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Review

Critical assessment of the enthalpy of fusion of metals used as enthalpy standards at moderate to high temperatures

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Abstract

Enthalpy of fusion values for metals used as enthalpy standards are critically assessed. Recent developments of high temperature DSCs imply that potential standards for higher temperature use must also be considered. The fusion values for Ga, In, Sn, Cd, Bi, Pb, Zn, Sb, Al, Ag, Au, Cu, Ni and Co are treated here. We are hence covering materials for use from ambient temperature and up to 1768 K. A detailed review of the enthalpy of fusion determinations reported for each individual metal is presented in terms of sample quality and the methodology used. The accompanying evaluation leads to recommended values for the enthalpy of fusion of the metals and estimates of the uncertainty of the mean. The statistical method used is discussed in some detail. In reaching the recommended values for the enthalpy of fusion of the metals, the uncertainty of each individual determination has been estimated. Arguments regarding the effects of sample quality, intrinsic defects, and thermal treatment to aid in the assignment of uncertainties as well as a short review of the main calorimetric techniques used are presented.

Keywords: Calibration; Calorimetry; Enthalpy of fusion; Metals; Standards

1. Introduction

Standard materials are in demand as calibrants for temperature, enthalpy and heat capacity. Temperature calibration of a measuring instrument is the simplest task and is most often achieved through melting of pure metals, alloys, and organic compounds. Only infinitely pure substances melt isothermally, while even very pure metals melt in a temperature interval which depends upon the type and amount of impurities. Thus, for demanding purposes the melting temperature interval of the standard material should be ascertained through fractional fusion experiments. The isothermal fusion – or triple point – temperature may be derived by extrapolation in case of a system containing a main impurity which causes the liquidus line to slope downwards (eutectic-like), while for impurities which cause the liquidus line to slope upwards (peritectic-like) significant errors in temperature calibration may result [1].

Most calorimetric techniques do not employ electrical calibration in relating enthalpy results to international standards. In adiabatic calorimetry, the energy supplied electrically to the sample is determined directly through measurement of the current through and potential over a heater, and time. For many other techniques, notably differential thermal analysis (DTA) and differential scanning calorimetry

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(DSC), enthalpy calibration is most often performed by means of standard materials. The calibration factor of a DTA/DSC varies with temperature and pressure in addition to other variables. It is thus necessary to calibrate the instrument throughout the temperature and pressure ranges of interest. Accordingly, a number of enthalpy and temperature standards may be needed. Although the uncertainty of an enthalpy increment determined, for example by DSC is most often dominated by factors other than that of the reference material, the measurand to be used in the calibration should preferably be known with an uncertainty which is negligible in the total calibration and measurement procedure.

A DSC may need separate calibrations with respect to heat (enthalpy) and to heat-flow rate (heat capacity) since the calibration factors are not identical even at the same temperature [2]. Highly accurate heat-capacity standards, like synthetic sapphire, α-Al_2O_3, and benzoic acid, are available. Thus, the uncertainty in the heat-capacity value of the reference material should not contribute significantly to the total uncertainty of a heat-capacity determination by DSC (although differences in heat diffusivity may). For enthalpy reference materials, the situation is not equally straightforward. Until recently the use of most commercial DSCs has been limited to temperatures below 900 K. Furthermore, reasonably accurate enthalpy standards have been available for intermediate temperature use only. The recent development of high temperature DSCs implies that enthalpy standards for higher temperature use must be considered.

Truly, the quality of the temperature, enthalpy, and heat-capacity standards is only one of several aspects of the total DSC measurement procedure. Standard procedures for use of DSCs have been recommended, e.g. by the German Gesellschaft für Thermische Analyse (GEFTA) [2–4] and the American Society for Testing of Materials (ASTM) [5,6]. Since DSCs are frequently used for quality assurance in industrial production processes, calibration, testing and analysis procedures must comply with strictly controlled standards. Quality assurance aspects of DSC have been treated elsewhere [7,8].

The present paper deals with the quality of enthalpy standards, and aims at presenting an assessment of enthalpy of fusion values of available and potential metallic standard materials for use at moderate to high temperatures. Fusion and transition of simple inorganic salts or compounds have frequently been proposed as temperature and enthalpy calibration standards for high temperatures use [9–12]. Such compounds are for several reasons not considered here. Firstly, because they are generally not available with purities comparable to those for readily available metals. Thus, their melting behaviour is less well defined. Secondly, the solid–solid transitions proceed much more sluggish than fusion, and with transition temperatures and enthalpies generally less accurately known. Furthermore, the enthalpy of transition is probably to a larger extent dependent on the purity and crystal perfection of the actual material than the enthalpy of fusion. Only metals are, hence, treated here. The available and potential enthalpy standards considered are Ga, In, Sn, Cd, Bi, Pb, Zn, Sb, Al, Ag, Au, Cu, Ni and Co. In general, reactions between metal melts and sample holders can not be excluded. In addition, the vapour pressure of the metal may constitute a problem in cases where calibration is performed in open sample holders.

The organization of the paper is as follows. In Section 2, the terms used to characterize the quality of the different data sets are presented. Some brief arguments are used to indicate the present status with regard to enthalpy standards. In Section 3, the evaluation approach is discussed. A description of the statistical method utilized is followed by considerations regarding the effects of sample quality, intrinsic defects and thermal treatment. A short review of the main calorimetric techniques is also given. In Section 4, a detailed discussion of all enthalpy of fusion determinations reported for each individual metal is given in terms of sample quality, investigators reliability and the methodology used. The discussion leads to recommended values for the enthalpy of fusion of the metals and estimates of the uncertainty of the mean.

2. Uncertainty, accuracy, repeatability, and reproducibility

DSC is potentially a quantitative technique since proper calibration allows thermodynamic parameters to be determined. When reporting the result of a measurement of a physical quantity some quantitative indication of the quality or uncertainty of the result should be given so that its reliability can be assessed. It is important to distinguish between the often used terms accuracy and precision. In the present paper, the terms uncertainty, accuracy, repeatability, and reproducibility will be used. The definitions of these terms are taken from the Guide to the Expression of Uncertainty in Measurement [13]:

The uncertainty of the result of a measurement reflects the lack of exact knowledge of the value of the measurand. The result of a measurement after correction for recognized systematic errors is still only an estimate of the value of the measurand because of the uncertainty arising from random effects and imperfect correction of the result for systematic effects. The uncertainty is thus a parameter that characterizes the dispersion of the values that could reasonably be attributed to the measurand. All components of uncertainty, including those arising from systematic effects, contribute to the dispersion.

The accuracy of measurement reflects the closeness of the agreement between the result of a measurement and a true value of the measurand. The true value is a value that would be obtained by a perfect measurement and should not be confused with the conventional true value of a quantity. This represents a value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose. The conventional true value is sometimes called assigned value, best estimate of the value, recommended value or reference value.

Repeatability refers to the closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement.

Reproducibility refers to the closeness of the agreement between the results of successive measurements of the same measurand carried out under changed conditions of measurement. The actual change of condition must be clearly stated.

The distinction between repeatability and reproducibility is often neglected. In a careful study by Zahra and Zahra [14] the importance of this difference is clearly shown. The repeatability of the determination of the enthalpy of fusion of In and Sn with a specific DSC was shown to be 0.1% whereas the reproducibility was significantly lower, 0.7 and 0.3%, respectively. The changed conditions referred in this case to changes in the position of the sample pan, or the sample and lids, relatively to the calorimeter cell since the cell was reloaded in each experiment. The manufacturer of the actual DSC characterized their instrument in terms of calorimetric uncertainty and calorimetric inaccuracy which was given as <0.1 and 1%, respectively.

In the same study, Zahra and Zahra [14] evaluated the accuracy of the DSC also with regard to determination of heat capacity. The heat capacity of Al measured with their DSC in the temperature range 373 to 773 K is reported to be within 0.5% of the recommended values for the heat capacity of Al by Desai [15] which, hence, were taken as conventional true values. The heat capacity of aluminium, as reported by four groups known for accurate calorimetry, is shown in Fig. 1. The heat capacity Al(s) is not known with an accuracy better than ca. 1 to 2% in the temperature interval 373 to 773 K, and at 773 K the deviation between the highest and lowest values is near 5%. The choice of the conventional true value is obviously crucial when comparing a given result with that of a standard. The values recommended by Desai

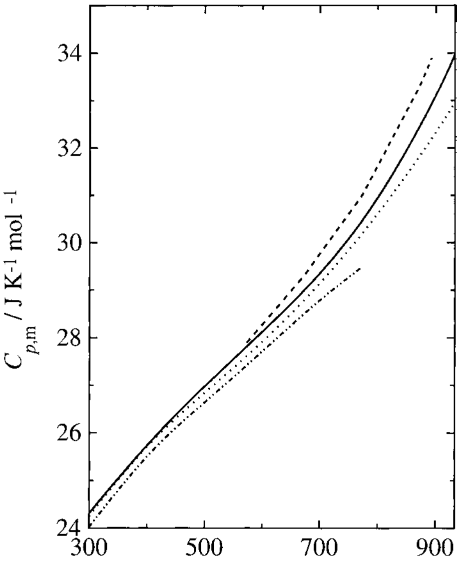

Fig. 1. Molar heat capacity of Al(s) as a function of temperature. ———, McDonald [16]; – – –, Brooks and Bingham [17]; ·–·–·–·, Leadbetter [18]; · · ·, Ditmars et al. [19].

[15] at 400, 600, and 700 K are 0.3% lower, 0.6, and 1.1% higher than the presumably more accurate values reported by Ditmars et al. [19]. Thus, the close agreement between the DSC results and the recommended values for the heat capacity of Al by Desai [15] is most probably coincidental.

This simple example shows the influence of the conventional true value chosen for a measurand. The choice is most often the result of a more or less well-founded evaluation process by a certain evaluator or organization. It is, hence, not surprising that the conventional true value in evaluations of instrument/measurement accuracies in literature varies in a somewhat arbitrary way. While the accuracy of the enthalpy of fusion determined by DSC is often claimed to be within 1%, the cited literature (conventional true) value used for calibration, or used for assessing the accuracy of the DSC, often varies to a comparable or larger extent. Values from 7028 [20] to 7190 [21] J mol^{-1} have been used as literature values for the enthalpy of fusion of tin, whereas values from 3261 [20] to 3296 [14] J mol^{-1} are used for indium. The spread in the cited 'true' values are, hence, 2.3 and 1.1% respectively. For other reference materials the situation is worse. One of the most often used enthalpy and temperature calibrant is zinc. Its enthalpy of fusion as reported by ASTM [6] and given in major data compilations [22–26] is ca. 4% above the most recently published experimental determination [27]. The rather confusing situation is further substantiated by consideration of the enthalpies of fusion of metals recommended in major data compilations [22–26,28], see Table 1. The values given for the metals considered there are also compared with the value recommended in a recent independent evaluation (when available). The deviation between the lowest and highest values is in some cases surprisingly high, e.g. 2.3 and 4.2% for Sn and Zn. In other cases, the different evaluators agree surprisingly well, e.g. for Co where the same value is reported in all compilations. This coincidence does, however, not imply that the enthalpy of fusion of Co is more accurately known than that of Sn or Zn.

