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Calorimetric measurements in metallurgy: remarks on calibration and some specific problems

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Abstract

A summary is reported on alloy thermodynamics with special reference to the measurements and evaluation of the formation enthalpies by means of calorimetric techniques. Also, advantages and drawbacks of direct and indirect reaction calorimetry are presented and discussed on the basis of the work in progress in the authors' laboratory. Comments are finally made about the problems of the calibration, intercalibration and assessment of the thermochemical data. Importance is given to the peculiar difficulties of alloy thermochemistry and to the need for a strict determination of the composition (elemental and phase composition) of the sample and of its equilibrium state.

Keywords: Alloy thermochemistry; Calorimetry; Direct calorimetry; High temperature calorimetry; Alloy thermodynamics

1. Introduction

Several recent developments in metallurgy and intermetallic chemistry (melting and casting procedures, synthesis methods, etc.) have highlighted the need for an ever deeper knowledge and understanding of a number of 'constitutional' properties of the alloy systems involved. Special attention has been paid to the thermodynamics and the investigation of the phase transformations and equilibria.

As in other fields of materials science (such as those concerning ceramic materials, oxides, inorganic, industrial chemistry, etc.) noteworthy advancements may be observed in the application and implementation of the so-called *Cal*culation of *Pha*se *D*iagrams (CALPHAD) methods [1–4].

Fundamental quantities for the calculation and prediction of phase equilibria (solid–solid and solid–liquid equilibria in intermetallic systems, in particular) are: the Gibbs free energy of the phases (G_φ) or the chemical potential of the elements in the phases (μ_A^φ), expressed as functions of the state variables (typically x and T, possibly P). Phase equilibria can then be calculated if the $G_\varphi(x,T,P)$ function is well-known for every phase φ.

It is important to underline that the calculation of the phase equilibria in a system requires G functions to be defined and calculable even for state variable values for which the phases are not stable. For example, $G_{\text{liq}}(x,T)$ must be defined and evaluated even for x,T values corresponding to states where only solid phases are stable. In other words, the Gibbs free energy must

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be evaluated, even for conditions for which it cannot be measured.

The best definition of the $G_\varphi(x,T,P)$ functions mainly depends on two factors:

1. A good choice of the interaction models defining the functional dependence of G on the state variables (e.g. depending on the adopted model, the selection of G may be linear or quadratic, etc., with respect to T)
2. The reliability of the experimental values used to explicitly define the above-mentioned functional dependence (e.g. if, according to the adopted model, G is linearly dependent with respect to T, the proportionality constant is defined by the condition that the $G(T')$ value is equal to the experimental value measured for $T = T'$).

It is important to recall that, in the calculations, as mentioned above, it is often necessary to use $G(T)$ (with $T \neq T'$) values corresponding to conditions different from the experimental ones. The reliability of these values depends on the reliability of the models adopted and of the experimental data.

The best definition of the $G_\varphi(x,T,P)$ functions also allows greater accuracy and reliability in the extrapolation of the calculation to higher order systems (systems with more components); that means it makes the 'prediction' of phase equilibria possible in more complex systems on the basis of the simpler ones, before any experimental determination.

The determination of the Gibbs free energy of the phases, which is essential to the thermodynamic calculation and prediction of phase equilibria, may be affected by different factors (such as measuring errors, uncertainty in the equilibrium state, approximation errors in the calculations, etc.). The most important measurements useful for this determination (in combination, possibly, with phase equilibria investigations) concern heat contents, enthalpies of solution, enthalpies of reaction (formation) and transformation, and chemical potential of the elements in a given phase (generally via electromotive force (emf) or partial vapor pressure measurements).

Considering the experimental aspects of the alloy investigation, among the consequences of this CALPHAD approach, we may underline, on one hand, the possible more rational and economic planning of the measurements, based on a repeated cross-checking on some crucial compositions or temperatures of experimental and computed data, and, on the other hand the increasing need for sound experimental thermodynamics.

Experimental alloy thermodynamics has a long history (see, for instance White [5], Kubaschewski [6], Wagner [7], Calvet and Prat [8], Lupis [9], Rao [10], Pelton [11]) and, as for the formation functions, techniques based on calorimetry and on electromotive force and vapour pressure measurements have long been employed. Advantages and disadvantages of the different techniques have often been compared and discussed: according to the more common general opinion, the best way to obtain thermodynamic data of formation is based on a combination of methods aiming at the independent determination of the $\Delta_f H^0$ (by calorimetry) and the $\Delta_f G^0$ (by emf or vapour pressure measurements), in order to obtain a more reliable, separate evaluation of the two, enthalpic and entropic, terms of ΔG. The problems, difficulties and errors frequently met in the evaluation of $\Delta_f H$ from emf or vapour pressure data have often been underlined [12–15].

In the following, a description will be given of calorimetric measurements. Attention will be paid to some specific characteristics and features of the application of some common calorimetric methods to the particular case of alloy systems.

For metallurgists, as for high temperature chemists, both thermophysical and thermochemical data are important; so, the results from calorimetry of both non-reacting and reacting systems are relevant. Several papers reviewing experimental thermodynamics and its application to metal-chemistry have been written. We may especially mention (in chronological order) those prepared by Kubaschewski [6,12], Calvet and Prat [8], Predel [13,16], Komarek [14], Hertz and Gachon [15,17], Hemminger and Höhne [18], Ipser and Komarek [19], Bruzzone [20], Rouquerol and Zielenkiewicz [21], Parrish [22], Stahl [23], Sommer [24], Bros [25,26], Castanet [27,28], Kleppa [29], Colinet [30], Rogez [31], Randzio [32].

On the basis of our own research work, however, we will place special emphasis on the *calorimetry of reacting systems*. In any case, it may be underlined (see for instance Komarek [14]) that the boundary between the two kinds of measurements cannot be clearly defined. So, for instance, valuable information about relative molar heat capacities may be obtained from accurate measurements of the enthalpies of mixing at different temperatures.

2. Calorimetric measurements of enthalpy of formation of alloys: remarks on calorimeter types

All people working in the calorimetric field know that several criteria may be and have been used for classifying the different calorimetric methods (based for instance on the working conditions, or on the structure of the calorimeter and its surroundings and auxiliary devices, or on the processes to be measured, etc.). Just as an illustration of this point and as a preliminary presentation of a few different instruments, Table 1 shows, according to some authoritative researchers, a list, which is not, however, exhaustive, of calorimeter types described on the basis of some alternative and complementary criteria.

In the following discussion, however, while summarizing the characteristic features and performance of some calorimeters employed in alloy chemistry and dealing with formation thermochemistry, more than on the overall instrumental characteristics, we will rely on the subdivision of the alloy calorimetry into *indirect-reaction* and *direct-reaction calorimetry.*

Indirect-reaction calorimetry, to which the first instruments used in alloy thermochemistry may be related, is based on the measurement of the enthalpy changes involved in a certain reaction carried out separately on the components and the compound respectively. The enthalpy of formation is then obtained by the difference between the two values.

For each specific reaction, different calorimeter types (corresponding to different characteristics summarized in Table 1) have generally been built and/or adapted. A large variety of instrumental features and operating conditions more or less approaching the ‘optimum’, are described in the literature.

2.1. Indirect reaction methods in alloy thermochemistry

2.1.1. Solution calorimetry

The application of solution calorimetry to alloy thermochemistry is based on the dissolution in separate runs of the compound (prepared before the calorimetric experiment) and its components (either separately or possibly all together as a mechanical mixture of the same overall composition) in a suitable solvent bath.

Different kinds of solvents have been used, each distinguished by certain advantages and disadvantages and specific instrumental and working characteristics.

