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CALORIMETRIC METHODS IN METALLURGY*

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ABSTRACT

After a brief introduction on the thermodynamics of alloy formation, the principles of calorimeter construction are discussed, considering mainly the isothermal and the adiabatic mode of operation as well as the methods of quantitative differential thermoanalysis (DTA) and the twin or differential calorimeter.

Several examples for the practical realization of these principles are given. Some important sources of errors are discussed. Finally, an outlook on the future prospect of calorimetry is given.

INTRODUCTION

Decisive for the formation of alloys and for their stability is the change of the free energy ΔG, which is related to the formation of the alloy from the pure components. The magnitude of this value is principally fixed by changes in the type and extent of the interatomic interactions. There are, in general, also influences from atomic radii differences, which cause lattice distortion in solid alloys and effects from structural changes. According to the Gibbs–Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

ΔH is the mixing enthalpy, ΔS is the mixing entropy and T is the temperature in K. Of the integral mixing values introduced in eqn (1), only ΔH can be directly determined experimentally. The single factors mentioned above which influence the formation of alloys, are of course, also affecting the sign and the magnitude of ΔH. Measurements of formation enthalpies are therefore often a goal of thermodynamic investigations in alloy systems.

It should be mentioned that the usual methods for the determination of free energies of mixing, for example partial vapor pressure measurements or e.m.f.

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measurements on suitable galvanic cells, primarily lead to the determination of the partial free energies of mixing of one component. From their concentration dependence, the partial values for the other component can be determined from:

$$\overline{\Delta G}_A = -\int_{x_B=0}^{x_B} \frac{x_B}{x_A}\, \mathrm{d}\,\overline{\Delta G}_B \tag{2}$$

This relation can often be evaluated only with a limited degree of precision. $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$ are the partial free energies of components A and B. The integral free energies of mixing are then obtained from

$$\Delta G = x_A \cdot \overline{\Delta G}_A + x_B \cdot \overline{\Delta G}_B \tag{3}$$

where x_A and x_B are the mole fractions of the components.

The integral mixing enthalpy, ΔH, is related to the corresponding partial values, $\overline{\Delta H}_A$ and $\overline{\Delta H}_B$, in an analogous way by:

$$\Delta H = x_A \cdot \overline{\Delta H}_A + x_B \cdot \overline{\Delta H}_B \tag{4}$$

and

$$\overline{\Delta H}_A = \Delta H + (1 - x_A)\left(\frac{\partial \Delta H}{\partial x_A}\right) \tag{5}$$

The partial molar enthalpies which are necessary for some considerations can be directly measured by calorimetry in suitable cases. They can also be determined from the temperature dependence of the partial free energy of mixing,

$$\overline{\Delta H}_A = \overline{\Delta G}_A - T\left(\frac{\partial \overline{\Delta G}_A}{\partial T}\right) \tag{6}$$

The precision, however, is in general relatively poor. An optimal assessment of the thermodynamic properties of an alloy can, in general, be given if the free energy of mixing is determined from equilibrium measurements (Eqns (2) and (3)) and the mixing enthalpy by calorimetry.

Furthermore, the heat contents H are often the subject of calorimetric investigations. The heat content is related to the mixing enthalpy ΔH and the molar specific heat, C_p, by the following equations:

$$\Delta H = H_{\mathrm{alloy}} - (x_A \cdot H_A + x_B \cdot H_B),\ T = \text{constant} \tag{7}$$

and

$$C_p = \left(\frac{\partial H}{\partial T}\right) \tag{8}$$

H_{alloy} is the heat content of the alloy and H_A and H_B are the heat contents of the pure components.

Further, melting and transformation enthalpies are significant for energetic considerations of melting reactions and transformation processes. They can be directly or indirectly determined from calorimetric investigations.

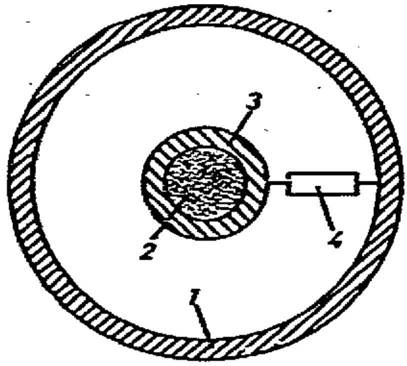
Calorimetric measurements consist in general of the measurement of temperature changes. These are related to enthalpy changes which are the result of changes of state. Initial and final states of the observed reaction must be defined exactly. This leads to many special difficulties in the case of alloys at low temperatures. Therefore, the major region for application of calorimetry in metallurgy is the temperature range well above room temperature. This can cause, on the other hand, considerable problems with the measurement of small temperature differences.

However, additional reactions can also result in significant errors. For example, reactions with the crucible or with remaining oxygen or nitrogen in the protective gas can lead to false results. Likewise, errors can occur through vaporization of one component.

Calorimetric measurements are frequently carried out as relative measurements. Calibration with a known quantity of heat should provide effects with like signs and approximately similar values as those occurring during the measurement of unknown thermal effects. In this case, the possible systematic errors of calorimetric measurements are minimal. Statistical errors are far less dangerous, since they can be recognized from the scatter of the measured values with adequately frequent repetition. In metallurgy, the measurement goals which can be attained by calorimetric methods and under special operating conditions which have to be observed are certainly numerous. Correspondingly, the number of calorimeter types which have been designed to meet the requirements for the best solution of the actual problem, is considerable[1a, 1b]. In the following, some calorimeter types will be described which are suitable for measurement of often required values. However, this discussion will not be so much with the theoretical background but will be directed more towards construction principles and practical boundaries of operation.

PRINCIPLES OF ISOTHERMAL AND ADIABATIC PROCEDURES

A calorimeter in principle consists of a calorimeter mantle (1), a sample (2) and a sample container (3) (Fig. 1)[2, 3]. The sample and container are coupled to the mantle by a thermal resistance, (4). In the simplest case of calorimetric experiments, the mantle is maintained at constant temperature and a quantity of heat is generated or absorbed by the sample. Therefore, at first a temperature difference occurs between the sample and the mantle. If the thermal resistance (4) is small, then a noticeable heat flux and temperature equalization occurs. This is isothermal operation. In the case that the temperature of the mantle is changed continuously, the temperature of the sample and sample holder follow this change. Such a heat exchange can be prevented if, by suitable measures, the temperature of the mantle and that of sample and sample holder are maintained equal. Calorimeters which operate according to this principle are known as adiabatic calorimeters. The adiabatic method is an advantage when amounts of heat are to be measured which only develop slowly. Isothermal operation



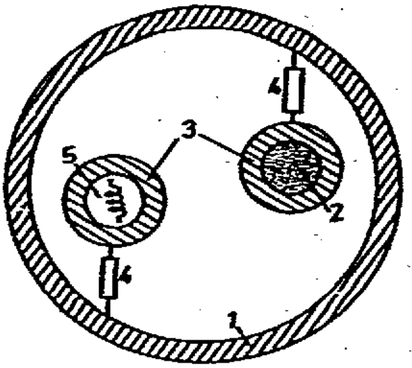


Fig. 1. Construction principle of a calorimeter. 1 = Calorimeter mantle; 2 = sample; 3 = container; 4 = thermal resistance.

Fig. 2. Construction principle of a twin or differential calorimeter. 1 = Calorimeter mantle; 2 = sample; 3 = containers; 4 = thermal resistance; 5 = heating coil.

would fail in this case. On the other hand, rapidly occurring thermal effects in adiabatic calorimetry can lead to considerable control difficulties due to thermal lag of the experimental equipment. Control difficulties are greater, the slower heat is produced in the sample.

It is to be mentioned further, that with adiabatic operation in which the thermal resistance (4) is very large, small temperature increases of the sample due to the occurrence of thermal effects produce no noticeable thermal flux. At higher temperatures, heat transfer between mantle and sample occurs by radiation; therefore the thermal resistance (4) decreases with increasing temperature. Preventive measures can be taken in this case by introduction of radiation shields between the sample and mantle.

Calorimeters which work strictly isothermally are the so-called phase transformation calorimeters. Here, the thermal effects associated with the reaction of interest are used to transform a substance which is present in the calorimeter. In the Bunsen ice calorimeter, ice is melted. No temperature difference between sample and mantle occurs. The quantity of heat introduced into the calorimeter is measured from the amount of the calorimeter substance transformed.

For many measurements, a twin arrangement in the calorimeter can be of advantage (Fig. 2). In such a twin or differential calorimeter, two sample containers, which should be as nearly equal as possible, are present. In one of these containers, the reaction occurs for which the heat effect is to be measured. In the other, the thermal effect is simulated through a corresponding development of Joule heat so that the temperature difference between both containers is always equal to zero. With this compensation method, which can be used not only for isothermal but also for adiabatic operations, the desired thermal effect is given directly by the applied electrical energy. If there is a certain asymmetry of the twin arrangement, this can be accounted for by a blank test, during which the same thermal energy is developed simultaneously in both sample holders with a heater. Another possibility to determine asymmetry is simply to exchange in two experiments, the heater and the sample in the containers.

CALORIMETERS FOR THE DETERMINATION OF MELTING AND TRANSFORMATION ENTHALPIES

Melting enthalpies and transformation enthalpies can be determined from measurement of the heat contents above and below the temperature of the corresponding phase transformation (for example ref. 4), by comparison of the hold times for thermal analysis[5, 6] or for similar procedures, or through a combination of heat content measurements and thermal analysis as applied in the "Thermodynamic Analysis" developed by Oelsen[7]. A procedure will be considered next which originates from differential thermal analysis.

QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS (DTA)

The "thermal effects" occurring during DTA in the case of phase transformations give information on the temperature at which the phase transformation takes place, and on the enthalpy changes accompanying the phase change, from the magnitude of the area under the recorded temperature difference–time or temperature difference–temperature curve. A simple quantitative determination of the melting or transformation enthalpy is carried out on this basis in general with high precision. The principle for a suitable calorimeter is shown in Fig. 3. As "reference sample" the DTA-system uses a massive metal block (7) which contains in addition to the control thermocouple, a cavity into which the crucible (9) with the material to be investigated (5) is inserted. The system is contained in a suitable furnace (4) which can be heated or cooled with appropiate rates. The large heat capacity of the metallic reference sample provides thermal stability against short-time disturbances of the surroundings so that electronic control devices are not necessary. The temperature difference between the reference thermocouple and the thermocouple which indicates the sample temperature can be used directly for the recording of a ΔT–time curve or a ΔT–T curve. As an example such a ΔT-time curve is shown in Fig. 4 for the solidification of a metal.

For the quantitative determination of the melting enthalpy, which corresponds to the area under the "thermal effect" curve, a calibration can be made using a heating coil (6) placed in the sample from which it is electrically insulated.

In order to have a sufficiently rapid decay of the temperature difference ΔT, in the ΔT-time curve to a final steady state value, a relatively small thermal resistance between sample and metal block is necessary with heating or cooling rates of the order of 1 °C min^{-1}. This assures an exact definition of the area between the "thermal effect" curve and the baseline (B–D) of the curve.

For solidification or transformation of a sample, which occurs at a constant temperature T_T, the temperature difference, ΔT, between the times $t = 0$ and $t = t_0$ (Fig. 4) is given by

$$\Delta T = (T_T - T_0) \cdot (1 - e^{-\beta t}) \tag{9}$$

if temperature equalization in the metal block rapidly occurs[8, 9]. For small values of βt this can be simply written as:

$$\Delta T = (T_T - T_0) \cdot \beta t \tag{10}$$

T_0 is the temperature approached by the calorimeter as a final value in the case of cooling, if at a temperature above T_T, the heating oven was shut off or its temperature decreased to a determined constant value below T_T.

As expected on the basis of eqn (10), ΔT–time curves are indeed found experimentally where the initial portion of the curve A–C (Fig. 4) is practically linear, whereas in the region of C (for longer times t) considerable deviations from a straight line occur.

On the basis of the heat transfer equations the segment of the ΔT–time curve for $t > t_0$ can also be expressed[8]. The total area is:

$$F = \int_0^{t_0} \Delta T \mathrm{d}t + \int_{t_0}^{\infty} \Delta T \mathrm{d}t \tag{11}$$

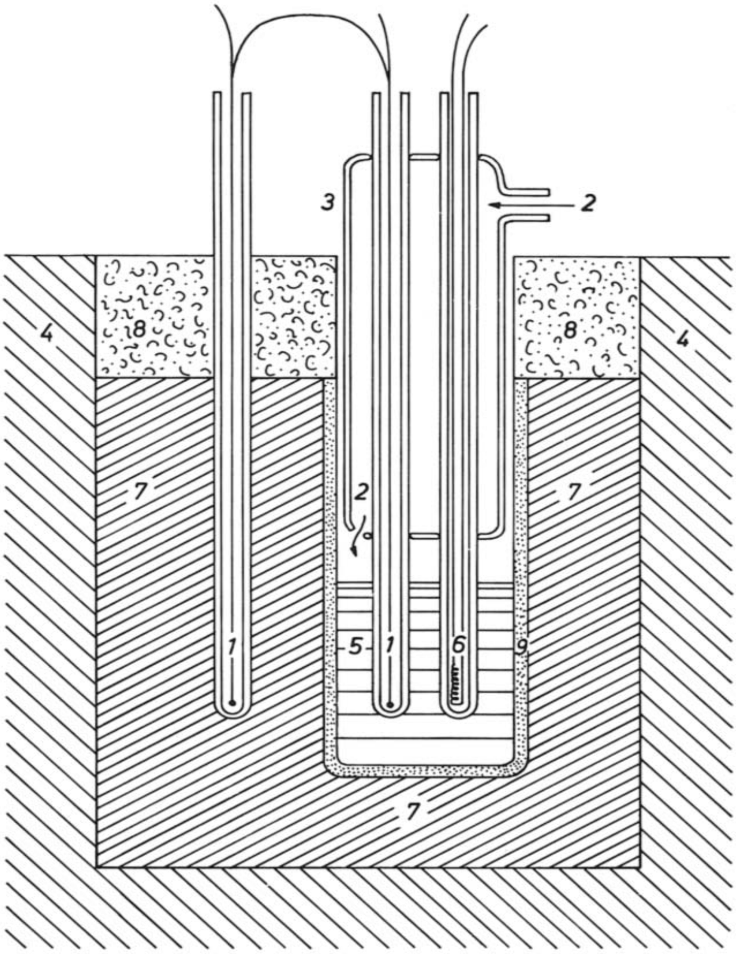


Fig. 3. Construction of a calorimeter according to the principle of quantitative DTA. 1 = Thermocouple; 2 = protective gas; 3 = insulating body; 4 = oven; 5 = alloy; 6 = heating coil; 7 = massive metal block; 8 = thermal insulation (ceramic material); 9 = crucible.

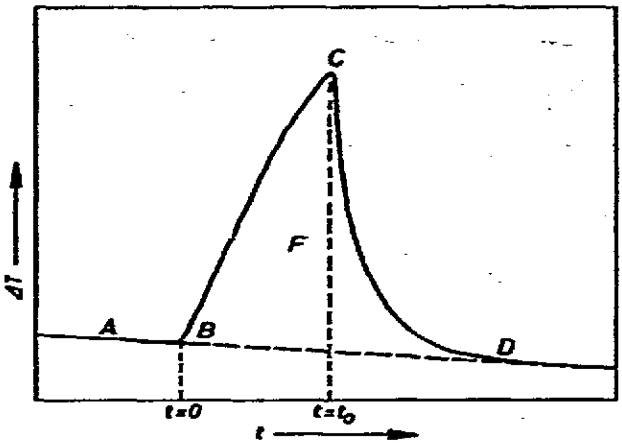


Fig. 4. Temperature difference–time curve for the solidification of a pure metal by quantitative DTA (clarification in text).

In the expression for ΔT as a function of time the mass, m, of the sample and its melting or transformation enthalpy L (in J g^{-1}) are contained in addition to apparatus constants (in which are included values such as, for example, mass and specific heat of the metal block as well as the thermal resistances). A simple relationship

$$F = \frac{L \cdot m}{b} \tag{12}$$

results from this where b is an "apparatus constant".

For the production of a "calibration effect" with the aid of a heating coil in the sample, the following equation is valid:

$$F = \frac{i \cdot U \cdot t_u}{b} \tag{13}$$

i is the electric current, U the voltage and t_u the time during which the Joule heating is produced.

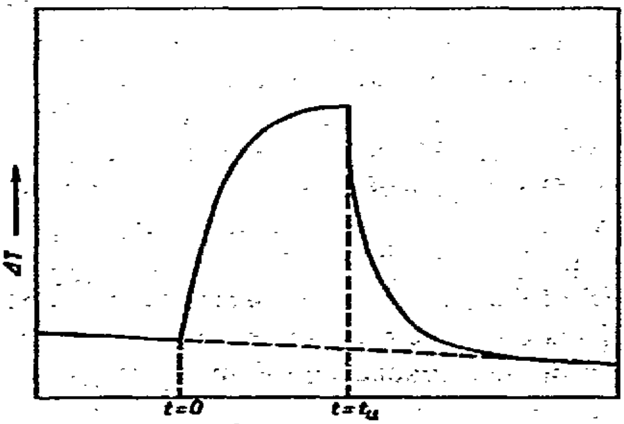


Fig. 5. Temperature difference–time curve for calibration with time constant electrical input for quantitative DTA (clarification in text).

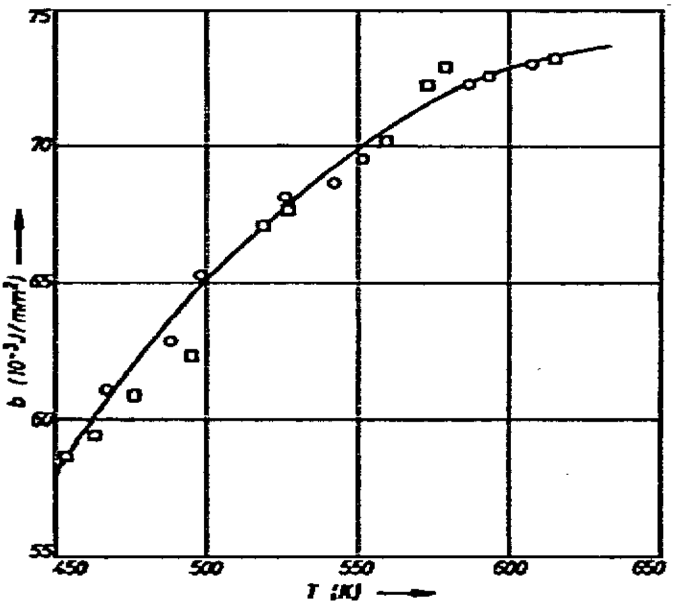


Fig. 6. Comparison of the calibration processes for quantitative DTA. ○ = Calibration with time variable input; □ = calibration with time constant input.

