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Heat capacity of solid zinc from 298.15 to 692.68 K and of liquid zinc from 692.68 to 940 K: thermodynamic function values

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Abstract

The heat capacity of zinc has been determined by adiabatic calorimetry from 298.15 to 940 K. For crystalline zinc $C_{p,\mathrm{m}}$ increases from 25.47 J K^{-1} mol^{-1} at the former temperature to an evenly extrapolated value of 30.96 J K^{-1} mol^{-1} at the triple-point temperature 692.681 K (ITS-90). The estimated heat capacity increment of fusion is 2.46 J K^{-1} mol^{-1}. For liquid zinc the heat capacity decreases from 33.42 J K^{-1} mol^{-1} at T_{fus} to 32.31 J K^{-1} mol^{-1} at 940 K. Thermodynamic function values have been derived and are tabulated for selected temperatures after revaluation of earlier low temperature results.

Keywords: Zinc; Heat capacity; Enthalpy of fusion; Thermodynamic properties

1. Introduction

In two recent thermodynamic property tables [1,2] the evaluations for solid and liquid zinc were based upon results from before 1978, cf. Hultgren et al. [3]. The close agreement between the evaluations is surprising in view of the spread in the results at temperatures above 500 K, see below. The common enthalpy of fusion value in the two evaluations, 7322 J mol^{-1}, is outdated by more recent determinations, and a critical evaluation [4] led to the much lower value of 7068 ± 28 J mol^{-1}. For liquid zinc the above evaluations arrived at a heat capacity $C_{p,\mathrm{m}} = 7.5$ cal K^{-1} mol^{-1} or 31.4 J K^{-1} mol^{-1} with considerable uncertainty. The experimental results spanned the range from ca. 25 J K^{-1} mol^{-1} [5] to ca. 34 J K^{-1} mol^{-1} [6–8].

In the present work the heat capacity of very pure zinc has been measured in the temperature range 300–900 K. Thermodynamic function values have been evaluated and tabulated for selected temperatures.

2. Experimental

The step-wise heated high-temperature adiabatic calorimeter and the measuring technique have been described [9,10]. Zinc shot of 6N purity from the Laboratory of the Government Chemist, Teddington, UK, was used in most of the experiments. The sample mass was about 141 g. The second sample with mass of about 138 g was 5N8 shot from Goodfellow, Cambridge, UK.

Temperatures were measured with an ASL F-18 resistance bridge using a locally constructed 25 Ω platinum-resistance thermometer. This system allows

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a temperature resolution of 3×10^{-5} K. Temperature calibration is performed according to the recommendations supplementing the ITS-90 [11] up to the fusion temperature of aluminium, 933.473 K. The accuracy in the temperature determinations is considered to be within ±0.02 K. Energy is supplied to the internal resistor ca. 20 Ω by a constant current source. The current through the heater is measured every 10 s and the potential drop across the heater every second in between. The potential is measured using a 8.5 digit Hewlett-Packard digital voltmeter. The current is determined by measuring the potential drop over a calibrated resistor. The total time as well as the triggering of the potential and current measurements are measured or controlled using a Keithley counter. The accuracy and precision of the heat capacity determinations are approximately ±0.2% [10].

3. Results and discussion

The experimental molar heat capacity values of solid and liquid zinc are given in Table 1 for $M(\mathrm{Zn}) = 65.409$ g mol^{-1} [12] and presented graphically in Fig. 1a and b. The heat capacity of solid zinc above 298.15 K is in good agreement with the previous determinations by Bronson and Wilson [13] and by Zabetakis [14] over the common region, to 393 and 304 K, respectively. Results by Behrens and Drucker [15] from 273 to 473 K (not shown in Fig. 1a) are at most 1% lower than the present, while those by Kramer and Nölting [16] are about 2% higher in the temperature range 350–550 K, increasing to 4% at 650 K and about 6% at 692.5 K. The results by Wüst et al. [17] indicated a steep rise with temperature up to 34 J K^{-1} mol^{-1} at the melting temperature, while a more moderate rise was observed by Jaeger and Poppema [18]. A close to linear rise extrapolating to ca. 30 J K^{-1} mol^{-1} was found by Umino [7] and Eastman et al. [19]. Similarly the results by Schübel [20] and Ruer and Kremers [21] extrapolate to ca. 28 and 27 J K^{-1} mol^{-1}, respectively. The results by Cordoba [22] from 330 to 680 K—not shown in Fig. 1a—agree with the present results within their reported variation of ±0.7%. Several old results collected by Wüst et al. [14], and three mean values by Awbery and Griffiths [5] are not shown in the figure.