2.1.1.1. Aqueous solvents.

The reactions involved in the simple case in which solvent and solutes are at the same, generally room temperature, are the following (s=solid, l=liquid):

$$xA(s,T_0) + (1-x)B(s,T_0) + \mathrm{solvent}(l,T_0) \Rightarrow \mathrm{solution}(l,T_0) \quad \Delta_r H_1$$

$$A_x B_{1-x}(s,T_0) + \mathrm{solvent}\,(l,T_0) \Rightarrow \mathrm{solution}\,(l,T_0) \quad \Delta_r H_2$$

The standard enthalpy of formation of A_xB_{1-x} according to the following reaction

$$xA(s,T_0) + (1-x)B(s,T_0) \Rightarrow A_xB_{1-x}(s,T_0)$$

is given by $\Delta_f H^0 = \Delta_r H_1 - \Delta_r H_2$.

$xA + (1-x)$ B is a mechanical mixture of the components which must be dissolved together if the interactions between the solutes are not negligible. However, if A and B may be considered at infinite dilution in the solvent, and the interactions between A and B in the solvent can be neglected, it is possible to use the data obtained by separate dissolution of A and B.

For measurements carried out near room temperature, the solvents used are aqueous acids or highly reactive inorganic liquids. However, with these compounds, the measured heat effects are large compared with the enthalpy of formation. This will generally result in large relative errors in the evaluation of $\Delta_r H_1 - \Delta_r H_2$. Consider, for instance, a compound such as $LaAl_2$ and the hypothetical determination of its enthalpy of formation by solution in hydrochloric acid: we have to take into account data such as $\Delta_f H^0$ of the alloy −50.5 kJ/mol of atoms [33], while the standard enthalpies of formation of aqueous La^{3+} and Al^{3+} correspond to $\cong -710$ and $\cong -531$ kJ/mol of ions, respectively [34].

A further disadvantage of the method is the slow rate of dissolution of many alloys, except those of reactive elements such as Mg, Al, and Zn, in aqueous

Table 1
Notes on calorimeter types and their possible description (see [6,14,18,21–23,26,28,30])

Characteristics considered	Alternative or complementary features[a]	
Heat exchange mode ($Q_{\mathrm{tot}}=Q_{\mathrm{accum}}+Q_{\mathrm{exch}}$)	$Q_{\mathrm{accum}}=0$	perfect heat flow
	$Q_{\mathrm{exch}}=0$	perfect adiabatic
	$Q_{\mathrm{accum}}\neq0$ $Q_{\mathrm{exch}}\neq0$	ordinary, inertial
Thermal resistance between calorimeter and surrounding	R very large	adiabatic
	R small	conduction, isothermal
	R intermediate	intermediate, isoperibol
Operational mode	isoperibol	$\mathrm{Ts}=K$
	isothermal	$\mathrm{Tc}=\mathrm{Ts}=K$
	adiabatic	$\mathrm{Tc}=\mathrm{Ts}\neq K$
	heat-flow	$(\mathrm{Tc}-\mathrm{Ts})=K$
	scanning of surroundings	$(\mathrm{Ts}(t)=\mathrm{Ts}_0+K't)$
	adiabatic scanning	$(\mathrm{Tc}(t)=\mathrm{Ts}(t)=\mathrm{Ts}_0+K't)$
	isoperibol scanning	$(\mathrm{Tc}(t)=\mathrm{Tc}_0+K't)$
Measuring principle	compensation of the heat effect	*electric compensation*:
		(i) Joule heating
		(ii) Peltier cooling
		thermochemical compensation:
		(i) phase change heat compensation, etc.
		(ii) chem. react. heat compensation
		(iii) gas compression, etc.
	no compensation of the heat effect	$\mathrm{Tc}(t)$ measurement
		thermal flux (vs. t) measurement
Calibration method	electric calibration	Joule effect
		Peltier effect
	use of standard reference samples	standard Cp samples (Al_2O_3, etc.)
		standard $\Delta_{\mathrm{fus}}H$ samples (In, Sn, Ag, Au, etc.)
	chemical calibration	combustion of standard samples
	radioactive calibration	mixing of standard substances, etc.
Process occurring in the sample inside the calorimetric cell	temperature change	instantaneous, continuous, step by step
	phase transformation	fusion, vaporization, solid state transformation
	chemical reaction	mixing, synthesis, combustion, etc.
Sample handling and loading method	loading time	at $t<t_0$
		at $t>t_0$ (drop calorimetry, etc.)
	loading mode	batch
		piece by piece
		Continuous:
		(i) continuous addition of one reagent to a fixed amount of the other: *titration calorimetry*;
		(ii) continuous addition of both reagents: *flow calorimetry*
	sample initial state	solid, liquid, compact of powder mixture, different liquids to be mixed, etc.
Calorimeter structure and components	calorimetric medium	liquid (presence of internal stirrers, etc.) *or* aneroid
	number of cells	single, *or* multiple (twin, differential measurements, presence of a reference, dummy, cell)
	surrounding thermostat	room temperature (water ultrathermostat) *or* high-temperature furnace (presence of thermal shields, etc.)
	sensors	thermocouples, thermistor, etc.

Table 1 (*Continued*)

Characteristics considered	Alternative or complementary features[a]	
	methods and devices for loading the sample(s)	'normal' calorimeter mixing calorimeter drop calorimeter titration calorimeter flow calorimeter (suitable sample dispenser, etc.)

[a] Note that generally the calorimeter properties and behaviour listed in each group may be combined in different ways with those of the other groups (Tc, calorimeter temperature; Ts, surrounding temperature; K, K', constant values independent of time (t); t_0, starting time for measurement; R, thermal resistance between calorimeter and surroundings).

solvents. The solvent must be carefully chosen in order that no reactions in addition to those considered take place. If hydrogen is produced during solution, it must either be completely evolved after complete heat exchange with the solution, or else completely oxidised by suitable reagents.

The solution should take place neither too slowly nor too rapidly, and the solution reaction must be quantitative, complete and reproducible. The advantages of working with this method may be related to the facility in working at room temperature and in using previously prepared and analyzed samples.

Different apparatuses have been used for the determination of enthalpies of solution in aqueous solvent. A survey of various calorimeters and of a number of aqueous solvents suggested for different alloys has been presented by Kubaschewski et al. [6]. Differential solution calorimeters (for instance of the type constructed by Buck et al. [35]) have been employed, and electric heaters placed in the vessel may be used for the calibration of the calorimeter. Generally, the components, contained in a glass vial, are added to the solvent by breaking this vial. In several cases, the control of the rate solution may be convenient: for instance a small quantity of platinic chloride has been used in the past to accelerate the solution of metals and alloys in hydrochloric acid [36] and, on the other hand, the violence of the reaction has been reduced by covering the alloy pieces with paraffin wax or with collodion [6]. Solvents containing nitric acid or bromine as an oxidising agent (e.g. such as the solvent by Herschkowitsch) have found useful applications.

The heats of formation of several rare earth (R) alloy systems such as R–Al [37,38], Pu–Al [39], R–In [40,41], R–Ga [42], Nd–Zn [43], La–Ni [44], have been determined by solution calorimetry in hydrochloric acid.

An interesting application of solution calorimetry in aqueous HCl has been described by Kaldis et al. [45] who performed measurements of $\Delta_f H$ of strongly exothermic compounds only partially metallic in their characteristics like CeN, Sm_2S_3 Sm_3S_4, $TmSe_x$, etc. A detailed description of the trends of $\Delta_f H$ as a function of the stoichiometries was presented and discussed in terms of mixed valence states.