Equation (13) applies for the case that the voltage U and current i are constant during the time t_u. The resulting "calibration effect" is reproduced in Fig. 5. It differs considerably in shape from the form of the normal "thermal effect". It is naturally possible with the help of suitable electrical control equipment to vary the values i and U with time, so that the "thermal effect" which occurs for the transformation is exactly reproduced, but this is not necessary in general as the following experiment shows.

Using indium as a sample, "thermal effects" were alternately produced (at a cooling rate of 1 °C min^{-1}) corresponding in form to Fig. 5 and a triangular shape, respectively. Time-independent and time-variable ($i \cdot U$)-values were used to generate the different shapes, giving areas F which were approximately equal. The determined b-values are shown in Fig. 6 as a function of the temperature. The average deviation of a single value from the best-fit curve is 1 %. No difference between the two calibration methods is observed which is greater than this scatter. Figure 6, however, indicates another possible error source. The apparatus constant b is noticeably dependent upon the temperature. This is due to the temperature dependence of the thermal resistance between the sample and the metal block. For the investigation leading to Fig. 6, glass was used as crucible material. The determined temperature dependence of b can indeed, as a comparison with corresponding data shows, be traced back to the temperature dependence of the thermal conductivity of the selected crucible material.

To avoid errors, it is therefore necessary, during the heating or cooling of the calorimeter, before and after the occurrence of the investigated phase transformation, to make several calibrations at different temperatures, and then to determine by interpolation the values of "b" valid for the temperature of the phase transformation. A determination of the constant "b" is unnecessary if the thermal effect of the phase transformation is compensated for by development of corresponding Joule heat with a heating element. In this way Wittig[10] has undertaken, in 1952, to determine the solidification enthalpy of germanium.

Quantitative DTA applies especially simply to the investigation of phase transformations which proceed at constant temperature or over very small temperature intervals. Considerable difficulties with calibration and determination of the lower boundary of the area, F, of the thermal effect can occur, if there are large melting or transformation intervals, as is usually the case for alloy systems. In general, this method applies especially well for the determination of melting enthalpies of pure metals, congruently melting intermetallic compounds, eutectic alloys and analogous solid-state reactions. It has also been shown that the melting enthalpy of binary alloys over the entire concentration range can be well determined when the melting interval is not extremely large. For example, the formation enthalpies of the solid alloys in the system Fe–Ni can be obtained from the so determined melting enthalpies, if the mixing enthalpies are known[11].

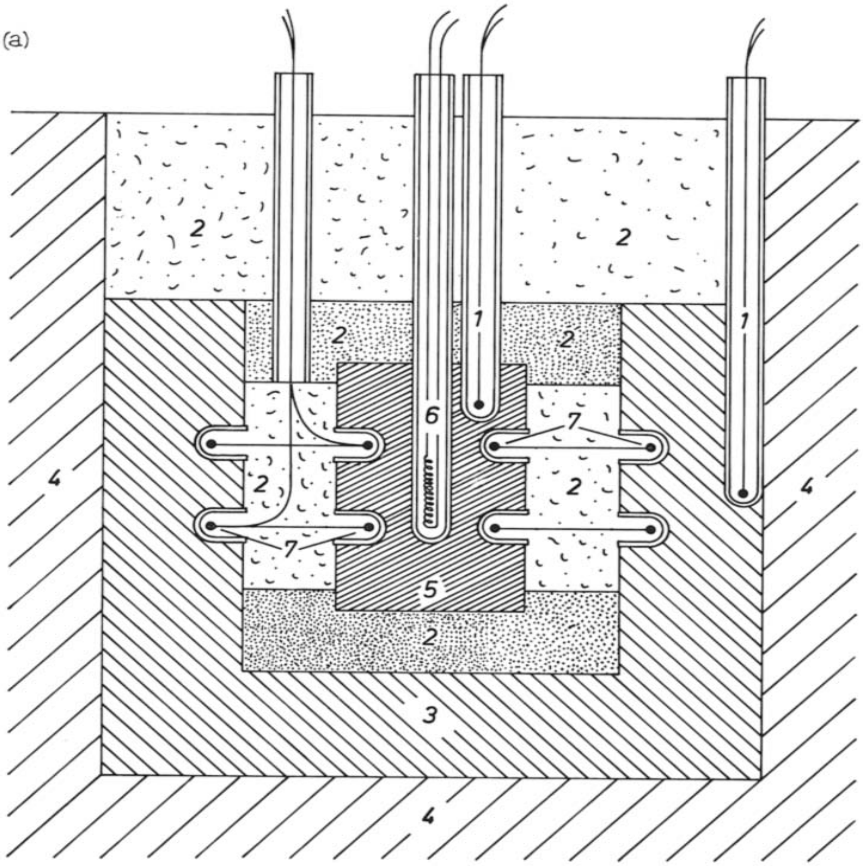


Fig. 7a. See p. 220 for legend.

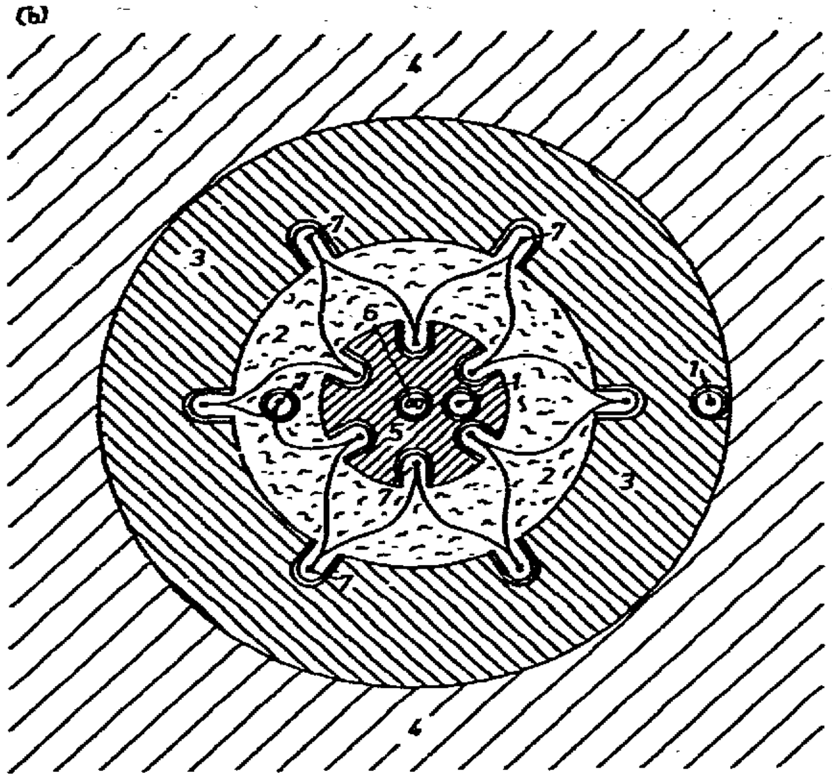


Fig. 7. (a, b). Calorimeter according to the principles of quantitative DTA for the determination of small transformation enthalpies. 1 = Thermocouple; 2 = ceramic; 3 = massive metal block; 4 = oven; 5 = sample; 6 = heating coil for calibration; 7 = thermopile.

The sensitivity of a calorimeter can naturally be considerably increased if, in place of a thermocouple pair, a thermopile is used. The utilization of a thermopile is especially applicable to the determination of small enthalpy changes accompanying phase transformations in the solid state. In Figs. 7 a and b, a simple experimental arrangement is shown, as an example, with which it was possible to determine the enthalpy change corresponding to a martensitic phase transformation in In–Tl solid solutions[12]. This value is only

$$\Delta H_t = 2.0 \pm 0.1 \text{ J mol}^{-1}$$

DETERMINATION OF TRANSFORMATION ENTHALPIES WITH AN ADIABATIC CALORIMETER

For the determination of enthalpy changes for sluggish transformations of iron alloys in the region between 680 and 1700 K, Sale and Normanton[13] have constructed a spherical adiabatic calorimeter. The structure is shown in Fig. 8 a/b. The spherical shape was selected in order to attain a good thermal symmetry. The outer oven (5), (6) is easily regulated thermally. It furnishes the heat which is necessary to bring the entire apparatus to the required temperature. The inner oven (3), (4) is equally easily regulated. The adiabatic conditions can be maintained at 1200 K to ± 0.005 K.

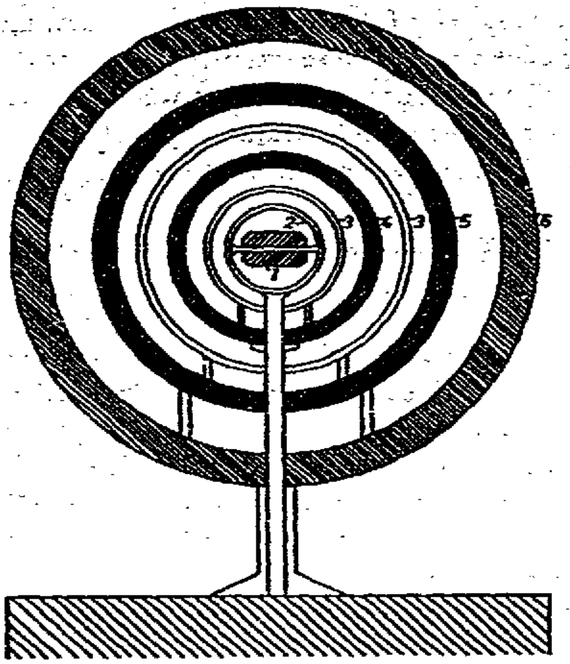


Fig. 8. (a) Spherical adiabatic calorimeter of Sale and Normanton[13]. 1 = Sample; 2 = sample holder from tantalum; 3 = molybdenum radiation shields; 4 = inner tantalum oven; 5 = outer tantalum oven; 6 = radiation shields and outer case.

