ,mJ mol^{-1} K^{-2}	θ_D,K
Dixon *et al.*[6]	4.780 4.779	463.7 ± 1.1 426.6 ± 1.8
Cheng *et al.*[7]	4.979	445 ± 15
Shinozaki and Arrott[8]	4.81 4.80 4.72	463 468 440
Arrott and Shinozaki[9]	4.80	
Marklund *et al.*[10]	4.72 ± 0.039	
Mazur and Zacharko[11]	4.90	468
Arp *et al.*[12]	4.90 ± 0.5	
Keesom and Kurrelmeyer[13]	5.021	462
Duyckaerts[14]	5.021	464.5
Recommended value	4.942 ± 0.11	465 ± 3

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

$$C_p^\circ = \gamma T + [1943.75/\theta_D^3]T^3.$$

Table 1. Recommended low-temperature heat capacity of iron

$\frac{T}{K}$	$\frac{C_p^o}{J\cdot mol^{-1}\cdot K^{-1}}$	$\frac{T}{K}$	$\frac{C_p^o}{J\cdot mol^{-1}\cdot K^{-1}}$
1	0.004961	130	16.067
2	0.01004	140	17.120
3	0.01535	150	18.080
4	0.02101	160	18.895
5	0.02713	170	19.652
6	0.0335	175	20.011
7	0.0406	180	20.336
8	0.0487	190	20.952
9	0.0583	200	21.503
10	0.0698	210	21.981
15	0.138	220	22.423
20	0.256	225	22.640
25	0.456	230	22.847
30	0.743	240	23.245
40	1.552	250	23.612
50	2.804	260	23.962
60	4.496	270	24.282
70	6.534	273.15	24.380
75	7.538	280	24.580
80	8.518	290	24.864
90	10.338	298.15	25.084
100	12.067		
110	13.555		
120	14.879		
125	15.482		

$C_{(electronic)} = \gamma T;\ \gamma = 4.942 \pm 0.11\ mJ\cdot mol^{-1}\cdot K^{-2}$

	Crystal, Fe(s)	Gas, Fe(g)
H^o(298.15 K)$-H^o$(0 K)	4481 ± 10 $J\cdot mol^{-1}$	6849 ± 0.3
S^o(298.15 K)	27.085 ± 0.08 $J\cdot mol^{-1}\cdot K^{-1}$	180.376 ± 0.002

The recommended values from 5 to 20 K agree well with the following measurements: Keesom and Kurrelmeyer,[13] Duyckaerts,[14] and of Eucken and Werth.[15] The recommended values from 20 to 298.15 K agree well with the measurements of Eucken and Werth,[15] Stepakoff and Kaufman,[16] Kelley,[17] Simon and Swain,[18] and of Reddy and Reddy.[20] Other results deviate from the recommended values as follows:

Source	Deviation, %
Griffiths and Griffiths[19]	up to 7
Schroder and MacInnes[21]	up to 26 (< 140 K), − 6 (> 140 K)
Rodebush and Michalek[22]	8
Gunther[23]	up to − 12
Bendick and Pepperhoff[24]	agree well (> 80 K) − 8 to 30 higher (< 80 K)

The recommended value of $C_p^\circ = 25.084$ J mol^{-1} K^{-1} at 298.15 K is based on the data of Stepakoff and Kaufmann,[16] Griffiths and Griffiths,[19] and the lower end of the high-temperature data discussed in the next section. Integration of the recommended C_p° values yields H°(298.15 K) H°(0 K) = 4481 ± 10 J mol^{-1} and integration of C_p°/T values yields S°(298.15 K) = 27.085 ± 0.08 J mol^{-1} K^{-1}. These values are tabulated in Table 1 and C_p° values are shown in Fig. 1 along with the experimental data.

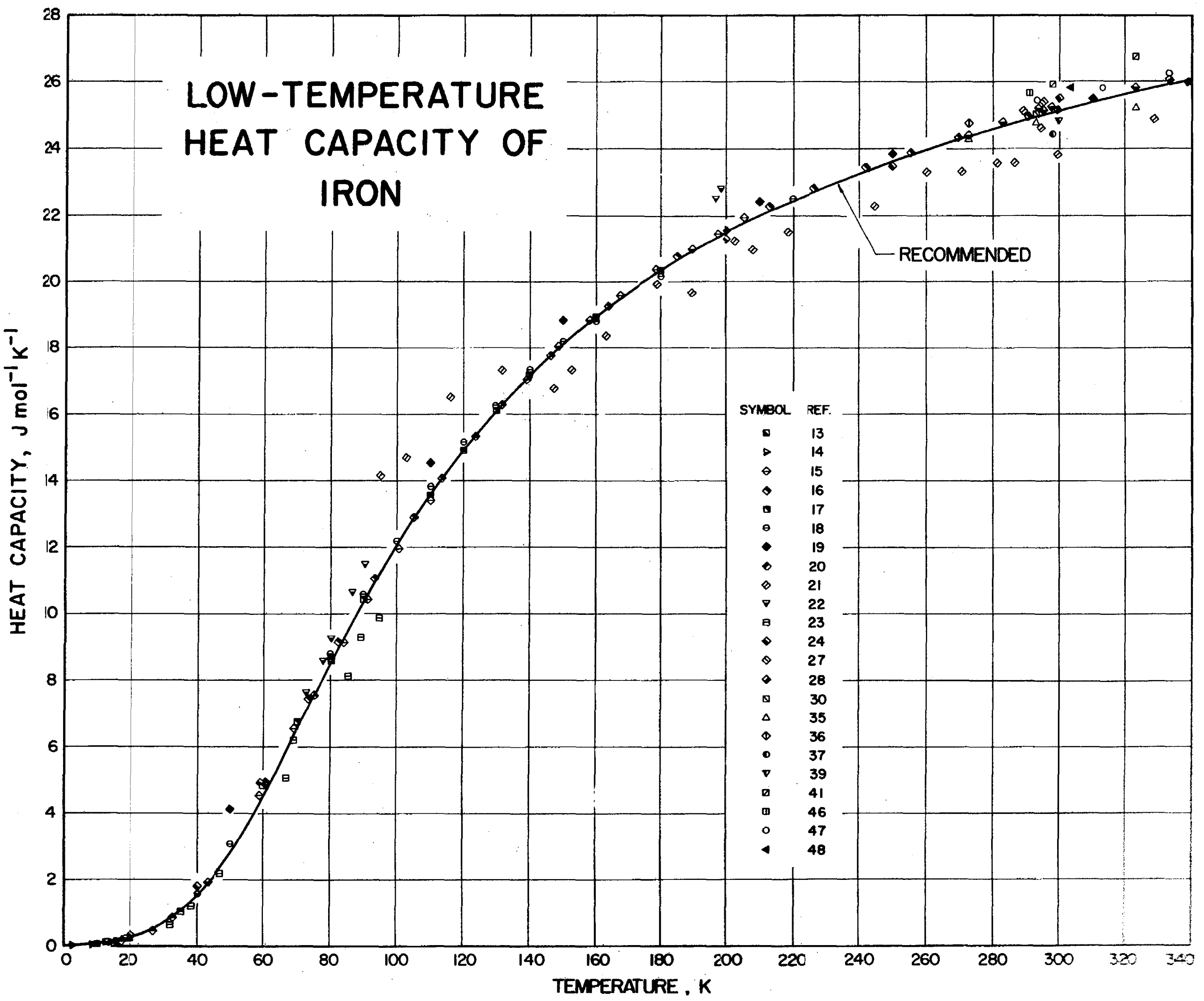

FIG. 1. Low-temperature heat capacity of iron.

2.3. High-Temperature Heat Capacity (Solid)

There have been numerous measurements of the heat capacity of α-iron. These generally agree with one another up to 1000 K. Near the Curie temperature, C_p° varies rapidly with temperature. In this region, from 1000 to 1060 K and in some cases up to 1185 K, comparatively large deviations in C_p° occur which could be, in many cases, reconciled by changing the temperature only slightly.

The recommended C_p° values for α-Fe in general agree well ($\pm 3\%$) except in the region near the Curie temperature region with the following measurements: Griffiths and Griffiths,[19] Bendick and Pepperhoff,[24] Pepperhoff and Ettwig,[25] Rogez and Le Coze,[26] Kollie *et al.*,[28] Tsuchiya *et al.*,[29] Lyusternik,[30] Awbery and Griffiths,[32] Sykes and Evans,[33] Normanton *et al.*,[34] Pallister,[35] Holetzko,[36] Wallace *et al.*,[37] Braun and Kohlhaas,[38] Braun,[39] and of Kraftmakher and Romashina.[44] Comparison of other measurements with the recommended values is as follows:

Source	Deviation, %
Schroder and MacInees[21]	− 5 (300–430 K), 12 (440–1000 K), 14 (> 1085 K)
Larikov *et al.*[27]	± 6
Dench and Kubaschewski[31]	6
Orehotsky and Schroder[40]	± 4
Shanks *et al.*[41]	9 (< 930 K), − 3 (> 1070 K)
Kollie[42]	± 6
McElroy[43]	± 4
Klinkhardt[45]	up to 6 (< 1000 K) ± 7 (> 1070 K)
Lapp[46]	3 to 12 (< 975 K) − 2 to − 10 (> 1060 K)
Esser and Baerlecken[47]	1 to 6 (< 1000 K) ± 6 (> 1070 K)
Kobayasi *et al.*[48]	± 5
Varchenko *et al.*[49]	− 2 to 12

Additionally, measurements of Lederman *et al.*[50] near the Curie temperature yield as much as 15% lower C_p° values.

α-Fe tranforms to γ-Fe at 1185 K and then to δ-Fe at 1667 K. The recommended values of $\Delta H_{\alpha-\gamma}$ and $\Delta H_{\gamma-\delta}$ are based on the following literature values:

Source	$\Delta H_{\alpha-\gamma}$	$\Delta H_{\gamma-\delta}$
Sale and Normanton[2]	923 ± 10	765 ± 22
Bendick and Pepperhoff[24]	820	
Rogez and Le Coze[26]	900 ± 20	850
Dench and Kubaschewski[31]	900	837 ± 30
Wallace *et al.*[37]	911 ± 80	
Braun and Kohlhaas[38]	910	850
McElroy[43]	901	
Anderson and Hultgren[51]	942 ± 80	
Olette and Ferrier[52]		1100 ± 290
Recommended value	900 ± 40	850 ± 80 J mol^{-1}

There appears to be an excellent agreement between several measurements reported for γ-Fe in the literature. The recommended values agree well ($\pm 2\%$) with the following measurements: Sale and Normanton,[2] Cezairliyan and McClure,[4] Dench and Kubaschewski,[31] Normanton *et al.*,[34] Wallace *et al.*,[37] Shanks *et al.*,[41] and Lapp.[46] Other measurements compare with the recommended values as follows:

Source	Deviation, %
Bendick and Pepperhoff[24]	− 5 to − 14
Rogez and Le Coze[26]	− 1 to − 4
Larikov *et al.*[27]	8
Kollie *et al.*[28]	1 to 6
Awbery and Griffiths[32]	− 5
Pallister[35]	− 1 to − 10
Holetzko[36]	± 7
Braun[39]	− 1 to − 4
Orehotsky and Schroder[40]	− 3
Kollie[42]	up to 8
Esser and Baerlecken[47]	10
Kobayasi[48]	± 5
Varchenko *et al.*[49]	+ 20

The recommended C_p° value for δ-Fe are based on the data of Cezairliyan and McClure.[4] Data of Sale and Normanton[2] and of Dench and Kubaschewski[31] are, respectively, 2% to 5% and 2.5% higher than the recommended values, and those of Braun[39] and of Morris *et al.*[54] are up to 7% and 9% lower, respectively, while those of Holetzko[36] are as much as 36% higher.

