Specific Heat of Aluminum from Zero to Its Melting Temperature and Beyond

Equation for Representation of the Specific Heat of Solids

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The available experimental data on the specific heat of aluminum have been reviewed, analyzed, and re-evaluated, and recommended values are presented in both tabular and graphical forms. The paper discusses in detail the considerations involved in arriving at the recommended values, with a full assessment of the experimental data and theoretical and empirical guidelines on which the evaluation was based. The recommended values were generated from a spline function representation of the reliable data in the literature.

The synthesis of existing fragments of knowledge is just as important as the original experimental observations, or even more so. The availability of adequate reference data is very essential to those engaged in theoretical research as well as to the applied scientists and engineers who are involved with design, construction, and operation of equipment.

The rapid growth of science and technology has brought a realization that the present limitations in many areas of scientific developments are a direct result of scarcity of knowledge of the properties of materials. A great deal of attention has been given to research studies on the thermophysical properties of materials in recent years. As a result, the volume of research literature has increased tremendously. Steps therefore have to be taken to ensure that this body of information be organized, synthesized, evaluated, and disseminated to the ultimate users, the engineers and scientists.

SPECIFIC HEAT CORRELATION EQUATIONS

Experimental investigations on the specific heats of solid substances may be divided into three subregions. The liquid helium region is roughly between 0.1° and 4° K; the intermediate temperature range is 4° to 300° K; and the high temperature range is 298.15° K and above, which sometimes extends beyond the melting point. In the range from 0.1° to 4° K, where $C_p = C_v$, theoretical expressions have been derived by several investigators (*4, 5, 6, 8, 11*) to account for the variations of C_v with temperature. Very recently the equation most widely used was the cube law with or without the higher order lattice term and linear electronic term—i.e.,

$$C_v = \gamma T + \beta T^3 + \delta T^5 \tag{1}$$

or

$$C_v = \gamma T + \beta T^3 \tag{2}$$

and for nonmetals

$$C_v = \beta T^3 \tag{3}$$

where γT represents the electronic specific heat, βT^3 the lattice specific heat, and δT^5 the second-order lattice specific heat term. Additional contributions to the specific heat, such as those arising from the excitation of spin waves, may also be present in some substances. In such cases, the equation for the specific heat may take the form

$$C_v = \gamma T + \beta T^3 + \alpha T^{3/2} \tag{4}$$

For some metals—for example, cobalt—there is a large nuclear contribution to the specific heat which masks any spin wave or additional lattice contributions in the temperature range between 0.1° and 4° K. For this case, the expression for the specific heat takes the form

$$C_v = \gamma T + \beta T^3 + \kappa T^{-2} \tag{5}$$

When applicable to a particular substance, the values of the constants, γ, β, α, and κ may be obtained by fitting the correct form of the equation to the measured values of specific heat.

The variation of the specific heat with temperature in the range 5° to 300° K has not been successfully represented by any type of theoretical or empirical equation. Part of the reason may be the rapid rise in values of specific heat in this region. Furthermore, the values measured are C_p instead of C_v and C_p is no longer equal to C_v in this temperature range.

The specific heat functions above 298.15° K are derived from relative enthalpy data. Several fitting schemes have been proposed for these functions, but the most successful ones are

$$C_p = a + bT \tag{6}$$

$$C_p = a + bT + cT^2 \tag{7}$$

$$C_p = a + bT + cT^{-2} \tag{8}$$

The last equation proposed by Maier and Kelley (*26*) has been used successfully by Kelley (*19*) in recommending and correlating high temperature thermal data of normally

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behaving substances in the solid state. The value of specific heat obtained from Equation 8 at 298.15° K usually does not agree with the result obtained from low temperature calorimetry measurements (5° to 300° K) unless the constants in Equation 8 have been obtained by using assumed correct C_p values derived from these low temperature measurements.

An empirical correlation equation that would represent the specific heat of solids, especially in the temperature range 5° to 300° K, has long been overdue. In this paper we propose a spline (*31*) function to represent the specific heat of aluminum over the entire range 0.1° to 933.2° K with an accuracy of from 0.1 to 5%. The term "spline function" is derived from a third-degree spline function that approximates the behavior of a mechanical spline used by draftsmen to draw a smooth curve. Those interested in the spline fit program may direct their inquiries to TPRC, in care of the director.