3. Evaluation approach

3.1. Evaluation of weighted mean and uncertainty of mean

In all experimental studies, non-random, systematic errors are expected to occur to some extent. Errors of this type are usually not coped with in the statistical analysis. They may result from inadequate measuring techniques, faulty calibration of the equipment or from bias on the part of the observer. The uncertainties

Table 1
Enthalpy of fusion in J mol^{-1} of possible enthalpy calibrants as recommended in some major data compilations. The last column gives the deviation between the largest and smallest value (%)

Element	JANAF [22]	CODATA [23]	Hultgren [24]	MALT [25]	SGTE [26]	IVTAN [28]	Evaluation	Deviation
Ga	5590 ± 40	—	5590 ± 40	5590	5572	5552 ± 1	5569 [29]	0.7
In	—	—	3264 ± 42	3286	3283	3283 ± 10	3286 [29]	0.6
Sn	—	7195	7029 ± 210	7190	7029	7195 ± 20	7170 [29]	2.3
Cd	—	6060	6192 ± 84	6190	6192	6060 ± 80	—	2.2
Bi	—	—	11297 ± 210	11300	11297	11131 ± 11	11250 [29]	1.5
Pb	4770 ± 10	4812	4799 ± 42	4770	4774	4812 ± 40	—	0.9
Zn	7322 ± 105	7300	7322	7320	7322	7026 ± 20	7026 [29]	4.2
Sb	—	—	19874 ± 628	19870	19874	20200 ± 400	—	1.6
Al	10711 ± 210	10700	10795 ± 125	10710	10711	10700 ± 100	10740 [29] 10580 [15]	1.5
Ag	—	11000	11297 ± 420	11300	11297	10920 ± 450	—	3.5
Au	—	—	12552 ± 420	12550	12552	12670 ± 400	—	0.9
Cu	13138 ± 411	13140	13054 ± 837	13140	13263	13140 ± 300	—	1.6
Ni	17150 ± 400	—	17472	17150	17480	17500 ± 400	17470 [30]	2.0
Co	16192 ± 250	—	16192 ± 250	16190	16200	16200 ± 300	16200 [31]	0.0

due to such systematic errors must be estimated from an analysis of the experimental conditions and techniques. Different experimental techniques will result in different uncertainties and different systematic errors. Although random errors will vary according to a probability density function for a certain instrument as operated, the systematic errors will not. Still, it may reasonably be assumed that the systematic errors arising in the various techniques, under varying operating conditions, etc. are in total randomly distributed about the mean. If this condition is fulfilled, the weighted mean, μ', of a series of determinations with nonuniform uncertainties [32] is:

$$\mu' = \sum N_i(x_i/\sigma_i^2)/\sum(N_i(1/\sigma_i^2))$$

where N_i, x_i, and σ_i represent the number of determinations, the reported value, and the uncertainty assigned to the ith series of experiments. The uncertainty of the mean can be evaluated if all errors are random and, hence, due to fluctuations in observations which are distributed according to a probability density function. For non-uniform uncertainties of the individual determinations the general formula for the uncertainty of the mean is given by

$$\sigma_\mu^2 = 1/\sum N_i(1/\sigma_i^2)$$

The number of determinations made of the measurand in a study should in general be included in the analysis. This is, for several reasons, not implemented here. First of all, the number of determinations is not always stated. Furthermore, a very large fraction of the reported enthalpy of fusion determinations are of relatively low quality. Low quality determinations would not constitute a large problem if the total number of determinations were high. However, only eight independent studies are reported for Ga and nine for Au. Using the above formula, an enthalpy of fusion obtained by taking the mean of 44 determinations with a method assessed with an uncertainty of 2% would have equal weight as one determination with a method assessed with an uncertainty of 0.3%. Such an evaluation procedure would put an unreasonable weight to DTA and DSC determinations. This weighting scheme is especially questionable since such instruments are often calibrated by means of standard materials. Alternatively, these determinations have to be disregarded in the evaluation since they can not be considered as independent. In the present evaluation we choose not to include the number of determinations, as it is taken into account, although indirectly in the assigned uncertainty of the mean value.

The most difficult task in the following evaluation of the enthalpy of fusion of metals is obviously the assignment of an uncertainty to each individual determination reported in the literature. The uncertainty will depend on a large number of parameters related to sample quality, instrumentation, operating procedures and data reduction. The sample quality, discussed in Section 3.2, is probably not the main reason for the large spread in literature values. Operating procedures and data reduction are not normally discussed at any length in scientific papers and can in general not be assessed. Hence, two factors can be singled out as parameters for evaluation of the quality of the result; the instrumental technique used and the scientist who uses it. In the evaluation of uncertainties, we will give weight to the instrumental technique used. Furthermore, since most of the scientist who have determined enthalpies of fusion have done so on more than one metal, it is often possible to evaluate the consistency of a certain researchers work. The scientist factor is given considerable weight in the present evaluation. An independent evaluation of the scientist factor is also possible in cases where performance tests of the calorimeter are reported. Calorimeter performance is usually demonstrated in terms of the heat capacity of α-Al_2O_3. In addition fractional enthalpy of fusion determinations, as well as heat-capacity measurements on first-order solid–solid transitions, should be considered as testing experiments. The quality of accurate calorimeters has often been evaluated through determination of the heat capacity of synthetic sapphire. Fractional fusion experiments are usually not reported and the negligibility of temperature gradients within the calorimeter is, hence, ordinarily not proved.

It should be noted that so-called outliers are not removed in the present evaluation. Our approach is based on assigning a realistic uncertainty to each individual determination in a way which assures the different determinations to be within 2σ of the mean value of the measurand. All results should, hence, be significant at the 0.05 level [32]. This is in our opinion a suitably strong test which assures that a not too high accuracy is ascribed to a determination.

3.2. Considerations regarding sample quality, intrinsic defects, and thermal treatment

In general, the condition of the sample is considered to affect the determined enthalpy of fusion only to a minor extent, provided that the sample is sufficiently pure. Significant effects of sample shape have, however, been reported by Andon et al. [33] and Callanan [34]. These results are somewhat surprising. An effect of the sample shape might be present in results by DSC if a special state of the sample is largely maintained after the first solidification, due to lack of coalescence of smaller parts, smeared out condition of a foil etc. Such conditions are not expected for larger samples in drop calorimetry or adiabatic calorimetry, and any sample shape effect thus relate to the instrumental method more than to the sample. Another possible reason for the observations might be that differently prepared samples have different purities.

The order of magnitude of the effect of impurities in a sample to be used for enthalpy of fusion calibration can be arrived at by considering tin contaminated with antimony [35] or bismuth [36] as representative examples. The enthalpy of fusion of Sn-samples with mole fraction 0.001 of Bi or Sb is $\approx$0.6 and 0.03% lower than that of pure tin. The decrements in the enthalpy of fusion depend on the differences in the excess enthalpy of the solid and liquid solutions as well as the slopes of the liquidus and solidus lines. The observations by Andon et al. [33] can, hence, not easily be rationalized from arguments related to sample purity or sample shape. Experimental studies of the effect of sample purity on the enthalpy of fusion agree in part with our qualitative arguments. The enthalpy of fusion of 3N Sn is reported to be $\approx$1% lower than observed for 5N and 6N samples [37]. The effect is much smaller for 4N and 7N In (0.2%) and within the accuracy of the method [37]. A systematic difference of 0.5% between 4N5 and 6N Bi reported by Raetz [38] is surprisingly high and may relate to the method more than to the sample. No effect of the sample purity (4N, 5N and 6N In) was observed by adiabatic calorimetry by Anscin [39].

In addition to affecting the enthalpy of fusion to a small extent the impurities also influence the fusion characteristics. Thus, the melting plateau is not at a constant temperature over its entire length [1]. The actual (detailed) heat-capacity contribution due to impurities is not easily evaluated. Tin is once more considered as an example. A sample contaminated with mole fraction 0.00001 of an solid-insoluble impurity which forms an ideal mixture in the liquid state will show a premelting enthalpy contribution of $\approx$250 J mol^{-1} at a temperature 80 mK away from the fusion temperature (see Fig. 2).

Further below the fusion temperature the heat capacity and enthalpy increments due to impurities are of negligible importance compared to those from thermally excited intrinsic defects. The heat-capacity contribution due to the formation of Schottky-type intrinsic defects [40] is:

$$C_V = \exp(\Delta_f S_V/R)\exp(-\Delta_f H_V/RT)$$

where $\Delta_f S_V$ and $\Delta_f H_V$ are the molar entropy and enthalpy of defect formation.

At the fusion temperature, the contribution is of the order 0.3 J K^{-1} mol^{-1} both for zinc and aluminium [40]. The fractional number of defects, the heat capacity of defect formation, and the integrated enthalpy of defect formation for aluminium are given as a function of temperature in Fig. 3. The estimates of the heat capacity of defect formation for tin at its fusion

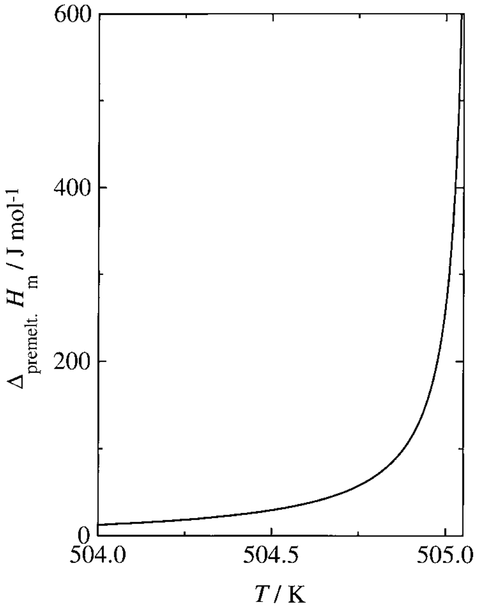

Fig. 2. Premelting contribution to the enthalpy of Sn(s) with mole fraction 0.00001 of an solid-insoluble impurity which forms an ideal mixture with liquid Sn.

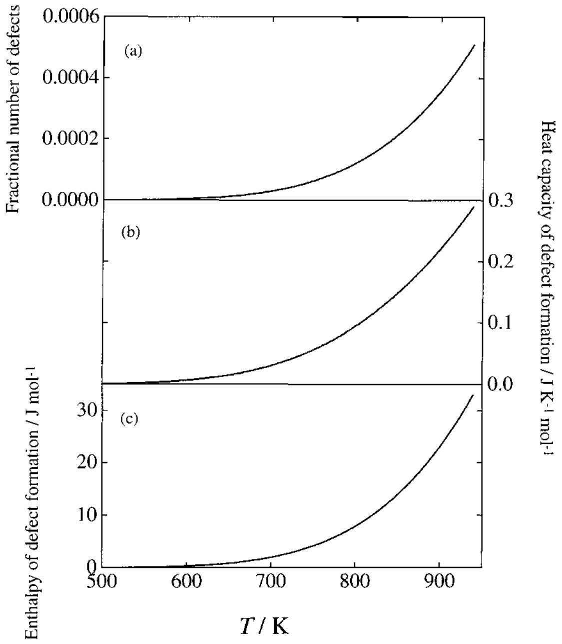

Fig. 3. (a) The number of thermally excited intrinsic defects in Al(s) according to Ref. [40]. (b) and (c) show the corresponding heat capacity contribution and enthalpy increments.

temperature are more uncertain and vary from 0.03 J K^{-1} mol^{-1} [41] to 0.5 J K^{-1} mol^{-1} [42], and 1.5 J K^{-1} mol^{-1} [43]. These effects should be observable in the heat-capacity results and we will consider them more closely for these three metals, as they have been studied both by accurate drop calorimetry and adiabatic-shield calorimetry.

According to Ditmars [44], the heat capacity of his tin sample was 30.30 J K^{-1} mol^{-1} and constant over the region 483 to 505.06 K, cf. Fig. 4. Our values [45,46] are ca. 2% higher at the former temperature and ca. 3.5% higher at 500 K. The deviations clearly exceed the experimental errors, and may indicate that the low heat capacity of tin in the region 483 to 505 K by drop calorimetry is related to sample quenching.

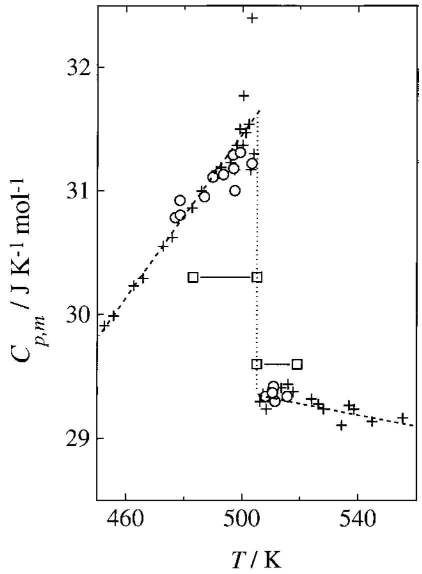

Fig. 4. Molar heat capacity of Sn(s) and Sn(l) as a function of temperature in the vicinity of the fusion temperature. □, Ditmars [44]; +, Grønvold [45]; ○, Grønvold [46]; · · ·, fusion temperature.

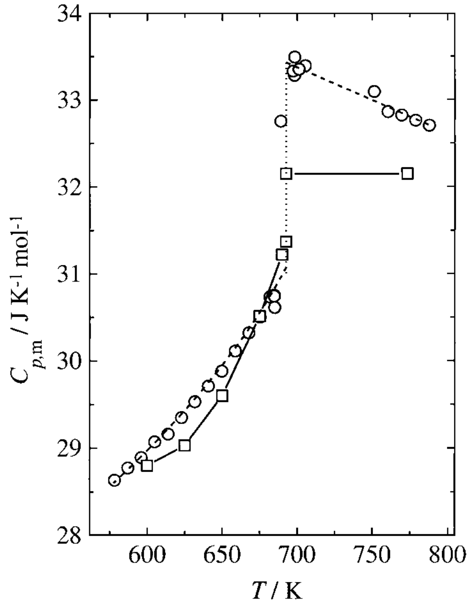

Fig. 5. Molar heat capacity of Zn(s) and Zn(l) as a function of temperature in the vicinity of the fusion temperature. □, Ditmars [27]; ○, Grønvold [47]; · · ·, fusion temperature.

