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Thermodynamic investigations of ternary liquid alloys

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Abstract

A review of different methods for determining thermodynamic quantities is given. The electromotive force (EMF) method with a liquid and solid electrolyte, the calorimetric and differential scanning calorimetry (DSC) methods, and vapour pressure experiments like the isopiestic and Knudsen effusion methods are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Knowledge of the thermodynamic properties of alloy systems is crucial for all metallurgical processes. The possibility of a reaction, the stability of phases, the reaction path, and many more physical properties depend on it. It is also necessary for all types of calculations, like phase diagram calculations, wetting behaviour and surface tension.

Many alloys in use today consist of several deliberately alloyed constituents to achieve the desired mechanical and physical properties. A reliable thermodynamic description of all the phases forming in the complex systems concerned must be available to allow a full account to be taken of reactions such as those associated with segregation during casting, with the formation of precipitated phases in a multicomponent alloy during heat treatment processes, or in vapour deposition of complex coatings on an alloy substrate as examples.

The aim of thermodynamic investigations is the determination of the partial and integral quantities of metallic systems depending on concentration, temperature and pressure. Various methods are available and can be chosen, depending on the system and on the properties that are to be determined.

Using the thermodynamic properties of binary and ternary systems, the properties of higher-order systems can be calculated. Various extrapolation and calculation models are available and are widely used [1–4].

For a complete thermodynamic description of an inorganic reaction, we need a knowledge of the equilibrium constant K or free energy ΔG of the reaction, the enthalpy ΔH of the reaction, the enthalpy of formation $\Delta_f H$ (298 K) at 298 K, the

standard entropy S_0 (298 K), the molar heat capacity $c_p(T)$, and the enthalpies of transformation $\Delta_{tr} H(T_{tr})$.

For the determination of $\Delta_f H$, $\Delta_{tr} H$ and c_p , S_0 calorimetry can be used. With vapour pressure and EMF (electromotive force) measurements, $p_i(T)$, $a_i(T)$, K and ΔG can be determined. The measurement of the EMF of a suitable galvanic cell is one of the most accurate methods for obtaining thermodynamic data of alloys.

None of the methods used for the investigation yields a complete description of the thermodynamic properties of a system but, by combining various methods, a complete set of thermodynamic data can be obtained.

2. EMF measurements

For the measurement of the EMF, two different kinds of electrolytes can be used. The partial Gibbs energy and therefore the activity of the most electropositive component can be calculated directly from the measured EMF (equation (1)):

$$\overline{\Delta G}_A = -nFE = RT \ln a_A. \quad (1)$$

$\overline{\Delta G}_A$ is the partial Gibbs energy of the less electro-negative element A, n is the number of exchanged electrons, F is the Faraday constant ($96\,486 \text{ C mol}^{-1}$), R is the gas constant ($8.314\,34 \text{ J mol}^{-1} \text{ grad}^{-1}$), T is the temperature in kelvin, and a_A is the thermodynamic activity of the component A.

The partial entropy is obtained from the slope of the EMF versus T curve and the partial enthalpy is obtained from the intersection of the EMF versus T curve with the Y axis. As

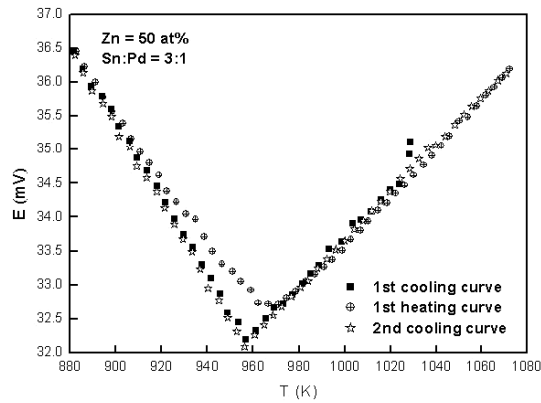


Figure 1. EMF versus T curve of the ternary Sn–Pd–Zn system at the cross section Sn:Pd = 3:1 with 50 at.% Zn.

an example, the EMF versus T curve of the ternary Sn–Pd–Zn system at the cross section Sn:Pd = 3:1, at 50 at.% Zn, is shown in figure 1. The values obtained from the first heating cycle differ from the values from the first and second cooling curves. From the kink of the EMF versus T curve, the melting temperature of the investigated alloy can be determined.

