Cryoscopic Constant, Heat and Enthalpy of Fusion of Metals and Water

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In thermometry the latent heat of fusion L is used for the calculation of the cryoscopic constant A of a material. High precision heat of fusion measurement results are generally published in terms of enthalpy of fusion $\Delta_{\mathrm{fus}}H$. The relationship between heat Q and enthalpy H is given by:

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p = \mathrm{d}Q + V\mathrm{d}p. \qquad (1)$$

At constant pressure p and if the influence of a volume change is negligible, enthalpy of fusion and heat of fusion agree.
The majority of information used here is based on a review article about enthalpy of fusion of metals by S. Stølen and F. Grønvold from 1999 [1]. An update of this recommended data was prepared and will be published as a IUPAC Technical Report [2]. The data are supplemented by recently published results of NIST [3, 4], PTB, and literature data of water [5, 6], and mercury [7].

Table 1 Enthalpy of fusion data

Substance	***M*** g mol^{-1}	**Reference**	$\Delta_{\mathrm{fus}}H$ / J mol^{-1}	$\Delta_{\mathrm{fus}}h$ / J g^{-1}
Hg	200.59	NIST, [7]	2301 ± 2	11.469 ± 0.008*
H_2O	18.01528	[5, 6]	6008 ± 4	333.50 ± 0.20
Ga	69.723	[1]	5576 ± 19	79.97 ± 0.27
		[2]	5583 ± 9	80.07 ± 0.13
		PTB	5588 ± 12	80.14 ± 0.18
		[3]	5585 ± 2	80.097 ± 0.032
In	114.818	[1]	3281 ± 8	28.576 ± 0.07
		[2]	3287 ± 5	28.62 ± 0.04
		[4]	3291 ± 1	28.6624 ± 0.0076
		LGC	3296 ± 9	28.71 ± 0.08
		NIST	3273 ± 22	28.51 ± 0.19
		PTB	3288 ± 7	28.64 ± 0.06
Sn	118.710	[1]	7173 ± 20	60.425 ± 0.17
		[2]	7168 ± 18	60.38 ± 0.15
		PTB	7151 ± 19	60.24 ± 0.16
		NIST	7147 ± 22	60.22 ± 0.19
Zn	65.409	[1, 2]	7068 ± 28	108.09 ± 0.43
		LGC	7103 ± 31	108.59 ± 0.47
Al	26.981538	[1, 2]	10789 ± 36	399.9 ± 1.3
		LGC	10827 ± 43	401.3 ± 1.6
Ag	107.8682	[1, 2]	11284 ± 225	104.6 ± 2.1
Au	196.96655	[1, 2]	12720 ± 304	64.6 ± 1.5
Cu	63.546	[1, 2]	12928 ± 277	203.4 ± 4.4

Atomic Weights of the Elements 2001, Pure Appl. Chem. 75 (2003) 1107-1122
LGC: Certified Reference Materials for Thermal Analysis, Office of Reference Materials, Laboratory of the Government Chemist, Teddington, Middlesex, UK,
The certification of the LGC enhalpy of fusion data was carried out by F. Grønvold and S. Stølen, University at Oslo, Norway.
NIST: Standard Reference Materials Catalog, SRM Program, National Institute of Standards and Technology. Gaithersburg. MD. USA.
PTB: Physikalisch-Technische Bundesanstalt, Fachbereich 3.3. Braunschweig, Germany
* Measurement uncertainty $\Delta_{\mathrm{fus}}h$(Hg) from NIST-SRM-2225 report

The measurement uncertainties were likewise adopted from the cited documents and therefore not determined on a unique basis. Although the assumption of a coverage factor of k=2 might be reasonable in most cases it should be mentioned here that there is disagreement among calorimetrists about some stated uncertainties.

Gallium
The recommended value of Stølen and Grønvold [1] for the enthalpy of fusion of Ga was based on three sources. One of them was questioned because it was about 0.6 % lower than the average of the two other determinations. Recent measurements of Archer [3] and at PTB have confirmed that. The measurements of Archer [3] and at PTB had an excellent agreement. The measurements of Archer are considered as the most accurate ones and his result is therefore recommended here as reference value.

Indium
The recent results of Archer and Rudtsch at NIST [4] on a certified reference material of PTB showed an excellent agreement. These results [4] are considered as the most accurate ones.

Tin
The deviations between the results of Ditmars and that of Grønvoldt are larger than the combined uncertainties. It was assumed that Ditmars drop calorimetry results might have been influenced by quenching in of disorder (see [1]), but recent measurements at PTB support Ditmars results. Here the unweighted mean of these measurements is recommended as reference value.
Ditmars (1989): (7148±22) J mol^{-1}
Grønvoldt (1998): (7187±11) J mol^{-1}
PTB (2003): (7151±19) J mol^{-1}
Mean: (7162±22) J mol^{-1}

For Zn, Al, Ag; Au and Cu the recommended values from [1] were adopted. For the calculation of the cryoscopic constants the value of R = 8.314471 J mol^{-1} K^{-1} was used.

Table 2 Recommended enthalpy of fusion data and cryoscopic constants

Substance	T_{ITS-90} / K	$\Delta_{fus}H$ / J mol^{-1}	A / K^{-1}
Hg	234.3156	2301	0.005041
H_2O	273.16	6008	0.009684
Ga	302.9146	5585	0.007321
In	429.7485	3291	0.002143
Sn	505.078	7162	0.003377
Zn	692.677	7068	0.001772
Al	933.473	10789	0.001489
Ag	1234.93	11284	0.000890
Au	1337.33	12720	0.000855
Cu	1357.77	12928	0.000843

References
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