In case of zinc, cf. Fig. 5, the heat capacities derived by Ditmars [27] are lower than the adiabatic ones [47] in the region 600–650 K, but rise slightly above in the 680 K region. For aluminium Ditmars' results [19], see Fig. 6, are lower than the adiabatic ones [48] over the region 800–930 K, which again point to possible quenching effects in the drop calorimetric results. The difference is larger than the contribution associated with formation of vacancies [40] and, points to the presence of further defect excitations as the melting temperature is approached, as suggested by Mitus and

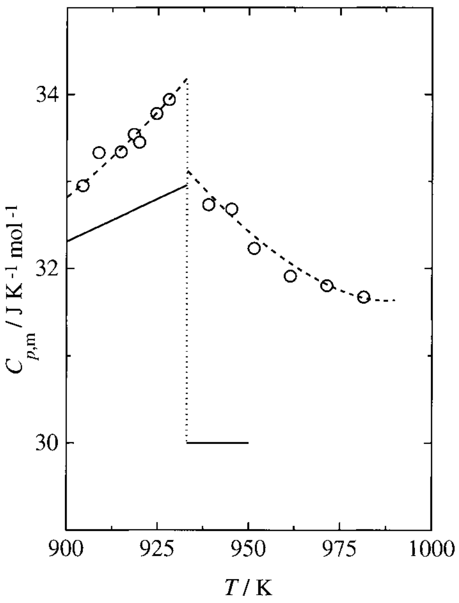

Fig. 6. Molar heat capacity of Al(s) and Al(l) as a function of temperature in the vicinity of its fusion temperature. ———, Ditmars et al. [19]; ○, Grønvold and Stølen [48]; · · ·, fusion temperature.

Patashinski [49], and revealed in the case of lead [50]. The more complex defects are assumed to have liquid-like structure, consisting of a central atom, or a vacancy, and its nearest neighbors.

The excess heat capacity of very pure tin, zinc and aluminium at temperatures within a fraction of 1 K to fusion is at present not uniquely separable into those of impurity defects and of intrinsic defects. In the case of tin $\Delta_{\mathrm{prem}}C_{\mathrm{p,m}} = 38$ J K^{-1} mol^{-1} and $\Delta_{\mathrm{prem}}H_{\mathrm{m}} = 25$ J mol^{-1} were observed over a 0.656 K temperature interval ending 11 mK below the triple-point temperature [45]. The behaviour contrasts with the complete absence of such components in Ditmars' drop-calorimetric experiments to within 17 mK of the fusion temperature for a slightly less pure (4N85) tin sample [44]. In the case of zinc (6N) $\Delta_{\mathrm{prem}}C_{\mathrm{p,m}} = 1.9$ J K^{-1} mol^{-1} and $\Delta_{\mathrm{prem}}H_{\mathrm{m}} = 13$ J mol^{-1} over a 7.06 K temperature interval ending 5 mK below the triple-point temperature [47]. In Ditmars drop-calorimetric experiments for a zinc sample of comparable purity $\Delta_{\mathrm{prem}}H_{\mathrm{m}} = 40$ J mol^{-1} at ca. 50 mK below the fusion temperature [27]. Thus, in contrast to Ditmars results for tin it appears that for zinc some defect formation enthalpy is released on quenching. For aluminium there are no results in the premelting region.

The molar enthalpy of defect formation of solid zinc and aluminium under equilibrium conditions at the melting temperature are of the order 25 and 31 J mol^{-1} [40]. The results for tin based on Refs. [41,42] are 1 and 28 J mol^{-1}. The different models used in Ref. [43] result partly in even higher enthalpies of defect formation. They are of comparable magnitude to the difference between the drop and calorimetric results for tin, zinc and aluminium, see Table 2. Thus, it appear that vacancy defects, as well as further pre-solidification effects may be retained on quenching. Another interesting parameter is the interpolated difference between solid and liquid heat capacity at the fusion temperature. Again results obtained by drop

Table 2
Enthalpy of fusion, $\Delta_{\mathrm{fus}}H$, and heat capacity change on fusion, $\Delta_{\mathrm{s}}^{\mathrm{l}}C_{\mathrm{p}}$ of tin, zinc and aluminium

Drop calorimetry		Ref.	Adiabatic calorimetry		Ref.
$\Delta_{\mathrm{fus}}H$/(J mol^{-1})	$\Delta_{\mathrm{s}}^{l}C_{\mathrm{p}}$/(J K^{-1} mol^{-1})		$\Delta_{\mathrm{fus}}H$/(J mol^{-1})	$\Delta_{\mathrm{s}}^{\mathrm{l}}C_{\mathrm{p}}$/(J K^{-1} mol^{-1})	
M(Sn) = 118.710 g mol^{-1}					
7148 ± 22	−0.7	[44]	7195 ± 7	−2.3	[45]
			7179 ± 15	−2.0	[46]
			7187		[47]
M(Zn) = 65.39 g mol^{-1}					
7026 ± 40	0.8	[27]	7103 ± 30	2.4	[47]
M(Al) = 26.981539 g mol^{-1}					
10760 ± 70	≈−3	[19]	10827 ± 42	−0.9	[47]
			10805		[48]

calorimetry and by adiabatic-shield calorimetry differ considerably, cf. Table 2. It appears that drop calorimetric data are not of an accuracy which allows determination of the temperature dependency of the heat capacity for the liquid close to fusion. Obviously, the amount of energy which is stored on quenching a molten metal to 273 K and not released within minutes needs further investigation. In addition to the energy of ordinary crystalline defects in the solidifying metal which are retained as a result of fast cooling in the drop-calorimetric results, the mechanical deformation energy in the quenching process must be considered (see below). Also pre-crystalline defects and impurity-containing traces may cause some additional energy storage.

An order of magnitude measure of the enthalpy increase of a metal due to deformation in the quenching process may be found in the molar uniaxial elastic energy at the elastic limit [51]:

$$\Delta_{\mathrm{el}}U_{\mathrm{m}} = (\sigma_{\mathrm{e}}^{2}\cdot V_{\mathrm{m}})(2E)^{-1} + \alpha\sigma_{\mathrm{e}}TV_{\mathrm{m}}$$

Here σ_e is the limiting elastic stress, V_m the molar volume, α the linear thermal expansivity coefficient, and E the modulus of elasticity.

The first term on the right side of the equation represents the (reversible) work done on the metal and is of the order 0.1 J mol^{-1}. The second term – heat transferred to the metal for maintaining its temperature constant – is of the order 1 J mol^{-1}. Values are given for Sn, Zn and Al in Table 3. The elastic energy actually stored in a drop calorimetric sample at 273 K is smaller than the sum, since parts since the sample is partly in extension and partly in compression. It is further influenced by adherence to the container wall. Some additional energy is stored in plastic deformation.

For slightly plastically deformed aluminium recovery and recrystallization expectedly occur above 273 K, and the grain growth at even higher temperatures, but these additional effects are presumably also an order of magnitude smaller than the difference between the adiabatic and drop calorimetric enthalpy of fusion results for tin, zinc and aluminium. Thus, the energies associated with crystalline and solid-like defects remaining after quenching of the liquid metal appear as a major cause of the deficit in enthalpy of fusion results obtained by drop calorimetry compared to adiabatic calorimetry for tin, zinc and aluminium. Since some doubt still exists as to describing the observed trend to methodic differences, and since the defect formation enthalpies and the quenchability of the defects are somewhat uncertain, we will in the following disregard the consequences of systematic differences between adiabatic and drop calorimetric results.

3.3. Calorimetric techniques: a brief survey and evaluation of uncertainty

Calorimeters can be arranged in groups according to particular characteristics and various classification systems have been proposed [56,57]. The present section is intended to give a background for the uncertainties assigned in Section 4 to each individual calorimetric determination of an enthalpy of fusion. A simple classification scheme which does not follow previously suggested ones is, hence, used. For simplicity, only a small number of techniques is treated. It is in general not possible to assign a specific uncertainty to a given technique. A common uncertainty may, however, with some justification be used as a starting point for evaluation of determinations obtained with commercial instruments, especially DTA and DSC. The accuracy of laboratory-constructed instruments varies to a large extent and must be assessed in each individual case.

Table 3
Selected thermal and physical properties of tin, zinc and aluminium. Here σ_e is the elastic stress limit, E the modulus of elasticity, V_m the molar volume, α the linear thermal expansivity, and $\Delta_{el}U_m$ the molar uniaxial elastic energy at the elastic limit

	σ_e/(MPa)	E/(GPa) [54]	$V_m\times10^6$/(m^3 mol^{-1}) [55]	$\alpha\times10^6$/K [55]	$\Delta_{el}U_m$/(J mol^{-1})
Sn	3.4 [52]	48	14.4	22.0	1.8
Zn	17 [53]	99	9.2	30.2	0.9
Al	12 [53]	70	10.0	23.1	1.8

3.3.1. Techniques based on heating or cooling curves

Some of the earliest determinations of enthalpies of fusion were based on cooling or heating curves. The time dependence of the temperature on cooling or on heating sample plus container in a surrounding of approximately constant temperature was recorded and related to the behaviour of a standard material or the empty container. In the calculations Newton's cooling law was some times applied, and in other cases the extension of the constant temperature plateau. These determinations are burdened by rather large uncertainties and σ is here generally taken to be 10%.

3.3.2. Differential thermal analysis and differential scanning calorimetry [58,59]

DTA and DSC are closely related techniques. The word differential emphasises that measurements involve both a sample and a reference sample. Two main types of DSCs exist: heat-flux and power-compensated instruments. In heat flux DSC, as in DTA, the temperature difference between sample and reference material is measured and there is no clear distinction between these two types of instruments. Only a part of the heat released or absorbed during a phase transition is detected. The thermocouple system used is, hence, of crucial importance for the quality of the instrument. Early DSC determinations tend to be less accurate than those by more recent instrumentation. The relationship between heat-flux DSCs and classical DTAs is seen in a number of DSC-constructions where both the sample and the reference material are contained within a single furnace chamber. The temperature sensors in these constructions are placed in a disk of good thermal conductivity. A quite different approach is that used by Calvet [60]. In his apparatus two cylindrical sample chambers are in a common calorimeter block and the heat flux determined by differential thermopiles. In the following discussion distinction will be made between DTA, disk-type heat-flux DSC (DSC-HF), Calvet type heat-flux DSC (DSC-C) and power-compensated DSC (DSC-PC).

While the heat-flux DSC measures the temperature difference between sample and reference sample, power-compensated DSCs are based on compensation of the heat to be measured by electrical energy. The time integral over the compensating heating power is proportional to the enthalpy consumed by or released from the sample.

Proper calibration of the instruments is crucial. The basis of the enthalpy calibration is generally the enthalpy of fusion of a standard material. For this reason DTA and DSC results generally do not provide independent determination of enthalpies of fusion, in contrast to the requirement by Griffin and Laye [61]. Electrical calibration is an alternative which has been used both in DTA [62] and DSC [63–65] instrumentations. A resistor is placed in or attached to the calorimeter cell and heat peaks are produced by electrical means just before and after a comparable effect caused by the sample. The different heat transfer conditions during calibration and measurement put limits to the improvement. The repeatability of the electrical calibration peak is reported to be ca. 0.55% [21] for one construction, while the accuracy in determination of the electric energy dissipated is ca. 0.25–0.3% [38].

DTA has gradually developed from being a purely qualitative technique into a quantitative technique, and the uncertainty in the energetic results is expected to diminish accordingly. In the present evaluation results from older DTA and DSC studies are given uncertainties of the order 5–3%. More recent determinations are considered to have lower uncertainty, but the uncertainty depends to a large extent on the skills of the investigator. An interesting study by Höhne et al. [66] should be mentioned. It shows a difference of the order 1–1.5% between enthalpies of transitions determined by a heat-flux and a power-compensated DSC.

3.3.3. Drop-calorimetry [67,68]

In this technique, a sample is heated to a known temperature and is then dropped into a receiving calorimeter which is usually operated around room temperature. The calorimeter provides for measurement of the heat evolved in cooling the sample to the calorimeter temperature. Furthermore, the calorimeter must allow the heat delivered by the sample to be measured with high accuracy. Usually the temperature developments of the calorimeter and of the sample plus calorimeter combined serve for determination of the enthalpy increments. Some times the temperature development of the sample during cooling in the calorimeter is also followed. Often a large mass at constant or approximately constant temperature surrounds the calorimeter, which is thus termed quasi-isothermal or isoperibol.