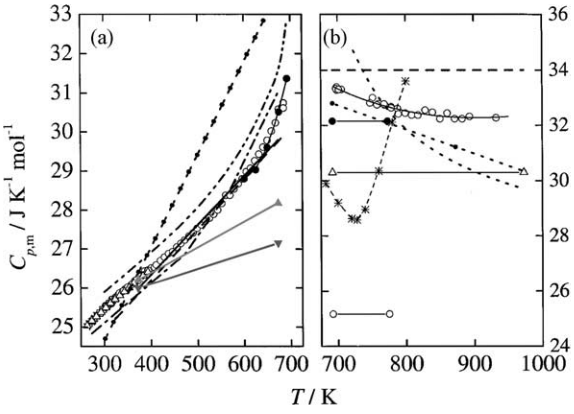

Fig. 1. Heat capacity of solid (a) and liquid (b) zinc. Experimental data: (○—○) Awbery and Griffiths [5], (– – –) Iitaka [6] and Umino [7], (- - -) Förster and Tschentke [8], (△) Bronson and Wilson [13], (+) Zabetakis [14], (– - - -) Kramer and Nölting [16], (- -●- -) Wüst et al. [17], (– - –) Jaeger and Poppema [18], (—) Eastman et al. [19], (—▲—) Schübel [20], (—▼—) Ruer and Kremers [21], (✳- -✳- -✳) Cordoba [22], (—●—●—) Ditmars [23], (△—△) Braune [24].

The heat capacity values by Ditmars [23] were obtained by derivation of the enthalpy increment equation $H(T) - H(273.15\,\mathrm{K})$ presented for results above 594 K. They fall slightly below those obtained here in the temperature region 600–650 K and cross over above to 31.383 J K^{-1} mol^{-1} at the melting temperature. The observed pre-melting enthalpy reached about 50 J mol^{-1} at a temperature 50 mK below the triple-point in Ditmars' experiments, and 13 J mol^{-1} at only 5 mK below for the present sample, in support of its very high purity.

For liquid zinc near the melting temperature, see Fig. 1b, the heat capacity ranges from ≈34.8 J K^{-1} mol^{-1} by Förster and Tschentke [8] to ca. 34 J K^{-1} mol^{-1} by Iitaka [6] and Umino [7] and to 32.8 JK^{-1} mol^{-1} by Wüst et al. [17], 32.165 J K^{-1} mol^{-1} by Ditmars [23], and 31.9 J K^{-1} mol^{-1} by Génot and Hagège [25] over the region 693 to 723 K. Braune [24] reported 30.3 J K^{-1} mol^{-1} from 693 to 1141 K, while Cordoba [22] found a steep decrease from about 29.5 J K^{-1} mol^{-1} at 700 K to 28.7 J K^{-1} mol^{-1} at 730 K, followed by an almost linear increase to 33.5 J K^{-1} mol^{-1} at 800 K. Awbery and Griffiths [5] on the other hand obtained 25.2 J K^{-1} mol^{-1} from 693 to 773 K. Results by Wüst et al. [17] and Förster and Tschentke [8] both show a decrease in heat capacity of the liquid with increasing temperature, which however,

Table 1
Experimental heat capacities of solid and liquid zinc, $M(\mathrm{Zn}) = 65.409\ \mathrm{g\ mol^{-1}}$

T (K)	$C_{p,\mathrm{m}}$ (J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$)
Solid zinc, sample 1	
302.24	25.56
309.26	25.57
316.25	25.72
323.23	25.75
330.24	25.84
337.25	25.91
344.24	25.98
351.24	26.00
358.27	26.10
365.28	26.19
372.30	26.20
379.30	26.31
386.28	26.44
393.26	26.47
400.24	26.52
407.22	26.54
315.21	25.61
323.99	25.77
332.77	25.88
341.53	25.94
350.27	26.03
359.01	26.10
367.73	26.21
376.45	26.31
385.17	26.35
393.88	26.46
411.30	26.60
420.01	26.71
428.72	26.80
437.44	26.89
446.17	26.94
454.91	27.06
463.67	27.15
472.43	27.24
481.20	27.34
489.98	27.42
498.77	27.54
507.59	27.63
516.41	27.72
525.24	27.80
534.35	27.90
542.93	28.01
551.79	28.18
560.64	28.39
569.50	28.39
578.39	28.55
587.29	28.68
596.15	28.81
605.13	28.99
614.04	29.08
622.96	29.27
631.92	29.44
640.91	29.62
649.91	29.79
658.91	30.03
667.92	30.24
674.45	30.59
682.05	30.65
684.81	30.76
684.85	30.75
685.15	30.62
Liquid zinc	
Sample 1	
698.52	33.40
705.56	33.31
751.49	33.01
760.58	32.79
769.71	32.74
778.84	32.68
788.03	32.62
698.33	33.29
697.39	33.34
701.37	33.31
Sample 2	
747.64	32.82
757.94	32.75
768.33	32.78
778.79	32.64
789.18	32.42
799.20	32.45
808.77	32.38
818.03	32.38
828.62	32.56
839.44	32.48
850.29	32.25
861.09	32.45
872.00	32.25
882.94	32.25
893.93	32.33
932.62	32.28

continues to higher temperatures, in contrast to what might be expected from the present results.