ASSESSMENT OF EXPERIMENTAL DATA

In arriving at the recommended values for specific heat from the available experimental data sources, several criteria were used. Considerations were given to the characterization of the specimens used: purity, thermal history, and final state of the specimens, environment under which measurements were made, and existence of phase or magnetic transitions. Consistencies with results obtained by the different methods of measurement over different temperature ranges were also given much weight in analyzing the data. The appropriate limits of experimental uncertainty were independently assessed. Large linear and logarithmic plots of the literature data helped in selecting the "best values." Some literature values may be judged better than others, for reasons that sometimes may be difficult to formulate. Finally, the reputations of the investigators and the laboratories which produced the experimental results were given careful consideration.

SPECIFIC HEAT OF ALUMINUM

The specific heat of aluminum was measured by Tilden (*36*) as early as 1903. Since then, there have appeared several independent experimental determinations. Measurements on high purity aluminum were reported by McDonald (*23*) for the range 298.15° to 1700° K and by Berg (*3*) between 2.7° and 20° K. Recently Brooks and Bingham (*7*) measured the specific heat of aluminum between 330° and 893° K and Leadbetter (*22*) between 300° and 772° K using adiabatic calorimeters. The specimens used by Berg (*3*) and McDonald (*23*) were supplied by the United Minerals and Chemical Corp., with a stated purity of 99.9999% aluminum. Subsequent spectrographic analysis showed this purity to be more nearly 99.99%. The specimen used by Brooks and Bingham is 99.991% pure, while that used by Leadbetter is 99.995% aluminum. Leadbetter's sample was annealed at 600° C for one hour and then slowly cooled. Selected values for the specific heat of aluminum were based on the experimental data obtained by McDonald (*23*) in the temperature range 298.15° to 1700° K. These values agree well with the data reported by Hirano *et al.* (*16*), Pochapsky (*29*), and Griffiths and Griffiths (*14*). The recommended values are about 4% higher than those given by Kelley (*19*), Stull and Sinke (*35*), and Hultgren *et al.* (*18*) at 900° K, decreasing to about 0.3 to 0.5% at 500° K. At 298.15° K, although the values agree precisely, the agreement may be considered fortuitous. The average specific heat values reported by Brooks and Bingham (*7*) are 0.84% higher at 500° K and about 2% higher at 850° K than the recommended values. Leadbetter's data are about 3.7% lower at 750° K and about 0.55% lower at 500° K than the recommended values. The specific heat value selected for liquid aluminum is 0.2813 cal g^{-1} K^{-1} from 933.2° to 1700° K and is based on the value given by McDonald (*23*). This value is about 8% higher than the value 0.2595 cal g^{-1} K^{-1} given by Kelley (*19*), Stull and Sinke (*35*), and Hultgren *et al.* (*18*). The liquid enthalpy data of Awbery and Griffiths (*2*) give a value of 0.33 cal g^{-1} K^{-1} for the mean specific heat of liquid aluminum between 933° and 1033° K instead of the value 0.66 cal g^{-1} K^{-1} given by the authors, while Umino (*37*) reported a value of 0.2309 cal g^{-1} K^{-1} between 933° and 1273° K.

The recommended values for the specific heat of aluminum for the temperature range between 20° and 298.15° K were based largely on the data reported by Giauque and Meads (*12*). These values were in agreement with those obtained by Maier and Anderson (*25*). The selected values are about 0.8% higher at 55° K and 1% higher at 296° K than the values given by Maier and Anderson for annealed aluminum. For hard-drawn aluminum, the specific heat values reported by Maier and Anderson agree to within 1.5% maximum deviation. At the overlapping temperature range of 15° to 20° K, the values reported by Kok and Keesom (*20*) are about 12% higher than those reported by Giauque and Meads (*12*). The specific heat values reported by Phillips (*28*) were selected below 4° K. These values are consistently lower by as much as 13% of the values obtained by Kok and Keesom (*20*) from 1.14° to 4.0° K. The recent measurements reported by Berg (*3*)