The main sources of errors relate to temperature measurement and the attainment of equilibrium in the furnace, to evaluation of heat losses during drop, to the measurements of the heat release in the calorimeter, and to the reproducibility of the initial and final states of the sample. Isothermal calorimeters are in general more accurate. Here the volume change of a solid to liquid transformation occurring in the receiving calorimeter – usually containing H_2O or diphenyl ether – is measured. Isothermal conditions are maintained by the presence of melting ice or diphenyl ether in the surroundings. This type of calorimeter is in principle unsurpassed for enthalpy-increment determinations of substances with negligible instrinsic or extrinsic defect concentrations in the region of interest, like high purity synthetic sapphire, α-Al_2O_3, except in the vicinity of the melting point. The calorimeter is, however, not isothermal or adiabatic with regard to the sample to be studied, which is quenched in the transfer to the receiver, with accompanying influences on the observed thermodynamic properties of the substance in question.

A special form for drop calorimetry has been developed for high temperature studies of metals and alloys. At high temperatures reactions between sample and container lead to serious errors. They may be avoided by electromagnetic levitation of the sample in a vacuum furnace, and levitation drop calorimetry is a very powerful high temperature technique [69].

Relatively large uncertainties are assigned to early drop-calorimetric determinations where the temperature rise of water in the receiving calorimeter is a measure of the enthalpy increment. Determinations made before 1940 are in general given uncertainties of the order of 7.5–20%.

3.3.4. *Adiabatic calorimetry [70,71]*

Calorimeters with electrically heated shields which follow the surface temperature of the calorimeter with its contained sample offer unique possibilities for accurate determination of thermodynamic properties. They can be operated either with intermittent energy inputs preceded and followed by equilibration periods, or alternatively with continuous input of energy. In the latter, dynamic mode, the characteristics resemble those of DSC. The energy or enthalpy increments are usually fairly accurate for instantaneous processes, but the corresponding temperatures might be slightly shifted. With step-wise operation the accuracy of enthalpy and temperature determinations can be increased.

The continuous heating technique reached a high level of performance with the work of Moser [72]. Time has shown that the results suffered somewhat from the difficulty in correctly accounting for the heat exchange and dissipitation during continuous heating. The intermittent technique was brought to a high level of perfection by West and Ginnings [70].

In spite of the generally high accuracy of adiabatic calorimeters it is not possible to assign a common uncertainty to determinations made by this type of technique. The name adiabatic calorimetry only implies that the construction is based on adiabatic shields surrounding the calorimeter proper and, hence, says nothing about to what degree adiabatic conditions are maintained. Stretching the definition far, also power-compensated DSCs may with some justification be denoted adiabatic.

3.3.5. *Pulse calorimetry [73]*

Conventional steady-state and quasi steady-state techniques for accurate measurement of heat capacity are generally limited to temperatures below 2000 K. A special technique for studies of metals at very high temperature is the so-called pulse calorimetry in which the sample reaches high temperatures and different thermophysical properties are recorded in short times – sub-microsecond techniques have been reported. The accuracy is lower than obtained by drop-calorimetry but it seem reasonable to assume an uncertainty of ca. 3–5%.

4. Enthalpy standards: literature review and recommendations

All experimental calorimetric determinations known to the authors of the enthalpy of fusion for the metals considered are presented below in separate tables. The tables include the main characteristics of the experimental studies and also the presently assessed uncertainty. Some comments regarding the determinations for each metal are given in the following subsections. From these considerations, recommended enthalpy of fusion values and estimated

Table 4
Recommended enthalpy of fusion values and estimated uncertainties

Metal	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}/(\mathrm{J\ mol}^{-1})$	Estimated uncertainty $-\ 2\sigma/(\mathrm{J\ mol}^{-1})$
Ga	5576	19
In	3281	8
Sn	7173	20
Bi	11145	54
Cd	6211	77
Pb	4782	22
Zn	7068	28
Sb	19792	598
Al	10789	36
Ag	11284	225
Au	12720	304
Cu	12928	277
Ni	17042	376
Co	16056	369

uncertainties of the mean are derived. The results of the evaluation are summarized in Table 4.

Outline of the content in Tables 5–18: Each table heading contains the fusion temperature and molar mass value for the metal in question. The fusion temperature is the defining fixed point of ITS-90 for Ga, In, Sn, Zn, Al, Ag, Au, Cu [74]. For the remaining metals approximate values on ITS-90 are taken from [75]. The molar mass values correspond to the Standard Atomic weights 1997 [76].

The first three columns from the left side of the tables contain the name of the first author of the publication, the year of publication, and the reference number.

In column 4 the calorimetric method is indicated, some times with additional comment related to change in the enthalpy of fusion value, e.g. due to a superseded molar mass value (indicated in parenthesis) for some highly precise determinations. The purity indication in column 5 is generally on a mass basis, and does most often not include non-metallic impurities. The mass value in column 6 is either a rounded value, or when preceded by $\approx$, an order of magnitude value when more precise information is lacking, or an intermediate value of widely differing sample masses. Column 7 gives either the total number of enthalpy of fusion determinations as a single number, or the number of drop experiments in solid and liquid states as $n_{\mathrm{s}}+n_{\mathrm{l}}$. The total number of samples measured is recorded in column 8.

The resulting enthalpy of fusion value is found in column 9 with units as given in the paper. Some uncertainty is attached to the conversion of calories and other 'heat units' to joule. The unit used by Rudberg [77] was the heat necessary to raise the temperature of 1 g of water from 0 to 1°C. The limiting value, $\mathrm{cal}_0 = 4.2174$ J [78,79]. Later the 15°C calorie was commonly used, $\mathrm{cal}_{15} = 4.1855$ J [78,79], and during the latter half of this century the thermochemical calorie $\mathrm{cal}_{\mathrm{th}} = 4.184$ J [80]. The actual caloric unit used is seldom stated in earlier work, but when so (cf. Malaspina [81]) the result is reported here in J. The international (steam) Table calorie, $\mathrm{cal}_{\mathrm{IT}} = 4.1868$ J [79] is never referred to. When not stated we have assumed cal_{15} in the conversion to joule up to 1970, and $\mathrm{cal}_{\mathrm{th}}$ after that date, as indicated. The uncertainty value given is that derived or estimated by the authors. Gay-Lussac [82] used the latent heat of fusion of ice as unit, $\Delta_{\mathrm{fus}}H^0(\mathrm{H_2O}) = 6009$ J/mol or 333.56 J/g [23].

In the conversion of specific enthalpy of fusion values to molar ones in column 9 the 1997 molar mass values in the table headings have been used. Earlier molar enthalpy of fusion values have generally been taken without change due to the smallness of the changes in the years since 1925 [83]. They are within 0.05%, except for Au (0.12%).

The last two columns relate to the evaluation made here, with uncertainty assigned to each determination, and the deviation of the determination in question from the recommended value derived in the present assessment.

4.1. Gallium – Table 5

The most accurate values are presumably those by Amitin et al. [88] and Adams et al. [87] (adiabatic calorimetry) and that by Lavut and Chelovskaya [90] (by isoperibol calorimetry). The calorimeters used by the two former groups were built for low-temperature studies, whereas the one used by the latter group was built for high-temperature studies. The enthalpy of fusion reported by Amitin et al. [88] is 0.6% lower than the average of the two other determinations and may be questioned. The uncertainties of all three determinations are presently judged to be 0.3%.

Table 5
Enthalpy of fusion of gallium at $T_{\mathrm{fus}} = 302.9146$ K. $M(\mathrm{Ga}) = 69.723$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Berthelot	1878	[84]	drop – water at 286 K		34	2	1	19.11 $\mathrm{cal_{15}/g}$			
			transformed to 303 K here					19.24 $\mathrm{cal_{15}/g}$	5616	5	0.7
Roth	1933	[85]	drop – water	0.17% Zn	24	15	2	19.15 ± 0.02 $\mathrm{cal_{15}/g}$			
		[86]	revised					19.16 ± 0.01 $\mathrm{cal_{15}/g}$	5591	1.5	0.3
Adams	1952	[87]	adiabatic shield	3N8	93	3	1	1335.2 ± 1.0 $\mathrm{cal_{15}/mol}$	5588	0.3	0.2
Bros	1964	[63]	DSC-C-EC	tres grande	0.1			19.20 $\mathrm{cal_{15}/g}$	5603	1	0.5
Amitin	1984	[88]	adiabatic shield	6N	39	2	1	5551.8 ± 0.7 J/mol	5551.8	0.3	−0.4
Kano	1991	[89]	adiabatic shield	5N	25			5.61 kJ/mol	5610	3	0.6
Wolf	1994	[21]	DSC-HF-EC	5N	0.01	2	1	5.55 kJ/mol	5550	2	−0.5
Lavut	1995	[90]	isoperibol	6N	1500	11	1	5584.7 ± 0.5 J/mol	5584.7	0.3	0.2

Table 6
Enthalpy of fusion of indium at $T_{\text{fus}} = 429.7485$ K. $M(\text{In}) = 114.818$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\text{fus}}H_{\text{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Roth	1933	[85]	drop – water	3N	≈20	3	1	6.807 ± 0.025 cal$_{15}$/g			
		[86]	revised					6.797 ± 0.025 cal$_{15}$/g	3266	1.5	−0.4
Oelsen	1955	[91]	drop – water – scanning		200	1	1	0.779 kcal$_{15}$/mol	3261	3	−0.6
Oelsen	1955	[92]	drop – water – scanning		200	1	1	0.76 kcal$_{15}$/mol	3181	3	−3.0
Oelsen	1955	[93]	drop – water – scanning		200	9	1	0.781 ± 0.004 kcal$_{15}$/mol	3269	3	−0.4
Schneider	1956	[94]	drop – Cu-block	3N	≈30	2	1	0.79 ± 0.01 kcal$_{15}$/mol	3307	3	0.8
Oelsen	1957	[95]	cool. curve – air stream – scanning		≈200	1	1	0.76 kcal$_{15}$/mol	3181	3	−3.0
David	1964	[96]	DTA		0.002	1	1	6.9 cal$_{15}$/g	3316	4	1.1
Predel	1964	[62]	DTA-EC		≈10			806 ± 4 cal$_{15}$/mol	3374	3	2.9
Tarwater	1965	[97]	according to Ref. [24]					910 cal$_{15}$/mol	3809	20	16
Alpaut	1965	[98]	DTA-EC	5N	13	<3	1	798 ± 9 cal$_{15}$/mol	3340	4	1.8
Bros	1966	[99]	DSC-C	very pure				781 cal$_{15}$/mol	3269	1	−0.4
Gwinup	1968	[100]	DSC-HF					825 ±6 cal$_{15}$/mol	3453	4	5.3
Mechkovskii	1969	[101]	DTA		≈1			804 ±24 cal$_{15}$/mol	3365	4	2.6
Reznitskii	1970	[64]	DSC-EC-HF		≈2			0.80 kcal$_{\text{th}}$/mol	3348	15	2.1
Nedumov	1970	[102]	DTA	5N	1.2			6.80 cal$_{\text{th}}$/g	3267	3	−0.4
Malaspina	1971	[81]	DSC-EC-C	5N	0.2	3		3319 ± 81 J/mol	3319	3	1.2
Brennan	1973	[103]	DSC-PC					3260 J/mol	3260	3	−0.6
Marti	1974	[104]	DSC	5N5				3238 ± 39 J/mol	3238	2	−1.3
Widmann	1975	[105]	DSC-isothermal shield	extr. pure	0.08	1	1	6.84 cal$_{\text{th}}$/g	3286	2	0.2
Richardson	1975	[106]	DSC-PC	6N	≈0.05	15	3	3.35 ± 0.03 kJ/mol			
			revised according to Ref. [33]					3.31 ± 0.03 kJ/mol	3310	2	0.9
Lowings	1978	[9]	DSC-PC			8		6.837 ± 0.025 cal$_{\text{th}}$/g	3284	2	0.1
Grønvold	1978	[107]	adiabatic shield	6N	250	4	1	3283 ± 7 J/mol			
			{$M = 114.82$ g/mol} revised					3283 ± 7 J/mol	3283	0.3	0.1
Andon	1979	[33]	adiabatic shield	5N8 pellet	100	9	1	3252 ± 6 J/mol	3252	0.7	−0.9
Andon	1979	[33]	adiabatic shield	5N shot	100	9	1	3273 ± 8 J/mol	3273	0.7	−0.2
Andon	1979	[33]	adiabatic shield	3N2 powd	100	6	1	3247 ± 13 J/mol	3247	0.7	−1.0
Marti	1982	[108]	DSC-PC	5N5				3332 ± 17 J/mol	3332	2	1.6
Breuer	1982	[10]	DSC-HF	5N	≈0.015	6		3.28 ± 0.02 kJ/mol	3280	1	0.0
Schönborn	1983	[65]	DSC-EC-HF	5N5	0.045	3		3289 ± 9 J/mol	3289	0.7	0.3
Ancsin	1985	[39]	adiabatic shield	4,5,6N	200	8	3	28.53 ± 0.02 J/g	3276	0.3	−0.1
Callanan	1985	[34]	DSC	5N gran	0.05	20	5	28.623 ± 0.26 J/g	3286	1.5	0.2
Callanan	1985	[34]	DSC	6N rod	0.05	20	5	28.761 ± 0.27 J/g	3302	1.5	0.7
Callanan	1985	[34]	DSC	5N foil	0.05	20	5	28.937 ± 0.15 J/g	3322	1.5	1.3
Hemminger	1989	[37]	DSC-EC-C	4,7 N	≈0.1	10	3	28.59 ± 0.11 J/g			
			revised according to Ref. [109]					28.64 J/g	3288	0.7	0.2
Ditmars	1990	[110]	drop – ice	5N8 pellet				3283 J/mol	3283	0.3	0.1
Ditmars	1990	[110]	drop – ice	6N foil				3275 J/mol	3275	0.3	−0.2