A systematic plot of percent deviation (up to $\pm 4\%$) in C_p° values from various measurements is shown in Fig. 2.

In addition to the direct C_p° measurements, there are several enthalpy studies reported in the literature. These compare with the enthalpy values obtained by integrating the recommended C_p° values as follows:

Source	Deviation, %
Anderson and Hultgren[51]	± 1.5
Olette and Ferrier[52]	± 1
Ferrier and Olette[53]	up to − 2
Morris *et al.*[54]	± 0.5
Jaeger *et al.*[55]	± 1.5
Rapson[56]	up to − 3.5
Pattison and Willows[57]	− 1.5
Umino[58]	− 4 (< 1185 K) ± 1 (> 1185 K)
Umino[59]	− 2.5 (< 1185 K) + 5 (> 1185 K)
Wust *et al.*[60]	± 3
Oberhoffer and Grosse[61]	+ 1

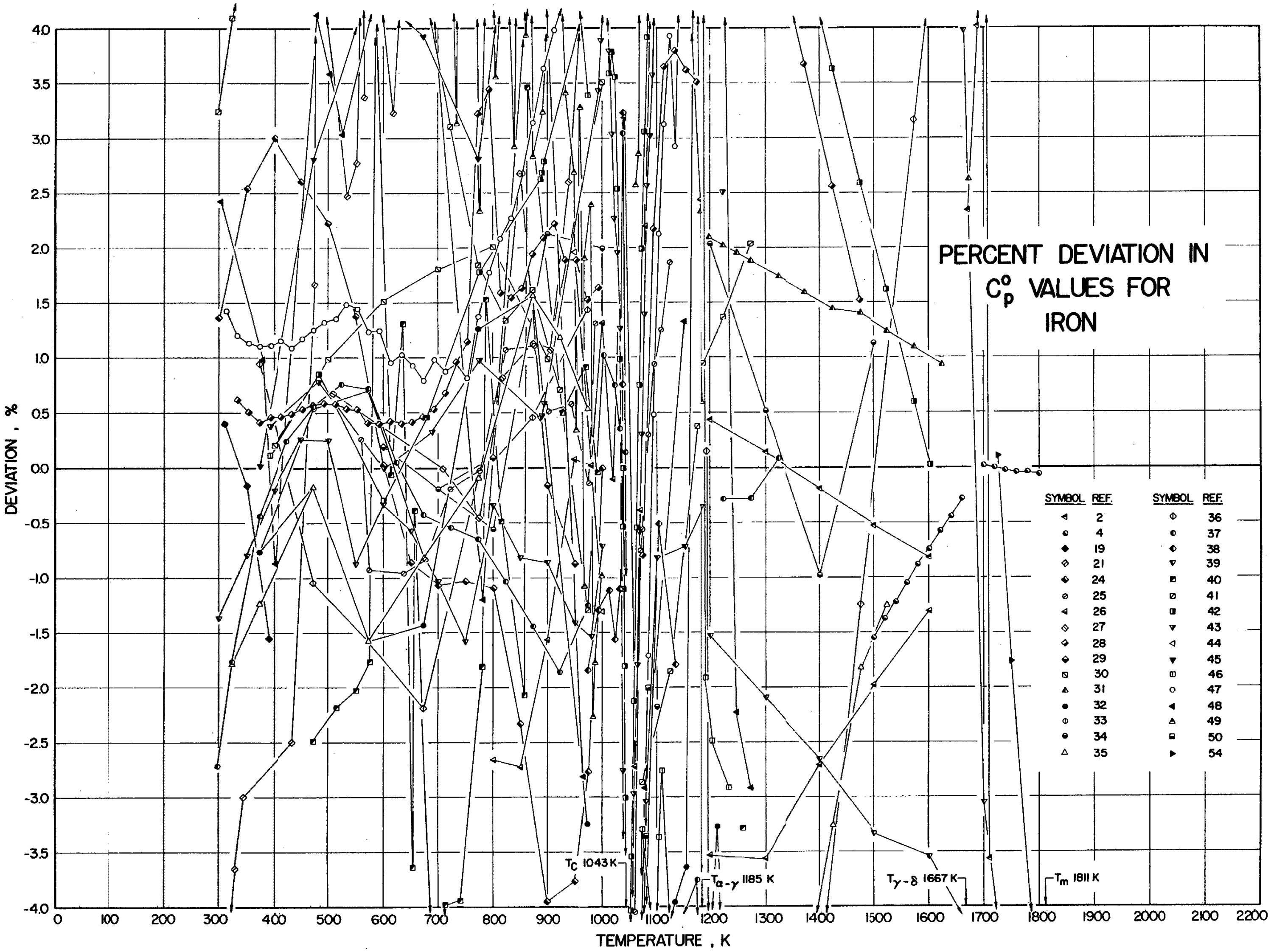

FIG. 2. Percent deviation in C_p° values for iron.

2.4. High-Temperature Heat Capacity (Liquid)

The recommended value for the enthalpy of melting, $\Delta_{\mathrm{fus}}H^\circ = 13\,810 \pm 300$ J mol^{-1}, was obtained by extrapolating solid and liquid enthalpies to the melting point, $T_{\mathrm{fus}} = 1811$ K. This compares with the following values reported in the literature:

Source	$\Delta_{\mathrm{fus}}H^\circ$, J mol^{-1}
Braun and Kohlhaas[38]	14 400 ± 300
Ferrier and Olette[53]	13 774 ± 380
Morris *et al.*[54]	13 799 ± 400
Umino[58]	16 170
Umino[59]	15 340
Wust *et al.*[60]	11 531
Oberhoffer and Grosse[61]	15 043
Treverton and Margrave[62]	13 836 ± 300
Mogutunov and Tomilin[63]	13 782
Vollmer *et al.*[64]	14 393 ± 400

The following investigators have reported constant values for the C_p° of molten iron from their enthalpy measurements in the limited temperature range:

Source	C_p°, J mol^{-1} K^{-1}
Ferrier and Olette[53]	46.970
Morris *et al.*[54]	40.481
Umino[58]	45.331
Treverton and Margrave[62]	43.062 ± 0.21
Mogutunov and Tomilin[63]	46.986
Vollmer *et al.*[64]	42.00
Margrave[65]	46.6 ± 1.8
Chetykhin *et al.*[93]	38.31
Recommended value	46.632 ± 3.0

Other quantities in Table 2 are calculated by integrating C_p° values. The recommended enthalpy values for liquid iron agree within ± 2% of the data of Ferrier and Olette,[53] Morris *et al.*,[54] Pattison and Willows,[57] Umino,[59] and of Treverton and Margrave.[62] The data of Umino[58] are up to 6% higher than the recommended values.

The recommended C_p° values reported in Table 2 are shown in Fig. 3 along with experimental data. Other quantities in Table 2 were calculated using the procedure outlined earlier.[1]

The estimated uncertainties in the heat capacity are ± 3% below 10 K, 1.5% from 10 to 298.15 K, ± 2% from 298.15 to 1000 K, ± 5% from 1060 to 1185 K, ± 2% from 1185 and 1667 K (γ-Fe) and 1667 to 1811 K (δ-Fe), and ± 3% in the liquid region. However, uncertainty near the Curie temperature is as much as ± 10%.

2.5. Ideal Gas Properties

Thermodynamic quantities for Fe(g) reported in Table 2 are calculated from C_p°(g) and S° (298.15 K) (g) values reported in Chase *et al.*[66]

2.6. Vapor Pressure Data

Application of the third law test to the vapor pressure measurements gave the following enthalpy of sublimation at 298.15 K.

Source	$\Delta_{\mathrm{sub}}H^\circ$ (298.15 K), kJ mol^{-1}
Smith and Shuttleworth,[67] 1273–1773 K, Knudsen method	422.07 ± 1.24
Nesmeyanov and Trapp,[68] 1327–1518 K, Knudsen method	417.97 ± 1.09
Myles and Aldred,[69] 1451–1677 K, Knudsen method	414.77 ± 0.76
Saxer,[70] 1507–1657 K, Knudsen method	414.72 ± 1.90
Gulbransen and Andrew,[71] 1298–1423 K, Langmuir method	423.10 ± 1.79
Turkdogan and Leake,[72] 1873 K, Transport method	424.44
Speiser *et al.*,[73] 1725–1826 K, Calculated from Knudsen method for Fe–Ni alloys	415.12 ± 2.32
McCabe *et al.*,[74] 1497, 1506 K, Knudsen method	417.47 ± 0.25
Burlakov,[75] 1302–1505 K, Langmuir method	
First sample	406.74 ± 1.92
1291–1529 K, second sample	405.67 ± 2.32
Ivanov,[76] 1360–1328 K, Isotope exchange method	406.64 ± 3.42
Morris *et al.*,[77] 1810–1889 K, Transport method	416.67 ± 0.33
Vintaikin,[78] 1400–1600 K, Knudsen method	417.54 ± 1.17
Kornev,[79] 1464–1623 K, Knudsen method	406.17 ± 3.47
Edwards *et al.*,[80] 1356–1519 K, Langmuir method	418.12 ± 0.96
Wessel,[81] 1500–1800 K, Knudsen method	408.22 ± 2.51
Darken and Gurry,[82] 1873 K, Langmuir method	420.84
Marshall *et al.*,[83] 1317–1579 K, Langmuir method	408.09 ± 2.34
Jones *et al.*,[84] 1270–1580 K, Langmuir method	405.27 ± 1.49
Alcock and Kubik,[85] 1810–1895 K, Knudsen method	416.73 ± 0.13
Lindscheid and Lange,[86]	
1765–1870 K, Knudsen method	413.43 ± 4.28
1773–1870 K, torsion method	417.27 ± 2.84
Svyazhin *et al.*,[87] 1993–2363 K Carrier gas transportation method	402.70 ± 0.40
Karasev *et al.*,[88] 1873–2023 K, Evaporation method	421.56 ± 3.22
Yavoyskii *et al.*,[89] 1908–2293 K, Carrier gas transportation method	409.35 + 3.97
Chegodaev *et al.*,[90] 1273–2200 K, Langmuir method	438.08 ± 1.60
Lindscheid and Lange,[91]	
1622–1878 K, Knudsen method	413.09 ± 2.20
1624–1875 K, torsion method	414.78 ± 2.28
Nemets and Nikolaev,[92] 1478–1665 K, Absorption method	403.65 ± 2.52
Recommended value	415.47 ± 1.25

