ELSEVIER

Thermochimica Acta 391 (2002) 169–174

thermochimica acta

www.elsevier.com/locate/tca

Heat capacity of solid cadmium from 298.15 to 594.22 K and of liquid cadmium from 594.22 to 700 K: enthalpy of fusion

Svein Stølen*, Fredrik Grønvold

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

Received 5 September 2001; accepted 9 November 2001

Abstract

The heat capacity of cadmium has been determined by adiabatic calorimetry from 298.15 to 700 K. The heat capacity of solid cadmium at 594 K is approximately 5% higher than recommended in the evaluation by Hultgren—recently accepted without change by Barin and only slightly modified in a CODATA evaluation. For liquid cadmium the presently obtained heat capacity is about 6% higher at 600 K than proposed by the same authors. The enthalpy of fusion derived from two series of experiments is 6166 ± 18 J mol^{-1}. The thermodynamic properties of cadmium at selected temperatures are derived.

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

1. Introduction

No determinations of the enthalpy of fusion of cadmium seem to exist by calorimeters proven to give highly accurate values [1]. In our recent evaluation of the enthalpy of fusion of metals used as enthalpy standards for thermal analysis the recommended enthalpy of fusion value and the estimated uncertainty was 6211 ± 77 J mol^{-1}. The uncertainty is considerably larger than for indium, tin, lead and zinc. We hence concluded that determinations by adiabatic calorimetry were needed for cadmium in order to use it as an enthalpy standard for accurate work.

The heat capacity of solid and liquid cadmium as derived from enthalpy increment results, scatter badly, see Fig. 1. That for solid cadmium by Wüst et al. [3] showed a moderate rise with temperature, which was supported by the results of Schneider and Hilmer [8] in the upper range. Those by Naccari [2] and Umino [5] increase rather steeply with temperature. These results were superseded by the heat capacity determinations by Saba et al. [9] up to 543 K, which fitted well with those by Bronson and Wilson [6] over the common temperature range 298–420 K. The rapidly increasing slope in the curve above 500 K need more accurate delineation, especially in view of the more pronounced effects reported by Khomyakov et al. [10] above 570 K.

For liquid cadmium the heat capacities have been derived exclusively from drop-calorimetric results. They range from 27.5 to about 36 J K^{-1} mol^{-1}.

2. Experimental

The step-wise heated high-temperature adiabatic calorimeter and the measuring technique have been

* Corresponding author. Tel.: +47-22-85-56-01; fax: +47-22-85-54-41.
E-mail address: svein.stolen@kjemi.uio.no (S. Stølen).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00174-0

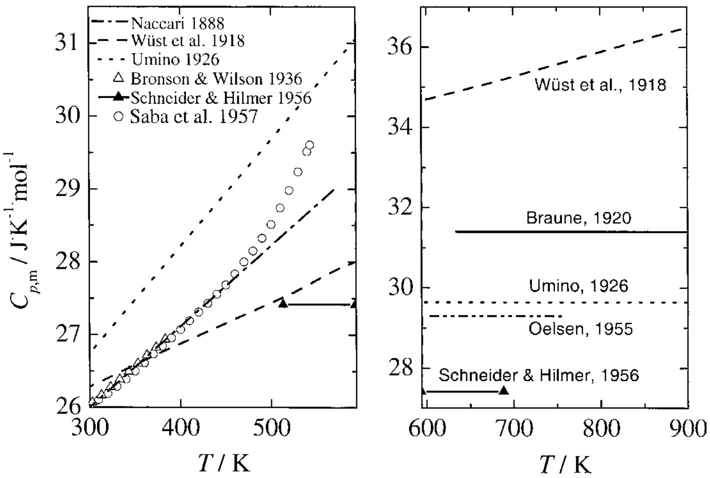

Fig. 1. Heat capacity of: (a) solid and (b) liquid cadmium. Experimental data are: (— - —) Naccari [2]; (– – –) Wüst et al. [3]; (—) Braune [4]; (- - -) Umino [5]; (△) Bronson and Wilson [6]; (– - - –) Oelsen [7]; (▲) Schneider and Hilmer [8]; (○) Saba et al. [9].

described [11,12]. Cadmium in the form of 1 mm diameter wire of 5 N purity from Koch-Light, Colnbrook, England, was used in the experiments. One sample had a mass of about 165 g and the other about 80 g. Temperature was measured with an ASL F-18 resistance bridge using locally constructed 25 Ω platinum-resistance thermometers. This system allows a temperature resolution of ca. 3×10^{-5} K. Temperature calibration is performed according to the recommendations supplementing the ITS-90 [13] up to the fusion temperature of aluminium, $T = 933.473$ K. The accuracy in temperature determination is considered to be within ±0.02 K. Energy is supplied electrically 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% [12].