Xiheng	1990	[111]	adiabatic shield	5N1	54			3265 J/mol	3265	0.5	−0.5
Kano	1991	[89]	adiabatic shield	6N	13			3.26 kJ/mol	3260	3	−0.6
Grønvold	1993	[46]	adiabatic shield	7N	200	5	1	3296 ± 9 J/mol	3296	0.3	0.5
Wolf	1994	[21]	DSC-EC-HF	5N5	≈0.01			3324 J/mol	3324	2	1.3
Wolf	1994	[21]	DSC-EC-HF	5N5	≈0.01	2	1	3.33 kJ/mol	3330	2	1.5
Zahra	1996	[14]	DSC-PC	4N+	0.0055	10		28.739 ± 0.20 J/g	3300	1.5	0.6

Table 7
Enthalpy of fusion of tin at $T_{\mathrm{fus}} = 505.078$ K. $M(\mathrm{Sn}) = 118.710\ \mathrm{g\ mol^{-1}}$

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}/(\mathrm{J\ mol^{-1}})$	Uncertainty (%)	Deviation (%)
Irvine Sr.	ca. 1780	[112]						33(5/9) $\mathrm{cal_{15}/g}$	9110	30	27
Rudberg	1829	[77]	cooling curve			1		13.314 $\mathrm{cal_{0}/g}$	6666	7.5	−7.1
Gay-Lussac	ca. 1830	[82]						$0.205\Delta_{\mathrm{fus}}H(\mathrm{H_2O})$ /g	8117	30	13
Person	1846	[113]	drop – water					14.3 $\mathrm{cal_{15}/g}$	7105	7.5	−1.3
Person	1848	[114]	drop – water		≈300	2		14.252 $\mathrm{cal_{15}/g}$	7081	7.5	−0.9
Spring	1886	[115]	cooling curve		≈25	1		14.651 $\mathrm{cal_{15}/g}$	7280	7.5	1.5
Mazzotto	1886	[116]	heating/cooling curve		485	7	1	13.617 $\mathrm{cal_{15}/g}$	6766	7.5	−5.7
Pionchon	1887	[117]	drop – water		≈25	0 + 6		14.6 $\mathrm{cal_{15}/g}$	7254	10	1.1
Richards	1893	[118]	drop – water					14.56 $\mathrm{cal_{15}/g}$	7234	10	0.9
Robertson	1902	[119]	drop – water		43	4 + 4	1	14.05 $\mathrm{cal_{15}/g}$	6981	10	−2.7
Glaser	1904	[120]	drop – water		≈2500	1 + 1	2	13.62 $\mathrm{cal_{15}/g}$	6767	15	−5.7
Guinchant	1907	[121]	cooling curve – EC		100	1		14.3 $\mathrm{cal_{15}/g}$	7105	20	−0.9
Wüst	1918	[122]	drop – ice	reinst	5	5 + 11		13.79 $\mathrm{cal_{15}/g}$	6852	15	−4.5
Iitaka	1919	[123]	drop – aniline	2N8				13.38 $\mathrm{cal_{15}/g}$	6648	10	−7.3
Umino	1926	[124]	drop –water	4N	15	4 + 8		14.2 $\mathrm{cal_{15}/g}$	7055	10	−1.6
Awbery	1926	[125]	drop – water	3N8	≈1000	4 + 4		14.6 $\mathrm{cal_{15}/g}$	7254	15	1.1
Möller	1928	[126]	drop – ice					13.8 ± 0.14 $\mathrm{cal_{15}/g}$	6857	10	−4.4
Cavallaro	1943	[127]	cooling curve		94			14.44 $\mathrm{cal_{15}/g}$	7175	10	0.0
Bartenev	1948	[128]	cooling curve	3N				13.96 $\mathrm{cal_{15}/g}$	6936	5	−3.3
Nagasaki	1952	[129]	heating cruve					1820 $\mathrm{cal_{15}/mol}$	7618	7.5	6.2
Khomyakov	1952	[130]	adiabatic scanning			3	3	15.7 ± 0.012 $\mathrm{cal_{15}/g}$	7801	15	8.8
Oelsen	1955	[91]	drop – water – scanning		200	2	2	1.72 ± 0.01 $\mathrm{kcal_{15}/mol}$	7199	3	0.4
Oelsen	1955	[91]	drop – water – scanning		200	2	1	1.71 $\mathrm{kcal_{15}/mol}$	7158	3	−0.2
Oelsen	1955	[92]	drop – water – scanning		200	1	1	1.64 $\mathrm{kcal_{15}/mol}$	6864	3	−4.3
Oelsen	1955	[93]	drop – water – scanning		200	8	1	1.69 ± 0.01 $\mathrm{kcal_{15}/mol}$	7073	3	−1.4
Oelsen	1957	[95]	cooling curve – air static – scanning		50	1	1	1.73 $\mathrm{kcal_{15}/mol}$	7241	3	1.0
Oelsen	1957	[95]	cool curve – air stream – scanning		200	1	1	1.66 $\mathrm{kcal_{15}/mol}$	6948	3	−3.1
Pascard	1959	[131]	DTA		1	2	1	14.7 $\mathrm{cal_{15}/g}$	7304	15	1.8
Genot	1960	[132]	drop – water – scanning		195			1720 ± 20 $\mathrm{cal_{15}/mol}$	7199	4	0.4
Schürmann	1961	[133]	drop – water – scanning		50			1.69 $\mathrm{kcal_{15}/mol}$	7073	3	−1.4

Table 7 (*Continued*)

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Speros	1963	[134,135]	DTA	5N	≈0.5	5		1692 cal$_{15}$/mol	7082	3	−1.3
David	1964	[96]	DTA		≈0.005	4	4	13.72 cal$_{15}$/g	6817	4	−5.0
Alpaut	1965	[98]	DTA-EC	3N6	13			1730 ± 19 cal$_{15}$/mol	7241	4	1.0
Yamaguchi	1966	[136]	cooling curve scanning		100	2		1730 ± 10 cal$_{15}$/mol	7241	7.5	1.0
Chiotti	1966	[137]	adiabatic scanning	5N		4		1645 ± 16 cal$_{15}$/mol	6885	3	−4.0
Plaza	1967	[138]	drop – diphenyl ether	5N8	7.28			1675 cal$_{15}$/mol	7011	2	−2.3
Gwinup	1968	[100]	DSC-HF					1739 ± 21 cal$_{15}$/mol	7279	4	1.5
Reznitskii	1970	[64]	DSC-EC-HF		≈2			1.77 kcal$_{\mathrm{th}}$/mol	7406	15	3.3
Nedumov	1970	[102]	DTA	5N	2.58			14.78 cal$_{\mathrm{th}}$/g	7341	3	2.3
Malaspina	1971	[81]	DSC-EC-C	5N	0.1	3	3	7108 ± 105 J/mol	7108	3	−0.9
Grønvold	1974	[45]	adiabatic shield	6N	300	3	1	7195 ± 7 J/mol			
			{M = 118.69 g/mol} revised					7196 ± 7 J/mol	7196	0.3	0.3
Breuer	1982	[10]	DSC-HF	5N	≈0.02	9		7.19 ± 0.03 J/mol	7190	1	0.2
Höhne	1983	[66]	DSC-PC	5N	0.01	5	5	7.14 ± 0.04 kJ/mol	7140	1.5	−0.5
Höhne	1983	[66]	DSC-HF	5N	0.01	5	5	7.19 ± 0.03 kJ/mol	7190	1.5	0.2
Hemminger	1989	[37]	DSC-EC-C	5,6N				60.14 ± 0.24 J/g			
			revised according to Ref. [109]					60.24 ± 0.24 J/g	7151	0.7	−0.3
Ditmars	1989	[44]	drop – ice	5N	25	25		7147 ± 22 J/mol			
			{M = 118.69 g/mol} revised					7148 ± 22 J/mol	7148	0.3	−0.3
Kano	1991	[89]	adiabatic shield	5N	5			7.20 kJ/mol	7200	3	0.4
Callanan	1992	[139]	DSC	5N				60.15 ± 0.15 J/g	7140	1.5	−0.5
Grønvold	1993	[46]	adiabatic shield	6N	213	3	1	7179 ± 15 J/mol	7179	0.3	0.1
Wolf	1994	[21]	DSC-EC-HF	5N	0.008			7.17 kJ/mol	7170	2	−0.2
Wolf	1994	[21]	DSC-EC-HF	5N	0.008	2		7.19 kJ/mol	7190	2	0.0
Wolf	1994	[21]	DSC-EC-HF	5N	0.008	20	10	60.33 ± 0.22 J/g	7162	2	0.2
Zahra	1996	[14]	DSC-PC	4N+	0.015			61.04 J/g	7246	1.5	1.0
Grønvold	1998	[47]	adiabatic shield	6N	151	5	1	7187 ± 11 J/mol	7187	0.3	0.2

Table 8
Enthalpy of fusion of bismuth at $T_{\text{fus}} = 544.55$ K. $M(\text{Bi}) = 208.98037$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\text{fus}}H_{\text{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Irvine Jr.	1804	[140]	drop – water		1500	7		23.65 (5/9) cal$_{15}$/g	11492	30	3.1
Gay-Lussac	ca 1830	[82]						0.22 $\Delta_{\text{fus}}H$ (H$_2$O)/g	15335	30	38
Person	1846	[113]	drop – water					12.4 cal$_{15}$/g	10846	7.5	−2.7
Person	1848	[114]	drop – water		≈500	1 + 2		12.64 cal$_{15}$/g	11056	7.5	−0.8
Mazzotto	1886	[116]	heating/cooling curve		694	3	1	12.393 cal$_{15}$/g	10840	7.5	−2.7
Roos	1916	[141]	cooling curve		50			12.5 ± 0.06 cal$_{15}$/g	10934	12.5	−1.9
Wüst	1918	[122]	drop – ice		5	5 + 9		10.23 cal$_{15}$/g	8948	15	−20
Iitaka	1919	[123]	drop – aniline	2N2		18 + 6		12.24 cal$_{15}$/g	10706	10	−3.9
Umino	1926	[124]	drop – water	3N	15	5 + 5		14.10 cal$_{15}$/g	12333	10	11
Awbery	1926	[125]	drop – water	3N8	1000	5 + 4		13.0 cal$_{15}$/g	11371	15	2.0
Kubasch.	1940	[142]	drop – water		28	6 + 6		2.63 kcal$_{15}$/mol	11008	5	−1.2
Cavarallo	1943	[127]	cooling curve		95			13.46 cal$_{15}$/g	11773	10	5.6
Nagasaki	1952	[129]	heating curve					2850 cal$_{15}$/mol	11929	7.5	7.0
Oelsen	1955	[91]	drop – water – scanning		200	2	1	2.72 ± 0.01 kcal$_{15}$/mol	11385	3	2.2
Oelsen	1955	[92]	drop – water – scanning		200	1	1	2.75 kcal$_{15}$/mol	11510	3	3.3
Oelsen	1955	[93]	drop – water –scanning		200	6	1	2728 ± 5 cal$_{15}$/mol	11418	3	2.4
Oelsen	1956	[143]	drop – water – scanning		200			2685 cal$_{15}$/mol	11238	3	0.8
Oelsen	1957	[95]	cooling curve – static air – scanning		50	1	1	2.68 kcal$_{15}$/mol	11217	3	0.6
Oelsen	1957	[95]	cooling curve – air stream – scanning		200	1	1	2.74 kcal$_{15}$/mol	11468	3	2.9
Pascard	1959	[131]	DTA		1.7	3	1	15.8 cal$_{15}$/g	13820	15	24
Oelsen	1961	[144]	drop – water – scanning		330			2.75 kcal$_{15}$/mol	11510	3	3.3
Schürmann	1961	[133]	drop – water – scanning		≈50			2.73 kcal$_{15}$/mol	11426	3	2.5
Chiotti	1966	[137]	adiabatic shield	5N		9		2755 ± 18 cal$_{15}$/mol	11531	3	3.5
Castanet	1968	[145]	DSC-C-EC	5N	1.5			2659 ± 15 cal$_{15}$/mol	11129	1	−0.1
Malaspina	1971	[81]	DSC-EC-C	5N		3	3	11252 ± 113 J/mol	11252	2.5	1.0
Grønvold	1975	[146]	adiabatic shield	6N	260	4	1	11131 ± 11 J/mol	11131	0.3	−0.1
Breuer	1982	[10]	DSC-HF	5N5	≈0.01	9		11.09 ± 0.12 kJ/mol	11090	1	−0.5
Höhne	1983	[66]	DSC-PC	5N5	0.01	5	5	11.01 ± 0.13 kJ/mol	11010	1.5	−1.2
Höhne	1983	[66]	DSC-HF	5N5	0.01	5	5	11.09 ± 0.12 kJ/mol	11090	1.5	−0.5
Raetz	1989	[38]	DSC-EC-HF	6N	0.20	1		52.93 ± 0.21 J/g			
			revised according to Ref. [109]					53.03 ± 0.21 J/g	11082	1	−0.6
Kano	1989	[147]	adiabatic shield	6N	90			11478 J/mol	11478	3	3.0
Wolf	1994	[21]	DSC-EC-HF	5N5	≈0.01	2	1	11360 J/mol	11360	2	1.9
Wolf	1994	[21]	DSC-EC-HF	5N5	≈0.01			11260 J/mol	11260	2	1.0