Table 2. Recommended high-temperature thermodynamic properties of iron[a]

	Condensed phase				Gas phase Fe(g)			
T	C_p^o	$H^o-H^o(Tr)$	S^o	$-[G^o-H^o(Tr)]/T$	C_p^o	$H^o-H^o(Tr)$	S^o	$-[G^o-H^o(Tr)]/T$
K	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$		$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	
298.15	25.084	0	0.000	27.085	25.673	0	0.000	180.376
300	25.131	48	0.155	27.085	25.681	48	0.159	180.376
350	26.321	1334	4.122	27.397	25.703	1334	4.123	180.689
400	27.427	2677	7.710	28.102	25.531	2615	7.545	181.385
450	28.532	4076	11.004	29.031	25.254	3885	10.538	182.280
500	29.639	5531	14.066	30.090	24.891	5139	13.180	183.279
550	30.810	7042	16.947	31.229	24.537	6374	15.535	184.322
600	32.008	8612	19.678	32.410	24.200	7593	17.656	185.378
650	33.260	10243	22.289	33.615	23.892	8795	19.580	186.426
700	34.618	11940	24.805	34.833	23.610	9982	21.341	187.457
750	36.153	13709	27.246	36.053	23.354	11156	22.960	188.462
800	37.924	15559	29.633	37.270	23.133	12318	24.461	189.439
850	40.170	17508	31.995	38.483	22.936	13470	25.857	190.386
900	43.157	19587	34.370	39.692	22.765	14612	27.163	191.304
925	45.152	20690	35.579	40.297	22.688	15180	27.786	191.751
950	47.642	21848	36.815	40.902	22.617	15747	28.390	192.190
975	50.691	23076	38.090	41.507	22.551	16312	28.977	192.623
1000	54.458	24389	39.419	42.115	22.489	16874	29.547	193.049
1010	56.815	24944	39.972	42.360	22.465	17099	29.771	193.217
1020	60.140	25528	40.548	42.605	22.442	17323	29.992	193.385
1030	65.490	26154	41.159	42.852	22.421	17548	30.211	193.550
1035	69.420	26491	41.486	42.976	22.411	17660	30.319	193.632
1040	74.900	26851	41.833	43.100	22.401	17772	30.427	193.748
1042	78.690	27004	41.980	43.149	22.397	17816	30.470	193.748
1043	83.770	27085	42.058	43.175	22.395	17839	30.492	193.764
1044	74.540	27163	42.133	43.199	22.393	17861	30.513	193.781
1046	68.270	27306	42.269	43.249	22.389	17906	30.556	193.813
1048	63.980	27438	42.395	43.298	22.384	17951	30.599	193.846
1050	60.900	27563	42.514	43.349	22.381	17996	30.641	193.878
1055	56.348	27854	42.791	43.474	22.372	18108	30.747	193.959
1060	53.850	28129	43.051	43.599	22.362	18220	30.853	194.040
1070	50.138	28642	43.533	43.849	22.344	18443	31.063	194.202
1080	47.462	29129	43.986	44.099	22.328	18667	31.271	194.362
1090	45.675	29595	44.414	44.348	22.311	18890	31.477	194.523
1100	44.350	30044	44.825	44.597	22.297	19113	31.681	194.681
1125	42.223	31124	45.795	45.214	22.260	19670	32.181	195.072
1150	41.063	32164	46.709	45.826	22.229	20226	32.670	195.458
1175	40.262	33178	47.583	46.431	22.203	20779	33.148	195.840
1185(α)	40.000	33581	47.923	46.669	22.195	21001	33.336	195.990
1185(γ)	33.775	34481	48.682	46.669	22.195	21001	33.336	195.990
1200	33.905	34989	49.108	47.036	22.184	21336	33.615	196.211
1250	34.353	36695	50.501	48.230	22.151	22445	34.520	196.940
1300	34.809	38424	51.857	49.385	22.138	23551	35.388	197.648
1350	35.280	40176	53.179	50.504	22.139	24659	36.224	198.334
1400	35.750	41952	54.471	51.590	22.154	25766	37.029	199.001
1450	36.220	43751	55.734	52.645	22.183	26874	37.807	199.649
1500	36.690	45574	56.970	53.672	22.230	27984	38.560	200.280
1550	37.161	47420	58.180	54.672	22.287	29097	39.290	200.893
1600	37.630	49290	59.368	55.646	22.355	30213	39.998	201.491
1650	38.100	51183	60.533	56.597	22.434	31333	40.687	202.073
1667(γ)	38.260	51832	60.924	56.916	22.463	31715	40.917	202.268
1667(δ)	40.400	52682	61.434	56.916	22.463	31715	40.917	202.268
1700	41.454	54033	62.236	57.537	22.522	32457	41.358	202.642
1750	43.051	56145	63.461	58.463	22.619	33585	42.012	203.197
1800	44.649	58338	64.696	59.371	22.727	34719	42.651	203.739
1811(δ)	45.000	58831	64.969	59.569	22.748	34969	42.790	203.857
1811(ℓ)	46.632	72641	72.595	59.569	22.748	34969	42.790	203.857
1900	46.632	76791	74.832	61.501	22.958	37003	43.986	204.787
2000	46.632	81388	77.190	63.581	23.213	39311	45.070	205.791
2200	46.632	90714	81.634	67.486	23.769	44008	47.308	207.680
2400	46.632	100041	85.692	71.093	24.363	48820	49.401	209.436
2600	46.632	109367	89.424	74.445	24.974	53754	51.375	211.077
2800	46.632	118693	92.880	77.575	25.589	58810	53.249	212.621
3000	46.632	128020	96.098	80.509	26.209	63989	55.035	214.081
3110	46.632	133149	97.627	81.899	26.554	66892	55.986	214.853
3200	46.632	137380	99.124	83.278	26.840	69295	56.747	215.468

$T_{\alpha-\gamma} = 1185$ K $\Delta H_{\alpha-\gamma} = 900 \pm 40$ J·mol^{-1} $\Delta S_{\alpha-\gamma} = 0.759 \pm 0.034$ J·mol^{-1}·K^{-1}

$T_{\gamma-\delta} = 1667$ K $\Delta H_{\gamma-\delta} = 850 \pm 80$ J·mol^{-1} $\Delta S_{\gamma-\delta} = 0.510 \pm 0.048$ J·mol^{-1}·K^{-1}

$T_{fus} = 1811$ K $\Delta_{fus}H^o = 13810 \pm 300$ J·mol^{-1} $\Delta_{fus}S^o = 7.626 \pm 0.160$ J·mol^{-1}·K^{-1}

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

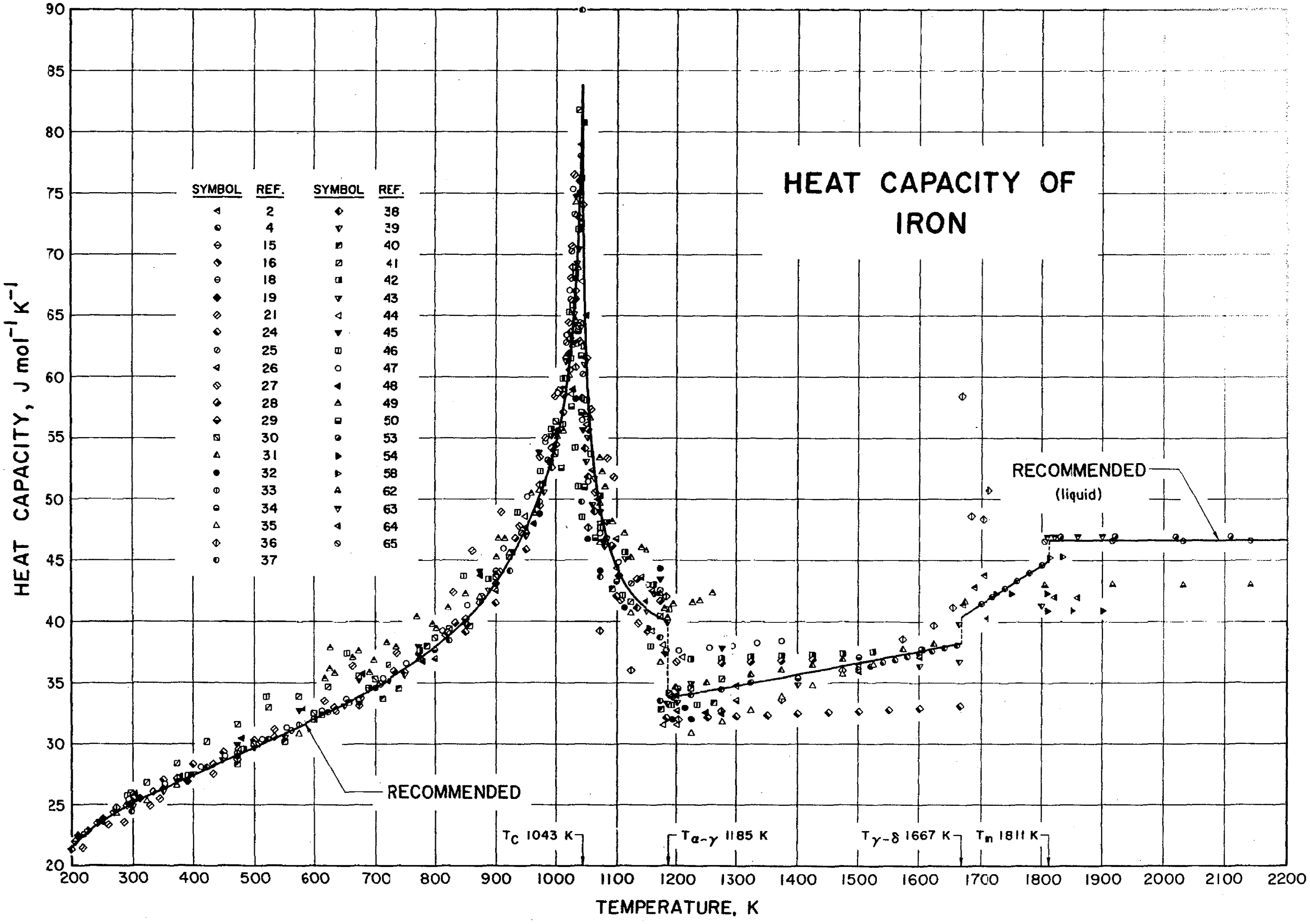

FIG. 3. Heat capacity of iron.