Table I. Recommended Specific Heat of Aluminum

T, K	Normal, C_p, Cal G^{-1} K^{-1}	Superconducting, C_p, Cal G^{-1} K^{-1}	T, K	Normal, C_p, Cal G^{-1} K^{-1}
0.118	1.580×10^{-6}		60.0	5.097×10^{-2}
0.150	1.942		70.0	6.851
0.189	. . .	5.847×10^{-8}	80.0	8.536
0.200	2.519	1.058×10^{-7}	90.0	1.010×10^{-1}
0.250	3.098	2.432	100.0	1.152
0.300	3.681	5.960	150.0	1.655
0.350	4.267	1.191×10^{-6}	200.0	1.922
0.400	4.858	2.033	250.0	2.070
0.450	5.453	3.107	273.15	2.116
0.500	6.651	4.394	298.15	2.156
0.550	6.655	5.866	300.0	2.159
0.600	7.261	7.500	350.0	2.222
0.650	7.872	9.275	400.0	2.273
0.700	8.487	1.117×10^{-5}	450.0	2.321
0.750	9.106	1.319	500.0	2.370
0.800	9.727	1.530	550.0	2.421
0.850	1.035×10^{-5}	1.751	600.0	2.478
0.900	1.098	1.982	650.0	2.539
0.950	1.162	2.222	700.0	2.606
1.000	1.225	2.471	750.0	2.679
1.196	1.473	3.294	800.0	2.758
1.50	1.878		850.0	2.844
2.00	2.571		900.0	2.935
3.00	4.171		(S) 933.2	3.000
4.00	6.170		(l) 933.2	2.813
5.00	8.678		950.0	2.813
6.00	1.180×10^{-4}		1000	2.813
7.00	1.566		1100	2.813
8.00	2.035		1200	2.813
9.00	2.599		1300	2.813
10.0	3.269		1400	2.813
20.0	1.992×10^{-3}		1500	2.813
30.0	7.608		1600	2.813
40.0	1.848×10^{-2}		1700	2.813
50.0	3.371			

1 calorie = 4.1840 absolute joules; atomic weight = 26.9815; 0° C = 273.15° K.

were the basis for the recommended values between 4° and 20° K. Between 2.5° and 4° K, Berg's results agree to within 1% with those of Phillips (*28*). The recommended values are about 9 to 20% lower than the values given by Hultgren *et al.* between 1.196° and 4° K. Their values were based on the data of Kok and Keesom (*20*), which are believed to be not sufficiently precise. At the overlapping temperature range (15° to 21° K), the data reported by Berg (*3*) are preferred to those of Giauque and Meads (*12*). Between 300° and 800° K, the recommended values are very close to the average of the values reported by Leadbetter (*22*) and Brooks and Bingham (*7*). At 800° K and above, the recommended values are much closer to Brooks and Bingham's data than to Leadbetter's. Since two of the most recent supposedly accurate measurements of Leadbetter (*22*) and Brooks and Bingham (*7*) differ by as much as 4% (300° < T < 900° K), the authors feel that the recommended values based on the data of McDonald, which are very close to the average of the former two measurements, should be accepted as tentative values until more accurate specific heat measurements on aluminum are reported in the literature, in order to resolve the discrepancy.