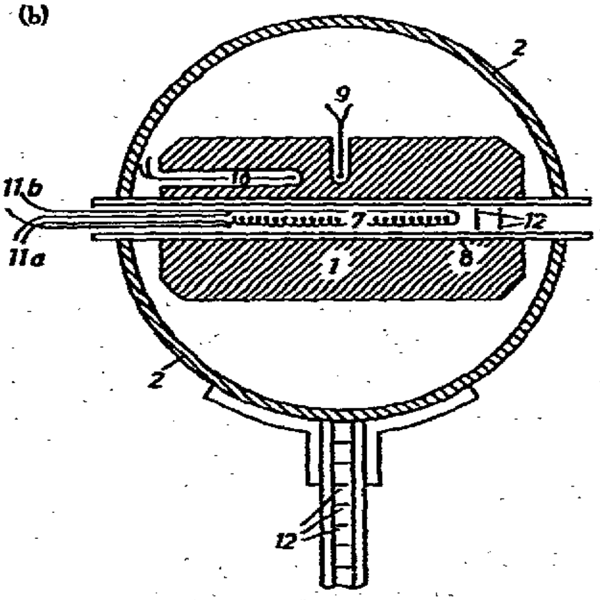


Fig. 8. (b) Central part of the apparatus shown in Fig. 8a. 1 = sample; 2 = sample holder cell (tantalum); 7 = heating coil; 8 = alumina sheath; 9 = differential thermocouple; 10 = sample temperature measurement thermocouple; 11 a, b = potential and current measuring leads; 12 = radiation shields.

The sample (1) is mounted on an alumina tube (8) which contains a heating element (7). This heating element serves for calibration. The thermal effect occurring while traversing a transformation point during heating or cooling of the whole system is compared with the effect which is simulated by the sample heater.

Likewise, this calorimeter can be used for the determination of specific heats.

DETERMINATION OF MELTING AND TRANSFORMATION ENTHALPIES BY HEAT CONTENT MEASUREMENTS

For a long time, methods for determination of melting and transformation enthalpies from heat contents have been practiced. The heat contents are determined in general as the enthalpy difference between a predetermined temperature, T_x, and the calorimeter temperature T. In the simplest case, T corresponds to 298.15 K (25°C; standard temperature; T_{St}). For temperatures $T_x > T$, heated samples are dropped into the calorimeter and the enthalpy difference $H_{T_x} - H_{St}$ measured ($H_{St} = H(T_{St})$; standard enthalpy). For this type of calorimeter, the known restricting conditions for high temperature calorimeter construction need not be considered. They can be built with such a high sensitivity that the error limits are determined through the accuracy of the temperature measurement of the sample before dropping and the circumstances of the drop of the sample into the calorimeter. The construction of various types of room temperature calorimeters, of which there are many, shall not be discussed here. As an example, the heat content of thallium, H_{T_x}–H_{St} is shown in Fig. 9 as a function of temperature as well as the melting enthalpy and the transformation enthalpy[14].

Analogously, heat contents and melting enthalpies of alloys can also be determined. An advantage of this method is, certainly, the fact that the measurements can be carried out at room temperature. Furthermore, this is often the only method for the determination of melting and transformation enthalpies for aggressive or easily vaporized substances. The material to be investigated can be enclosed in suitable containers, the heat content of which must be determined in blank experiments. As an example, the determination of the mixing enthalpy of liquid alloys of the system Bi–BiI_3 can be mentioned[15]. During the rapid solidification of the Bi–BiI_3 alloys, which exist in the liquid state at sufficiently high temperatures as homogeneous solutions, a separation into practically pure Bi and BiI_3 occurs. The solidification enthalpy, ΔH^f_{alloy}, determined from the heat content curve, combined with knowledge of the solidification enthalpies of the components (ΔH^f_{Bi} and $\Delta H^f_{BiI_3}$) yields the mixing enthalpies, ΔH, of the liquid alloys.

$$\Delta H = \Delta H^f_{alloy} - (x_{Bi}\,\Delta H^f_{Bi} + x_{BiI_3}\,\Delta H^f_{BiI_3}) \qquad (14)$$

Liquid Bi–BiI_3 alloys are very sensitive to moisture and air, and, moreover, the partial pressure of BiI_3 is considerable. Through encapsulation in glass or quartz ampoules, these error factors are eliminated. The use of other methods for the determination of the mixing enthalpies would be connected with considerable experimental difficulties. Nevertheless, the melting or transformation enthalpies determined

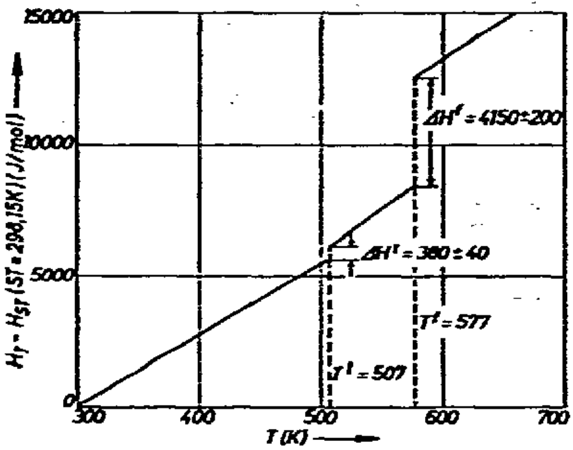


Fig. 9. Heat content, melting enthalpy and transformation enthalpy of thallium[14].

by this method often include considerable errors, since they result as small differences of two large numbers. This method of drop calorimetry is up to now the only possibility to carry out calorimetric measurements for extremely high temperatures. Leibowitz et al.[16] have measured the heat content of tungsten to 3600 K using this technique.

MEASUREMENT OF MELTING ENTHALPIES AND HEAT CONTENTS ACCORDING TO OELSEN

Oelsen et al.[17] have developed, through combination of simple classical thermal analysis with classical calorimetry at room temperature, a procedure with which the heat content curve of a material can be determined relatively rapidly over large temperature ranges in a single experiment. Moreover, the melting and transformation enthalpies of metals and alloys are simultaneously easily obtainable.

The schematic diagram of a simple experimental apparatus is shown in Fig. 10. It is an ordinary water calorimeter which consists of a Dewar flask (1) with about 4 liters of water (2), a stirrer (4) and a thermometer (3). This calorimeter contains a housing from copper sheet (8) into which the iron holder (7) with the sample (6) to be investigated is added, after these have been heated in a separate oven to the initial temperature. With the help of a wire frame, the sample holder is held in the center of the housing in the manner indicated in Fig. 10. The air cushion between container and housing provides a relatively slow thermal exchange with the calorimeter water. The temperature of the sample is followed with a thermocouple (5) during cooling and simultaneously the temperature of the calorimeter water is measured. After a run time of about 1 minute a steady-state heat flow occurs. The pair of values of a temperature measurement in the sample and in the calorimeter water leads to a point on the heat content curve. The total heat content curve can be determined within 1 to 2 hours. Material amounts of 0.2 to 1 kg are used.

The method is often applied to determine the thermodynamic properties of liquid alloys. Figure 11 gives a simple example of this. Shown are the measured heat

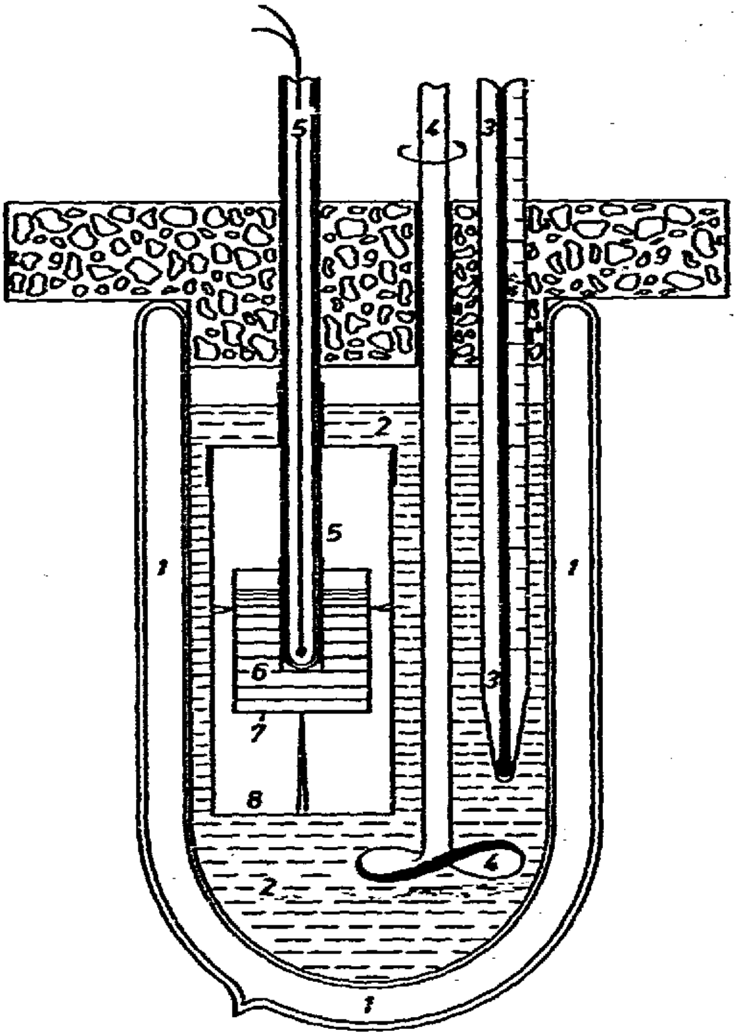


Fig. 10. Calorimeter for the determination of melting enthalpies and heat contents from Oelsen[17]. 1 = Dewar flask; 2 = water; 3 = thermometer; 4 = stirrer; 5 = thermocouple; 6 = sample; 7 = sample holder; 8 = sheet housing for damping the heat exchange between sample and calorimeter water; 9 = thermal insulation.