Table 3. Recommended vapor pressure of iron[a,b]

$Fe_{(s,\ell)} = Fe_{(g)}$

T/K	p/atm	ΔG°	ΔH°	p/atm	T/K
		J·mol^{-1}			
298.15	1.65×10^{-65}	369766	415470	10^{-10}	1220
300	4.65×10^{-65}	369483	415470	10^{-9}	1296
400	5.65×10^{-47}	354157	415408	10^{-8}	1382
500	3.96×10^{-36}	338876	415078	10^{-7}	1480
600	6.61×10^{-29}	323689	414451	10^{-6}	1593
				10^{-5}	1726
700	9.32×10^{-24}	308633	413512	10^{-4}	1888
800	6.62×10^{-20}	293735	412229	10^{-3}	2091
900	6.40×10^{-17}	279019	410495	10^{-2}	2346
1000	1.52×10^{-14}	264536	407955	10^{-1}	2678
1100	1.29×10^{-12}	250378	404539	1	3110
1185(α)	3.06×10^{-11}	238525	402890		
1185(γ)	3.06×10^{-11}	238525	401990		
1200	5.10×10^{-11}	236460	401817		
1300	1.12×10^{-9}	222728	400597		
1400	1.58×10^{-8}	209095	399284		
1500	1.55×10^{-7}	195558	397880		
1600	1.13×10^{-6}	182118	396393		
1667(γ)	3.75×10^{-6}	173168	395353		
1667(δ)	3.75×10^{-6}	173168	394503		
1700	6.51×10^{-6}	168792	393894		
1800	3.05×10^{-5}	155608	391851		
1811(δ)	3.58×10^{-5}	154164	391608		
1811(ℓ)	3.58×10^{-5}	154164	377798		
2000	3.78×10^{-4}	131050	373393		
2200	2.87×10^{-3}	107043	368764		
2400	1.53×10^{-2}	83447	364249		
2600	6.17×10^{-2}	60227	359857		
2800	0.201	37341	355587		
3000	0.553	14754	351439		
3110	1.000	0	349213		
3200	1.328	−7538	347385		

$\Delta_{vap}S^\circ(3110\ K) = 112.29 \pm 0.40$ J·mol^{-1}·K^{-1}

$\Delta_{sub}H^\circ(0\ K) = 413.102 \pm (1.26)$ kJ·mol^{-1}

[a] 1 atm = 101325 Pa

[b] ΔG° refers to $\Delta_{sub}G^\circ$ when $T < T_{fus}$ and $\Delta_{vap}G^\circ$ when $T > T_{fus}$ (and similarly for ΔH°).

The values for ΔG°, p, and ΔH° reported in Table 3 are calculated using $\Delta_{sub}H^\circ$ (298.15 K) and the Gibbs energy values for Fe(s,l) and Fe(g) from Table 2.

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 well within the uncertainty of these values.

2.7. References

[1] P. D. Desai, "Thermodynamic Properties of Aluminum, Nickel, and Titanium," J. Phys. Chem. Ref. Data (to be published).

[2] F. R. Sale and A. S. Normanton, "A Spherical Adiabatic Calorimeter," in *Metallurgical Chemistry Symposium 1971* (National Physical Laboratory, Teddington, England, 1972), pp. 19–28.

[3] J. A. Treverton and J. L. Margrave, J. Chem. Thermodyn. **3**, 473 (1971).

[4] A. Cezairliyan and J. L. McClure, J. Res. Natl. Bur. Stand. Sect. A **78**, 1 (1974).

[5] C. Boulanger, C. R. Acad. Sci. **241**, 1133 (1955).

[6] M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. R. Soc. London Ser. A **285**, 561 (1965).

[7] C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. **120**, 426 (1960).

[8] S. S. Shinozaki and A. Arrott, Phys. Rev. **152**, 611 (1966).

[9] A. Arrott and S. Shinozaki, Ann. Acad. Sci. Fenn. Ser. A **210**, 31 (1966).

[10] K. Marklund, L. Hoel, K. Spahr, and T. Lindqvist, J. Low Temp. Phys. **5**, 227 (1971).

[11] J. Mazur and W. Zacharko, Acta Phys. Pol. **32**, 501 (1967).

[12] V. Arp, D. Edmonds, and R. Petersen, Phys. Rev. Lett. **3**, 212 (1959).

[13] W. H. Keesom and B. Kurrelmeyer, Physica (The Hague) **6**, 633 (1939).

[14] G. Duyckaerts, Physica (The Hague) **6**, 401 (1939).

[15] A. Eucken and H. Werth, Z. Anorg. Allg. Chem. **188**, 152 (1930).

[16] G. L. Stepakoff and L. Kaufman, Acta Metall. **16**, 13 (1968).

[17] K. K. Kelley, J. Chem. Phys. **11**, 16 (1943).

[18] F. Simon and R. C. Swain, Z. Phys. Chem. Abt. B **28**, 189 (1935).

[19] E. H. Griffiths and E. Griffiths, Proc. R. Soc. London Ser. A **90**, 557 (1914).

[20] B. P. N. Reddy and P. J. Reddy, Phys. Status Solidi A **22**, 219 (1974).

[21] K. Schroder and W. M. MacInnes, J. Sci. Instrum. Suppl. 2, **2**, 959 (1969).

[22] W. H. Rodebush and J. C. Michalek, J. Am. Chem. Soc. **47**, 2117 (1925).

[23] P. Gunther, Ann. Phys. (Paris) **51**, 828 (1916).

[24] W. Bendick and W. Pepperhoff, Acta Metall. **30**, 679 (1982).

[25] W. Pepperhoff, and H. H. Ettwig, Z. Angew. Phys. **22**, 496 (1967).

[26] J. Rogez and J. Le Coze, Rev. Phys. Appl. **15**, 341 (1980).

[27] L. N. Larikov, Yu. V. Usov, and A. V. Zolotukhin, Metallofizika (75), 55 (1979).

[28] T. G. Kollie, D. L. McElroy, M. Barisoni, and C. R. Brooks, ORNL Report No. ORNL-4380, 1969, 33 pp. [N69-27239].

[29] M. Tsuchiya, M. Izumiyama, and Y. Imai, J. Jpn. Inst. Met. **35**, 839 (1971).

[30] V. Ye. Lyusternik, Phys. Met. Metallogr. (USSR) **19**, 48 (1965).

[31] W. A. Dench and O. Kubaschewski, J. Iron Steel Inst. London **201**, 140 (1963).

[32] J. H. Awbery and E. Griffiths, Proc. R. Soc. London Ser. A **174**, 1 (1940).

[33] C. Sykes and H. Evans, J. Iron Steel Inst. London **138**, 125 (1938).

[34] A. S. Normanton, P. E. Bloomfield, F. R. Sale, and B. B. Argent, Met. Sci. J. **9**, 510 (1975).

[35] P. R. Pallister, J. Iron Steel Inst. London **161**, 87 (1949).

[36] H. Holetzko, dissertation (University of Koln, 1958); quoted by F. Krauss, Z. Metallkd. **49**, 386 (1958).

[37] D. C. Wallace, P. H. Sidles, and G. C. Danielson, J. Appl. Phys. **31**, 168 (1960).

[38] M. Braun and R. Kohlhaas, Phys. Status Solidi **12**, 429 (1965).

[39] M. Braun, Inaugural dissertation (University of Koln, 1964).

[40] J. L. Orehotsky and K. Schroder, J. Phys. E **3**, 889 (1970).

[41] H. R. Shanks, A. H. Klein, and G. C. Danielson, J. Appl. Phys. **38**, 2885 (1967).

[42] T. G. Kollie, ORNL Report No. ORNL-TM-1187, 1965.

[43] D. L. McElroy, Ph.D. thesis (University of Tennessee, Knoxville, 1957).

[44] Ya. A. Kraftmakher and T. Ya. Romashina, Tverd. Tela. **7**, 2532 (1965).

[45] H. Klinkhardt, Ann. Phys. (Paris) **84**, 167 (1927).

[46] C. Lapp, Ann. Phys. (Paris) **6**, 826 (1936).

[47] H. Esser and H. Baerlecken, Arch. Eisenhuttenw. **14**, 617 (1941).

[48] K. Kobayasi, T. Ohmori, and Y. Fujimura, High Temp.–High Pressures **11**, 459 (1979).

[49] A. A. Varchenko, Ya. A. Kraftmakher, and T. Yu. Pinegina, High Temp. (USSR) **16**, 720 (1978).

[50] F. L. Lederman, M. B. Salamon, and L. W. Shacklette, Phys. Rev. B **9**, 2981 (1974).

[51] P. D. Anderson and R. Hultgren, Trans. Metall. Soc. AIME **224**, 842 (1962).

[52] M. Olette and A. Ferrier, in *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds* (National Physical Laboratory, Teddington, England, 1959), Symposium No. 9, Paper 4H, pp. 100–109.

[53] A. Ferrier and M. Olette, C. R. Acad. Sci. **254**, 2322 (1962).

[54] J. P. Morris, E. F. Foerster, C. W. Schultz, and G. R. Zellars, U.S. Bur. Mines Rep. Invest. 6723 (1966).

[55] F. M. Jaeger, E. Rosenbohm, and A. J. Zuithoff, Recl. Trav. Chim. Pays-Bas **57**, 1313 (1938).

[56] R. L. Rapson, M. S. thesis (Air Force Institute of Technology, WPAFB, 1965) (School of Engineering Report No. GME/ME/65-1).

[57] J. R. Pattison and P. W. Willows, J. Iron Steel Inst. London **183**, 390 (1956).

[58] S. Umino, Sci. Rep. Tohoku Imp. Univ. Ser. 1 **18**, 91 (1929).

[59] S. Umino, Sci. Rep. Tohoku Imp. Univ. Ser. 1 **15**, 597 (1926).

[60] F. Wust, A. Meuthen, and R. Durrer, Forsch. Geb. Ingenieurwes. VDI-Forsch. **204** (1918).

[61] P. Oberhoffer and W. Grosse, Stahl Eisen **47**, 576 (1927).

[62] J. A. Treverton and J. L. Margrave, J. Chem. Thermodyn. **3**, 473 (1971).

[63] B. M. Mogutunov and I. A. Tomilin, Izv. Akad Nauk SSSR Met. **4**, 28 (1967).

[64] O. Vollmer, R. Kohlhaas, and M. Braun, Z. Naturforsch. Teil A **21**, 181 (1966).

[65] J. L. Margrave, Rice University Report No. N71-20542, 1970.

[66] M. W. Chase, Jr., J. L. Curnutt, J. R. Downey, Jr., R. A. McDonald, A. N. Syverud, and E. A. Valenzuela, J. Phys. Chem. Ref. Data **11**, 695 (1982).

[67] R. Smith and R. Shuttleworth, Trans. Metall. Soc. AIME **233**, 806 (1965).

[68] N. Nesmeyanov and G. Trapp, Zh. Fiz. Khim. **38**, 2931 (1964) [Russ. J.

Phys. Chem. **38** (12), 1593 (1964)].

[69]K. M. Myles and A. T. Aldred, J. Phys. Chem. **68**, 64 (1964).

[70]R. K. Saxer, Ph.D. thesis (Ohio State University, 1962) [Univ. Microfilms No. 63-81].

[71]E. A. Gulbransen and K. F. Andrew, Trans. Metall. Soc. AIME **221**, 1247 (1961).