2.1.1.2. *Metallic solvents.*

The use of molten metals as a solvent of intermetallic compounds avoids the problem connected with large solution enthalpy effects. Here, the enthalpy of solution of the metals in liquid metallic solvents is much smaller than the enthalpy of solution in aqueous solvents, so that the main objection of the acid solution method is removed; the enthalpies of solution and of reaction are now, in fact, comparable.

Generally, for solution calorimetry in molten metals, we have a calorimeter at high temperature and the alloy under investigation is dropped inside the calorimeter from a room temperature thermostat. In this case, the heat effect observed includes the variation of enthalpy due to the ΔT of components and compound, and the reaction. To reduce the contribution of the ΔT effect, a two-step drop method (so-called indirect drop method [25,27]) has been devised. The added metal is kept in a funnel close to the reaction crucible. After a convenient time, when thermal equilibrium is reached, the sample is dropped into the solvent; to this end the funnel is opened by means, for instance, of a magnetic device and the recorded effect corresponds directly to the enthalpy of mixing.

In the general case of metal solution calorimetry, the dissolution experiments are performed at high temperature. However, mercury may be a useful solvent for alloys; its use was introduced by Tayler for alloys of Pb with tin, bismuth, and zinc [46], and the most favourable conditions are obtained when mercury itself is one of the alloying elements. Enthalpies of solution of a number of transition metals in mercury at 150°C have been determined calorimetrically by Kleppa [47]. Carling [48] adapted a commercially available oxygen bomb calorimeter to obtain a calorimeter for the direct determination of the enthalpies of reaction of alkali metals with mercury. The reaction vessel was modified and two containers were inserted into it, an upper one containing Hg, and a lower one containing the alkali metal. The mercury container was attached to a fuse wire and could pivot at the other end, so that Hg could be poured (by fusing the wire) into the other less dense metal.

If possible, a solvent metal must have a low melting temperature and a negligible vapour pressure in the working temperature range, it must be resistant to oxidization, available in pure form, and have a low specific density and a surface tension that allows good wettability of the sample and prevents floating of the solid solute on the liquid solvent.

Liquid tin serves all these requirements and has been applied as a preferable solvent for many years. Unfortunately, as highlighted by Colinet [30], molten tin is not a good solvent for most transition metals. For this reason, molten aluminium has often been employed. At higher temperatures, copper or germanium can be used [49,50]. The use of a molten alloy (near an eutectic composition) as a solvent may be advantageous. Kleppa and coworkers, by using $Mn_{0.4}Ni_{0.6}$, have determined the enthalpies of formation of carbides, sulfides, etc. [51].

Ga and In have also been suggested as suitable solvents. The thermodynamics of Si+Ga and Si+In mixtures have been studied at ≅700°C by Tmar et al. [52] by using a suitable calorimeter. It is made of a heavy block of nickel and surrounded, in a high vacuum, by a system of Ni screens for reducing the temperature oscillations of the oven [53]. Problems related to the very low dissolution rates in Ga and In were discussed. Colinet [54] employed the same apparatus to determine enthalpies of formation of many liquid rare earth binary alloys.

The twin Calvet high-temperature calorimeter has been extensively used in Marseille [25,55]. Numerous researchers [15,56,57] made modifications of the experimental cells of a very high temperature heat flow calorimeter commercially available (Setaram company) to perform measurements up to 1800 K.

Several isoperibol high-temperature calorimeters have been built by Predel and coworkers [16,24,58] in order to determine directly, at temperatures up to 1800 K, the mixing enthalpies of liquid alloys by adding a liquid metal A to the experimental crucible which contains the second liquid metal B.

A twin-solution calorimeter having a massive molybdenum block where the working and reference cells are placed, and operating up to temperatures of 1900 K, has been used to carry out experimental studies on liquid copper lanthanide alloys [59]. Isoperibol calorimeters have also been built by Nikolaenko and coworkers [60] and high temperature enthalpies of mixing, up to 1850 K, have been reported for transition metal-rare earth alloys [61]. The instrument was calibrated generally by addition of weighed quantities of the solvent, at the beginning, and of tungsten later in the course of the experiment.

This solution calorimetry technique may be particularly convenient when one of the components of the system corresponds to the solvent S (molten tin for tin alloys, mercury for the amalgams, etc.). The enthalpy of formation is then deduced from only two measurements, the enthalpies of dissolution obtained by dropping M and the compound MS_n and from the knowledge of the enthalpy difference of the solvent between the temperature T_0 and the temperature T.

As a final comment, we may mention a particular case of solution calorimetry developed by Kleppa and co-workers to obtain the enthalpies of formation of RB_2, RB_4, and RB_6 compounds (R=rare earths) and for thermochemical studies of refractory materials. The key point in this method is to generate in the calorimetric cell the same liquid phase while using the compound and, in a different run, the components. Platinum or palladium foils have been used to generate the liquid phase. For instance, the enthalpy of formation of YB_4 was obtained by measuring the heat involved during the dropping of two different kinds of samples in the calorimetric cell: ($Pt+YB_4$) and ($Pt+Y+B$) to obtain the same liquid alloy $Pt_{0.70}B_{0.24}Y_{0.06}$ [62].

2.1.2. Combustion calorimetry

Among the reactions which can be carried out on the components and the compound in order to have the enthalpy of formation, we have to mention combustion reaction with a gaseous reactant, mainly with O_2 and F_2. In this case, too, we have strongly exothermic reactions. However, oxygen bomb combustion calorimetry is a well-developed technique which can be used when no other method is available. The same technique may be used, of course, in the investigation of the enthalpy of formation of oxides or halogenides, for which combustion calorimetry is a direct calorimetric method.

Oxidation or fluorination calorimetry, besides the case of oxides and fluorides, has been used in the study of sulfides, silicides, etc. [63]. Good results have also been recently obtained in the investigation of the borides of several metals for which the $\Delta_f H$ may be obtained with difficulty using different methods [64,65].

The fluorination method is generally preferred because the metal fluorides show less deviation from stoichiometry than do the oxides, reducing the error due to this source in computing the enthalpy of formation of the intermetallic phase. Details of experimental procedures, sample purity requirements, demands of careful handling, etc. have been given by O'Hare. Commercial fluorine, distilled and then treated with NaF to remove any HF present, has adequate purity. Besides, the absence of water should be meticulously checked. Generally, the sample reacts readily when placed on a nickel saucer on the head of the bomb. In several cases, the F_2 has had to be diluted with an inert gas in order to moderate the reaction. In other cases, however, it may be convenient to resort to some 'device' in order to promote the reaction. For instance, owing to the vigorous reaction of W with F_2 to form WF_6, the presence of W may help to fluorinate even the most refractory of compounds [64]. Similarly a few milligrams of sulfur as igniter were added to vanadium sulfide to initiate the reaction with F_2 [66]. Most materials and fluorine, on the other hand, combine spontaneously to some extent and, therefore, must be kept apart during the fore-rating period of a calorimetric experiment. For this reason, the majority of fluorine-bomb measurements have required two-compartment calorimetric vessels [67,68].

Two kinds of apparatus have recently been described [64,69]. The apparatus by O'Hare [64], essentially consists of a storage tank charged with F_2 at typical initial pressure of 1–1.5 MPa connected to a combustion bomb. This entire assembly sits within the water-filled calorimeter can. An isolation valve on the side of the tank is opened by remote control to admit the F_2 and initiate the combustion.

Another kind of fluorine-bomb has been described by Kim and Oishi [69]. The combustion was initiated by passing an electric current through a nickel fuse wire. Electrical energy supplied for the ignition was determined with an electric-current integrating device.