The thermodynamic properties of zinc at selected temperatures are given in Table 2. For solid zinc the present experimental heat capacities were combined with those by Zabetakis [14] and Bronson and Wilson [13] in a polynomial fit and integrated numerically. A similar fit for the liquid metal was obtained exclusively from the present results. The enthalpy and entropy values at 298.15 K were reintegrated from

Table 2
Thermodynamic properties of zinc at selected temperatures, $M(\text{Zn}) = 65.409$ g mol^{-1}

T (K)	$C_{p,\text{m}}$ (J K^{-1} mol^{-1})	$\Delta_0^T H_\text{m}$ (J mol^{-1})	$\Delta_0^T S_\text{m}$ (J K^{-1} mol^{-1})	$-(\Delta_0^T G_\text{m} - \Delta_0^0 H_\text{m})/T$ (J K^{-1} mol^{-1})
0	0	0	0	0
0.5	0.0004	0.00007	0.00026	0.00012
0.84	0.0012	0.00035	0.00066	0.00024
1	0.0007	0.00045	0.00078	0.00033
2	0.0018	0.0016	0.0016	0.00080
4	0.0071	0.0095	0.0041	0.00173
5	0.012	0.019	0.0061	0.00230
10	0.158	0.325	0.043	0.0105
15	0.731	2.325	0.198	0.0430
20	1.798	8.473	0.544	0.120
30	4.851	40.90	1.817	0.454
40	8.133	106.05	3.669	1.018
50	11.009	202.16	5.802	1.758
60	13.400	324.60	8.027	2.617
80	16.939	630.39	12.40	4.522
100	19.335	994.58	16.45	6.509
120	21.041	1399.3	20.14	8.479
140	22.255	1833.0	23.48	10.39
160	23.055	2286.7	26.51	12.22
180	23.564	2753.2	29.25	13.96
200	23.989	3228.7	31.76	15.62
220	24.364	3712.4	34.06	17.19
240	24.693	4203.0	36.20	18.69
260	24.988	4699.9	38.19	20.11
280	25.252	5202.3	40.05	21.47
298.15	25.470	5662.7	41.64	22.65
300	25.492	5709.8	41.80	22.77
350	26.02	6997.9	45.77	25.77
400	26.51	8311.3	49.28	28.50
450	27.01	9649.1	52.43	30.98
500	27.54	11013	55.30	33.27
550	28.14	12404	57.95	35.40
600	28.87	13829	60.43	37.38
650	29.84	15295	62.78	39.25
692.681	30.96	16591	64.71	40.76
$\Delta_\text{fus}H_\text{m} = 7070$ J mol^{-1}				
692.681	33.42	23661	74.91	40.76
700	33.34	23905	75.26	41.12
750	32.85	25559	77.55	43.47
800	32.53	27193	79.65	45.67
850	32.35	28815	81.62	47.72
900	32.28	30430	83.47	49.66
940	32.31	31722	84.87	51.13

earlier results, as the heat capacity reported by Chase [1] at 250 K appeared to be slightly high.

The heat capacities by Keesom and Seidel [26], Phillips [27] and Martin [28,29] were used through the superconductivity maximum at 0.84 K. Above this temperature and up to 25 K additional results by Keesom and van der Ende [30] (up to 18 K), Smith [31], Zimmerman [32], and Cetas et al. [33] were also used up to 25 K. The results by Silvidi and Daunt [34] and Srinivasan [35] in the region 1–4 K were not considered accurate enough for incorporation. The results of Clusius and Harteck [36] were used from 25 to 100 K, those by Eichenauer and Schulze [37] from 12 to 273 K, and in addition the earlier mentioned results by Bronson and Wilson [13] from 193 K, and those by Zabetakis [14] from 12 to 200 K and above 260 K. The revised values at 298.15 K are

$$\Delta_0^{298.15\,\mathrm{K}} H_\mathrm{m} = 5663\ \mathrm{J\,mol^{-1}},$$
$$\Delta_0^{298.15\,\mathrm{K}} S_\mathrm{m} = 41.64\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

The enthalpy of fusion value for zinc, 7070 J mol^{-1}, was adopted from our earlier evaluation [3] after adjustment to the new molar mass value $M(\mathrm{Zn}) = 65.409\ \mathrm{g\,mol^{-1}}$ [12]. Quenching rate experiments, in which the release of stored energy related to crystalline defects, effects of interphase conditions between sample and container, and other factors might be revealed are still lacking. Thus, the decrement in enthalpy of fusion related to the severity of quenching remained uncertain and could not be allowed for in the earlier evaluation.

When comparing Ditmars' [23] enthalpy results, obtained in a melting ice receiving calorimeter, with the present ones, very good agreement is noted in the range 600 K to the triple-point temperature. Thus, the value of $H(692.745\,\mathrm{K}, T_\mathrm{trp}\ \mathrm{on\ IPTS\text{-}68}) - H(273.15\,\mathrm{K}) = 11\,532\ \mathrm{J\,mol^{-1}}$ excluding pre-melting, is only 29 J mol^{-1} lower than that obtained here after adding $H(298.15\,\mathrm{K}) - H(273.15\,\mathrm{K}) = 633\ \mathrm{J\,mol^{-1}}$. This difference is within the combined error limits. A comparison at two higher temperatures, 703.14 and 773.41 K results in differences of −88 and −143 J mol^{-1}, respectively. The difference between the two latter figures is independent of the selected value of the enthalpy of fusion value. It is considerably larger than expected from the accuracies of the methods in question, and is presently unresolved.

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