[72]E. T. Turkdogan and L. E. Leake, Trans. Metall. Soc. AIME **218**, 1136 (1960).

[73]R. Speiser, A. J. Jacobs, and J. W. Spretnak, Trans. Metall. Soc. AIME **215**, 185 (1959).

[74]C. L. McCabe, R. G. Hudson, and H. W. Paxton, Trans. Metall. Soc. AIME **212**, 102 (1958).

[75]V. D. Burlakov, Fiz. Met. Metalloved. **5**, 91 (1957) [Phys. Met. Metallogr. (USSR) **5**, 72 (1957)].

[76]L. I. Ivanov, thesis (Metallurgy Institute, Academy of Sciences of the USSR, 1957).

[77]J. P. Morris, G. R. Zellars, S. L. Payne, and R. L. Kipp, U.S. Bur. Mines Rep. Invest. 5364 (1957).

[78]E. Z. Vintaikin, Dokl. Akad. Nauk SSSR **117**, 632 (1957).

[79]Yu. V. Kornev, Probl. Metalloved. Fiz. Met. **4**, 432 (1955).

[80]J. W. Edwards, H. L. Johnston, and W. E. Ditmars, J. Am. Chem. Soc. **75**, 4729 (1951).

[81]G. Wessel, Z. Phys. **130**, 539 (1951).

[82]L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. **68**, 798 (1946).

[83]A. L. Marshall, R. W. Dornte, and F. J. Norton, J. Am. Chem. Soc. **59**, 1161 (1937).

[84]H. A. Jones, I. Langmuir, and G. M. J. Mackay, Phys. Rev. **30**, 201 (1927).

[85]C. B. Alcock and A. Kubik, Trans. Inst. Mining Met. Sec. C **77**, 220 (1968).

[86]H. Lindscheid and K. W. Lange, Z. Metallkd. **61**, 193 (1970).

[87]A. G. Svyazhin, A. F. Vishkarev, and V. I. Yovoisky, Russ. Metall. **5**, 42 (1968).

[88]Yu. A. Karasev, L. Sh. Tsemekhman, and S. E. Vaisburd, Russ. J. Phys. Chem. **45**, 1172 (1971).

[89]V. I. Yavoyskii, A. G. Svyazhin, A. F. Vishkarev, N. K. Pin, D. A. Romanovich, and G. M. Chursin, Russ. Metall. **3**, 24 (1971).

[90]A. I. Chegodaev, E. L. Dubinin, A. I. Timofeev, N. A. Vatolin, and V. I. Kapitanov, Russ. J. Phys. Chem. **52**, 1229 (1978).

[91]H. Lindscheid and K. W. Lange, Z. Metallkd. **66**, 546 (1975).

[92]A. M. Nemets and G. I. Nokolaev, J. Appl. Spectrosc. (USSR) **21**, 1145 (1974).

[93]V. I. Chetykhin, I. N. Zedina, and S. Ye. Vaisburd, Inzh. Fiz. Zh. **34**, 870 (1978).

3. Thermodynamic Properties of Silicon

3.1. Phase and Structure

Silicon has an fcc (A4) crystal structure isotypic with diamond.[1] Its atomic weight is 28.0855 and melting point is 1687 ± 2 K (IPTS-68). The melting point is based on the following measurements (IPTS-68):

Source	T_{fus}, K
Lucas and Urbain[2]	1685 ± 1
Kantor *et al.*[3]	1692 ± 4
Olette[4]	1687 ± 2
Hansen *et al.*[5]	1685 ± 5
Gayler[6]	1690 ± 2
Hoffman and Schulze[7]	1685 ± 2

Table 4. Recommended low-temperature heat capacity of silicon

T/K	C_p°/J·mol^{-1}·K^{-1}	T/K	C_p°/J·mol^{-1}·K^{-1}
1	0.000007740	120	9.250
2	0.00006192	125	9.721
3	0.0002092	130	10.186
4	0.0004937	140	11.107
5	0.0009665	150	11.955
6	0.001669	160	12.776
7	0.002651	170	13.556
8	0.003960	175	13.921
9	0.005637	180	14.286
10	0.007740	190	14.990
15	0.03054	200	15.642
20	0.09456	210	16.223
25	0.2385	220	16.761
30	0.481	225	17.037
35	0.810	230	17.291
40	1.237	240	17.778
45	1.710	250	18.219
50	2.205	260	18.625
60	3.230	270	19.015
70	4.251	273.15	19.133
75	4.765	280	19.381
80	5.283	290	19.738
90	6.293	298.15	20.007
100	7.296	300	20.066
110	8.285		

$C_{(\mathrm{electronic})} = \gamma T$ $\gamma = 0.000$ J·mol^{-1}·K^{-2}

Crystal, Si(s)	Gas, Si(g)	1/2 Si_2(g)	1/3 Si_3(g)
H°(298.15 K)−H°(0 K) = 3214±10	7550±0.3	4632±0.3	4651±0.6 J·mol^{-1}
S°(298.15 K) = 18.806±0.08	167.870±0.0008	114.843±0.42	89.495±2.0 J·mol^{-1}·K^{-1}

3.2. Low-Temperature Heat Capacity

The recommended values agree well with the data of Keesom and Seidel,[8] Flubacher *et al.*,[9] Kalishevich *et al.*,[10] and of Anderson.[11] The data of Gul'tyaev and Petrov[12] are up to 4% lower and those of Russell[13] are up to 6% higher near 300 K. Additionally, three data sets reported graphically in small figures which appeared to be a one-and-the-same investigation by Letun *et al.*,[14] Gel'd and Krentis,[15] and by Letun and Gel'd[16] are in fair agreement with the recommended values. The data of Pearlman and Keesom[17] are up to 30% higher below 4 K, 7% higher from 50 to 100 K, agree slightly higher from 12 to 50 K. The recommended values of C_p° are in agreement with the values of Hultgren *et al.*[18] and of Glushko *et al.*[19]

Within the experimental uncertainty, the electronic specific heat coefficient γ is equal to 0.000 J mol^{-1} K^{-2} and Debye temperature $\theta_{\mathrm{D}} = 631$ K. Mertig *et al.*[43] report a value of 528 ± 20 K for the Debye temperature of amorphous silicon. Integration of the recommended C_p° values yield $H^\circ(298.15\ \mathrm{K}) - H^\circ(0\ \mathrm{K}) = 3214$ J mol^{-1} and integration of C_p°/T values yield $S^\circ(298.15\ \mathrm{K}) = 18.806\ (\pm 0.08)$ J mol^{-1} K^{-1} which are in agreement with those recommended by the CODATA Task Group.[20] These values are reported in Table 4 and C_p° values are shown in Fig. 4 along with the experimental data.

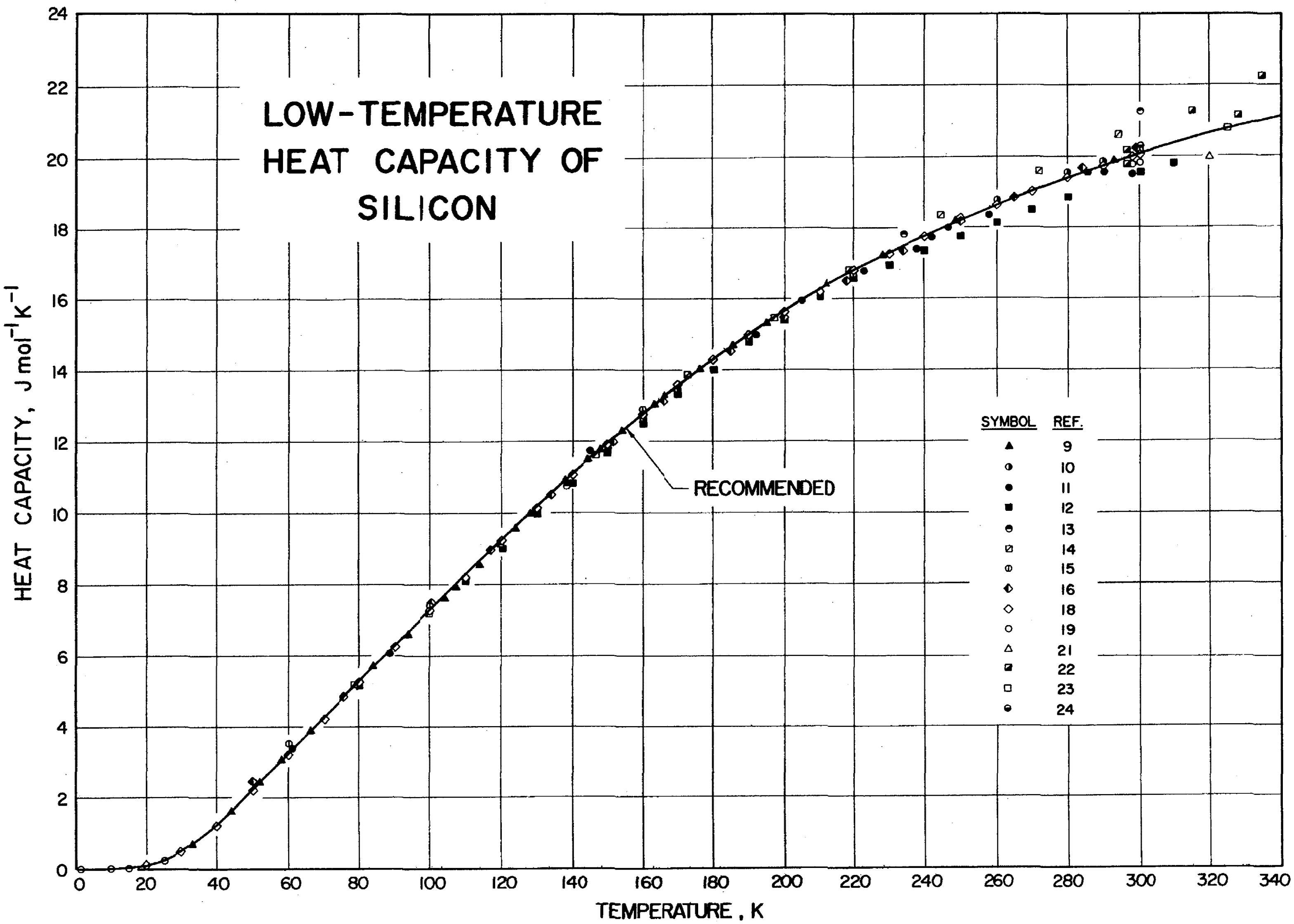

FIG. 4. Low-temperature heat capacity of silicon.