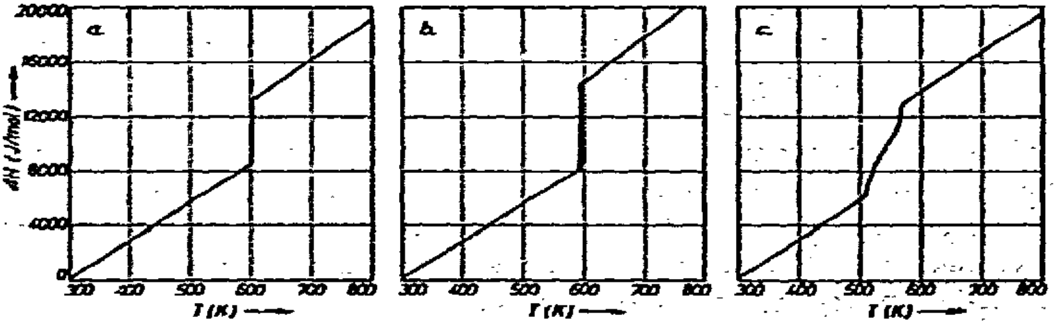


Fig. 11. Heat content curves of lead (a), cadmium (b) and a lead–8.84 at.% Cd alloy (c) determined by the Oelsen calorimeter[17].

content curves of Pb, Cd and a Pb–Cd alloy with 8.84 at.% Cd[17]. From the heat content curve of the alloy, for example, the following information is obtained: liquidus temperature, eutectic temperature, total melting enthalpy of the alloy, melting enthalpy for each alloy between 8.84 at.% Cd and the eutectic concentration as well as specific heats of the liquid alloy and the mixture of the solid phases. Among other things, the mixing enthalpy of the melt can be determined from these data.

CALORIMETERS FOR THE MEASUREMENT OF MIXING ENTHALPIES

The mixing enthalpies of liquid alloys can be directly determined through measurement of the enthalpy changes during the mixing of the liquid components. Because of the high measurement temperatures, the necessity of suitable heat transfer conditions for the realization of an adequate measurement sensitivity and the probability of reactions between the metal melts and the usual crucible materials as well as air, the choice of construction materials for the calorimeter core is limited and there are only very simple mechanisms applicable for the mixing of the components in question.

ISOTHERMAL CALORIMETERS FOR THE MEASUREMENT OF MIXING ENTHALPIES

Of the different proven concepts, the next to be discussed is a high-temperature calorimeter, the basis of which is the differential principle of quantitative DTA. In order to achieve a change of state, during measurements of the mixing enthalpies for the alloys from the liquid components, it is of course not necessary to provide a temperature change as in the case of measurements of melting and transformation enthalpies. Therefore, the system can be operated at constant temperature. Figure 12 shows the construction principles of such a high-temperature calorimeter[18, 19]. Through raising of the stopper (6), the liquid component A in the top crucible (4) can flow into the bottom crucible (7) which contains the melt of component B. A stirrer (8) ensures rapid mixing, and an argon stream the protection of the melt from oxidation. Both crucibles are imbedded in a 2-part massive metal block (3) which provides a constant temperature of the components before mixing. This temperature equality can be controlled with the thermocouples (5a) and (5b). The temperature change in the crucible (7) with respect to the massive metal block and the corresponding time change of this temperature difference, ΔT, due to the mixing of the components, is followed with the thermocouples (5b) and (5c). The resulting ΔT–time curve is schematically shown in Fig. 13. The sudden mixing of the components leads to a rapid increase of the temperature difference to a maximum value. The area, F, under the ΔT–time curve is a measure of the mixing enthalpy.

Calibration can be carried out by introduction of a determined amount of Joule heating, with the help of a heating element (9) in the alloy melt, after the mixing process. More simple and certainly equally reliable, is the calibration by introduction of a suitable metal sample into a bottom-closed tube which replaces the tube with the

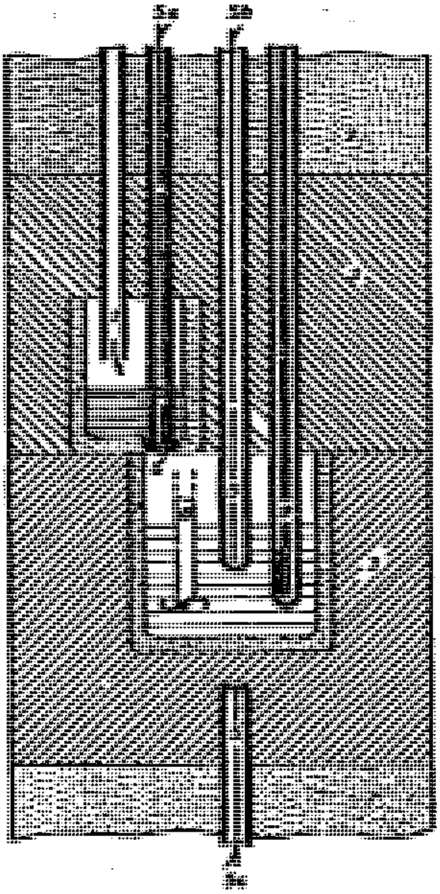


Fig. 12. Schematic structure of an isothermal high-temperature calorimeter for the determination of mixing enthalpies and alloys[18, 19]. 1 = Argon stream; 2 = ceramic; 3 = massive metal block; 4 = charge crucible; 5 (a, b, c) = thermocouples; 6 = stopper; 7 = lower crucible; 8 = stirrer; 9 = heating coil for calibration.

heating element immersed in the alloy melt. Especially good results are obtained for calibration by addition of cylindrical metal samples in the calibration tube which melt at the calorimeter temperature and assure a good heat transfer from the alloy melt to the calibration sample. Naturally, the calibration samples are dropped from room temperature into the calorimeter. The heat contents and melting enthalpies of metals which have been used as calibration substances (for example tin, silver) are well known (for example Hultgren et al.[14]).

In the case of calibration with Joule heating, the calibration effects in the T–time plot has a distinctly different shape from that of the thermal effect for mixing of the components. The thermal effect for calibration by introduction of a suitable metal sample into the calibration tube has, however, practically the same form as the mixing effect. It should be mentioned that it has been attempted to calibrate by the addition of small metal cylinders, through an open calibration tube, directly into the alloy melt. However, the calibration sample may not react with the alloy melt. In many cases, tantalum, tungsten or molybdenum fulfill this requirement.

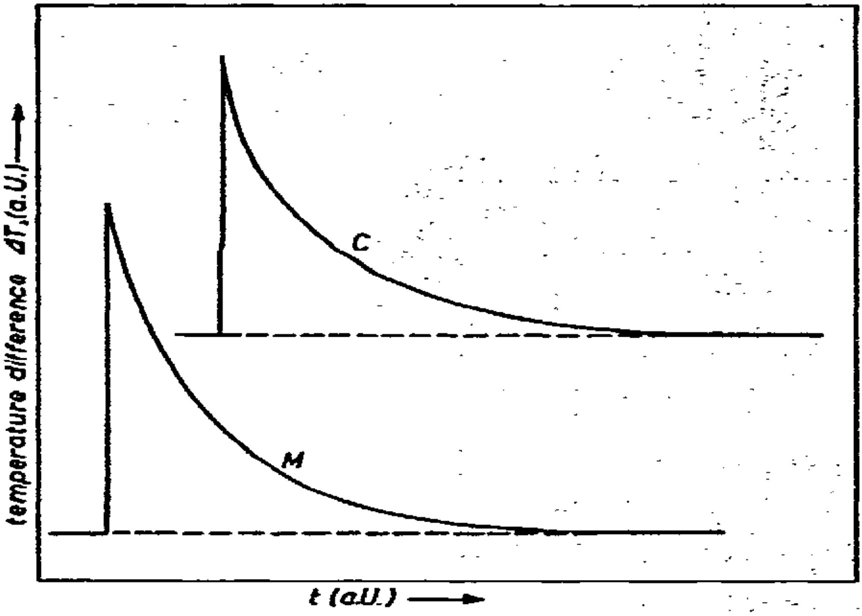


Fig. 13. Temperature difference–time curve of the mixing effect and a calibration effect due to addition of pure tin as the calibration substance in an isothermal high-temperature calorimeter of the type shown in Fig. 12.

An example of a high-temperature calorimeter for the determination of mixing enthalpies up to temperatures of 1870 K is shown schematically in Fig. 14[11]. The massive metal block (5) consists of a compact cylinder of 7 kg molybdenum. The large heat capacity of this block ensures that the operation is relatively stable against slight outer temperature variations without use of complicated electronic temperature control. This calorimeter can also be used for the determination of solidification enthalpies. After the mixing process is finished and the mixing enthalpy measured, the calorimeter temperature is lowered and the solidification enthalpy of the alloy determined. Thus, as mentioned previously, the formation enthalpy of the solid alloy can also be determined.