The integral quantities are calculated using the Gibbs Duhem equation given by Elliot and Chipman [5].

2.1. Liquid electrolyte

The most often used liquid electrolyte is the eutectic mixture of LiCl/KCl with a small amount of the chloride of the less electro-negative element, to suppress the solubility of the metal in the electrolyte. This electrolyte shows good thermal stability, and has a low vapour pressure at high temperatures.

Advantages. It can be used at rather low temperatures (the melting point is 359 °C). It covers the alloys, which hinders the evaporation of volatile components. No cracks occur (which can falsify the measurements). Equilibrium is reached much more quickly than with a solid electrolyte, where diffusion processes have to be taken into account.

Disadvantages. The electrolyte has to be prepared carefully and is time consuming, and it can be used only for one experiment. At higher temperatures, electronic conductivity can occur. The reactions of the electrode wire and the container with the electrolyte have to be taken into account.

2.2. Preparation of the electrolyte

A large quartz apparatus is evacuated and purged with argon. The salt is melted in a furnace and argon is passed through the melt. Afterwards, chlorine gas is flown through the liquid electrolyte to remove all traces of water, hydroxide ions and oxygen ions. To get rid of the remaining chlorine, argon gas is again passed through the molten salt mixture for some hours. Finally, the salt is filtered through a glass frit into an ampoule and sealed. Shortly before the measurement, the ampoule is opened and transferred into the measuring cell. A schematic representation of the EMF cell is shown in figure 2 and an extensive overview has been given by Karlhuber [6].

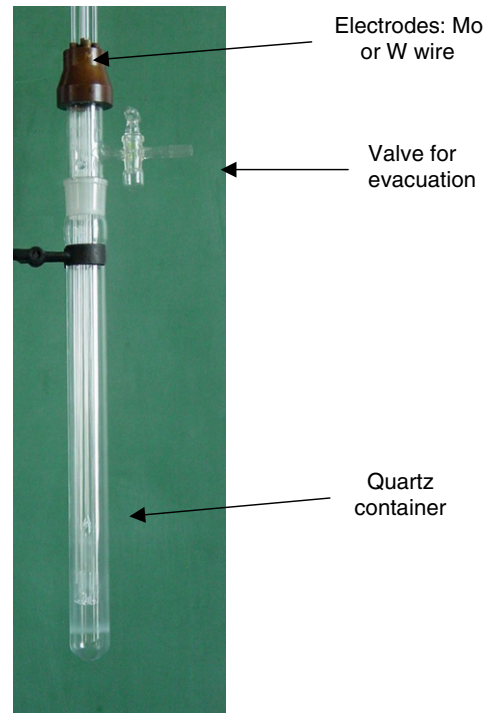


Figure 2. Picture of the EMF apparatus.

As electrode Mo or W wire is used, depending on the system being measured.

2.3. Measurements

The apparatus has to be gas tight, which is controlled before each measurement. Afterwards, the samples of the pure metal and the metal alloys will be put into the sample holder (approximately 2 g for each measurement). The electrolyte is transferred very quickly into the tube and flushed several times with argon. During the measurements the argon pressure in the cell is around 1.0 atm.

The measurement starts at a temperature higher than the melting temperature of the electrolyte. After the melting of the electrolyte the sample holder is lowered and the measurement is started. Two cooling and two heating cycles are recorded during one measurement, with both cooling and heating rates of 10 K h⁻¹.

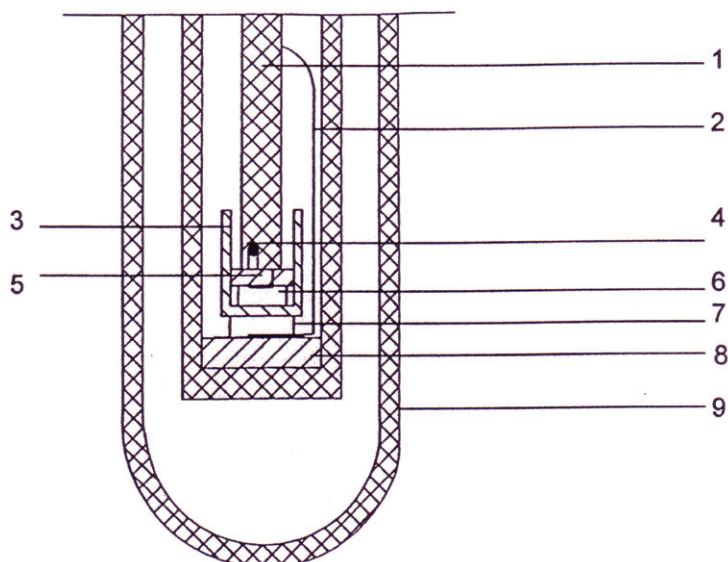
As a pure electrode the less electronegative element is used and three alloys can be measured in each experiment. The EMF values are registered every 5 min using a connected PC.