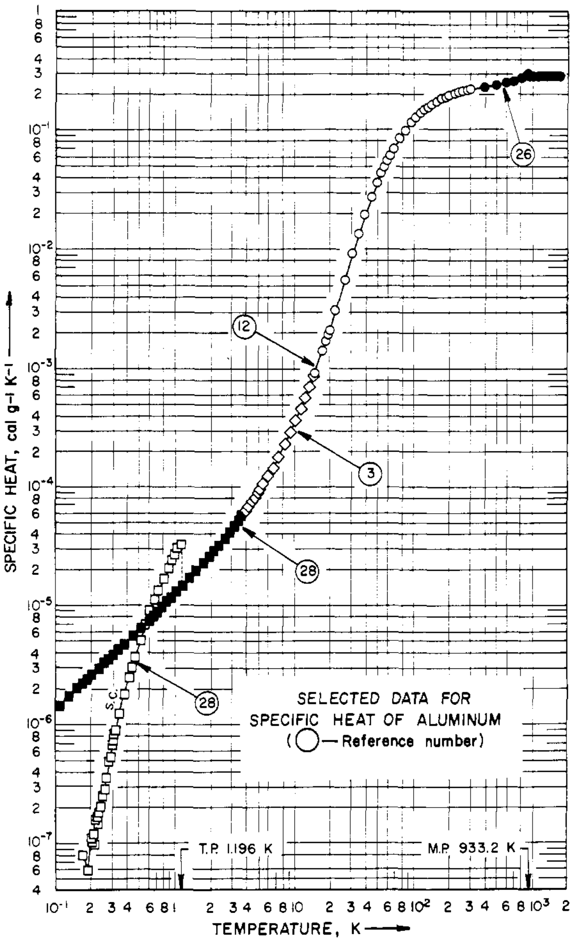

Figure 1. Relation of selected specific heat to temperature

Table I gives smoothed recommended values for the specific heat of aluminum from 0.1° to 1700° K, and the derived thermodynamic values are presented in Table II. The melting temperature of aluminum is taken as 933.2° K. The graph of the selected specific heat *vs.* temperature is shown in Figure 1. The available high temperature data have been plotted on a large linear scale for comparative evaluation. It is based on this large plot that several sets of data reported by Laemmel (*21*), Schubel (*33*), Griffiths and Griffiths (*15*), Eastman *et al.* (*10*), Goodman (*13*), Seekamp (*34*), Quinney and Taylor (*30*), Avramescu (*1*), Mader (*24*), Parker *et al.* (*27*), Hopkins (*17*), Rorer *et al.* (*32*), Yurkov and Ivoniskaya (*38*), and Dixon *et al.* (*9*) were eliminated from the final selection. This plot is not presented here, because its reduction in size has made the points indistinguishable. Figure 2 shows the departure plot of the selected data from the recommended values. The recommended values represent the selected experimental data with an average deviation of 0.5% and a maximum deviation of 4.6% from 0.1° to 1700° K. The accuracy of the selected data from which the recommended values were generated may be taken to be less than 5% above 298.15° K and from 0.1 to 3% between 0.1° and 298.15° K.

The constants for Equation 9 were determined by Phillips (*28*), which he used to represent the liquid helium range (0.1° to 4.0° K) for the specific heat at the normal state of aluminum. This equation is given by

$$C_v = \gamma T + \frac{12}{5}\pi R\left(\frac{T}{\theta_D}\right)^3 \qquad (9)$$

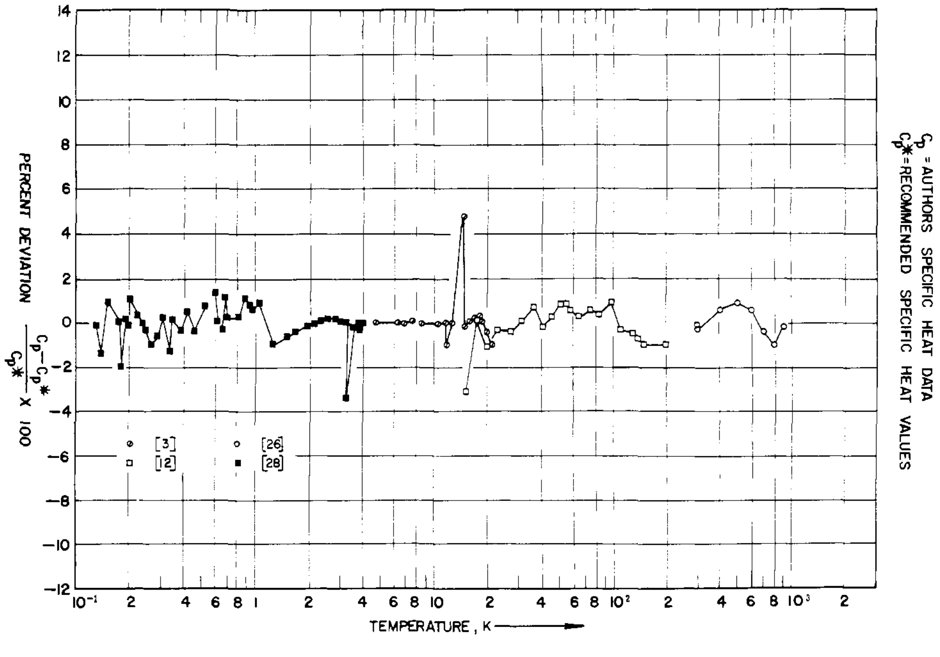

Figure 2. Departure plot for aluminum

where

T = temperature, ° K
$\gamma = 1.350 \times 10^{-3}$ joule mole^{-1} K^{-2}
$\theta_D = 427.7°$ K limiting Debye temperature
$R = 8.3143$ joules mole^{-1} K^{-1}