As for the *calibration*, following [64], the reaction between high purity rhombohedral sulfur and F_2 to form SF_6, for which the enthalpy change is well known, could be used. According to Kim et al. [70], the energy equivalent of the calorimetric system was determined in a standard manner by combustion of the reference benzoic acid in oxygen gas under the standardized conditions. O'Hare et al. underlined that, as in other calorimetric techniques, the complete characterization of the specimens is very important: an accurate qualitative and quantitative determination of the reagents and products is a sine qua non-condition for reliable calorimetry. In particular, considering the properties of the pentatungsten trisilicides, Tomaszkiewicz et al. [65] underlined that conversion of massic to molar values, such as $\Delta_f H^0$, can require a great deal of analytical chemistry as well as an intuitive understanding and interpretation of the analytical values, for substances contaminated with non-trivial quantities of impurity or shown to be non-stoichiometric.

2.2. Direct reaction calorimetry

According to this technique, the reaction of interest itself, that is the synthesis of the alloy, takes place in the calorimeter. In boundary cases, the reaction and the kind of calorimeter may be coincident with those already presented in the previous paragraph: study of stannides by reaction with the tin solvent, synthesis of fluorides, oxides, etc.

Several examples, however, have been presented of a number of intermetallic compounds synthesized inside the calorimeter from a convenient mixture of the component metals. A special case is that of the 'self-propagating reactions' (gas-free combustion synthesis). Many mixtures of solid substances (capable of reacting with a strong thermal evolution) if heated up to a certain characteristic temperature, may give rise to a self-substained reaction running to the combination of the initial substances.

Different kinds of calorimeters have been employed for measuring the heat evolved by these reactions. A point common to all these techniques is the necessity of starting the reaction inside the mixture and having it running in a controlled manner. *Different ignition methods* have been suggested and used; reference can be made to them for a classification of these calorimeters.

2.2.1. Room-temperature synthesis direct calorimetry

This type of instrument is enclosed inside a room temperature water-thermostat and, even if at the start of the reaction there is self-heating of the sample, during the measurement the temperature of the calorimeter (and of the sample inside it, etc.) cools down again to room temperature. A peculiar calorimetric method related to direct calorimetry and going back to the origin of alloy thermochemistry is that used by Oelsen et al. [71,72] and often affectionately and graphically described by Kubaschewski. Briefly the method consisted in pouring the one molten component on to the other which is contained in a calorimeter at room temperature. If reaction was incomplete under these conditions, then both components were heated above their melting points and poured into the calorimeter simultaneously. The heat content of the molten components had to be subtracted from the measured heat effect, but the error involved was much smaller than those in computing the heats of formation from heats of combustion or solution using Hess's law: this was the great advantage of this direct method. The calorimeter used by Oelsen et al. [71,72] was large and consisted of a can containing 6.3 dm^3 of water supplied with a Beckmann thermometer and insulated from its surroundings by wood fibre. The calorimeter vessel containing the cold component was temporarily removed from its jacket for the addition of the other substance melted under a protective slag. To ensure complete reaction the vessel was shaken, and then replaced in the calorimeter. The whole manipulation required two or three operators, and the time during which the vessel was out of the water had not to exceed 20–40 s. It was claimed, however, that the manipulation itself gave rise to small errors, owing to the large water equivalent of the calorimeter.

An improved popular calorimeter of this group, is the so-called *small-furnace calorimeter* (Öfchen-Kalorimeter). This technique has been suggested by Kubaschewski (see, for instance [73]). In principle a mixture of the powders of the two component metals is heated by a small furnace within a calorimeter until alloying takes place. The electrical energy supplied is measured and subtracted from the total heat evolved. The mixture of the component metals (for instance Ti–Al, Al–Fe, Fe–Ti) in the form of a compact inside the small furnace is inserted in an Al-block (the calorimeter proper) suspended in a container placed in a thermostat controlled at 25°C. Using the same principle Capelli et al. [74] designed an aneroid-isoperibol calorimetric apparatus containing four calorimeters. The temperature trend of each calorimeter is followed by 80 thermocouples in series, so it is possible to carry out differential measurements. Each calorimeter consists of a thick Al cylinder containing two small furnaces (these are used for starting the reaction in the sample and for electrical calibration respectively). When the apparatus, inside a thermostat, is in thermal equilibrium, the pellet is heated until the reaction starts. The electric energy dissipated in the calorimeter in the reaction run is then compared with that needed to obtain the same temperature/time response in a number of calibration runs. The construction features of the calorimeter, the adjustments of its thermal characteristics and its behaviour as an 'integrating' instrument have been described and discussed. This apparatus has been applied to systems with one low-melting metal, the other metal being chosen to produce fairly exothermic heat effects. Examples of systems studied by means of this calorimeter are Au–Al, Pd–Al, Mg–Ge, Mg–Bi [75] and several alloys of the rare earth metals (with Al, In, Pb, Sb, Bi, etc.) [76].

A similar procedure was used by Robins and Jenkins [77] to determine the strongly negative formation enthalpies of some silicides of the transition elements (Ti, Zr, V, Nb, Ta, Cr, Mo, W). In this case, the ignition procedure was a combination of brief electrical heating with a subsequent deflagration of a small pellet (accurately weighed) of a material such as the thermite mixture (chromium oxide and aluminum powder) attached to the compact of the metals under investigation.

2.2.1.1. Comments on the '(gas-less) self-propagating combustion synthesis'.

It could be underlined that several self-propagating reactions, to which the above described calorimetric technique may be applied, are interesting not only from a fundamental point of view, but also for the possible technological applications. This process represents a relatively new and promising method for the synthesis of different materials such as many intermetallic compounds (NiAl, CoAl) and ceramics (borides, carbides, silicides, chalcogenides) advanced alloys and composites. For several of these systems conventional melting processes have been modified to effectively utilize the exothermic reaction, as in the case of the combustion-synthesis technique, which can result in substantial energy saving and in the reduction of the time needed for melting (exo-melt process) [78]. The possibility of producing transition metal silicides has also been proved and the application of a novel one-step in situ synthesis technique for the production of ceramic-metal interpenetrating phase composites (IPC) has been described in Ref. [79].

In the discussion of these processes, several points have been underlined; for instance the effects of the shape, packing density, etc. of the compact on the advancement rate of the reaction front. The way to carry out the reaction, both by heating the pellet locally at one point (propagating mode) or by heating the whole pellet to the ignition temperature of the exothermic reaction (simultaneous combustion mode), has been discussed in Refs. [79,80].

In this framework, different methods for supplying the ignition energy have been considered: by electrical heating or by electron-beam or laser irradiation [81,82]. The effects of the simultaneous presence of an electric field have also been examined [82]. All these points may provide valuable suggestions for calorimetric techniques, which, on the other hand, may be useful in determining interesting parameters for these non-traditional synthesis routes.

We have to note now that small negative enthalpies of reaction (and of course endothermic) are more difficult to measure directly by this method, since there is insufficient self-heating of the compact (no self-supporting reaction). These reactions may be studied at a sufficiently high temperature in order to have spontaneous transformation. The measurement of the absorption or evolution of heat, as the reaction proceeds, should be done at high temperature, as will be described in the following paragraph.

2.2.2. High-temperature synthesis calorimetry

As previously mentioned, in several cases, the direct synthesis of the alloys can be conveniently carried out in a high-temperature calorimeter. Working at appropriate temperatures, depending on the melting point of alloys and on the rate of the reaction, the enthalpies of formation of low-exothermic or even endothermic reactions may be obtained. Different varieties of calorimeters have been designed to this end and used in alloy thermochemistry. A distinctive feature (on which building and operating characteristics depend) may be the operating temperature: for instance calorimeters working up to 800°C [83], or up to 1000°C (Tian–Calvet calorimeter [25,26]), or up to 1200°C [29,84] and up to 1500°C [15,16,24,56]. The different operating temperature ranges depend on a compromise between the need for having fast and complete reactions and for avoiding side reactions, attack of the crucible, and to have as small as possible, in comparison with $\Delta_f H$, the $\Delta H(T-T_0)$ due to the heating of the sample from room to calorimeter temperature. To the different temperatures and related working conditions corresponds the use of different building materials (calorimetric blocks of Ni, Mo, Al_2O_3), measurement thermocouples (Chromel, Pt/Rh, etc.) and auxiliary devices (screens, gates, protective atmosphere, getters, etc.).