Table 9
Enthalpy of fusion of cadmium at $T_{fus} = 594.22$ K. $M(\text{Cd}) = 112.411$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{fus}H_m$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Person	1848	[148]	drop – water					13.66 cal$_{15}$/g	6427	7.5	3.5
Roos	1916	[141]	cooling curve		43			13.7 ± 0.06 cal$_{15}$/g	6446	7.5	3.8
Wüst	1918	[122]	drop – ice		5	6 + 8		10.81 cal$_{15}$/g	5086	15	−18
Umino	1926	[124]	drop – water	3N6	16	6 + 5		12.90 cal$_{15}$/g	6069	10	−2.3
Cavarallo	1943	[127]	cooling curve		75			12.9 cal$_{15}$/g	6069	10	−2.3
Nagasaki	1952	[129]	heating curve					1540 cal$_{15}$/mol	6446	7.5	3.8
Khomyakov	1952	[130]	adiabatic scanning	2N6		1		15.2 cal$_{15}$/g	7152	15	15
Oelsen	1955	[91]	drop – water – scanning		≈500	4	2	1.49 ± 0.02 kcal$_{15}$/mol	6236	3	0.4
Oelsen	1955	[92]	drop – water – scanning		200	1	1	1.46 kcal$_{15}$/mol	6111	3	−1.6
Oelsen	1955	[93]	drop – water – scanning		≈500	10	2	1484 ± 7 cal$_{15}$/mol	6211	3	0.0
Schneider	1956	[94]	drop – Cu-block	rein	≈10	2	1	1.52 ± 0.01 kcal$_{15}$/mol	6362	5	2.4
Oelsen	1956	[143]	drop – water – scanning		200			1456 cal$_{15}$/mol	6094	3	−1.9
Oelsen	1956	[149]	drop – water – scanning		200			1.54 kcal$_{15}$/mol	6446	3	3.8
Oelsen	1957	[95]	cooling curve – air stream – scanning		200	1	1	1.46 kcal$_{15}$/mol	6111	3	−1.6
Pascard	1959	[131]	DTA		1.5	2	1	14.1 cal$_{15}$/g	6634	15	6.8
Heumann	1960	[150]	DTA-EC		≈10			1503 ± 7 cal$_{15}$/mol	6291	3	1.3
Schürman	1961	[133]	drop – water – scanning		≈50			1.50 kcal$_{15}$/mol	6278	3	1.1
Malaspina	1971	[151]	DSC-EC	5N	0.1	4	2	6199 ± 75 J/mol	6199	3	−0.2
Breuer	1982	[10]	DSC-HF	5N8	0.02	5		6.21 ± 0.11 kJ/mol	6210	1	0.0
Zahra	1996	[14]	DSC-PC	4N+	0.01			54.92 J/g	6174	1.5	−0.6

Table 10
Enthalpy of fusion of lead at $T_{fus} = 600.61$ K. $M(Pb) = 207.2$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{fus}H_m$/(J mol^{-1})	Uncertainty (%)	Deviation (%)
Irvine Jr.	1804	[140]	drop – water			5		5.604 (5/9) cal_{15}/g	2700	30	−44
Rudberg	1830	[77]	cooling curve					5.86 cal_0/g	5121	7.5	7.0
Gay-Lussac	ca 1830	[82]						0.08 $\Delta_{fus}H$ (H_2O) /g	5529	30	16
Person	1846	[113]	drop – water					5.15 cal_{15}/g	4466	7.5	−6.6
Person	1848	[114]	drop – water		≈500	1 + 2		5.37 cal_{15}/g	4657	7.5	−2.6
Spring	1886	[115]	cooling curve					5.320 cal_{15}/g	4614	7.5	−3.5
Mazzotto	1891	[116]	extrap heat/cool curve					5.37 cal_{15}/g	4657	7.5	−2.6
Robertson	1903	[119]	drop – water	100.15	45	4 + 3		6.45 cal_{15}/g	5594	10	17
Glaser	1904	[120]	drop – water		≈5000	1 + 3		4.78 cal_{15}/g	4145	15	−13
Roos	1916	[141]	cooling curve		57			6.37 ± 0.03 cal_{15}/g	5524	12.5	16
Wüst	1918	[122]	drop – ice		5	7 + 10		5.47 cal_{15}/g	4744	15	−0.8
Iitaka	1919	[123]	drop – aniline	3N		?		5.53 cal_{15}/g	4796	10	0.3
Umino	1926	[124]	drop – water	3N8	15	6 + 6		5.50 cal_{15}/g	4770	10	−0.2
Awbery	1926	[125]	drop – water	3N7	≈3000	4 + 4		6.26 cal_{15}/g	5429	15	14
Klinkhardt	1927	[152]	electron bombardment		70	5		5.65 ± 0.06 cal_{15}/g	4900	10	2.5
Cavallaro	1943	[127]	cooling curve		100			6.0 cal_{15}/g	5203	10	8.8
Bartenev	1947	[128]	cooling curve	3N				5.45 cal_{15}/g	4726	5	−1.2
Nagasaki	1952	[129]	heating curve					1190 cal_{15}/mol	4981	7.5	4.2
Douglas	1954	[153]	drop – ice	3N	45	3 + 7		23.03 ± 0.05 J/g	4772	0.5	−0.2
Oelsen	1955	[91]	drop – water – scanning		≈700	4	3	1.17 ± 0.02 $kcal_{15}$/mol	4897	3	2.4
Oelsen	1955	[92]	drop – water – scanning		300	1	1	1.18 $kcal_{15}$/mol	4939	3	3.3
Oelsen	1955	[93]	drop – water – scanning		≈700	10	3	1158 ± 5 cal_{15}/mol	4847	3	1.4
Oelsen	1956	[149]	drop – water – scanning					1.20 $kcal_{15}$/mol	5023	3	5.0
Oelsen	1957	[95]	cooling curve – air stream – scanning		≈300	1	1	1.16 $kcal_{15}$/mol	4855	3	1.5
Pascard	1959	[131]	DTA		2.0	4	1	5.9 cal_{15}/g	5117	15	7.0
Lazarev	1959	[154]	heating curve					6.0 cal_{15}/g	5203	10	8.8
Heumann	1960	[150]	DTA-EC		≈10			1164 ± 10 cal_{15}/mol	4872	2.5	1.9
Schürmann	1961	[133]	drop – water – scanning		80			1.20 $kcal_{15}$/mol	5023	3	5.0
Speros	1963	[134, 135]	DTA-PC	5N	≈1	5		1134 ± 6 cal_{15}/mol	4746	3	−0.7
Yamaguchi	1966	[136]	cooling curve – scanning		176	2		1220 cal_{15}/mol	5106	7.5	6.8
Schürmann	1965	[155]	drop – water – scanning		380	4		1.18 $kcal_{15}$/mol	4939	3	3.3
Chiotti	1966	[137]	adiabatic scanning	5N		6		1175 ± 9 cal_{15}/mol	4918	3	2.8
Gwinup	1967	[100]	DSC-HF					1143 ± 3 cal_{15}/mol	4784	4	0.0
Reznitskii	1970	[64]	DSC-EC-HF		≈2			1.31 $kcal_{th}$/mol	5481	15	15
Dosch	1970	[156]	adiabatic scanning		1.5	2		5.6 cal_{th}/g	4855	2	1.5
Malaspina	1971	[81]	DSC-EC	5N	~0.3	3	3	4626 ± 100 J/mol	4626	3	−3.3
Breuer	1982	[10]	DSC-HF	5N	0.015	3		4.79 ± 0.07 kJ/mol	4790	1	0.2
Kano	1991	[89]	adiabatic shield	5N				5.44 kJ/mol	5440	4	14
Wolf	1994	[21]	DSC-EC-HF	5N5	≈0.01	2		4.77 kJ/mol	4770	2	−0.2
Zahra	1996	[14]	DSC-PC	4N+	0.018			23.26 J/g	4819	1.5	0.8
Grønvold	1998	[47]	adiabatic shield	5N5	209	5	1	4765 ± 11 J/mol	4766	0.3	−0.3

Table 11
Enthalpy of fusion of zinc at $T_{\mathrm{fus}} = 692.677$ K. $M(\mathrm{Zn}) = 65.39$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Irvine Jr.	1804	[140]	drop – water			3		48.3 (5/9) cal$_{15}$/g	7344	30	3.9
Person	1846	[113]	drop – water					27.46 cal$_{15}$/g	7516	7.5	6.3
Person	1848	[114]	drop – water		$\approx$200	0 + 3		28.13 ± 0.46 cal$_{15}$/g	7699	7.5	8.9
Mazzotto	1886	[116]	drop – water					28 cal$_{15}$/g	7663	7.5	8.0
Glaser	1904	[120]	drop – water		$\approx$3000	3 + 2		29.86 cal$_{15}$/g	8172	15	16
Greenwood	1911	[157]	drop					26 cal$_{15}$/g	7116	10	0.7
Lashchenko	1913	[158]	drop – water		5	13 + 3		26.5 cal$_{15}$/g	7253	10	2.6
Wüst	1918	[122]	drop – ice		5	9 + 10		23.01 cal$_{15}$/g	6298	15	-11
Iitaka	1919	[123]	drop – aniline	98.7		?		23.1 cal$_{15}$/g	6322	10	-11
Umino	1926	[124]	drop – water	3N5	15	8 + 6		23.60 cal$_{15}$/g	6459	10	-8.6
Awbery	1926	[125]	drop – water	very pure	$\approx$3000	4 + 4		26.58 cal$_{15}$/g	7275	15	2.9
Cavallaro	1943	[127]	cooling curve		100			28.67 cal$_{15}$/g	7847	10	11
Oelsen	1955	[91]	drop – water – scanning		$\approx$650	2	2	1.71 ± 0.02 kcal$_{15}$/mol	7157	3	1.3
Oelsen	1955	[93]	drop – water – scanning		140	5	5	1.70 ± 0.02 kcal$_{15}$/mol	7115	3	0.7
Oelsen	1957	[95]	cooling curve – air stream – scanning		200	1	1	1.71 kcal$_{15}$/mol	7157	3	1.3
Oelsen	1957	[95]	cooling curve – air static – scanning		50	1	1	1.75 kcal$_{15}$/mol	7325	3	3.6
Pascard	1959	[131]	DTA		1.4	2	1	27.4 cal$_{15}$/g	7499	15	6.1
Génot	1960	[132]	drop – water – scanning		195			1750 ± 20 cal$_{15}$/mol	7325	4	3.6
Dobovisek	1960	[159]	DTA		4			1670 cal$_{15}$/mol	6990	10	-1.1
Schürmann	1961	[133]	drop – water – scanning		50			1.66 kcal$_{15}$/mol	6948	3	-1.7
Chiotti	1966	[137]	adiabatic shield	4N		9		1755 ± 20 cal$_{15}$/mol	7346	3	3.9
Gwinup	1967	[100]	DSC-HF					1762 ± 10 cal$_{15}$/mol	7375	4	4.3
Reznitskii	1970	[64]	DSC-EC-HF		$\approx$2			1.35 kcal$_{\mathrm{th}}$/mol	5648	15	-20
Malaspina	1971	[151]	DSC-EC	5N	0.1	4	2	7183 ± 84 J/mol	7184	3	1.6
Breuer	1982	[10]	DSC-HF	5N	0.013	5		7.1 ± 0.04 kJ/mol	7100	1	0.5
Ditmars	1990	[27]	drop – ice	6N	ca. 20	20 + 12	2	7026 ± 40 J/mol			
			{$M = 65.38$ g/mol} revised					7027 ± 40 J/mol	7027	0.3	-0.6
Wolf	1994	[21]	DSC-EC-HF	5N				6.86 kJ/mol	6860	2	-2.9
Zahra	1996	[14]	DSC-PC	4N+	0.003	10		107.50 ± 0.32 J/g	7030	1.5	-0.5
Grønvold	1998	[47]	adiabatic shield	6N	140	5	1	7103 ± 31 J/mol	7103	0.3	0.5