Equation 9 represents Phillips' experimental data to within 7% between 0.1° and 4° K. A spline (*31*) fitting technique has been applied to Phillips' specific heat data between 0.1° and 4° K, and the equation was found to be of the form

$$\ln C_p = A + B \ln T + C(\ln T)^2 + D(\ln T)^3 \qquad (10)$$

This represents his data to within 1%. A computer program was also used to generate the values for the specific heat of aluminum between 0.1° and 933.2° K, using the same

Table II. Thermodynamic Functions for Aluminum

(Cal, g, ° K)

T	C_p'	$\frac{H_T^0 - H_0^0}{T}$	$H_T^0 - H_0^0$	S_T^0	$\frac{-(G_T^0 - H_0^0)}{T}$	$-(G_T^0 - H_0^0)$	$H_T - H_{298.15}$
0.1186	1.156×10^{-5}	8.032×10^{-8}	9.526×10^{-9}	1.593×10^{-7}	7.899×10^{-8}	9.368×10^{-9}	
0.15	1.154	4.322×10^{-7}	6.482×10^{-8}	5.713	1.391×10^{-7}	2.087×10^{-8}	
0.20	1.156	8.818	1.764×10^{-7}	1.209×10^{-6}	3.272	6.545	
0.25	1.161	1.267×10^{-6}	3.168	1.833	5.662	1.416×10^{-7}	
0.30	1.169	1.621	4.863	2.450	8.288	2.487	
0.35	1.177	1.957	6.849	3.061	1.104×10^{-6}	3.864	
0.40	1.185	2.283	9.131	3.669	1.387	5.547	
0.45	1.194	2.602	1.171×10^{-6}	4.276	1.674	7.533	
0.50	1.202	2.917	1.458	4.881	1.965	9.823	
0.60	1.218	3.540	2.124	6.091	2.552	1.531×10^{-6}	
0.70	1.233	4.159	2.911	7.302	3.144	2.201	
0.80	1.248	4.777	3.822	8.517	3.739	2.992	
0.90	1.262	5.397	4.857	9.735	4.338	3.904	
1.0	1.275	6.019	6.019	1.096×10^{-5}	4.939	4.939	
1.5	1.337	9.176	1.376×10^{-5}	1.715	7.973	1.196×10^{-5}	
2.0	1.443	1.243×10^{-5}	2.487	2.349	1.106×10^{-5}	2.211	
2.5	1.595	1.583	3.958	3.003	1.419	3.548	
3.0	1.780	1.943	5.829	3.683	1.739	5.218	
3.5	1.994	2.328	8.146	4.395	2.067	7.236	
4.0	2.236	2.741	1.096×10^{-4}	5.145	2.405	9.619	
4.5	2.504	3.186	1.434	5.939	2.753	1.239×10^{-4}	
5.0	2.799	3.668	1.834	6.781	3.113	1.557	
6.0	3.475	4.754	2.853	8.630	3.875	2.325	
7.0	4.254	6.027	4.219	1.073×10^{-4}	4.701	3.291	
8.0	5.143	7.515	6.012	1.312	5.601	4.481	
9.0	6.151	9.245	8.321	1.583	6.583	5.925	
10.0	7.288	1.125×10^{-4}	1.125×10^{-3}	1.890	7.658	7.658	
15.0	1.529×10^{-4}	2.640	3.960	4.116	1.476×10^{-4}	2.214×10^{-3}	
20.0	3.197	5.390	1.078×10^{-2}	7.965	2.575	5.149	
25.0	5.559	1.029×10^{-3}	2.571	1.454×10^{-3}	4.254	1.063×10^{-2}	
30.0	8.206×10^{-4}	1.821×10^{-3}	5.462×10^{-2}	2.498×10^{-3}	6.778×10^{-4}	2.033×10^{-2}	
35.0	1.092×10^{-3}	2.973	1.041×10^{-1}	4.013	1.040×10^{-3}	3.640	
40.0	1.338	4.518	1.807	6.052	1.534	6.134	
45.0	1.534	6.461	2.907	8.635	2.174	9.783	
50.0	1.664	8.779	4.390	1.175×10^{-2}	2.972	1.486×10^{-1}	
60.0	1.761	1.436×10^{-2}	8.616	1.941	5.048	3.029	
70.0	1.731	2.085	1.459×10^{0}	2.859	7.740	5.418	
80.0	1.629	2.787	2.229	3.885	1.098×10^{-2}	8.782	
90.0	1.492	3.514	3.162	4.981	1.468	1.321×10^{0}	
100.0	1.344	4.244	4.244	6.120	1.876	1.876	
150.0	7.216×10^{-4}	7.595	1.139×10^{1}	1.185×10^{-1}	4.253	6.379	
200.0	3.857	1.020×10^{-1}	2.041	1.702	6.812	1.362×10^{1}	
250.0	2.225	1.217	3.042	2.148	9.310	2.328	
273.15	1.793	1.291	3.527	2.333	1.042×10^{-1}	2.847	
298.15	1.471	1.362	4.061	2.520	1.158	3.453	
300.0	1.451	1.367	4.101	2.534	1.167	3.500	0.40
350.0	1.104	1.485	5.197	2.871	1.387	4.853	11.36
400.0	9.729×10^{-5}	1.580	6.320	3.171	1.591	6.365	22.60
450.0	9.559	1.660	7.469	3.442	1.782	8.020	34.08
500.0	1.000×10^{-4}	1.728	8.641	3.689	1.961	9.803	45.81
550.0	1.079	1.789	9.839	3.917	2.128	1.171×10^{2}	57.78
600.0	1.176	1.844	1.106×10^{2}	4.130	2.286	1.372	70.03
650.0	1.285	1.895	1.232	4.330	2.435	1.583	82.57
700.0	1.400	1.943	1.360	4.522	2.578	1.805	95.43
750.0	1.520	1.990	1.493	4.704	2.714	2.035	108.6
800.0	1.643	2.036	1.628	4.879	2.844	2.275	122.2
850.0	1.769	2.081	1.768	5.049	2.969	2.523	136.2
900.0	1.897	2.125	1.913	5.214	3.089	2.780	150.7
933.2	1.984	2.155	2.011	5.322	3.166	2.955	160.5