3. Results and discussion

The experimental molar heat capacity values of solid and liquid cadmium are given in Table 1 and presented graphically in Fig. 2. The heat capacity of solid cadmium in the temperature region 298–543 K is in good agreement with the previous determinations by Bronson and Wilson [6], Craig et al. [14] and Saba et al. [9]. Above 543 K the heat capacity rises faster than suggested by Hultgren et al. [15], Barin [16] and CODATA [17] and near the melting temperature it is about 5% higher than in the tabulations. Similarly, the heat capacity of liquid cadmium is about 6% higher and decreases with increasing temperature. The enormous premelting effect observed by Khomyakov et al. [10] starting just above 580 K contributing about 50% of the total enthalpy of fusion did not show up in the present study. Thus, the work by Ubbelohde [18] regarding the anomalous melting behaviour of group B metals, Sn and Cd, seems now also for Cd to relate to "trivial liquid formation". Both impurities and temperature gradients are among possible causes of the anomalous results by Khomyakov et al. [10].

The enthalpy of fusion was determined in two series of experiments using two different samples, see Table 2. The average enthalpy of fusion, $\Delta_f H_m = 6166$ J mol^{-1}, is 0.4% lower than recommended by Hultgren et al. [15] and Barin [16] and 1.7% higher than suggested by CODATA [17]. The uncertainty of the present enthalpy of fusion determination is judged to be around 0.3%, see discussion in [1]. The triple point of cadmium taken as the temperature after

Table 1
Experimental heat capacities for solid and liquid cadmium

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
Solid cadmium					
322.54	26.355	421.50	27.425	516.27	28.726
330.36	26.357	429.26	27.511	524.38	28.799
338.13	26.528	437.01	27.599	532.49	29.106
345.85	26.548	444.79	27.693	540.50	29.271
353.54	26.563	452.60	27.876	548.14	29.636
361.19	26.668	460.44	27.9	555.81	29.641
368.80	26.775	468.32	27.933	563.45	30.164
376.44	26.789	476.22	28.08	571.13	30.134
390.74	27.11	484.16	28.247	578.79	30.555
398.41	27.07	492.13	28.323	582.58	30.785
406.10	27.188	500.14	28.49	590.45	35.409
413.78	27.286	508.19	28.588		
Liquid cadmium					
600.02	31.774	633.58	31.476	666.69	31.236
608.01	31.724	641.79	31.309	675.12	31.242
616.08	31.483	650.05	31.305	683.62	30.960
624.08	31.301	658.35	31.113		

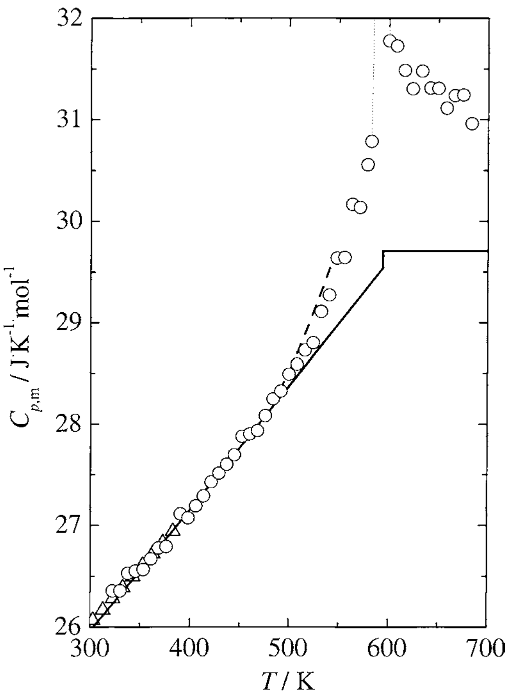

Fig. 2. Heat capacity of cadmium from 298.15 to 700 K. Experimental data are: (△) Bronson and Wilson [6]; (– – –) Saba et al. [9]; (—) Hultgren et al. [15]; (○) present data.

energy input 1 for sample 1, 594.273 K, is slightly higher than the IPTS-68 value [19] adjusted to ITS-90; $T_{trp}(Cd) = 594.22$ K. It is not clear whether this effect is due to the non-uniqueness of the temperature scale or non-ideal calibration of the resistance thermometer.

A recommended enthalpy of fusion of cadmium based on all experimental calorimetric determinations can be deduced in terms of the procedures outlined in [1]. All experimental determinations are presented in Table 3. Crucial in the evaluation is the uncertainty assigned to each individual determination and this figure is given in the second column from right. The recommended enthalpy of fusion is 6174 ± 17 J mol^{-1}. The deviation of the determination in question from the recommended value is given in the far right column.