The thermodynamic properties of several ternary alloys have been investigated by the authors [7–11].

Other possible electrolytes are an equimolar mixture of NaCl–AlCl₃ [12], NaCl + 3 wt% CuCl [13] and, respectively, MgCl₂ and MgCl₂ (20–80 mol%) with CaCl₂ [14].

2.4. Solid electrolyte

Because of the improvement in the performance of solid electrolytes, the use of solid electrolytes has increased. The basic requirements of these electrolytes are thermal stability



1. Spring loaded Al_2O_3 tube with four holes
2. Pt-wire to lower electrode
3. Electrolyte crucible
4. Thermocouple
5. Boron nitride disk
6. Upper electrode
7. Lower electrode
8. Al_2O_3 disk
9. Outer Al_2O_3 tube

Figure 3. Cell arrangement of an EMF measurement with solid electrolyte.

and ionic conduction. A conductivity of less than $10^{-6} \Omega$ is necessary to establish a stable EMF.

Advantages. These electrolytes are stable at higher temperatures and are commercially available. The measurements can be performed with solid and liquid samples. In the case of liquid samples, tubes must be used.

Disadvantages. Microcracks can occur and the material shows poor shock resistance. The oxygen partial pressure has to be known. Because of the poor ionic conduction, measurements can only be carried out at temperatures higher than 873 K. Due to this high temperature, it is not possible to determine the thermodynamic properties of volatile components.

For our measurements we used ZrO_2 , which shows a fluorite structure at T higher than 2573 K, but can be stabilized with the addition of 10–15 mol% MgO, CaO or Y_2O_3 at room temperature. Doping with other oxides produces vacancies in the oxygen lattice which are responsible for the ionic conductivity of this material. The cell arrangement is presented in figure 3. Figure 4 shows the EMF versus T curve of the In–Ag–Pd system at the composition 50.4 at.% In, 5.6 at.% Ag, and 44.0 at.% Pd [15].

Other solid electrolytes are fluoride electrolytes like CaF_2 [16], proton-conducting ceramics [17] like SrCeO_3 , and β' alumina ($\text{NaAl}_{11}\text{O}_{17}$) and β'' alumina (NaAl_5O_8) [18].

An extensive summary of thermodynamic investigations with different solid electrolytes has been given by Pratt [19].

3. Thermal analysis

The idea of thermal analysis means a group of methods where a physical property of a substance is measured as a function of temperature and time, respectively, while a regular temperature programme is running.

The term thermal analysis also includes the isothermal and quasi-isothermal performance, and in many cases the change of properties at a constant temperature is investigated.

3.1. Calorimetry

Calorimetric measurements mean the determination of heat quantities which are absorbed or emitted by physical bodies under constant conditions like pressure, volume, magnetic strength or composition if their temperature or physical or chemical state is changed.

Calorimeters can be divided into three different types:

- (1) Isothermal calorimeter— $T_C = T_S = \text{const}$; Q changes.
- (2) Adiabatic calorimeter— $T_C = T_S$ but not constant; T_C and T_S change with temperature.
- (3) Isoperibol calorimeter— $T_S = \text{const}$; T_C changes with temperature.

T_S is the temperature in the reaction chamber, T_C is the temperature of the calorimeter, and Q is the total produced heat.