Table III. Spline Function Coefficients

Temp. Range, °K	*a*	*b*	*c*	*d*
		NORMAL STATE ALUMINUM		
0.1185–1.3699	-1.3359×10	8.6800×10^{-1}	4.9412×10^{-2}	-2.7849×10^{-3}
1.3699–5.5639	-1.0979×10	1.0598	2.8963×10^{-2}	9.5029×10^{-2}
5.5639–15.2306	−9.1753	1.7010	4.2853×10^{-1}	2.4758×10^{-2}
15.2306–19.7069	−7.0025	2.6394	5.0337×10^{-1}	1.3519
19.7069–21.8306	−6.2659	3.1681	1.5487	−4.8023
21.8306–50.2698	−5.9306	3.3342	7.4521×10^{-2}	-4.8073×10^{-1}
50.2698–933.2	−3.3767	2.4552	−1.1284	1.8572×10^{-1}
		SUPERCONDUCTING STATE ALUMINUM		
0.1887–0.2051	-1.6655×10	1.7500×10	-1.6109×10^{2}	5.516×10^{2}
0.2051–0.2259	-1.5996×10	2.1489	-2.3362×10	2.5052×10^{2}
0.2259–0.2371	-1.5781×10	4.6494	4.9246×10	-5.0617×10^{2}
0.2371–0.2488	-1.5498×10	5.8638	-2.4105×10	1.7893×10^{2}
0.2488–0.3018	-1.5251×10	4.7876	1.8246	−6.4960
0.3018–1.1526	-1.4305×10	4.7652	−1.9408	4.4993×10^{-1}

spline technique. The experimental data reported by Phillips (*28*), Berg (*3*), Giauque and Meads (*12*), and McDonald (*23*) were used as the basis for the recommended values over the entire range 0.1° to 933.2° K with the aid of the spline function (*10*). The spline function has six knots, each represented within a temperature interval by Equation 10. The four term coefficients for the function Equation 11 are given in Table III.

$$\ln C_p = a + b[\ln T - \ln T_i] + c[\ln T - \ln T_i]^2 + d[\ln T - \ln T_i]^3 \quad (11)$$

where T = variable temperature in a given interval, and T_i = minimum temperature in the interval.