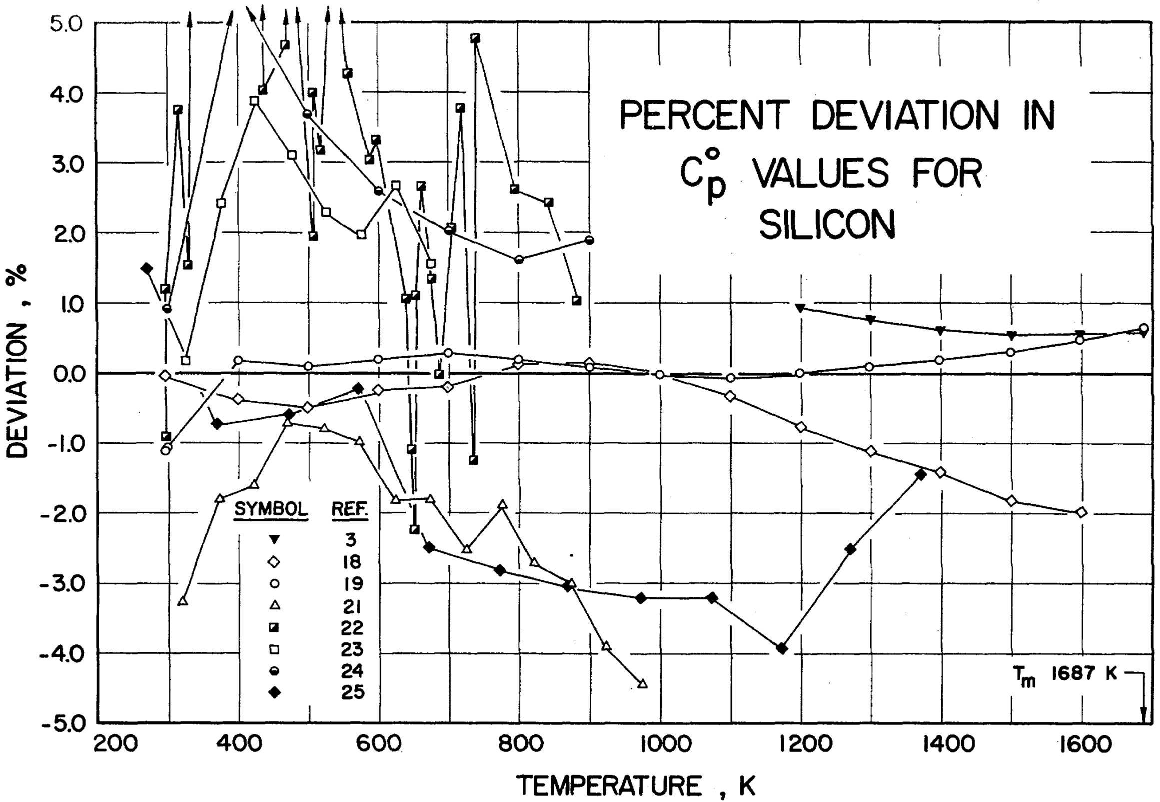

FIG. 5. Percent deviation in C_p° values for silicon.

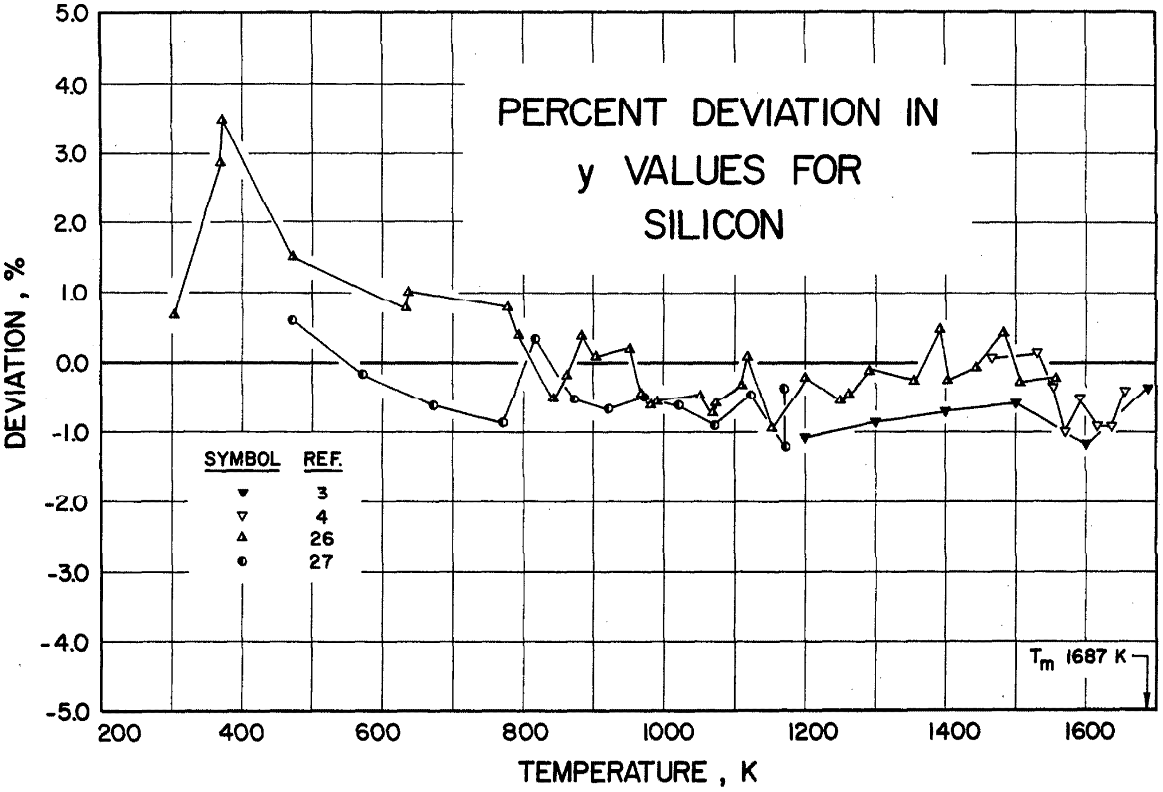

FIG. 6. Percent deviation in *y* values for silicon.

3.3. High-Temperature Heat Capacity (Solid)

There are only a few data sets available in this temperature range. The recommended C_p° values are generated by critically evaluating heat capacity and enthalpy data simultaneously. Agreement between C_p° and enthalpy data available in the literature and the recommended values is as follows:

Source	C_p° deviation, %
Kantor *et al.*[3]	up to 0.9
Hultgren *et al.*[18]	up to − 0.5 (< 700 K) up to − 1.0 (> 1000 K)
Glushko *et al.*[19]	− 1 (< 300 K)
North and Gilchrist[21]	up to − 4
Dismukes *et al.*[22]	− 1 to 10 (scatter considerably)
Kurosawa *et al.*[23]	up to 4
Gerlich *et al.*[24]	up to 5
Dennison[25]	− 0.2 to − 3.9

Source	y deviation, %
Kantor *et al.*[3]	− 0.4 to − 1.2
Olette[4]	up to − 1.0
Serebrennikov and Gel'd[26]	up to 3.5 (< 800 K) up to − 1.0 (> 800 K)
Magnus[27]	up to − 1.0
Golutvin and Maslennikova[28]	8–16

A systematic plot of percent deviation in C_p° values from various measurements is shown in Fig. 5. A systematic plot of percent deviation in y values

$$y = [H^\circ(T) - H^\circ(298.15\ \mathrm{K})]/(T - 298.15)$$

from various measurements is shown in Fig. 6.

3.4. High-Temperature Heat Capacity (Liquid)

The recommended value for the enthalpy of melting, $\Delta_{\mathrm{fus}}H^\circ = 50\,250 \pm 600\ \mathrm{J\ mol^{-1}}$ was obtained by extrapo-

Table 5. Recommended high-temperature thermodynamic properties of silicon[a]

T	Condensed phase				Gas phase Fe(g)			
	C_p°	$H^\circ-H^\circ(Tr)$	S°	$-[G^\circ-H^\circ(Tr)]/T$	C_p°	$H^\circ-H^\circ(Tr)$	S°	$-[G^\circ-H^\circ(Tr)]/T$
K	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$		$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	
298.15	20.007	0	0.000	18.806	22.251	0	0.000	167.870
300	20.066	37	0.124	18.806	22.234	41	0.138	167.870
350	21.324	1075	3.320	19.056	21.852	1143	3.533	168.138
400	22.258	2164	6.228	19.624	21.613	2229	6.436	168.734
450	23.000	3297	8.897	20.376	21.441	3305	8.970	169.495
500	23.588	4462	11.349	21.232	21.316	4374	11.223	170.346
550	24.047	5654	13.623	22.149	21.222	5437	13.249	171.233
600	24.420	6865	15.728	23.093	21.153	6496	15.094	172.137
650	24.748	8095	17.699	24.051	21.098	7553	16.783	173.034
700	25.050	9339	19.541	25.006	21.057	8606	18.346	173.922
750	25.334	10600	21.282	25.955	21.025	9659	19.797	174.789
800	25.608	11872	22.923	26.889	21.000	10709	21.154	175.638
850	25.865	13160	24.487	27.810	20.982	11759	22.420	176.462
900	26.110	14459	25.969	28.710	20.971	12807	23.626	177.265
950	26.344	15771	27.390	29.595	20.967	13856	24.758	178.043
1000	26.569	17093	28.744	30.457	20.968	14904	25.835	178.801
1100	26.988	19771	31.296	32.128	20.989	17002	27.834	180.248
1200	27.360	22489	33.661	33.726	21.033	19102	29.662	181.613
1300	27.707	25242	35.864	35.253	21.099	21209	31.348	182.904
1400	28.045	28030	37.930	36.715	21.183	23323	32.915	184.126
1500	28.372	30851	39.876	38.115	21.282	25446	34.379	185.285
1600	28.674	33703	41.717	39.458	21.394	27580	35.757	186.389
1687(s)	28.930	36210	43.245	40.587	21.497	29446	36.891	187.307
1687(ℓ)	27.200	86460	73.032	40.587	21.497	29446	36.891	187.307
1700	27.200	86814	73.241	40.980	21.513	29725	37.057	187.442
1800	27.200	89534	74.796	43.861	21.638	31882	38.290	188.448
1900	27.200	92254	76.266	46.518	21.764	34053	39.463	189.411
2000	27.200	94974	77.661	48.981	21.889	36235	40.583	190.335
2200	27.200	100414	80.254	53.417	22.129	40637	42.681	192.079
2400	27.200	105854	82.620	57.321	22.346	45085	44.615	193.700
2600	27.200	111294	84.798	60.798	22.535	49574	46.412	195.215
2800	27.200	116734	86.813	63.929	22.692	54097	48.088	196.637
3000	27.200	122174	88.690	66.771	22.819	58648	49.658	197.978
3200	27.200	127614	90.445	69.372	22.918	63222	51.134	199.247
3400	27.200	133054	92.094	71.767	22.992	67813	52.525	200.450
3490	27.200	135502	92.796	72.776	23.018	69863	53.126	200.972
3500	27.200	135774	92.883	72.896	23.021	70114	53.192	201.030
3514	27.200	136155	92.992	73.052	23.025	70436	53.284	201.110
3600	27.200	138494	93.649	73.985	23.046	72418	53.840	201.594