Another distinctive property may be the adopted *heating regime* for reaching the working temperature. The programmed final temperature of the calorimetric cell may be reached *by continuous heating mode*, as in the differential thermal analysis technique (scanning or differential dynamic calorimetry) [85–87]. In this case the sample, previously inserted in the calorimetric cell, is heated until the reaction takes place. The method is substantially based on the observation of the cell temperature changes with or without reaction (but under otherwise identical conditions). Calibration runs may be performed by using the known enthalpies of fusion of elements and compounds or a small electric calibration heater.

Instead of using a continuous heating mode, in some types of calorimeter the reaction temperature is reached *by step-heating*. An example was reported by Kubaschewski and Dench [73]. The whole calorimetric assembly (and the powder compact sample inside it) is, as the first step, heated up to a maximum safe temperature (that is a temperature at which the sample may be held without any appreciable reaction). The specimen is then heated adiabatically from the safe temperature (previously determined in a number of preliminary experiments) to the reaction temperature using an internal heater which is eventually switched off; the heat effect is recorded. Repeating the experiment with the reacted alloy, the difference in heat effects gives the enthalpy of formation at the safe temperature. In the measurement of the $\Delta_f H$ of Cr–Mo, Cr–Ta, etc. alloys, an estimated accuracy of ca. ±1.0 kJ/mol of atoms was stated.

More frequent application has been found by *high-temperature calorimeters thermostatted* at a temperature high enough to ensure that the reaction occurs.

In this case, of course, the calorimeter structure should be designed in such a way as to be able to start the reaction at a well-defined time. In the case of liquid metals and alloys, for instance, the components may be kept at the same temperature in separate containers inside the calorimeter and, at the right moment, can be mixed by opening from outside the connection between the containers. After the flow of one of the liquids inside the other, the operation of a stirrer guarantees a complete and rapid mixing [24,25,55].

The reaction in a high-temperature calorimeter alternatively may be started by dropping into it samples from a lower temperature thermostat (a special very frequently used case is from a room temperature thermostat; see also the two-step drop previously described in Section 2.1.1).

A particular case of direct synthesis can be considered, namely when one component of the system is liquid at working temperature and can act as a solvent (S) in which the solubility of the solute-partner A is small. By dropping A, saturation of the liquid may be reached and a solid alloy may be formed and precipitate from the solvent (*precipitation calorimetry*). The enthalpy of formation of the alloy may be deduced from the thermal effect involved, according to the following scheme [30]:

$$\begin{aligned} &x\mathrm{A}(s,T_0) + \text{solution}\,(l,T) \\ &\quad \rightarrow \mathrm{A}_x\mathrm{S}(s,T) + \text{solution}\,(l,T) \quad \Delta_\mathrm{r}H_1 \end{aligned}$$

The reaction of formation of the A_xS compound is:

$$x\mathrm{A}(s,T) + \mathrm{S}(l,T) \rightarrow \mathrm{A}_x\mathrm{S}(s,T)$$

The enthalpy of formation of A_xS is given by:

$$\begin{aligned} &\Delta_\mathrm{f}H^0(\mathrm{A}_x\mathrm{S},s,T) \\ &\quad = \Delta_\mathrm{r}H_1 - x[H_\mathrm{A}(s,T) - H_\mathrm{A}(s,T_0)]. \end{aligned}$$

A more general case of precipitation may be one in which the intermetallic phase under investigation is precipitated from the calorimetric solvent by the addition of one of its components in the solid state to a dilute solution of the other component in the liquid solvent. The first example was given by Bryant and Pratt [88] who determined, at a certain temperature T, the enthalpies of formation of the aluminides of nickel and palladium by precipitation of Pd–Al (or Ni–Al) alloys from the addition of Al to a tin solution of palladium.

$$\begin{aligned} &0.5\ \mathrm{Pd}\,(\text{liquid tin solution, } T) + 0.5\mathrm{Al}\,(s,T) \\ &\quad \rightarrow \mathrm{Pd}_{0.5}\mathrm{Al}_{0.5}\,(s,T) \quad \Delta_\mathrm{r}H_1 \end{aligned}$$

$$\begin{aligned} &0.5\ \mathrm{Pd}\,(s,T) \\ &\quad \rightarrow 0.5\ \mathrm{Pd}\,(\text{liquid tin solution, } T) \quad \Delta_\mathrm{r}H_2 \end{aligned}$$

$$\begin{aligned} &0.5\ \mathrm{Al}\,(s,T) + 0.5\ \mathrm{Pd}\,(s,T) \\ &\quad \rightarrow \mathrm{Pd}_{0.5}\mathrm{Al}_{0.5}(s,T) \quad \Delta_\mathrm{f}H = \Delta_\mathrm{r}H_1 + \Delta_\mathrm{r}H_2 \end{aligned}$$

3. Specific problems in thermochemical data accuracy

A number of problems in the calibration of the calorimeters and on the evaluation of the thermochemical data are, of course, dependent on the construction and operating characteristics of the instrument and independent of the specific application to a certain group of compounds (metallic or not). These questions have been largely discussed in a number of reviews.

The subdivision of the calibration procedures as based on electric methods (Joule and/or Peltier effects), on thermochemical methods (reference reactions, see Table 1), etc. may be applied also to the instruments used in alloy thermochemistry. General references to these points may be found in Refs. [6,8,14,18,21].

In these notes, however, it may be useful to underline some special points which, even if not peculiar to alloy thermochemistry, play in this case a special role and may affect the overall accuracy to a greater or lesser extent. The following is a short list of the points we consider especially noteworthy.

3.1. Operating at high temperature

Working at high temperature may be necessary in several cases in order to have a more complete and faster reaction and to reach a true equilibrium state. In the case of liquid alloys, of course, the need for high temperature is related to their melting points.

Disadvantages and problems regarding high temperature operations are connected with

- undesirable side reactions (with the crucible or gas atmosphere)
- possible vaporization of the components
- small size of experimental heat effects to be determined in comparison with the total heat involved
- greater problems in thermal insulation (heat leaks by conduction, radiation, etc.)
- more difficult selection of the materials of construction.

Some of these drawbacks may be counterbalanced by a convenient design of the calorimeter and of its component parts. For instance, a mixture of volatile metals to be reacted may be enclosed in tightly welded Fe or Ta crucibles [83] or in fused silica capsules [89].

The reactivity of the atmosphere may be reduced by a convenient getter, introducing for instance into the calorimetric ensemble, to be filled with high purity argon, thin foils of Zr [90].

A wise design of the high temperature calorimeter (centering in the furnace, symmetry, the features of the support and of the shields, etc.) may improve its thermal characteristics and reproducibility.

3.2. Temperature measurements

A number of problems, moreover, are related to temperature measurements both of a ΔT (temperature difference between the calorimeter and its surroundings, or the calorimeter and a reference block, etc.) and of T (the absolute temperature at which the calorimeter is working). Both measurements are very often made by means of thermocouples (for the ΔT evaluation a thermopile is generally used). An extensive discussion of this point and of all the underlying features may be found in the classic papers and books describing the Calvet-type calorimeters [8,26]. Characteristics, behaviour, and optimization of simple thermopiles (for high temperature calorimeters) have been discussed in Refs. [15,56,91], with reference both to commercial apparatus and to laboratory-made instruments.