Alloys which react with the usual ceramic crucible materials can be handled with this simple calorimeter construction very easily by substitution of other materials (for example, ref. 20). Further, the mixing enthalpy can also be determined if one of the components is solid at the calorimeter temperature and the other component, as well as the resulting alloy, is liquid. In this case, the melting enthalpy of the higher melting component at the calorimeter temperature must necessarily be known for the evaluation.

An advantage of the construction shown in Fig. 12 is, that the upper crucible (4) can be filled again with a definite amount of component A after any measurement. The hole in the crucible is sealed by the stopper (6) and the desired quantity of component A is added to the crucible through the protective gas inlet tube (1). The integral mixing enthalpy for several alloy concentrations can be determined in this way by a single test by the summation of all previous thermal effects. If the concentra-

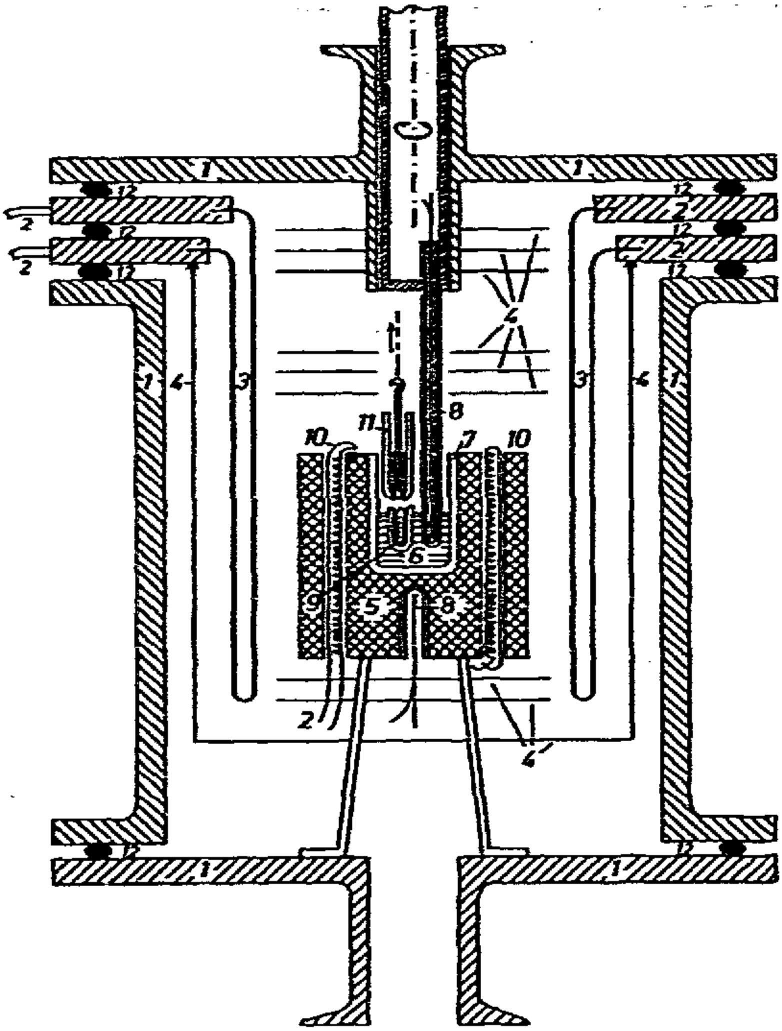


Fig. 14. Isothermal high-temperature calorimeter for the determination of mixing and solidification enthalpies up to a temperature of 1870 K[11]. 1 = Vacuum tank; 2 = power supply; 3 = molybdenum short circuit heater; 4 = radiation shields; 5 = massive molybdenum block; 6 = sample; 7 = crucible; 8 = thermoelement; 9 = heating coil for calibration; 10 = additional heater; 11 = charge crucible with stopper; 12 = rubber O-rings.

tion difference of a single step is chosen adequately small (approximately 1 at. %), the method leads to a direct determination of the first derivative of the mixing enthalpy with respect to the concentration for different concentrations[21].

ADIABATIC CALORIMETRY FOR THE MEASUREMENT OF MIXING ENTHALPIES

Itagaki and Yazawa[22] have used an adiabatic calorimeter for the determination of mixing enthalpies. The construction principle is shown in Fig. 15. The adiabatic block (9) is placed in a suitable resistance oven (10). In the middle of the adiabatic block is the cylindrical calorimeter block (6) of nickel. It contains both alloy compo-

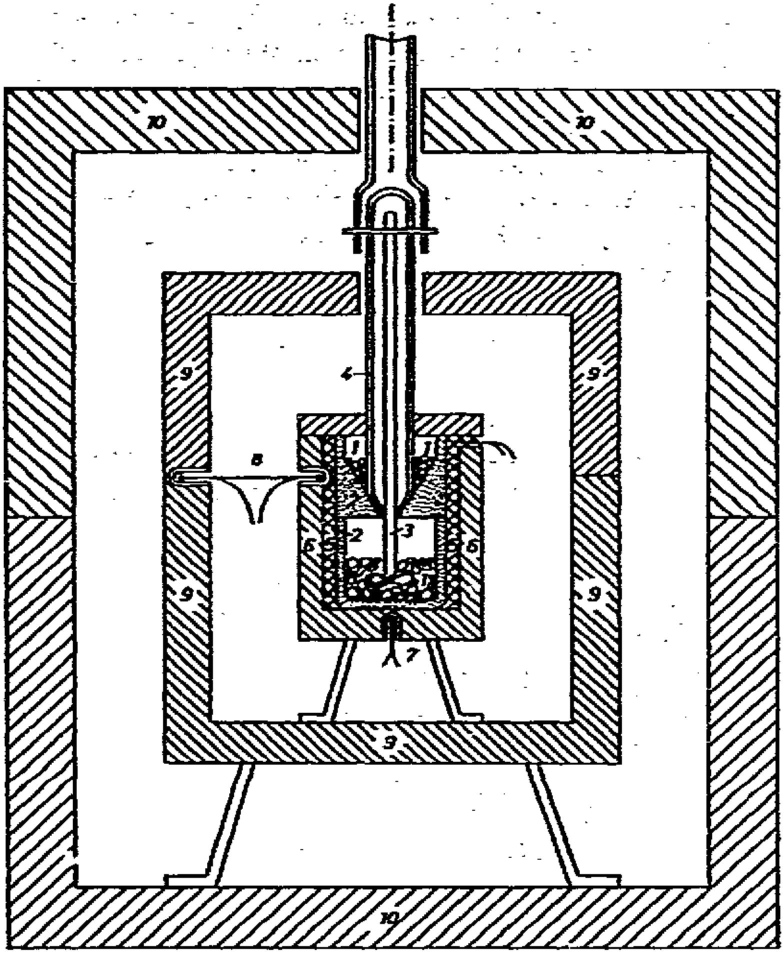


Fig. 15. Adiabatic high-temperature calorimeter for the determination of mixing enthalpies of alloys[22]. 1 = Sample; 2 = mixing container (graphite); 3 = stirrer (silica); 4 = silica charging device; 5 = constant wattage heater; 6 = calorimeter block (nickel); 7 = measuring thermocouple; 8 = differential thermocouple; 9 = adiabatic block (nickel); 10 = kanthal furnace and Al_2O_3 core.

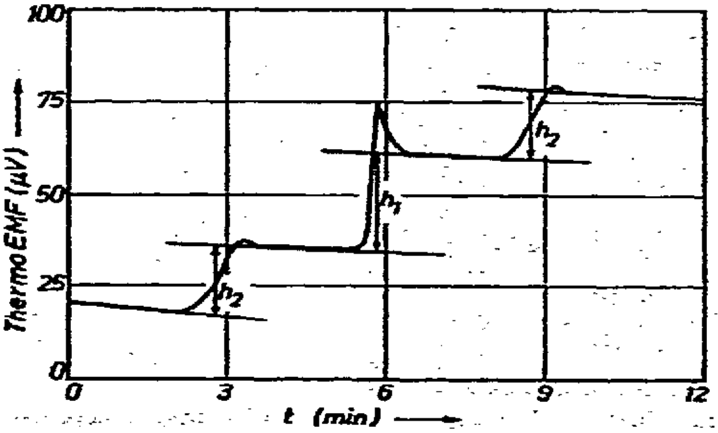


Fig. 16. A graphical representation of a measurement on the Pb–Bi system at 417 °C ($N_{Pb} = 0.701$, $m = 0.084$, $(i \cdot U \cdot t_0) = 55.9$ J g-at.$^{-1}$ (ref. 22)).

nents (1) in the mixing device (2). Calibration is carried out by introduction of electrical energy into the winding (5) of the calorimeter block. With the help of the differential thermocouples (8) and connected controls, an exact maintenance of the adiabatic conditions is assured through rapid regulation of the oven current. The temperature of the calorimeter block is registered as a function of time with the thermocouple (7). As an example, the temperature of the calorimeter block as a function of time is reproduced schematically in Fig. 16 for the case of a calibration, a following mixing reaction and an additional calibration.