$T_{\mathrm{fus}} = 1687\ \mathrm{K}$ $\Delta_{\mathrm{fus}}H^\circ = 50250 \pm 600\ \mathrm{J\cdot mol^{-1}}$ $\Delta_{\mathrm{fus}}S^\circ = 29.787 \pm 0.356\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$

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

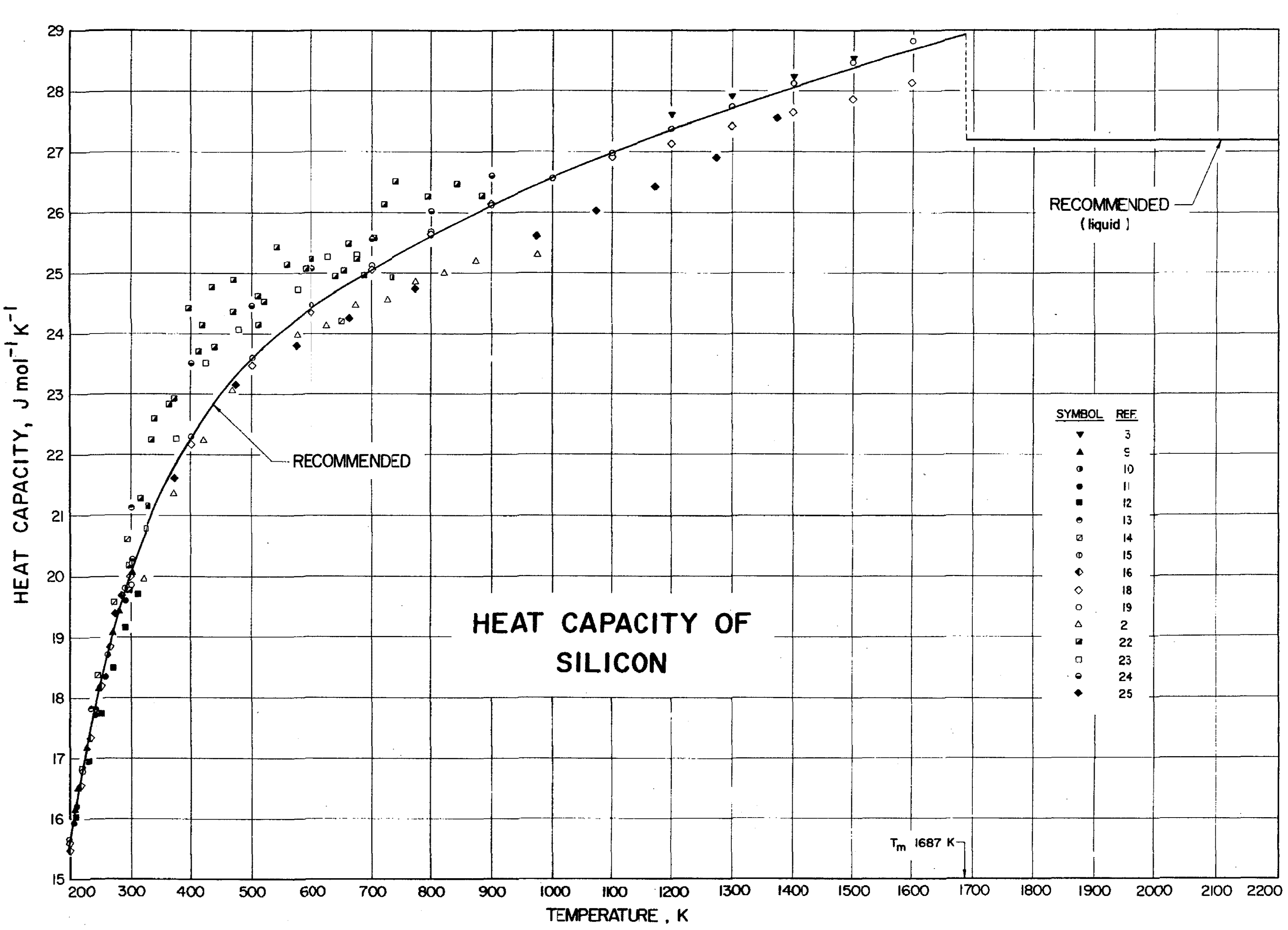

FIG. 7. Heat capacity of silicon.

Table 6. Recommended high-temperature thermodynamic properties of Si_2 and Si_3[a]

	Gas phase 1/2 $Si_2(g)$				Gas phase 1/3 $Si_3(g)$			
$\frac{T}{K}$	C_p° J·mol^{-1}·K^{-1}	$H^\circ-H^\circ(Tr)$ J·mol^{-1}	S° J·mol^{-1}·K^{-1}	$-[G^\circ-H^\circ(Tr)]/T$ J·mol^{-1}·K^{-1}	C_p° J·mol^{-1}·K^{-1}	$H^\circ-H^\circ(Tr)$ J·mol^{-1}	S° J·mol^{-1}·K^{-1}	$-[G^\circ-H^\circ(Tr)]/T$ J·mol^{-1}·K^{-1}
298.15	17.235	0	0.000	114.843	18.932	0	0.000	89.495
300	17.252	32	0.107	114.843	18.948	35	0.117	89.495
400	18.152	1802	5.193	115.531	19.641	1968	5.672	90.248
500	19.083	3663	9.343	116.859	20.015	3952	10.099	91.690
600	20.031	5619	12.906	118.384	20.234	5965	13.769	93.322
700	20.881	7666	16.060	119.951	20.373	7996	16.899	94.971
800	21.549	9789	18.894	121.500	20.467	10038	19.626	96.573
900	22.017	11969	21.461	123.005	20.531	12088	22.041	98.104
1000	22.304	14187	23.797	124.453	20.578	14144	24.207	99.557
1100	22.450	16425	25.931	125.841	20.615	16204	26.170	100.934
1200	22.495	18673	27.887	127.168	20.642	18267	27.965	102.237
1300	22.475	20922	29.687	128.436	20.662	20332	29.618	103.473
1400	22.414	23167	31.350	129.645	20.678	22399	31.150	104.645
1500	22.331	25404	32.894	130.801	20.692	24468	32.577	105.760
1600	22.239	27633	34.332	131.905	20.703	26537	33.913	106.822
1687	22.156	29564	35.507	132.825	20.712	28339	35.008	107.705
1700	22.144	29852	35.678	132.961	20.713	28608	35.168	107.835
1800	22.052	32062	36.941	133.972	20.722	30680	36.352	108.803
1900	21.964	34263	38.131	134.941	20.728	32753	37.473	109.730
2000	21.884	36455	39.255	135.871	20.733	34826	38.536	110.618
2200	21.743	40817	41.334	137.624	20.741	38973	40.512	112.292
2400	21.628	45154	43.221	139.250	20.750	43122	42.318	113.845
2600	21.535	49470	44.948	140.764	20.755	47273	43.979	115.292
2800	21.458	53769	46.541	142.181	20.758	51424	45.517	116.646
3000	21.389	58053	48.019	143.511	20.761	55576	46.949	117.919
3200	21.324	62325	49.398	144.764	20.760	59728	48.289	119.119
3400	21.255	66583	50.688	145.948	20.760	63880	49.548	120.254
3490	21.220	68494	51.243	146.460	20.760	65749	50.091	120.747
3500	21.217	68706	51.304	146.516	20.760	65956	50.149	120.800
3514	21.210	69003	51.389	146.595	20.760	66247	50.232	120.875
3600	21.177	70826	51.900	147.069	20.760	68032	50.733	121.330

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

lating solid and liquid enthalpies to the melting point, $T_{fus} = 1687$ K. This compares with the value of $50\,000 \pm 750$ J mol^{-1} reported by Kantor *et al.*[3] and of $50\,600 \pm 400$ J mol^{-1} given by Olette.[4] C_p° (l) $= 27.200 \pm 1.50$ J mol^{-1} K^{-1} was assumed to be constant to the boiling point based on the constant value 29.71 J mol^{-1} K^{-1} of Kantor *et al.*,[3] 25.52 J mol^{-1} K^{-1} of Olette,[4] and 26.20 J mol^{-1} K^{-1} of Chetykhin *et al.*[45]

Other thermodynamic quantities reported in Table 5 are calculated from C_p° values. The recommended C_p° values are shown in Fig. 7 along with experimental data.

The estimated uncertainties in the heat capacity are about $\pm 3\%$ below 10 K, $\pm 2\%$ from 10 to 298.15 K, $\pm 3\%$ from 298.15 to the melting point, and $\pm 5\%$ in the liquid region.

3.5. Ideal Gas Properties

Thermodynamic quantities for Si(g), Si_2(g), and Si_3(g) reported in Tables 5 and 6 are calculated from C_p° and S° (298.15 K) values reported by Glushko *et al.*[19] for Si(g) and Si_2 and by Brewer[44] for Si_3.

Brewer's calculation for Si_3(g) was preferred since it provided a smaller vibrational partition function. This is based on theoretical calculations indicating that the bending frequency, which is very anharmonic, should increase rapidly as the end atoms start approaching one another more closely with higher vibrational energies.

3.6. Vapor Pressure Data

Various vapor pressure measurements were tested with the aid of the third law. At experimental temperatures the vapor is predominantly monatomic Si(g) (99% at 2000 K). These numerical third law calculations yielded the following $\Delta_{sub}H^\circ$ (298.15 K) values:

Source	$\Delta_{sub}H^\circ$ (298.15 K), kJ mol^{-1}
Chegodaev *et al.*,[29] 1273–2223 K, Evaporation method	444.46 ± 3.2
Nannichi,[30] 1399–1527 K, Langmuir method	451.45 ± 2.2
Davis *et al.*,[31] 1848–2003 K, Knudsen method	453.71 ± 3.9
Grieveson and Alcock,[32] 1640–2054 K, Transport method	448.74 ± 4.4
Batdorf and Smits,[33] 1473–1601 K, Langmuir method	455.79 ± 2.2

Gulbransen *et al.*,[34] 1373–1623 K	448.10 ± 2.7
Alcock and Grieveson,[35] 1680–1785 K, Knudsen method	451.01 ± 0.21
Drowart and De Maria,[36] 1703–2160 K, Mass spectrometer	447.37 ± 0.64
Bodrov *et al.*,[37] 1697–2085 K, Atomic absorption method	457.05 ± 1.4
Tseplyaeva *et al.*,[38] 1485–1593 K, Knudsen method	383.97 ± 1.8
Baur and Brunner,[39] 1980–2160 K, Boiling point method	374.19 ± 3.7
Ruff and Konschak,[40] 2163–2468 K, Boiling point method	362.63 ± 10.6
Van Wartenberg,[41] 1473–1873 K, Transport method	371.68 ± 8.5
Recommended value	450.00 ± 4.0

Stull *et al.*[42] indicated that earlier boiling point measurements yielded considerably lower $\Delta_{sub}H^\circ$ (298.15 K) values possibly due to decomposition of the alumina and silicon carbide containers. Recently Bodrov *et al.*[37] pointed out that these lower values might be due to the formation of SiO. Therefore, no weight was given to these low values.