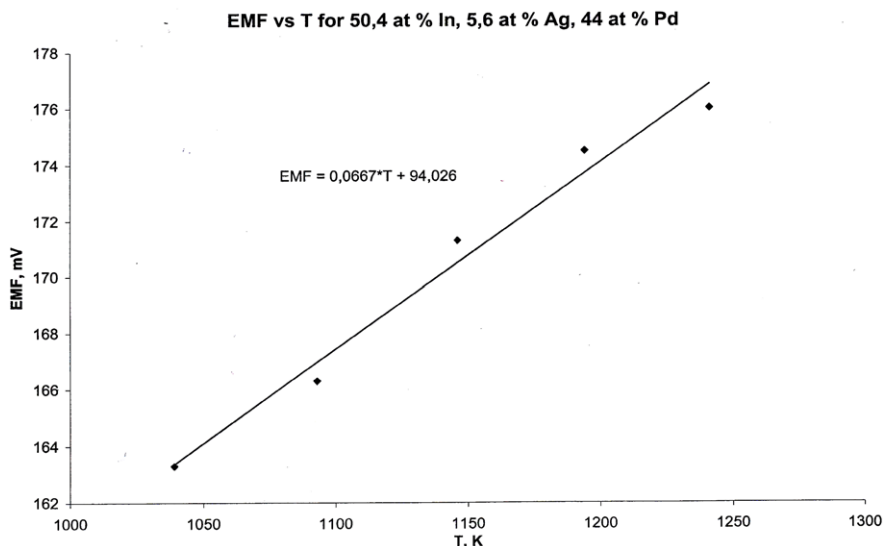


Figure 4. EMF versus T curve of the ternary In–Ag–Pd system at 50.4 at.% In, 5.6 at.% Ag, and 44.0 at.% Pd.

An extensive review of different calorimeters has been given by Komarek [20]. For our investigations, a Calvet-type microcalorimeter—an isoperibol calorimeter (Fa SETARAM; Lyon, France)—is used. The surroundings of the furnace were adapted to our requirements [21]. The measurements are performed with a direct drop method with an automatic sample drop device under Ar flow. The calorimeter is a twin calorimeter with two separate calorimeter cells, surrounded by thermopiles (TPs) with more than 200 pairs of thermocouples each. Each TP is mounted as a ring formed by two concentric cylinders measuring the temperature difference between the inner and outer surfaces. In this way, the EMF of a TP gives direct information on the heat flow absorbed or produced in the calorimeter cell.

The calorimeter cells are located in a large calorimeter block made of alumina and kanthal, which is surrounded by thermally isolating bricks and the electric resistance heating. The cells are connected in opposition, and variations in the temperature differences down to 10^{-5} K can be detected. The oscillations of the furnace are compensated. One cell is usually permanently loaded with a block of about 25 g alumina and serves as the reference cell. The alumina block provides similar heat capacity and thermal conductivity for the two cells in order to avoid secondary effects of the calorimeter signal. The furnace further contains two single thermocouples. One measures the sample temperature and the other is used to control the furnace temperature together with a Eurotherm 818 Controller.

All thermocouples are of type S (Pt/Pt–10 wt% Rh). The furnace can be operated from ambient temperature up to 1100 °C. The measuring cell is charged with a quartz tube which contains the sample crucible. This quartz tube is connected to the automatic sample introducing unit. The entire system is gas tight and can be evacuated and flushed with a protective gas. Our measurements are performed under a continuous argon flow ($30 \text{ cm}^3 \text{ min}^{-1}$). The signals that are obtained are recorded and automatically integrated.

The calorimeter is described in more detail in [21]. After each series of drops the calorimeter is calibrated by adding five pieces of $\alpha\text{-Al}_2\text{O}_3$ standard of NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA). The temperature in the drop device (DT) and the furnace temperature (FT) are measured before each drop.

The measured enthalpy is given by

$$H_{\text{Signal}} = n_i \cdot (H_{\text{Sample,FT}} - H_{\text{Sample,DT}}) + H_{\text{Reaction}} \quad (2)$$

where n_i is the amount of the added sample. The relative enthalpy, $H_{\text{Sample,FT}} - H_{\text{Sample,DT}}$, is calculated using the polynomials from Dinsdale [22] for the thermodynamic data of pure elements. The approximate partial enthalpies of each component of a system can be determined directly from

$$\overline{\Delta H}_i = \left(\frac{H_{\text{Signal}}}{n_i} \right) - (H_{\text{Sample,FT}} - H_{\text{Sample,DT}}) \quad (3)$$

The integral enthalpy of mixing is calculated from

$$\Delta H_{\text{MIX}} = H_{\text{bin}} + \frac{\sum H_{\text{Reaction}}}{(n + \sum ni)} \quad (4)$$

where n is the molar amount and H_{bin} is the integral enthalpy of the metals that can be used in the crucible.