Alternative positioning of the hot junctions of the thermopile around the calorimetric vessel have been considered and the effects observed in connection with partial or complete filling of the vessel discussed in Refs. [15,26,92].

Special problems related to high temperature operation and measurement have been described by Kleppa et al. [93]. They used calorimeters, the working part of which consisted of two superimposed cells, the reference and the sample cells. The heat effect (caused by the drop of a sample in the calorimetric cell) is evaluated by means of a thermopile Pt–Rh/Pt, the junctions of which are placed around the reference and the sample cell respectively. Typically, in subsequent runs the samples consist of a pellet formed from a mixture of fine powders of the components and of a specimen of the synthesised alloy. The calorimeter is inserted in a furnace having a heating element made from $Pt_{40}Rh$ wire. One calorimeter of this type was maintained, for three years, nearly continuously at ca. 1200°C. Both calorimeter and furnace were found to have acceptable lifetimes at this temperature. As a general rule, the calorimeter was calibrated about every two weeks, on the basis of the known heat content of pure copper at 1200°C. The change in the calibration factor over a period of ca. 1000 days at 1200°C, corresponded to a decline in sensitivity by a factor larger than 2. This decline was ascribed mainly to an alteration of the differential thermopile probably due to the diffusion of Rh from the Pt/Rh wires into those of pure Pt.

As for the measurement of the temperature at which the calorimeter is working, this is especially important in drop calorimetry, where also the ΔT from the reservoir to the calorimeter, and the corresponding ΔH, have to be accurately evaluated. To this point different errors can be related. The first one is in the measurement itself. For a recent discussion on the precision of the thermocouples (see Ref. [94]). Problems in thermocouple calibration (against reference metal melting points) and in performing this calibration in conditions as close as possible to the working ones, have been underlined. A good definition of the reference, cold-junctions of the thermocouple is equally necessary. Note moreover, according to Tye and Gardner [94], that even if the melting points of reference materials are known to a high precision level, these have been defined under steady-state conditions using sophisticated experimental apparatus and temperature measurement systems having very much higher orders of precision than that which can be obtained using only one thermocouple placed in an uncertain position and being heated and cooled under varying transient conditions.

Another source of error in the drop procedure, moreover, may be due to the heat exchange during the descent of the specimen from the upper, room temperature, to the lower containers. This could be partially minimized by dropping the sample enclosed in a suitable crucible (useful also as protection against reactions with the atmosphere), and comparing the results with the drop of the empty crucible. Alternatively, an evaluation of this heat exchange ('heat pick-up') may be made by computation. See, for instance, Kleppa and Hong [95] for a correction which they applied in their drop calorimetry. In conclusion to this chapter, we may underline that the reliability of the measurements is also closely connected to problems of temperature control and thermostatting.

3.3. *Composition control*

As already mentioned, checking of the real composition of the sample (which, of course, is an important point in all measurements) is particularly relevant in thermochemistry. This may be more difficult in alloy investigation especially at high temperature.

State and composition of the sample have to be checked (preferably, when possible, before and after the measurements) that is, the elemental as well as the phase composition have to be clearly defined. We may summarize these points by observing that the samples used in the calorimetric measurements (especially those synthesized in a direct calorimeter) should be compared with 'standard' samples. These have to be prepared by conventional techniques (melting, annealing, etc.) defined on the basis of the phase diagram. For the comparison, methods such as micrographic examinations, X-ray diffraction analysis, microprobe analysis, etc., should be routinely used. This means that the number of coexisting phases should be determined in the samples and their compositions checked. The possible appearance of metastable states (metastable phases, supersaturation and/or disorder in solid solution phases, etc.) should also be kept in mind. This may be due, for instance, to a 'quenching' of the sample if subjected to a fast temperature change.

It has been underlined [96] moreover that, in order to minimize ambiguities and consequent errors on these points, instead of studying a certain A_mB_n compound, it may be much better to investigate the complete range of composition, from A to B. A plot of the $\Delta_f H$ (conveniently reported in J or kJ per mol of atoms versus the mol fraction of A and B), generally has a shape corresponding to established rules and which can easily be related to the shape of the phase diagram and its characteristic points such as the congruent or incongruent formation of point or line intermediate phases [6,7]. An example of the problems which may be encountered on examining one single compound can be deduced, for instance, from the previously mentioned work by Tomaszkiewicz et al. [65] on the investigation of tungsten silicides, the stoichiometry of which, however, seemed not to be well-defined.

The role of impurities and side reactions (especially formation of small quantities of oxides, oxygen transfer from oxide crucibles to the alloy, reaction with metallic container, etc.) has been underlined by several authors [6,97].

3.4. *Calibration*

Several techniques have been developed for the calorimeter calibration and applied to the instruments used in alloy thermochemistry.

3.4.1. *Joule effect*

This method suggested for the calibration of exothermic processes, and accurately discussed since 1928 by White [5], uses an electrical heater inserted in the sample holder. The main concerted problems (measuring instrument, accurate timing, position and structure of the heater, reproducibility of the heating regimes, dimensions, arrangement of the connecting wires, etc.) have been presented and analysed [6,98]. Tachoire [99] discussed the procedures of electric calibration with particular attention to the problem of the accurate measurement of electrical energy dissipated by the heater and effectively transferred to the calorimetric cell and to the question of reproducing the heat-flow path in the reaction and in the calibration (to this end, see also the special design of the calorimeter reported in Refs. [74,83]).

3.4.2. Peltier effect

This type of calibration seems to have been applied only to the Tian–Calvet calorimeter type. In this instrument a certain number of thermocouples (independent of the measuring ones) can be used for the production of the Peltier effect. The Peltier cooling, however, may be used to compensate only small heat fluxes. An extensive treatment of this subject and of the corresponding devices may be found in the classic book by Calvet and Prat [8].

3.4.3. Radioactive materials

These materials (radium or, perhaps, preferably plutonium) are constant power sources independent of temperature and free from the disadvantages of the Joule effect (no connecting wires are needed).

This technique, besides handling and safety problems, may be very useful at ordinary temperature, but not at high temperature owing to the perturbation produced by the introduction or removal of the standard.

3.4.4. Enthalpy of fusion (or transformation) of standards

This method may be especially useful for scanning, differential dynamic calorimeters. A number of standard materials (for instance Ga, In, Bi, Sn, Pb, Zn, Al, Ag, Au) have been suggested. Alternatively, salts may be used in the cases where their physical properties are closer to those of the materials under investigation.

A drawback of this method may be related to the fact that, each calibration may be carried out only at a specific temperature (see, for instance [100,101]).

3.4.5. Heat content

The enthalpy change of a standard sample, on passing from one temperature to another is generally used in drop calorimetric instruments. Several substances may be useful, besides the certified standard Al_2O_3, such as Cu [95], Ag [83]. Difficulties are related to the accuracy with which the ΔT corresponding to the drop may be determined, the heat pick-up during the transfer, to the chemical and mechanical stability of the sample, etc.

Special problems may arise when a liquid metal bath is inside the calorimetric cell (as in the determination of mixing enthalpies). In this case, the calibration cannot be done by using, for instance Al_2O_3, because this material may not dip into the melt. The local heat-flux is different as compared with a heavy metal sample addition. The calibration factor, indeed, depends on the filling height of the calorimetric cell (a calibration curve therefore has to be determined as a function of the filling). This has been underlined, for instance, by Stoltz et al. [58] who, in the investigation of the enthalpy of mixing of liquid Al–Cu, Al–Ni and Cu–Ni alloys, used for the calibration, the dropping of solid cylindrical samples of the pure metal used as liquid bath material. The calibration rests in this case on the heat content and heat of fusion of the metal.