Table 12
Enthalpy of fusion of antimony at $T_{\mathrm{fus}} = 903.78$ K. $M(\mathrm{Sb}) = 121.760\ \mathrm{g\ mol^{-1}}$

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ ($\mathrm{J\ mol^{-1}}$)	Uncertainty (%)	Deviation (%)
Lashchenko	1914	[160]	drop – water	2N	5	17 + 3		40.5 $\mathrm{cal_{15}/g}$	20640	10	4.3
Wüst	1918	[122]	drop – ice		5	10 + 8		38.86 $\mathrm{cal_{15}/g}$	19804	15	0.1
Umino	1926	[124]	drop – water	2N7	15	6 + 5		40.75 $\mathrm{cal_{15}/g}$	20767	10	4.9
Awbery	1926	[125]	drop – water	3N5	1000	2 + 2		24.3 $\mathrm{cal_{15}/g}$	12384	15	−37
Richnow	1941	[161]	heating curve		35	1		20.6 ± 0.33 $\mathrm{cal_{15}/g}$	10498	50	−47
Cavallaro	1943	[127]	cooling curve		71	1		39.4 $\mathrm{cal_{15}/g}$	20079	10	1.5
Wittig	1950	[162]	DTA-EC		15			37.9 ± 2.1 $\mathrm{cal_{15}/g}$	19315	4	−2.4
Oelsen	1955	[93]	drop – water – scanning		≈135	7	2	4875 ± 20 $\mathrm{cal_{15}/mol}$	20404	3	3.1
Schürmann	1961	[133]	drop – water – scanning		50			4.83 $\mathrm{kcal_{15}/mol}$	20216	3	2.1
Reznitskii	1970	[64]	DSC-EC-HF		≈2			4.23 $\mathrm{kcal_{th}/mol}$	17698	15	−11
Malaspina	1971	[81]	DSC-EC	5N	0.1	3	3	19879 ± 318 J/mol	19879	3	0.4

Table 13
Enthalpy of fusion of aluminium at $T_{\mathrm{fus}} = 933.473$ K. $M(\mathrm{Al}) = 26.981539$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Pionchon	1892	[163]	drop – water	2N1		21 + 5		80 cal_{15}/g	9034	20	−16
Richards	1893	[118]	drop – water			0 + 4		100 cal_{15}/g	11293	10	4.7
Glaser	1904	[120]	drop – water		2000	2 + 2		76.80 cal_{15}/g	8673	15	−20
Greenwood	1911	[157]	drop					95 cal_{15}/g	10728	10	−0.6
Lashchenko	1914	[160]	drop – water	2N	≈1	25 + 3		87.1 cal_{15}/g	9836	10	−8.8
Roos	1916	[141]	cooling curve		13.5			80.3 cal_{15}/g	9068	12.5	−16
Roos	1916	[141]	drop – water		15	4		82.0 cal_{15}/g	9260	12.5	−14
Wüst	1918	[122]	drop – ice		5	10 + 8		93.96 cal_{15}/g	10611	15	−1.7
Umino	1926	[124]	drop – water	90.1	15	12 + 7		79.64 cal_{15}/g	8994	10	−17
Awbery	1926	[125]	drop – water	2N7	782	6 + 6		92.4 cal_{15}/g	10435	15	−3.3
Oelsen	1937	[164]	drop liquid Al	2N4	50	3 + 7		96 cal_{15}/g	10841	3	0.5
Awbery	1938	[165]	heating–cooling curve	4N		6		91 cal_{15}/g	10277	15	−4.7
Richnow	1941	[161]	heating curve		19	1		89.7 ± 2.1 cal_{15}/g	10130	30	−6.1
Cavarallo	1943	[127]	cooling curve					81.5 cal_{15}/g	9204	10	−15
Wittig	1952	[166]	DTA-EC	5N		15		383.8 ± 6.2 J/g	10356	4	−4.0
Oelsen	1955	[91]	drop – water – scanning		250	2	1	2.66 ± 0.05 kcal_{15}/mol	11133	3	3.2
Oelsen	1955	[93]	drop – water – scanning		≈150	5	2	2.63 ± 0.03 kcal_{15}/mol	11008	3	2.0
Pascard	1959	[131]	DTA		0.4	3	1	81 cal_{15}/g	9147	15	−15
Schürmann	1961	[133]	drop – water – scanning					2.57 kcal_{15}/mol	10757	3	−0.3
Speros	1963	[134,135]	DTA-quantitative	5N	≈0.1	6		2566 cal_{15}/mol	10740	3	−0.5
Chiotti	1966	[137]	adiabatic shield	4N+		4		2630 ± 8 cal_{15}/mol	11008	3	2.0
McDonald	1967	[16]	drop – Cu-block	5N	6	16 + 10		2560 ± 50 cal_{15}/mol	10715	0.7	−0.7
Schmidt	1970	[167]	adiabatic scanning	4N	45			10700 ± 100 mol	10700	1.5	−0.8
Ditmars	1985	[19]	drop – ice					10760 ± 70 J/mol	10760	0.3	−0.3
Grønvold	1998	[47]	adiabatic shield	5N	35	3	1	10827 ± 42 J/mol	10827	0.3	0.4
Grønvold	1998	[48]	adiabatic shield	4N	55	1	1	10805 J/mol	10805	0.3	0.1

Table 14
Enthalpy of fusion of silver at $T_{\mathrm{fus}} = 1234.93$ K. $M(\mathrm{Ag}) = 107.8682$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Person	1848	[148]	drop – water					21.07 cal$_{15}$/g	9513	7.5	−16
Pionchon	1887	[117]	drop – water		≈40	14 + 5		24.72 cal$_{15}$/g	11161	10	−1.1
Wüst	1918	[122]	drop – ice		5	15 + 8		26.02 cal$_{15}$/g	11748	15	4.1
Umino	1926	[124]	drop – water		15	9 + 4		24.90 cal$_{15}$/g	11242	10	−0.4
Cavallaro	1943	[127]	cooling curve		85	1		24.15 cal$_{15}$/g	10903	10	−3.4
Wittig	1950	[162]	DTA-EC		40			24.2 ± 0.9 cal$_{15}$/g	10926	4	−3.2
Oelsen	1957	[95]	cooling curve – air stream – scanning		200	1		2.61 kcal$_{15}$/mol	10924	3	−3.2
Speros	1963	[134]	DTA-quant.	5N	0.5			2728 cal$_{15}$/mol	11418	3	1.2
Dokken	1965	[169]	drop – liquid Ag – alloy	4N		2		2890 ± 250 cal$_{15}$/mol	12096	7.5	7.2
Vollmer	1968	[170]	adiabatic scanning	3N7	200			11400 ± 150 J/mol	11400	1.5	1.0
Callanan	1995	[171]	DTA			9		106.7 ± 6.7 J/g	11510	4	2.0
Callanan	1995	[171]	DTA			10		108.4 ± 3.3 J/g	11693	4	3.6

Table 15
Enthalpy of fusion of gold at $T_{\mathrm{fus}} = 1337.33$ K. $M(\mathrm{Au}) = 196.96654$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Roberts-Austen	1891	[172]	DTA					16.33 cal$_{15}$/g	13463	15	5.0
Ludwik	1914	[173]						14.7 cal$_{15}$/g	12119	15	−4.7
Wüst	1918	[122]	drop – ice		5	16 + 7		15.87 cal$_{15}$/g	13083	15	2.9
Umino	1926	[124]	drop – water		15	10 + 3		15.73 cal$_{15}$/g	12968	10	2.0
Plaza	1967	[138]	drop – diphenyl ether	5N+	ca. 15			2946 cal$_{15}$/mol	12330	3	−3.1
Vollmer	1968	[170]	adiabatic scanning	3N6	300			12700 ± 200 J/mol	12700	1.5	−0.2
Nedumov	1970	[102]	DTA	5N	4.8			16.75 cal$_{\mathrm{th}}$/g	13804	5	8.5
Lebedev	1973	[174]	pulse heating	4N		17		70 ± 3.5 J/g	13788	5	8.4
Kaschnitz	1993	[175]	pulse heating	5N				62 ± 3 J/g	12212	5	−4.0

Table 16
Enthalpy of fusion of copper at $T_{\mathrm{fus}} = 1357.77$ K. $M(\mathrm{Cu}) = 63.546$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Richards	1897	[118]	drop – water			0 + 6		43.3 cal$_{15}$/g	11517	10	−11
Glaser	1904	[120]	drop – water		3000	2 + 2		41.63 cal$_{15}$/g	11072	15	−14
Wüst	1918	[122]	drop – ice		5	14 + 7		40.97 cal$_{15}$/g			
			corrected [176]					50.97 cal$_{15}$/g	13557	15	4.9
Umino	1926	[124]	drop – water		15	11 + 7		49.95 cal$_{15}$/g	13285	10	2.8
Esser	1933	[176]	drop – metal block	electrol		14 + 4		50.9 cal$_{15}$/g	13538	7.5	4.7
Oelsen	1961	[144]	drop – water		300			3.03 kcal$_{15}$/mol	12682	3	−1.9
Schürmann	1965	[155]	drop – water		300			3.08 kcal$_{15}$/mol	12891	3	−0.3
Dokken	1965	[169]	drop – liquid Cu 1200°C	3N+		5		3290 ± 275 cal$_{15}$/mol	13770	7.5	6.5
Vollmer	1968	[170]	adiabatic scanning	5N	150			13000 ± 200 J/mol	13000	1.5	0.6
Nedumov	1970	[102]	DTA	3N	2.07			47.85 cal$_{\mathrm{th}}$/g	12722	5	1.6
Baricco	1995	[177]	DSC-C		0.2			13.1 ± 0.4 kJ/mol	13100	4	1.3
Pottlacher	1997	[178]	pulse heating					203 ± 10 J/g	12900	5	−0.2

Table 17
Enthalpy of fusion of nickel at $T_{\mathrm{fus}} = 1728.15$ K. $M(\mathrm{Ni}) = 58.6934$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Wüst	1918	[122]	drop – ice		5	33 + 4		56.08 cal$_{15}$/g	13777	15	−19
White	1921	[179]	drop – water	2N1	27	2 + 2		73 cal$_{15}$/g	17933	10	5.2
Umino	1926	[124]	drop – water	3N2	15	16 + 3		70.40 cal$_{15}$/g	17295	10	1.5
Geoffray	1963	[180]	drop – metal-block – adiabatic	3N5		27 + 33		4176 ± 54 cal$_{15}$/mol	17479	7.5	2.6
Vollmer	1966	[181]	adiabatic scanning	3N8	150			16900 ± 250 J/mol	16900	1.5	−0.8
Nedumov	1970	[102]	DTA	2N5	1.76			68.0 cal$_{\mathrm{th}}$/g	16699	5	−2.0
Predel	1970	[182]	DSC	4N	100			4070 ± 150 cal$_{\mathrm{th}}$/mol	17029	4	−0.1
Lebedev	1971	[183]	pulse heating	2N5				318 ± 9 J/g	18665	10	9.5
Seydel	1977	[184]	pulse heating	4N		6		322 ± 18 J/g	18899	10	11
Seydel	1979	[185]	pulse heating					306 J/g	17960	10	5.4
Pottlacher	1987	[186]	pulse heating					292 ± 15 J/g	17138	5	0.6
Bonell	1988	[187]	levitation drop					14900 ± 360 J/mol	14900	5	−13
Korobenko	1990	[188]	pulse heating	3N8				292 ± 15 J/g	17138	5	0.6
Obendrauf	1993	[189]	pulse heating	3N8				307 ± 9 J/g	18019	5	5.7
Kaschnitz	1994	[190]	pulse heating	3N8		5		17.03 ± 0.85 kJ/mol	17030	5	−0.1
Baricco	1995	[177]	DSC		0.2			17.5 ± 0.1 kJ/mol	17500	4	2.7