The time interval between the drops can be chosen individually for each measurement. The Calvet calorimeter shows high sensitivity and a stable base line, but only slow heating and cooling is possible and thermal equilibrium is reached only slowly. A graph for the Calvet calorimeter is shown in figure 5.

Figure 6 shows the integral enthalpies of mixing of liquid Bi–In–Zn alloys at 773 K. This system is very interesting, because there is a miscibility gap in the binary Bi–Zn system, which extends into the ternary system. The limits of this miscibility gap were determined at 773 K. Measurements were carried out at nine different cross sections, namely at Bi:In = 2:1, 1:1, and 1:2, Bi:Zn = 2:1, 1:1, and 1:2, and In:Zn = 2:1,

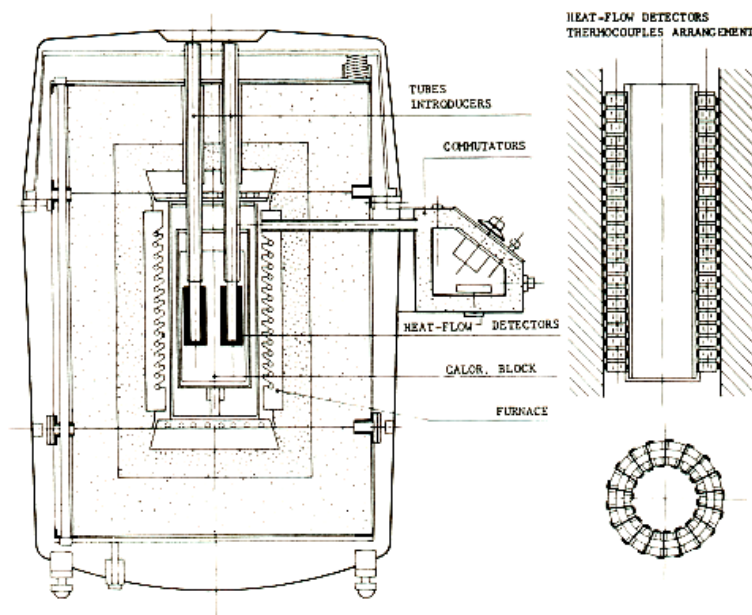


Figure 5. Schematic presentation of a Calvet-type calorimeter.

1:1, and 1:2. In each case the third component was added in the concentration range between 0 and approximately 55 at.%. From the kinks in the curves, the limits of the miscibility gap were determined [23].

3.2. DSC (differential scanning calorimetry)

DSC is a dynamic method, i.e. the measurement is performed at a constant heating rate. The heat flow between the sample and an inert reference is determined from the ΔT between the sample and the reference.

The device used for our measurements is a heat flow DSC. The difference in the energy supply, in this case the electrical power, between a substance and a reference is measured. Heat is flowing from the furnace to the sample and to the reference crucible. If reactions in the sample occur which either absorb or release heat, then equilibrium is disturbed and the sample temperature rises or drops to greater than or less than the temperature of the reference. The change in the temperature difference between the sample and the furnace can be seen as the heat flow for the reaction. A scheme of the apparatus can be seen in figure 7.

It is possible to determine three different quantities with the DSC method:

- (1) The reaction temperatures (DTA mode) from an evaluation of the onset, kink, and peak temperatures.
- (2) The heat of reaction from the peak area integration.
- (3) The heat capacities using the following approach—three different measurements have to be carried out for one experiment: (1) the baseline with two empty crucibles (2) the sapphire (NIST standard α -Al₂O₃, Gaithersburg, MD, USA) versus the empty crucible, and (3) the sample

versus the empty crucible. Using equation (5), the c_p value was evaluated:

$$c_p^{\text{Sample}} = \frac{m^{\text{Sapphire}} \cdot c_p^{\text{Sapphire}}}{m^{\text{Sample}}} \times \frac{\text{DSC}^{\text{Sample}}(T) - \text{DSC}^{\text{Baseline}}(T)}{\text{DSC}^{\text{Sapphire}}(T) - \text{DSC}^{\text{Baseline}}(T)} \quad (5)$$

where m represents the masses of the sample and the sapphire, and DSC is the heat flow effect (in micro-volts) caused by the empty crucible for the baseline, sapphire and sample at the respective temperatures T during the measurement. Also, information about phase equilibria can be obtained from the DSC curves.