3.4.6. Chemical calibration

This is based on the use for calibration of a reaction having a well defined $\Delta_r H$. This method has been applied to thermochemical investigations of several types of materials. Its main advantage lies in the fact that the reaction and the calibration may be very similar, so that many errors may be minimized as underlined here below. Typical examples may be combustion of standard substances in combustion calorimetry with O_2 [6,100,101], F_2 [64]. For a detailed discussion about this point see for instance [142].

In the metallurgical field we may mention Yokokawa and Kleppa [102] who employed the known mixing enthalpy of liquid Cu + Ag for calibration in the investigation of liquid Ti–Cu alloys.

A disadvantage of the method in alloy thermochemistry is that, for the different kind of calorimetric procedures, only a few intermetallic reactions can be identified for which the $\Delta_r H$ is well known and assessed.

One typical reaction for which several measurements performed with good agreement by using different techniques are available is the synthesis of a compound such as $CeAl_2$. The experimental data are $\Delta_f H$ $CeAl_2$(kJ/mol of atoms): −50.5±1.0 (emf [103]), −50.0±2.0 (direct calorimetry [104]), −53.0±1.0 (high-temperature drop calorimetry [83]), −52.2±1.0 [105] and −48.9±2.0 [106] (Al solution calorimetry). The average value −51.0±1.0 kJ/mol of atoms can be considered very reliable.

A similar situation may be found for instance for the reactions of Sn with Au, Pd, etc.

As a final comment to this point, however, we may observe that it is difficult to identify a single reference process (dissolution, chemical reaction, etc.) the enthalpy of which may be used as a general 'calibrant' for thermochemical measurements on all kinds of substances. This is due to the different properties (heat capacity, thermal conductivity, etc.) of various chemical compounds and the different operating conditions often needed (for instance different temperature). As a consequence the application of well-known chemical calibration procedures to metallurgical thermochemistry seems, unfortunately, to have for the moment only a marginal interest. We are referring to calibrants such as TRIS (tris(hydroxymethyl)aminomethane) standard samples of which may be purchased. Its negative enthalpy of dissolution in excess dilute HCl solution has been frequently used as a reference for room-temperature operating calorimeters (water solution, mixing calorimetry, etc.). Similarly, the positive dissolution enthalpy of KCl in water has been used. This point has been debated for instance by Skinner et al. [143].

4. Final remarks and conclusions

In Table 2, as a concluding example, a short summary is reported of the $\Delta_f H^0$ of formation data relevant to a group of silicides and aluminides (those of the

Table 2
Standard enthapies of formation at 298 K of aluminides and silicides of the 8, 9, 10 group elements

Phase	$\Delta_f H^0$ (kJ/mol of atoms)	Error (kJ/mol of atoms)	Measurement temperature and method[a]	Comments	Reference
FeAl	−26.5		rT drop dir cal		[72] quoted in [107]
	−25.1	0.8	rT dir cal		[73]
	−23.8	0.8	rT dir cal		[108]
	−25.1		n.i.		[109] quoted in [110]
	−32.0		calculated		[111]
$FeAl_2$	−26.5		rT drop dir cal		[72] quoted in [107]
	−26.2	1.2	rT dir cal		[73]
	−25.0		calculated		[111]
$FeAl_3$	−25.0		acid sol cal		[112] quoted in [107]
	−29.5		rT drop dir cal		[72] quoted in [107]
	−27.9	0.7	rT dir cal		[73]
	−19.0		calculated		[111]
CoAl	−64.0		acid sol cal		[112] quoted in [107]
	−54.1	2.9	rT drop dir cal		[72] quoted in [107]
	−60.0		Al sol cal at 1100 K	Ref. Al fcc at 1100 K	[113] quoted in [111]
	−65.7	1.0 (a)	Al sol cal at 1100 K	Ref. Al liq. at 1100 K	[113]
	−61.3	1.9	Al sol cal at 1030 K		[110]
	−59.5		emf at 900–1000 K	Ref. Al fcc at 980 K	[114] quoted in [110]
	−61.0		emf at 900–1050 K	Ref. Al fcc at 1000 K	[115] quoted in [111]
	−67.5	2.0 (a)	emf at 900–1050 K	Ref. Al liq. at 1000 K	[115]
	−60.3		n.i.		[116] quoted in [110]
	−67.4		n.i.		[117] quoted in [110]
	−62.9		n.i.		[109] quoted in [110]
	−43.0		calculated		[111]
Co_2Al_5	−41.8	3.0 (a)	rT drop dir cal		[72] quoted in [107]
$CoAl_3$	−32.0	3.0 (a)	rT drop dir cal		[72] quoted in [107]
	−25.0		calculated		[111]

Table 2 (*Continued*)

Phase	$\Delta_f H^0$ (kJ/mol of atoms)	Error (kJ/mol of atoms)	Measurement temperature and method[a]	Comments	Reference
Co_2Al_9	−29.7	3.0 (a)	rT drop dir cal		[72] quoted in [107]
Ni_3Al	−40.2		rT drop dir cal		[72] quoted in [119]
	−37.6	4.0 (a)	rT dir cal		[118] quoted in [119]
	−40.6	1.0	Al sol cal		[119]
	−41.3	1.3	Al sol cal		[120]
	−41.4	4.9	mass spec at 1389–1734 K	Ref. Al liq. at 1600 K	[121]
	−47.0		emf at 933–1030 K	Ref. Al fcc at 980 K	[122] quoted in [111]
	−36.8		emf at 1061–1278 K	Ref. Al fcc at 1273 K	[123]
	−37.7	4.0	assessment		[107]
	−33.0		calculated		[111]
NiAl	−58.8	4.2 (a)	rT dir cal		[118]
	−71.3	2.0 (a)	Al sol cal at 1023 K	Ref. Al liq. at 1023 K	[124]
	−72.2	1.0 (a)	Al sol cal at 1100 K	Ref. Al liq. at 1100 K	[125]
	−67.0	1.0	Al sol cal at 1100 K	Ref. Al fcc at 1023 K	[125] quoted in [111]
	−67.0		emf at 933–1030 K	Ref. Al fcc at 980 K	[122] quoted in [111]
	−62.0		emf at 1061–1278 K	Ref. Al fcc at 1273 K	[123]
	−62.9		n.i.		[109] quoted in [110]
	−63.0		n.i.		[116] quoted in [111]
	−58.8	4.2	assessment		[107]
	−48.0		calculated		[111]
Ni_2Al_3	−57.7	4.0	rT dir cal		[118]
	−70.0		emf at 933–1030 K	Ref. Al fcc at 980 K	[122] quoted in [111]
	−59.8		emf at 1061–1278 K	Ref. Al fcc at 1273 K	[123]
	−56.5	4.0	assessment		[107]
	−43.0		calculated		[111]
$NiAl_3$	−37.7	4.0	rT dir cal		[118]
	−56.0		emf at 933–1030 K	Ref. Al fcc at 980 K	[122] quoted in [111]
	−37.7	4.0	assessment		[107]
	−28.0		calculated		[111]
RuAl	−62.1	1.7	hT dir cal at 1473 K		[126]
	−48.0		calculated		[111]
RhAl	−106.3	1.6	hT dir cal at 1473 K		[126]
	−64.0		calculated		[111]
Pd_2Al	−81.6	4.2	rT dir cal		[75]
	−87.3	1.8	hT dir cal at 1473 K		[127]
	−81.0	4.0 (a)	isopiestic at 1090–1490 K	Ref. temp. 373 K	[128]
	−80.0		calculated		[111]
Pd_5Al_3	−91.0	4.0 (a)	isopiestic at 1090–1490 K	Ref. temp. 373 K	[128]
	−74.0		calculated		[111]
PdAl	−100.4	6.3	rT dir cal		[75]
	−92.5	0.8	precipit cal		[88]
	−91.3	1.9	hT dir cal at 1473 K		[129]
	−95.0	4.0 (a)	isopiestic at 1090–1490 K	Ref. temp. 373 K	[128]
	−84.0		calculated		[111]
Pd_2Al_3	−80.3	4.2	rT dir cal		[75]
	−80.0	4.0 (a)	isopiestic at 1090–1490 K	Ref. temp. 373 K	[128]
	−80.0		calculated		[111]
$PdAl_3$	−51.0	3.3	rT dir cal		[75]
	−51.0	4.0 (a)	isopiestic at 1090–1490 K	Ref. temp. 373 K	[128]
	−55.0		calculated		[111]