TWIN CALORIMETER FOR THE DETERMINATION OF MIXING ENTHALPIES

Kleppa[23] has constructed a twin calorimeter for investigations up to 770 K. It is based on the construction principle which was developed by Calvet[24]. The apparatus is shown in Fig. 17. Both calorimeter cells (1) are placed in a massive aluminum block

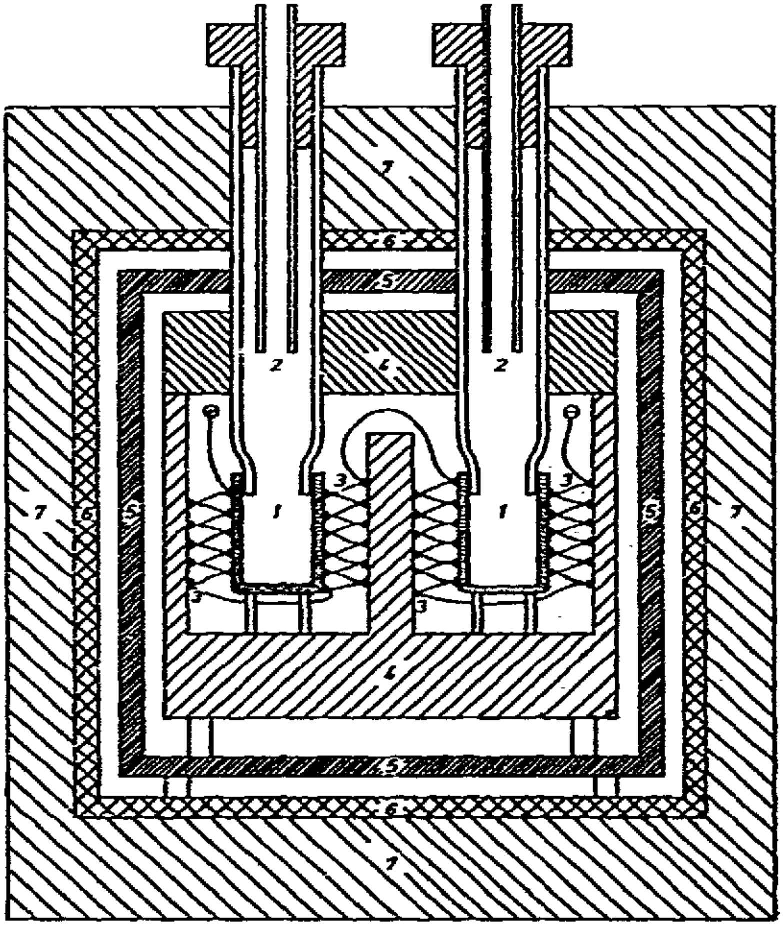


Fig. 17. Twin calorimeter for the determination of mixing enthalpies[23]. 1 = Sample crucibles; 2 = manipulation tubes; 3 = thermopile; 4 = calorimeter block; 5 = inner shield; 6 = heating element; 7 = thermal insulation.

(4). The thermopiles (3) measure the temperature difference between cell and aluminum block and are connected with each other. In one of the cells, the substance to be investigated is present. The other contains a blank sample which shows no reaction. The principle corresponds to that of differential thermoanalysis. In the previously described method, the massive metal block acts as comparison sample and calorimeter mantle simultaneously.

In the calorimeter of Kleppa, the total heat capacity was kept small in order to make a rapid temperature regulation possible. Thus, a high sensitivity was obtained simultaneously. The experimental arrangement operates as a heat flux calorimeter. The differential thermo-electric voltage of both thermopiles is registered as a function of time. This results in curves similar to those shown in Fig. 13. Calibration is carried out by the Joule heating produced by an electric heater introduced into the substance to be investigated or by addition of an inert substance of known heat content.

MEASUREMENT OF SOLUTION ENTHALPIES AND PRECIPITATION ENTHALPIES

The liquid alloy resulting from the mixing of liquid components can also be obtained if one of the initial components is solid and is dissolved in the other (liquid) component. The corresponding enthalpy change for the formation of the liquid solution in the second case is different from that in the first case. The difference is given by the melting enthalpy of the added solid component at the calorimeter temperature.

$$\Delta H = \Delta H_{\text{sol}} - \Delta H^{\text{f}} \tag{15}$$

ΔH = the mixing enthalpy; ΔH_{sol} = the solution enthalpy; ΔH^{f} = melting enthalpy of the solid component.

In addition to the determination of the mixing enthalpies of liquid alloys with one high-melting component and one low-melting component, which are often carried out below the melting temperature of the higher-melting component, the measurement of solution enthalpies can be used for the determination of formation enthalpies of solid alloys. For this purpose, a suitable liquid metal is introduced in the calorimeter and the solid alloy to be investigated dissolved in it. In a second experiment under similar conditions, the unalloyed mixture of the components of the solid alloy is dissolved in the metal bath. The difference of these solution enthalpies yields the formation enthalpy of the solid alloy directly.

In many cases, liquid tin is especially suitable as the solution substance. It has a low melting point, is not very sensitive to traces of oxygen, has a relatively low vapor pressure below 1300 K and is able to dissolve many metals. Liquid zinc, aluminum or copper have been used less frequently as bath substances. Liquid uranium has been used successfully for the determination of the solution enthalpies of iron, chromium, vanadium and nickel[25].

Calorimetric methods for the determination of solution enthalpies basically do not differ from those for the determination of mixing enthalpies. With these methods, the thermal effects, which are caused by precipitation reactions in liquid phases, can also be measured. The method of precipitation calorimetry was, for example, applied very successfully by Martosudirdjo and Pratt[26] for the determination of the formation enthalpies of semiconducting intermetallic compounds. While the formation enthalpies of III–V compounds, such as InSb or GaSb can be easily determined by solution calorimetry with liquid tin as the solution medium[27], this is not possible for compounds such as GaAs or AlSb since these have a very small solubility in liquid tin at the usual calorimeter operation temperatures. The condition of limited solubility can be used as the basis for the operation of precipitation calorimeters. First, one of the components (A, in general the VB element) is dissolved in liquid tin. By addition of the second component (B, in general the IIIB element), a solid compound AB is precipitated. The formation enthalpy is obtained from the thermal effect considering the initial and final states of the total reaction.

CALORIMETER FOR THE DIRECT DETERMINATION OF FORMATION ENTHALPIES OF SOLID ALLOYS

The determination of formation enthalpies by solution calorimetry or precipitation calorimetry represent indirect processes which are not applicable in all interesting cases. For example, this method cannot be applied for a compound of very high-melting point components when the compound as well as its components are not sufficiently soluble in the normal metallic solvents. A direct determination of the formation enthalpy is often possible, if the solid components react in the calorimeter adequately rapidly to form the desired compound. The reaction rate is essentially determined by the diffusion velocity. To minimize the diffusion paths, one logically starts from compacts of the mixture of the finely-powdered components. They are brought to a sufficiently high temperature in the calorimeter to initiate and maintain the reaction. A suitable calorimeter for this purpose was developed by Kubaschewski et al.[28]. The principle is shown in Fig. 18. The sample (1) is contained in a thin-walled steel container which has a heating coil (2) around it. This container is surrounded by an inner shell (2a). At further distances this apparatus is enclosed in a reference shell (5). Between the inner and the reference shells is placed a thermocouple hot junction (4). The total apparatus is surrounded by a main heater (6), by radiation shields (7) and an outer case (8). The sample—a cylindrical powder compact of 1 cm height—is heated in the calorimeter to the highest temperature at which the reaction of the components is still negligeably small. A degassing of the sample in the evacuated calorimeter results. Next, the sample is quickly heated to a temperature at which the reaction is finished within two hours. During the reaction period the thermal electric power of the differential thermocouple (3) between the inner shell and the reference shell is recorded as a function of the temperature. For the totally reacted sample, a thermal program equal to the above is carried out. The difference between the two recorded curves corresponds to the reaction enthalpy for the first experiment. Calibration results from Joule heating which is carried out with the help of the heater for the

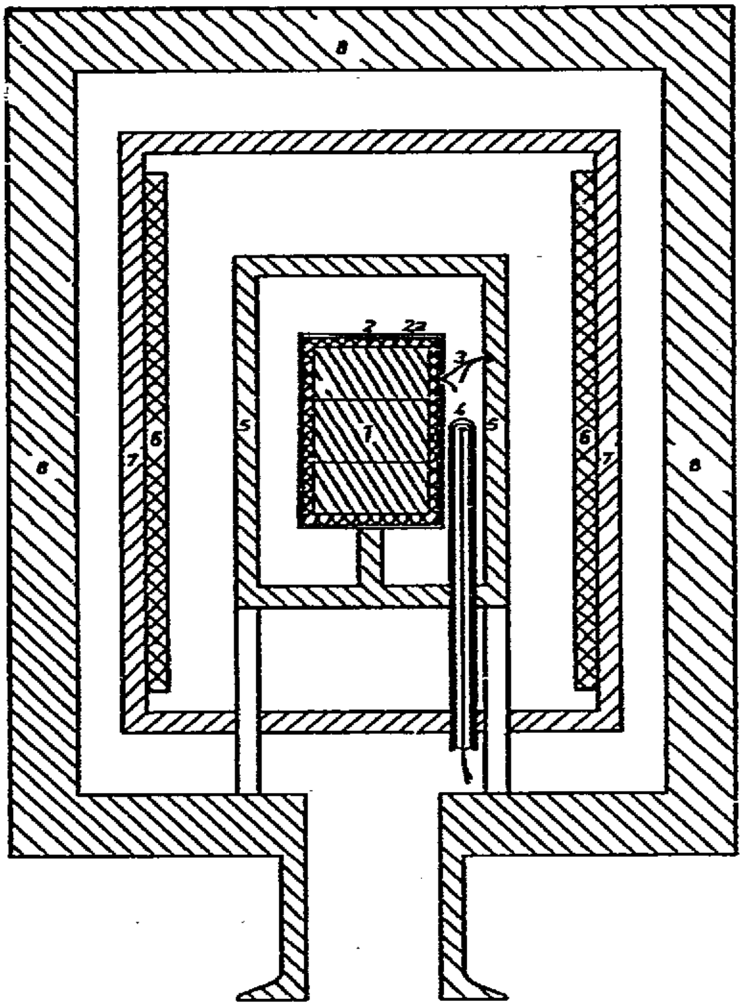


Fig. 18. Adiabatic high temperature calorimeter for the determination of formation enthalpies of solid alloys[28]. 1 = Compacted powder sample; 2 = sample holder with heater and inner shell; 3 = differential thermocouple; 4 = thermocouple; 5 = reference shell; 6 = main heater; 7 = multiple radiation shields; 8 = outer case (water-cooled).

sample. As an example a temperature of 710 K is suitable for the outgassing of Ni–Cu powder compacts with 50 at. % Cu. The alloy reaction occurs at 995 K. The total error in the determination of the formation enthalpy was given as ± 18%.