The same Equation 11 was also applied to the superconducting state specific heat data of Phillips, with constants also given in Table III. The recommended specific heat values presented in Table I were generated from Equation 11 with coefficients given in Table III. Earlier attempts to represent the specific heat of aluminum over the entire range 0.1° to 933.2° K by any other continuous function with reasonable accuracy have been unsuccessful, because C_p values change rapidly from about 10^{-6} cal g^{-1} K^{-1} at 0.1° K to 10^{-1} cal g^{-1} K^{-1} at 933.2° K. The spline function is the only continuous function that best represents the specific heat data for aluminum over the entire range of temperature, with an average deviation of 0.5%. The spline function could also provide an attractive approach for representing the specific heat of other solid substances over a wide range of temperatures. Thermodynamic functions given in Table III were calculated from the recommended smoothed specific heat values by numerical integration with the aid of the computer. The thermodynamic equations used were

$$H_T^0 - H_0^0 = \int_0^T C_p^0 dT \quad (12)$$

$$S_T^0 = \int_0^T \frac{C_p dT}{T} \quad (13)$$

$$G_T^0 - H_0^0 = \int_0^T S^0 dT = (H_T^0 - H_0^0) - T S_T^0 \quad (14)$$

The enthalpy function, $(H_T^0 - H_0^0)/T$, and the Gibbs energy function, $(G_T^0 - H_0^0)/T$, were obtained from values of Equations 12 and 14 by dividing by the corresponding temperature. The function (dC_p/dT) indicates the smoothness of the recommended values of C_p and in general shows the manner in which the specific heat changes with temperature.

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Estimates of Thermodynamic Properties of H_2O in Equilibrium with H, H_2, O, O_2, and OH

Temperature 1000° to 6000° C and Pressure 10 to 250,000 Bars

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Pressure-volume-temperature measurements made at temperatures less than 1000° C. and pressures up to 250,000 bars are combined with chemical equilibrium calculations to give the thermodynamic properties of water from 1000° to 6000° C. and from 10 to 250,000 bars.

Pressure-volume-temperature measurements for water have been made at temperatures less than 1000° C. and pressures up to 250 kbars (*4, 9-12, 14*). These data have been used to determine thermodynamic properties in this pressure-temperature range (*8, 11, 16*). At higher pressures and temperatures, theoretical models have been used to estimate thermodynamic properties (*7, 13*). The present work combines chemical equilibrium calculations of dissociated water made by the present author with the data of Holser and Kennedy (*10*) and Rice and Walsh (*14*) to give thermodynamic functions for water in the temperature range 1000° to 6000° C. and pressures from 10 bars to 250 kbars. The chemical equilibrium calculations are similar to those Rybakov (*15*), but Rybakov does not list the reference conditions he assumed for his calculations and, consequently, his work cannot be compared with existing data. A reference energy state of the molecular species as ideal gases at 0° K. and 1 bar is used for the functions reported here. (0° K. is taken to be −273° C.)

The chemical equilibrium calculations were performed using the method due to Brinkley (*5, 6*), which is incorporated in the HUG computer code (*2*). Brinkley's method is based on a chemically reacting mixture of perfect gases in thermodynamic equilibrium. Dissociation products considered to be in the mixture are H, H_2, O, O_2, OH, and H_2O. The thermochemical data for these species were taken from the JANEF thermochemical tables, where they are tabulated up to 6000° K. (There is a slight extrapolation of these data, since the calculations were performed to 6000° C. = 6273° K.) Ionization was included in the calculations, but was found to be unimportant.

The perfect gas assumption is invalid if the specific volume is so small that intermolecular forces become important. Accordingly, the chemical equilibrium calculations were considered in error for specific volumes smaller than twice the critical volume, or about 6.4 cm^3 per gram. This criterion is based on comparison of experimental data with the perfect gas law.

METHOD

In general, a change in the Gibbs function is given by

$$dG = -SdT + VdP + \sum_i \frac{\partial G}{\partial n_i} dn_i$$

A change involving only equilibrium states at constant T and P requires

$$\sum_i \frac{\partial G}{\partial n_i} dn_i = 0$$

A closed system consisting of H_2O and its dissociation products in equilibrium is considered here. A change in this system involves only equilibrium states. Consequently,