Table 18
Enthalpy of fusion of cobalt at $T_{\mathrm{fus}} = 1768.15$ K. $M(\mathrm{Co}) = 58.9332$ g mol^{-1}

First author	Year	Ref.	Method	Purity	Mass/g	n	p	Value reported	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/ (J mol^{-1})	Uncertainty (%)	Deviation (%)
Wüst	1918	[122]	drop – ice		5	21 + 5		58.23 cal$_{15}$/g	14363	15	−11
Umino	1926	[124]	drop – water	98.1%	15	18 + 3		67.00 cal$_{15}$/g	16527	10	2.9
Vollmer	1966	[181]	adiabatic scanning	5N	150			16200 ± 250 J/mol	16200	1.5	0.9
Nedumov	1970	[102]	DTA	98%	1.7			67.79 cal$_{15}$/g	16715	5	4.1
Predel	1970	[182]	DSC	2N6	100			3740 ± 160 cal$_{15}$/mol	15648	4	−2.5
Treverton	1971	[191]	levitation drop	3N5		? + 12		3670 ± 70 cal$_{15}$/mol	15355	3	−4.4
Seydel	1977	[184]	pulse heating	4N		6		300.7 ± 18 J/g	17721	10	11
Seydel	1979	[185]	pulse heating	—				302 J/g	17798	10	10
Hess	1994	[192]	pulse heating	4N				273 J/g	16089	5	0.2

Early determinations by Roth et al. [85,86], using an isoperibol calorimeter, as well as the more recent Calvet-calorimetry determination by Bros et al. [63] concord. Both Kano [89] and Wolf et al. [21] have determined the enthalpy of fusion of several metals, with results scattering around the more plausible values. The determinations by Wolf et al. [21] are within 2% of the presently recommended values. Larger deviations are observed for the values reported by Kano [89], e.g. near 14% for lead, see below. The very early determination by Berthelot [84] (1878) who used a phase change calorimeter is only 0.7% higher than the presently recommended value.

4.2. Indium – Table 6

Indium is the most used metal for temperature and enthalpy calibration and a large number of experimental determinations have been reported. Highest weight (lowest uncertainty) is given to the determinations by Grønvold [46,107] and by Ancsin [39] (by adiabatic calorimetry) and to those by Ditmars [110] (by drop calorimetry). These are in relatively good agreement and are presumably the most accurate. Accurate determinations have also been made by Andon et al. [33], Schönborn et al. [65] and Hemminger and Raetz [37]. The latter two determinations were made by groups using a carefully electrically calibrated DSC to which an uncertainty of 0.7% is presently assigned. It should be noted that a reduction of this uncertainty to 0.5% does not change the derived value of the enthalpy of fusion, nor the associated uncertainty of the mean given in Table 3. Andon et al. [33] at the National Physical Laboratory of UK used an adiabatic calorimeter. Slightly low enthalpies of fusion where obtained and the standard material was later withdrawn. Less weight is accordingly given to their determinations than to the other determinations by adiabatic calorimetry.

Some additional accurate determinations are grouped in a third category, e.g. those reported by Roth et al. [85,86], Bros [99], Breuer and Eysel [10], Callanan et al. [34], and Zahra and Zahra [14]. They seem to be slightly more accurate than the remaining DSC determinations. More recent DSC/DTA determinations are in general judged to have a lower uncertainty than the older ones. We have assigned uncertainties from 5 to 2% to most of the DSC/DTA determinations on this basis.

Four of the determinations in Table 5 and a large number of the determinations to be presented in the following sections were made by Oelsen and coworkers in the mid-fifties. They used a range of different calorimeters. The enthalpy of fusion determinations are in general estimated to have uncertainties of the order 3%.

4.3. Tin – Table 7

Tin is another metal which is frequently used for enthalpy calibration. The situation with regard to the types of enthalpy of fusion determinations available is similar to that for indium. However, in addition to some determinations by adiabatic calorimetry and many by DSC, a number of early drop-calorimetric determinations exist. Ten of them were made before 1900 and the first one by Irvine Sr. and Black at around 1780 [112]. Most of the early determinations are not of the highest accuracy, but still impressing taking their age into consideration. The uncertainties are of the order 10%.

Among the more accurate determinations, the adiabatic calorimetric results by Grønvold [45–47] are higher than the drop calorimetric data by Ditmars [44]. The possibility of quenching in of disorder in drop calorimetric experiments might explain the discrepancy. Equal uncertainties are assigned to all these determinations.

Among the DSC-determinations, highest weight is given to the results by Hemminger and Raetz [37], but also the determinations by Breuer and Eysel [10], Höhne et al. [66], Callanan et al. [139], and Zahra and Zahra [14] seem to be of better than average quality.

4.4. Bismuth – Table 8

The spread in the reported values of the enthalpy of fusion is larger than for the previously considered metals. Furthermore, the only determination to which an uncertainty below 1% can reasonably be given is the one by Grønvold [146]. The more reliable DSC-determinations, e.g. those by Castanet et al. [145], Breuer and Eysel [10], Höhne et al. [66] and Raetz

[38] agree with the adiabatic calorimetry result by Grønvold [146].

The value recommended by Sarge et al. [2] is considerably higher, since they gave equal weight to the result by Grønvold [146] and that by Kano [147]. Kano's calorimeter was primarily built for heat-capacity studies of supercooled metals and the quality of the instrument was not evaluated through measurements of the heat capacity of synthetic sapphire. Nor are fractional fusion data reported. Result by Kano for the fusion of other metals [89] show that the calorimeter is not of the highest accuracy and the determinations with this calorimeter are given uncertainties of 3% in the present evaluation.

4.5. Cadmium – Table 9

No determinations of the enthalpy of fusion appear to exist by calorimeters proven to give highly accurate values. Hence, the standard deviation of the mean value is larger than for the previously treated metals. Determinations by adiabatic calorimetry are needed for Cd before using it as an enthalpy standard for accurate work. Highest weight is given to the determinations by Breuer and Eysel [10], Zahra and Zahra [14], Heumann and Predel [150] and Malaspina et al. [151]. The two latter groups used electrically calibrated instruments.

4.6. Lead – Table 10

Lowest uncertainty and, hence, the highest weight are given to the determinations by Douglas and Dever [153] and to that by Grønvold [47] which are in good agreement. Among the DSC determinations, those by Breuer and Eysel [10], and Zahra and Zahra [14] are given most weight. Adiabatic scanning results by Dosch and Wendlandt [156] have also been given considerable weight. The determination by Kano [89] is 14% higher than presently recommended.

4.7. Zinc – Table 11

As observed for tin, the enthalpy of fusion determined by adiabatic calorimetry by Grønvold [47] is larger, nearly 1%, than the drop calorimetric determination by Ditmars [27]. The deviation is larger than the combined uncertainties of the two determinations and suggests the presence of systematic errors. Both these determinations are significantly lower, 3–4%, than the values recommended in major data compilations (see Table 1).

Among other accurate determinations that by Breuer and Eysel [10] supports [47], while that by Zahra and Zahra [14] supports [27].

Sarge et al. [2] reports that zinc is less applicable as an enthalpy standard than for example indium, since the shape of the peak as observed by DSC changes on repeated melting.

4.8. Antimony – Table 12

Few experimental determinations are reported. They are neither of high accuracy nor of recent date. Highest weights are given to the determinations by Malaspina et al. [81], Wittig [162], Oelsen et al. [93], and Schürmann and Träger [133].

4.9. Aluminium – Table 13

Three determinations of low uncertainty are reported: two by adiabatic calorimetry [47,48] and one by drop-calorimetry [19]. In this case the determinations by Grønvold [47,48] and Ditmars [19] agree more closely than in the case of zinc. The determination by McDonald [16] and also that by Schmidt et al. [167] concord within experimental uncertainty. The latter determination [167] by the group of Vollmer is made by a high temperature adiabatic scanning calorimeter with an upper temperature limit of 2173 K [168]. The group has made enthalpy of fusion determinations for several other metals to be discussed, and the calorimeter seems to be the most accurate one used in this temperature range.

4.10. Silver – Table 14

Results for potential enthalpy standards for use above 1000 K are in general of lower quality than those for use below. Adiabatic calorimetry becomes even more difficult at these temperatures, and the drop calorimetric results also seem to be of lower quality. In many cases the spread in reported values is large. Silver is no exception. In accordance with the arguments given above the highest weight is assigned to the determination by Vollmer and Kohlhaas [170], but the determinations by Speros and Woodhouse [134,135], Oelsen [95], and Callanan [171] are also given considerable weight.

4.11. Gold – Table 15

Surprisingly few enthalpies of fusion are reported in literature. Only two of them have been assigned uncertainties below 10%; the determinations by Vollmer and Kohlhaas [170] and that by Kashnitz et al. [175]. The latter determination was made using a pulse calorimeter – a type of calorimeter frequently used in studies of thermophysical properties of metals at high temperature. The accuracy of this type of calorimeter appears to be ca. 5%. The early determination by Roberts-Austen [172], the inventor of DTA, is 6.2% higher than the recommended value.

4.12. Copper – Table 16

The value by Vollmer and Kohlhaas [170] is most trustworthy, but also the determinations by Oelsen et al. [144], Schürmann and Kaune [155], Baricco et al. [177] and Pottlacher and Jäger [178] are given considerable weight. Barrico et al. [177] have used a commercial high-temperature DSC of the Calvet-type to determine the enthalpy of solidification. Calibration was achieved through melting of Al, Ag, Au, and Ni.

4.13. Nickel – Table 17

The properties of nickel have recently (1987) been evaluated by Desai [30]. The recommended enthalpy of fusion value, 17470 J mol^{-1}, was obtained from the literature data which show considerable spread. The uncertainty is evaluated to be 200 J mol^{-1}. Six more recent determinations also need to be considered. The results by Vollmer et al. [181] is given the lowest uncertainty. The determinations reported by Seydel et al. [184,185] spread largely and a higher uncertainty is given to these determinations than to the others by pulse calorimetry. Results by Predel and Mohs [182], Pottlacher et al. [186], Korobenko and Savvatimskii [188], Obendrauf et al. [189], Kaschnitz et al. [190] and Baricco et al. [177] are given considerable weight.

4.14. Cobalt – Table 18

The properties of cobalt have been evaluated by Fernandez-Guillermet [31]. The recommended enthalpy of fusion value, 16200 J mol^{-1}, was obtained from the literature data which show considerable spread. The inaccuracy is evaluated to be 250 J mol^{-1}. Determinations by adiabatic scanning calorimetry by Vollmer et al. [181], electrically calibrated DSC by Predel and Mohs [182], levitation drop calorimetry by Treverton and Margrave [191] and pulse calorimetry by Hess et al. [192] are given much weight.

5. Concluding remarks

The aim of the present study was to review all reported enthalpy of fusion determinations for a range of metals and to assess their quality. From this exercise a set of recommended enthalpies of fusion values and associated uncertainties of the mean are obtained. Obviously, the most difficult part of a study like this is the assignment of individual uncertainties to all experimental determinations. The values given here may of course be questioned, and other scientists with different experiences might choose differently. The fact remains, however, that small changes in the uncertainties of the individual determinations will not affect the resulting values significantly. The present study may thus serve as a starting point for further evaluations.

From our point of view, it is evident that the majority of the results reported are made on samples of sufficiently high purity. Hence, the spread in values is primarily due to differences in experimental techniques and procedures. In our opinion, it would be advantageous to derive a set of recommended enthalpy of fusion values to be used, e.g. for quantitative DSC. Thereby, the value of DSC determinations reported in literature will be enhanced. The enthalpy of fusion values for most of the certified metals are in accordance with the recommended values given here within twice the given standard deviation, or within twice the assessed uncertainty.

The uncertainty of the mean which results from the statistical analysis appears as unreasonably low, especially so for the high-temperature determinations. The statistical analysis would be less questionable if a larger number of determinations with realistic uncertainties were at our disposal. Presently, relatively few determinations are reported and the presence of even larger systematic errors than suggested here can not be excluded.

The lack of high quality data is obvious for the metals melting above 1000 K. New experimental determinations are badly needed. The estimated uncertainty of the mean varies considerably even for the metals melting at lower temperatures and new experimental determinations by adiabatic calorimetry are needed.

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