The thermodynamic properties of cadmium at selected temperatures are given in Table 4. The experimental heat capacities for solid and liquid cadmium were represented by polynomials in temperature and integrated numerically. The heat capacity of cadmium was revised using the same heat capacity values as used in the CODATA evaluation above 200 K (Craig et al. [14] from 200 to 320 K; Bronson and Wilson [6] from 193 to 393 K; Griffiths and Griffiths [35] from 108 to 371 K; Saba et al. [9] from 298 to 543 K)

Table 2
Enthalpy of fusion of cadmium

ΔU_{input} (J)	ΔU_{tare} (J)	ΔU_{drift} (J)	t (min)	T (K)	$\Delta_f H_m$ (J mol^{-1})
Sample 1 (1.44842 mol)					
				586.621	
1134.99	1084.7	−8.7	68	594.273	40.7
9103.66	256.8	−33.3	225	596.056	6130.9
					6171.6
Sample 2 (0.65768 mol)					
				590.684	
4695.8	627.8	16.3	185	596.055	6160.6

Table 3
Enthalpy of fusion of cadmium ($T_f = 594.22$ K, M(Cd) = 112.411 g mol^{-1})

Reference	Method	$\Delta_f H_m$ (J mol^{-1})	Uncertainty (%)	Deviation (%)
[20]	Drop-water	6427	7.5	4.1
[21]	Cooling curve	6446	7.5	4.4
[3]	Drop-ice	5086	15	−17
[5]	Drop-water	6069	10	−1.7
[22]	Cooling curve	6069	10	−1.7
[23]	Heating curve	6446	7.5	4.4
[10]	Adiabatic scanning	7152	15	16
[24]	Drop-water—scanning	6236	3	1.0
[7]	Drop-water—scanning	6111	3	−1.0
[25]	Drop-water—scanning	6211	3	0.6
[8]	Drop-Cu-block	6362	5	3.0
[26]	Drop-water—scanning	6094	3	−1.3
[27]	Drop-water—scanning	6446	3	4.4
[28]	Cooling curve—air stream—scanning	6111	3	−1.0
[29]	DTA	6634	15	7.4
[30]	DTA—electric calibration	6291	3	1.9
[31]	Drop-water—scanning	6278	3	1.7
[32]	DSC—electric calibration	6199	3	0.4
[33]	DSC—heat flux	6210	1	0.6
[34]	DSC—power compensated	6174	1.5	0.0
Present study	Adiabatic	6166 ± 18	0.3	−0.1

Table 4
Thermodynamic properties of cadmium at selected temperatures

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	$\Delta_0^T H_m$ (J mol^{-1})	$\Delta_0^T S_m$ (J K^{-1} mol^{-1})	$-\frac{\Delta_0^T H_m - T\Delta_0^T S_m}{T}$ (J mol^{-1})
298.15	26.04	6247.0	51.80	30.85
300	26.05	6295.2	51.96	30.98
310	26.16	6556.3	52.82	31.67
320	26.26	6818.4	53.65	32.34
330	26.37	7081.5	54.46	33.00
340	26.47	7345.7	55.25	33.64
350	26.57	7610.9	56.02	34.27
360	26.67	7877.2	56.77	34.89

Table 4 (*Continued*)

T (K)	$C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	$\Delta_0^T H_\mathrm{m}$ (J mol^{-1})	$\Delta_0^T S_\mathrm{m}$ (J K^{-1} mol^{-1})	$-\frac{\Delta_0^T H_\mathrm{m} - T\Delta_0^T S_\mathrm{m}}{T}$ (J mol^{-1})
370	26.78	8144.4	57.50	35.49
380	26.88	8412.7	58.21	36.08
390	26.99	8682.0	58.91	36.65
400	27.09	8952.4	59.60	37.22
410	27.21	9223.9	60.27	37.77
420	27.32	9496.5	60.93	38.31
430	27.44	9770.3	61.57	38.85
440	27.57	10045	62.20	39.37
450	27.70	10322	62.83	39.89
460	27.85	10599	63.43	40.39
470	28.00	10879	64.03	40.89
480	28.16	11159	64.62	41.38
490	28.33	11442	65.21	41.86
500	28.51	11726	65.78	42.33
510	28.71	12012	66.35	42.80
520	28.92	12300	66.91	43.25
530	29.14	12590	67.46	43.70
540	29.39	12883	68.01	44.15
550	29.65	13178	68.55	44.59
560	29.93	13476	69.09	45.02
570	30.23	13777	69.62	45.45
580	30.55	14081	70.15	45.87
590	30.90	14388	70.67	46.29
594.22	31.06	14519	70.89	46.46
$\Delta_\mathrm{f} H_\mathrm{m} = 6174$ J mol^{-1}				
594.22	31.85	20693	81.28	46.46
600	31.76	20877	81.59	46.80
610	31.62	21194	82.11	47.37
620	31.50	21509	82.63	47.94
630	31.40	21824	83.13	48.49
640	31.32	22137	83.62	49.04
650	31.25	22450	84.11	49.57
660	31.20	22762	84.59	50.10
670	31.16	23074	85.06	60.63
680	31.13	23385	85.52	51.13
690	31.12	23697	85.97	51.63
700	31.12	24008	86.42	52.12