Table 2 (*Continued*)

Phase	$\Delta_f H^0$ (kJ/mol of atoms)	Error (kJ/mol of atoms)	Measurement temperature and method[a]	Comments	Reference
OsAl	−38.6	0.9	hT dir cal at 1473 K		[126]
	−43.0		calculated		[111]
IrAl	−92.8	1.8	hT dir cal at 1473 K		[126]
	−60.0		calculated		[111]
Pt_3Al	−71.1	2.1	rT dir cal		[130]
	−63.6	2.1	hT dir cal at 1473 K		[131]
	−50.0		calculated		[111]
Pt_3Al_2	−92.9	2.1	rT dir cal		[130]
	−75.0		calculated		[111]
PtAl	−100.4	2.1	rT dir cal		[130]
	−97.6	5.1	hT dir cal at 1473 K		[129]
	−82.0		calculated		[111]
Pt_2Al_3	−95.0	1.3	rT dir cal		[130]
	−96.5	1.2	hT dir cal at 1473 K		[131]
	−79.0		calculated		[111]
$PtAl_4$	−57.3	1.7	rT dir cal		[130]
FeSi	−39.3	1.9	Al sol cal, T n.i.		[132] quoted in [133]
	−37.7	4.2	comb cal		[134] quoted in [133]
	−38.6	1.8	hT dir cal at 1473 K		[133]
	−35.9	7.8	mass spectrometry		[135] quoted in [133]
	−26.0		calculated		[111]
Co_2Si	−38.5	4.0 (a)	rT dir cal		[72] quoted in [133]
	−37.9	2.0	hT dir cal at 1473 K		[133]
	−41.0	2.0	mass spectrometry		[136] quoted in [133]
	−30.0		calculated		[111]
CoSi	−49.3	1.3	hT dir cal at 1473 K		[133]
	−47.3	2.0	mass spectrometry		[136] quoted in [133]
	−31.0		calculated		[111]
$CoSi_2$	−34.3	4.0 (a)	rT dir cal		[72] quoted in [133]
	−34.9	1.1	hT dir cal at 1473 K		[133]
	−32.9	2.0	mass spectrometry		[136] quoted in [133]
	−15.0		calculated		[111]
Ni_5Si_2	−45.1	1.4	hT dir cal at 1473 K		[133]
NiSi	−42.0		hT dir cal at 1473 K		[137] quoted in [111]
Ni_2Si	−46.9	4.0 (a)	rT dir cal		[138] quoted in [133]
	−50.6	1.7	hT dir cal at 1473 K		[133]
	−32.0		calculated		[111]
RuSi	−58.1	3.7	hT sol cal at 1400 and 1473 K		[139]
	−58.3	2.1	hT dir cal at 1473 K		[140]
	−32.0		calculated		[111]
Ru_2Si_3	−60.7	1.7	hT dir cal at 1473 K		[140]
	−26.0		calculated		[111]
Rh_2Si	−63.9	2.4	hT dir cal at 1473 K		[140]
	−38.0		calculated		[111]
RhSi	−75.0	2.5	hT sol cal at 1400 and 1473 K		[139]
	−75.8	1.6	hT dir cal at 1473 K		[140]
	−44.0		calculated		[111]

Table 2 (*Continued*)

Phase	$\Delta_f H^0$ (kJ/mol of atoms)	Error (kJ/mol of atoms)	Measurement temperature and method[a]	Comments	Reference
Pd_3Si	−57.9	1.9	hT dir cal at 1473 K		[140]
	−37.0		calculated		[111]
Pd_2Si	−64.5	2.5	hT sol cal at 1473 K		[137] quoted in [140]
	−64.2	2.4	hT dir cal at 1473 K		[140]
	−48.0		calculated		[111]
Os_2Si_3	−30.5	2.1	hT dir cal at 1473 K		[141]
	−23.0		calculated		[111]
IrSi	−63.8	3.7	hT sol cal at 1400 and 1473 K		[139]
	−64.4	2.6	hT dir cal at 1473 K		[141]
	−40.0		calculated		[111]
Pt_2Si	−61.7	2.3	hT sol cal at 1473 K		[137] quoted in [140]
	−63.3	2.3	hT dir cal at 1473 K		[141]
	−47.0		calculated		[111]
PtSi	−59.4	2.6	hT sol cal at 1473 K		[137] quoted in [140]
	−59.6	2.1	hT dir cal at 1473 K		[141]
	−56.0		calculated		[111]

[a] Errors, not indicated by authors, marked with (a), have been assumed by analogy with similar measurements. Default reference state is the component elements in the phase stable at 298 K. In a few cases, indicated in the table, different reference phases or temperatures are assumed (rT, room temperature; hT, high temperature; n.i., not indicated; dir cal, direct calorimetry; Al sol cal, solution calorimetry in liquid Al; comb cal, combustion calorimetry).

metals of the 8th, 9th and 10th groups of the Periodic Table). Experimental values obtained both by different calorimetric techniques and by indirect methods (mainly via vapour pressure measurements) are listed together with those computed according to the Miedema model and taken from Ref. [111]. We note a wide range of $\Delta_f H$ values in this group of alloys. The compounds with the noble Pt family metals, show values of the $\Delta_f H$ close to the most negative ones relevant to the intermetallic phases. Generally, more negative values are obtained only with the combinations of metals with non-metals or semi-metals.

Even if still incomplete these data, which have generally been obtained in leading laboratories, may give an indication of the reproducibility and accuracy and precision which presently may be obtained in alloy thermochemistry. Note the discrepancies between the data relevant to a given compound and the errors assigned to each individual measurement.

A certain regular trend of the values as a function of the position in the Periodic Table of the components is also apparent. The usefulness and the limits of the values obtained by computation (via the well-known Miedema's formula [111]) may also be noticed.

We may finally underline that the uncertainties and errors ascribed to the different measurements are generally due to chemical problems (purity of the sample, side reactions, complete or incomplete reaction, etc.) more than to instrumental problems.

The need, therefore, of thermochemical investigations carried out by using different techniques should be stressed. Systematic side errors could possibly be more easily recognized and minimized by comparing the results of different procedures.

As for the ΔH of formation, the higher reliability of calorimetric methods should be on principle accepted, even if indirect methods (vapour pressure, emf, etc. measurements) should be used to complete the thermodynamic description of the system. A greater understanding and more accurate analysis of the reasons for which large discrepancies can sometimes be found in the experimental values obtained both by direct and indirect methods could be an important aim for the future development of experimental alloy thermodynamics.

Another point of future progress, as already mentioned, may be the identification, with the joint cooperation of different laboratories, of certain groups of alloys to be recommended as thermochemical standards for the calibration, not only for calorimetric apparatus, but for the entire measurement procedure (sample preparation, manipulation, etc.).

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