Robins and Jenkins[29] use for the determination of formation enthalpies of intermetallic compounds, the fact that it is only necessary for compounds with strong exothermic reaction enthalpies, to start the reaction of the components. The formation enthalpy developed is so negatively large that it assures completion of the reaction. For example, the formation enthalpies of some silicides of the transition metals were determined in this way. In this case, the samples are made from a mixture of the powdered components which is pressed into a compact. As is evident from Fig. 19, this cylindrical compact (1) is placed in a suitable container (7) and a tablet of chro-

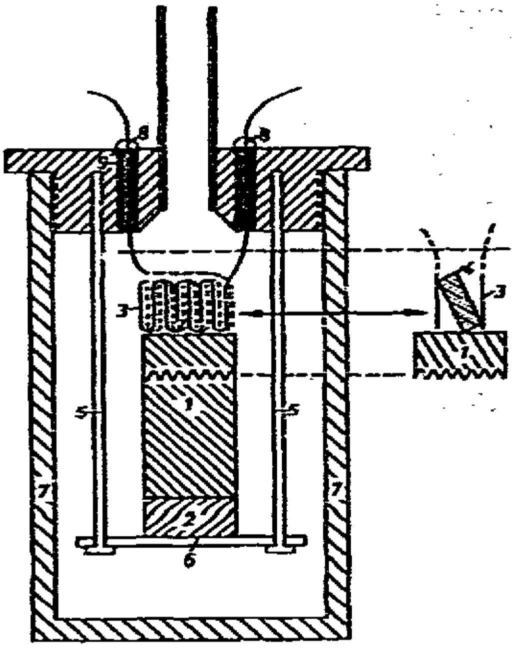


Fig. 19. Core of the calorimeter to determine formation enthalpies of intermetallic compounds[29]. 1 = Metal–silicon mixture; 2 = metal silicide; 3 = molybdenum heating element; 4 = thermite pellet; 5 = support rods; 6 = support plate for sample; 7 = outer case; 8 = wax insulation; 9 = refractory tube.

mium oxide and aluminum powder (4) (thermite mixture) placed above it between the windings of a molybdenum heater (3). The thermite tablet is ignited with the heater. The reaction heat melts the molybdenum heater and interrupts the heating current. Simultaneously, the strong local heating initiates the reaction of silicon with the metal. The complete apparatus is in a water calorimeter at room temperature. The Joule heating introduced and the heat resulting from the thermite tablet can be measured in a blank experiment and be taken into consideration in the corresponding calculation. For example, the formation enthalpies of the silicides of titanium and vanadium have been determined in this way. They have values ranging from -120 to -600 kJ mol^{-1}. This method is only useful when a highly exothermic reaction occurs.

DETERMINATION OF SPECIFIC HEATS

As already mentioned, specific heats can be determined from the slope of the heat content curves. The experimental procedures are discontinuous methods in most cases, where a sample at high temperature is dropped into a calorimeter at room temperature. For many alloys, however, the above procedure does not guarantee that the quenched sample is in the equilibrium state. Thus, this method is not always suitable to produce reliable values of heat contents and specific heats for alloys which undergo order–disorder transformations or where precipitation reactions are possible.

Several calorimeter types have been developed which make possible a direct determination of the specific heats at high temperatures. They are adiabatic high-temperature calorimeters. For example, the spherical adiabatic high-temperature calorimeter for the determination of transformation enthalpies of Sale and Normanton[13] as well as the previously discussed calorimeter of Kubaschewski et al.[28] for direct determination of the formation enthalpies of solid alloys are suitable for the determination of specific heats at high temperature.

FURTHER APPLICATIONS OF CALORIMETRY IN METALLURGY

Not all possibilities for the use of calorimetry in metallurgy and for optimal calorimeter construction have been treated here. It should be mentioned that, for example, the progress of precipitation reactions in solid solutions can be followed calorimetrically. Further applications are investigations for the determination of the stored energy of deformed metals and the determination of grain boundary energies. In these cases, very sensitive high-temperature calorimeters are necessary.

Modern electronic possibilities, development of new high-temperature materials and the general technological progress lead to new calorimeter constructions and further application possibilities for calorimetry in metallurgy. For instance, preparations are being made to perform calorimetric experiments on reactive metals, such as elements of the IVB or VB groups of the periodic system, in a gravity-free state during space flight, to avoid reactions with the container material. The expense of such an experiment using satellites is justified, since the knowledge of the thermodynamic properties of alloys of these elements is necessary for the development of new high-temperature technology. However, also for the high-temperature calorimeters on earth, there are still many metallurgical problems which wait for a solution.

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REFERENCES

1a K. L. Komarek, *Z. Metallkd.*, 64 (1973) 325.
1b J. S. L. Leach, in R. A. Rapp (Ed.), *Techniques of Metals Research*, Vol. IV, *Physicochemical Measurements in Metals Research*, Part 1, *Calorimetry*, Interscience, New York, 1970.
2 W. A. Roth and P. Becker, *Kalorimetrische Methoden*, Vieweg, Braunschweig, 1956.
3 M. Laffitte, in O. Kubaschewski (Ed.), *Metallurgical Chemistry Symposium, 1971*, National Physical Laboratory, Her Majesty's Stationery Office, London, 1972.
4 O. Kubaschewski, *Z. Elektrochem.*, 54 (1950) 275.
5 K. Hüttner and G. Tammann, *Z. Anorg. Chem.*, 43 (1905) 215.
6 G. D. Roos, *Z. Anorg. Chem.*, 94 (1916) 329.
7 W. Oelsen, O. Oelsen and D. Thiel, *Z. Metallkd.*, 46 (1955) 555.
8 T. Heumann and B. Predel, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.*, 63 (1959) 988.
9 T. Heumann and B. Predel, *Z. Metallkd.*, 51 (1960) 509.
10 F. E. Wittig, *Z. Metallkd.*, 43 (1952) 158.

11 B. Predel and R. Mohs, *Arch. Eisenhüttenwes.*, 41 (1970) 61.
12 B. Predel, *Z. Metallkd.*, 55 (1964) 117.
13 F. R. Sale and A. S. Normanton, in O. Kubaschewski (Ed.), *Metallurgical Chemistry Symposium, 1971*, National Physical Laboratory, Her Majesty's Stationery Office, London, 1972.
14 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, *Selected Values of the Thermodynamic Properties of the Elements*, Amer. Soc. Metals, Metals Park, Ohio, 1973.
15 B. Predel and D. Rothacker, *Thermochim. Acta*, 2 (1971) 25.
16 L. Leibowitz, M. G. Chasanov and L. W. Mishler, *Trans. Met. Soc. AIME*, 245 (1969) 981.
17 W. Oelsen, K. H. Rieskamp and O. Oelsen, *Arch. Eisenhüttenwes.*, 26 (1955) 253.
18 B. Predel and D. W. Stein, *J. Less-Common Met.*, 17 (1969) 377.
19 B. Predel and D. W. Stein, *Z. Metallkd.*, 61 (1970) 909.
20 B. Predel and F. Sommer, *Phys. Cond. Matter*, 17 (1974) 249.
21 B. Predel and G. Oehme, *Z. Metallkd.*, 67 (1976) 826.
22 K. Itagaki and A. Yazawa, *Trans. J. Inst. Met.*, 10 (1969) 259.
23 O. J. Kleppa, *J. Phys. Chem.*, 64 (1960) 1937.
24 E. Calvet and H. Prat, *Microcalorimetrie*, Masson, Paris, 1956.
25 D. L. Vieth, *Ph. D. Dissertation*, University of Cincinnati, 1972.
26 S. Martosudirdjo and J. N. Pratt, *Thermochim. Acta*, 10 (1974) 23.
27 W. F. Schottky and M. B. Bever, *Acta Met.*, 6 (1958) 320.
28 O. Kubaschewski, W. A. Dench and V. Genta, *The Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, in O. Kubaschewski (Ed.), National Physical Laboratory Symposium No. 9, Ed. O. Kubaschewski, Her Majesty's Stationery Office, London, 1959.
29 D. A. Robins and J. Jenkins, *Acta Met.*, 3 (1955) 598.
30 F. H. Haessner, W. Hemminger and W. L. Lukas, AIAA/ASME, 1974, *Thermophysics and Heat Transfer Conference, Boston, Mass., U.S.A.*, 1974.