combined with the present values for the temperature region from 323 to 582 K.

References

[1] S. Stølen, F. Grønvold, Thermochim. Acta 327 (1999) 1.
[2] A. Naccari, Atti. Accad. Sci. Torino 23 (1888) 107.
[3] F. Wüst, A. Meuthen, R. Durrer, Forsch. Gebiete Ingenieurw. VDI 204 (1918).
[4] H. Braune, Z. Anorg. Chem. 111 (1920) 109.
[5] S. Umino, Sci. Rep. Tohoku Imp. Univ. 15 (1926) 597.
[6] H.L. Bronson, A.J.C. Wilson, Can. J. Res. A 14 (1936) 181.
[7] W. Oelsen, Arch. Eisenhüttenw. 26 (1955) 519.
[8] A. Schneider, O. Hilmer, Z. Anorg. Allg. Chem. 286 (1956) 97.
[9] W.G. Saba, K.F. Sterrett, R.S. Craig, W.E. Wallace, J. Am. Chem. Soc. 79 (1957) 3637.
[10] K.G. Khomyakov, V.A. Kholler, S.A. Zhvanko, Vestn. Mosk. Univ., Ser. Fiz.-Mater. Est. Nauk. 2 (1952) 41.
[11] F. Grønvold, Acta Chem. Scand. 21 (1967) 1695.
[12] S. Stølen, R. Glöckner, F. Grønvold, J. Chem. Thermodyn. 28 (1996) 1263.
[13] H. Preston-Thomas, Supplementary Information for the International Temperature Scale of 1990, Bureau International des Poids et Mesures, Paris, 1990, Metrologia 27 (1990) 3.

[14] R.S. Craig, C.A. Krier, L.W. Coffer, E.A. Bates, W.E. Wallace, J. Am. Ceram. Soc. 76 (1954) 238.
[15] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Keller, D.D. Wagman, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, OH, 1973.
[16] I. Barin, Thermochemical Data of Pure Substances, VCH, Verlagsgesellschaft mbH, Weinheim, 1993.
[17] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
[18] A.R. Ubbelohde, The Molten State of Matter, Wiley, Chichester, UK, 1978, p. 335.
[19] The International Practical Temperature Scale of 1968, Metrologia 5 (1969) 35.
[20] C.C. Person, Comput. Rend. 27 (1848) 258;
C.C. Person, Ann. Phys. 75 (1848) 460.
[21] G.D. Roos, Z. Anorg. Allg. Chem. 94 (1916) 329.
[22] U. Cavallaro, Atti Reale Accad. Italia 4 (1943) 520.
[23] S. Nagasaki, E. Fujita, Nippon Kinzoku Gak. 16 (1952) 313, 317.
[24] W. Oelsen, K.H. Rieskamp, O. Oelsen, Arch. Eisenhüttenw. 26 (1955) 253.
[25] W. Oelsen, O. Oelsen, D. Thiel, Z. Metall. 46 (1955) 555.
[26] W. Oelsen, K. Bierett, G. Schwabe, Arch. Eisenhüttenw. 27 (1956) 607.
[27] W. Oelsen, E. Schürmann, H.J. Weigt, O. Oelsen, Arch. Eisenhüttenw. 27 (1956) 487.
[28] W. Oelsen, Arch. Eisenhüttenw. 28 (1957) 1.
[29] R. Pascard, Acta Met. 7 (1959) 305.
[30] T. Heumann, B. Predel, Z. Metall. 51 (1960) 509.
[31] E. Schürmann, H. Träger, Arch. Eisenhüttenw. 32 (1961) 397.
[32] L. Malaspina, R. Gigli, V. Piacente, Gazz. Chim. Italia 101 (1971) 197.
[33] K.H. Breuer, W. Eysel, Thermochim. Acta 57 (1982) 317.
[34] C.Y. Zahra, A.M. Zahra, Thermochim. Acta 276 (1996) 161.
[35] E.A. Griffiths, E. Griffiths, Philos. Trans. R. Soc. London A 214 (1914) 319.