For completeness of this report, the values for p_{total} reported in Table 7 are calculated using $\Delta_{sub}H^\circ$ (298.15 K) and the Gibbs energy values for Si(s,l) and Si(g) from Table 5 and $\Delta_{sub}H^\circ$ (298.15 K) = 294 972 J mol^{-1} for 1/2 Si_2 and $\Delta_{sub}H^\circ$ (298.15 K) = 212 000 J mol^{-1} for 1/3 Si_3, both values taken from Stull *et al.*[42]

Table 7. Recommended vapor pressure of silicon[a]

[Temperature, K; vapor pressure, atm.]

T	P_{Si}	P_{Si_2}	P_{Si_3}	P_{total}
298.15	8.875×10^{-72}	4.768×10^{-94}	4.482×10^{-101}	8.88×10^{-72}
300	2.719×10^{-71}	2.069×10^{-93}	2.181×10^{-100}	2.72×10^{-71}
400	1.059×10^{-51}	9.580×10^{-68}	1.031×10^{-72}	1.06×10^{-51}
500	5.994×10^{-40}	2.289×10^{-52}	3.962×10^{-56}	5.99×10^{-40}
600	4.067×10^{-32}	3.947×10^{-42}	4.324×10^{-45}	4.07×10^{-32}
700	1.582×10^{-26}	7.890×10^{-35}	3.195×10^{-37}	1.58×10^{-26}
800	2.443×10^{-22}	2.317×10^{-29}	2.471×10^{-31}	2.44×10^{-22}
900	4.389×10^{-19}	4.090×10^{-25}	9.152×10^{-27}	4.39×10^{-19}
1000	1.552×10^{-16}	1.010×10^{-21}	4.043×10^{-23}	1.55×10^{-16}
1100	2.335×10^{-14}	5.974×10^{-19}	3.809×10^{-20}	2.34×10^{-14}
1200	1.370×10^{-12}	1.209×10^{-16}	1.126×10^{-17}	1.37×10^{-12}
1300	4.278×10^{-11}	1.073×10^{-14}	1.369×10^{-15}	4.28×10^{-11}
1400	8.133×10^{-10}	4.982×10^{-13}	8.228×10^{-14}	8.14×10^{-10}
1500	1.040×10^{-8}	1.378×10^{-11}	2.835×10^{-12}	1.04×10^{-8}
1600	9.636×10^{-8}	2.502×10^{-10}	6.206×10^{-11}	9.67×10^{-8}
1687(s)	5.377×10^{-7}	2.343×10^{-9}	6.684×10^{-10}	5.41×10^{-7}
1687(ℓ)	5.377×10^{-7}	2.343×10^{-9}	6.684×10^{-10}	5.41×10^{-7}
1700	6.662×10^{-7}	3.038×10^{-9}	8.599×10^{-10}	6.70×10^{-7}
1800	3.117×10^{-6}	1.969×10^{-8}	5.252×10^{-9}	3.14×10^{-6}
1900	1.238×10^{-5}	1.044×10^{-7}	2.634×10^{-8}	1.25×10^{-5}
2000	4.274×10^{-5}	4.674×10^{-7}	1.117×10^{-7}	4.33×10^{-5}
2200	3.619×10^{-4}	6.167×10^{-6}	1.335×10^{-6}	3.69×10^{-4}
2400	2.137×10^{-3}	5.240×10^{-5}	1.036×10^{-5}	2.20×10^{-3}
2600	9.563×10^{-3}	3.176×10^{-4}	5.781×10^{-5}	9.94×10^{-3}
2800	3.444×10^{-2}	1.477×10^{-3}	2.490×10^{-4}	3.62×10^{-2}
3000	0.104	5.561×10^{-3}	8.736×10^{-4}	0.110
3200	0.274	1.763×10^{-2}	2.594×10^{-3}	0.294
3400	0.643	4.856×10^{-2}	6.716×10^{-3}	0.698
3490	0.914	7.380×10^{-2}	9.960×10^{-3}	0.998
3500	0.949	7.702×10^{-2}	1.035×10^{-2}	1.036
3514	1.000	8.196×10^{-2}	1.097×10^{-2}	1.093
3600	1.369	0.119	1.552×10^{-2}	1.504

[a] 1 atm = 101325 Pa

Si(s,l) = Si(g,1 atm)

$\Delta_{sub}H^\circ$ (298.15 K) = 450.000 ± 4.2
$\Delta_{sub}H^\circ$ (0 K) = 445.664
$\Delta_{vap}S^\circ$ (3513 K) = 109.380 ± 1.14

Si(s,l) = 1/2 Si_2(g,1 atm)

$\Delta_{sub}H^\circ$ (298.15 K) = 294.972 ± 6.3
$\Delta_{sub}H^\circ$ (0 K) = 293.554

Si(s,l) = 1/3 Si_3(g,1 atm)

$\Delta_{sub}H^\circ$ (298.15 K) = 212.000 ± 14.0
$\Delta_{sub}H^\circ$ (0 K) = 210.563

p_{total}, atm	T, K
10^{-10}	1329
10^{-9}	1408
10^{-8}	1499
10^{-7}	1602
10^{-6}	1725
10^{-5}	1883
10^{-4}	2074
10^{-3}	2308
10^{-2}	2601
10^{-1}	2980
1	3490

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

3.7. References

[1] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1984), Vol. 2.
[2] L. D. Lucas and G. Urbain, C. R. Acad. Sci. **225**, 2414 (1962).
[3] P. B. Kantor, A. N. Kisel, and E. N. Fomichev, Ukr. Fiz. Zh. (Ukr. Ed.) **5**, 358 (1960).
[4] M. Olette, C. R. Acad. Sci. **244**, 1033 (1957).
[5] M. Hansen, H. D. Kessler, and D. J. McPherson, Trans. Am. Soc. Met. **44**, 518 (1952).
[6] M. L. V. Gayler, Nature (London) **142**, 478 (1938).
[7] F. Hoffman and A. Schulze, Phys. Z. **38**, 901 (1938).
[8] P. H. Keesom and G. Seidel, Phys. Rev. **113**, 33 (1959).
[9] P. Flubacher, A. J. Leadbetter, and J. A. Morrison , Philos. Mag. **4**, 273 (1959).
[10] G. I. Kalishevich, P. V. Gel'd, and R. P. Krentis, Russ. J. Phys. Chem. **39**, 1602 (1965).
[11] C. T. Anderson, J. Am. Chem. Soc. **52**, 2301 (1930).
[12] P. V. Gul'tyaev and A. V. Petrov, Sov. Phys.-Solid State **1**, 330 (1959).
[13] A. S. Russell, Phys. Z. **13**, 59 (1912).
[14] S. M. Letun, P. V. Gel'd, and N. N. Serebrennikov, Russ. Metall. **6**, 97 (1965).
[15] P. V. Gel'd and R. P. Krentis, in *Experimental Techniques and Methods for High Temperature Measurements* (Nauka, Moscow, 1966), pp. 197–205.
[16] S. M. Letun and P. V. Gel'd, Elektrokhim. Margantsa Akad. Nauk Gruz. SSR **3**, 287 (1967).
[17] N. Pearlman and P. H. Keesom, Phys. Rev. **88**, 398 (1952).
[18] R. H. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, *Selected Values of Thermodynamic Properties of the Elements* (ASM, Metals Park, OH, 1973).
[19] V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veitz, V. A. Medvedev, G. A. Khachkuruzov, and V. S. Yungman, *Thermodynamic Properties of Individual Substances* (High Temperature Institute, Academy of Sciences of the USSR, Moscow, 1979), Vol. II.
[20] Report of the CODATA Task Group, J. Chem. Thermodyn. **10**, 903 (1978).
[21] B. North and K. E. Gilchrist, Ceram. Bull. **60**, 549 (1981).
[22] J. P. Dismukes, L. Ekstrom, E. F. Hockings, I. Kudman, N. E. Lindenblad, R. E. Miller, F. D. Rosi, and E. F. Steigmeier, "Thermoelectric Materials for Power Conversion," RCA Laboratories Quarterly Progress Report, 1963 [AD 441 793].

[23]T. Kurosawa, R. Hasegawa, and T. Yogihashi, Trans. Natl. Res. Inst. Metals (Tokyo) **7**, 222 (1965).
[24]D. Gerlich, B. Abeles, and R. E. Miller, J. Appl. Phys. **36**, 76 (1965).
[25]D. H. Dennison, Institute for Atomic Research, Ames, IA: quoted by H. R. Shanks, P. D. Maycock, P. H. Sidles, and G. C. Danielson, Phys. Rev. **130**, 1743 (1963).
[26]N. M. Serebrennikov and P. V. Gel'd, Dokl. Akad. Nauk SSSR **87**, 1021 (1952).
[27]A. Magnus, Ann. Phys. (Leipzig) **70**, 303 (1923).
[28]Yu. M. Golutvin and E. G. Maslennikova, Russ. Metall. (2), 129 (1968).
[29]A. I. Chegodaev, E. L. Dubinin, A. I. Timofeev, N. A. Vatolin, and V. I. Kapitanov, Russ. J. Phys. Chem. **52**, 1229 (1978).
[30]Y. Nannichi, Jpn. J. Appl. Phys. **2**, 586 (1963).
[31]S. G. Davis, D. F. Anthrop, and A. W. Searcy, J. Chem. Phys. **34**, 659 (1961).
[32]P. Grieveson and C. B. Alcock, in *Special Ceramics*, edited by P. Popper (Heywood, London, 1960), pp. 183–208.
[33]R. L. Batdorf and F. M. Smits, J. Appl. Phys. **30**, 259 (1959).
[34]E. A. Gulbransen, K. F. Andrew, and F. A. Brassart, J. Electrochem. **113**, 834 (1966).
[35]C. B. Alcock and P. Grieveson, J. Inst. Met. **90**, 304 (1961).
[36]J. Drowart and G. De Maria, in *Proceedings of the Conference on Silicon Carbide*, edited by J. R. O'Connor and J. Smiltens (Pergamon, New York, 1960), pp. 16–23.
[37]N. V. Bodrov, G. I. Nikolaev, and A. M. Nemets, Inorg. Mater. (USSR) **19**, 639 (1983).
[38]A. V. Tseplyaeva, Yu. A. Priselkov, and V. V. Karelin, Vestn. Mosk. Univ. **15**, 36 (1960).
[39]E. Baur and R. Brunner, Helv. Chim. Acta **17**, 958 (1934).
[40]O. Ruff and M. Konschak, Z. Elektrochem. **32**, 515 (1926).
[41]H. Van Wartenberg, Z. Elektrochem. **19**, 482 (1913).
[42]D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed., (U.S. GPO, Washington, DC, 1971), NSRDS-NBS 37.
[43]M. Mertig, G. Pompe, and E. Hegenbarth, Solid State Commun. **49**, 369 (1984).
[44]L. Brewer (private communications, University of California, Berkeley, 1984).
[45]V. I. Chetykhin, I. N. Zedina, and S. Ye. Vaisburd, Inzh. Fiz. Zh. **34**, 870 (1978).

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