A thermodynamic characterization of liquid Bi–Ga alloys has been performed by Huber *et al* [24].

4. Vapour pressure methods

It is possible to divide vapour pressure methods into four different groups. (1) Static methods, where the pressure of a closed system at a constant temperature is determined by mechanical gauges or optical absorption. (2) Dynamic methods, i.e. the transpiration method, where a constant flow of inert gas is used as a carrier of the gas species for the measurement. The focus in this paper is on the equilibrium methods (where a condensed sample is equilibrated with the vapour of a volatile component and the pressure is kept constant by an external reservoir) and on the effusion methods (where the vapour effuses through a small hole into a high vacuum chamber).

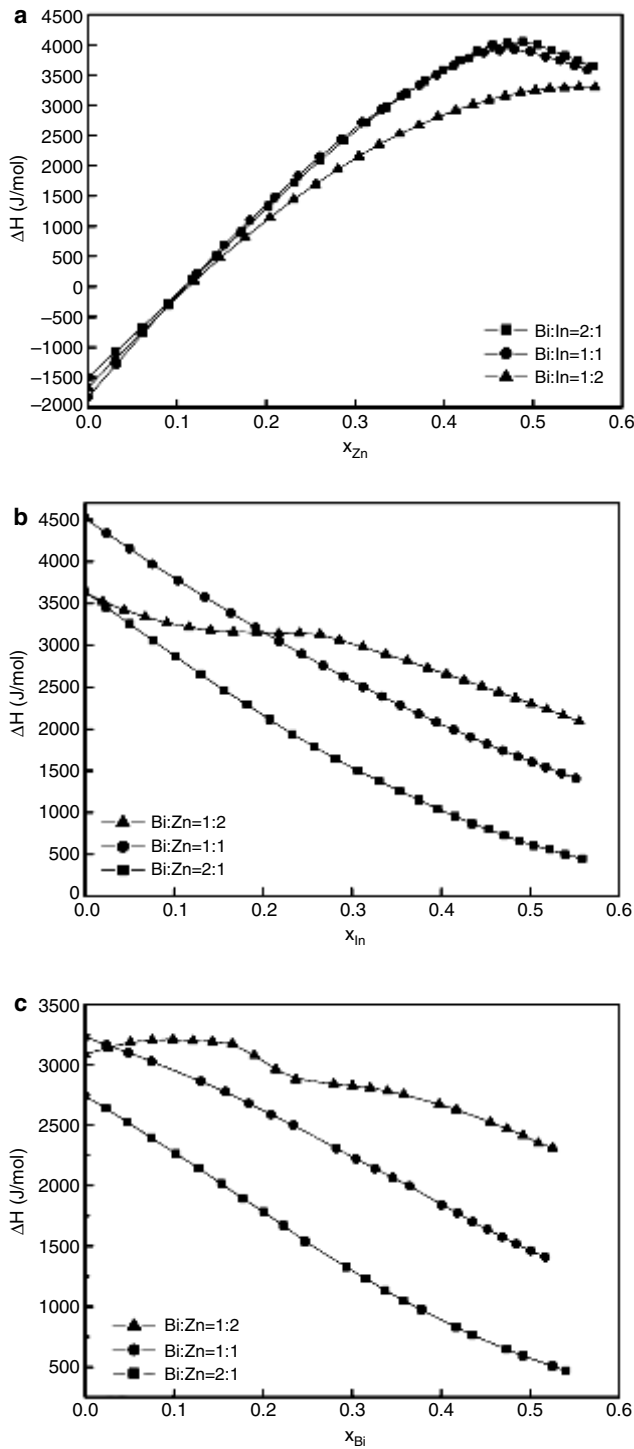


Figure 6. Integral enthalpies of mixing of the liquid Bi–In–Zn alloys at 500 °C: (a) pure zinc drop into molten Bi–In alloys; (b) pure indium drop into molten Bi–Zn alloys; and (c) pure bismuth drop into molten In–Zn alloys.

4.1. Isopiestic method

The isopiestic method is presented as an example of an equilibrium method. Using this method, the vapour pressure, activities and partial thermodynamic quantities can be determined. In a closed system, several non-volatile

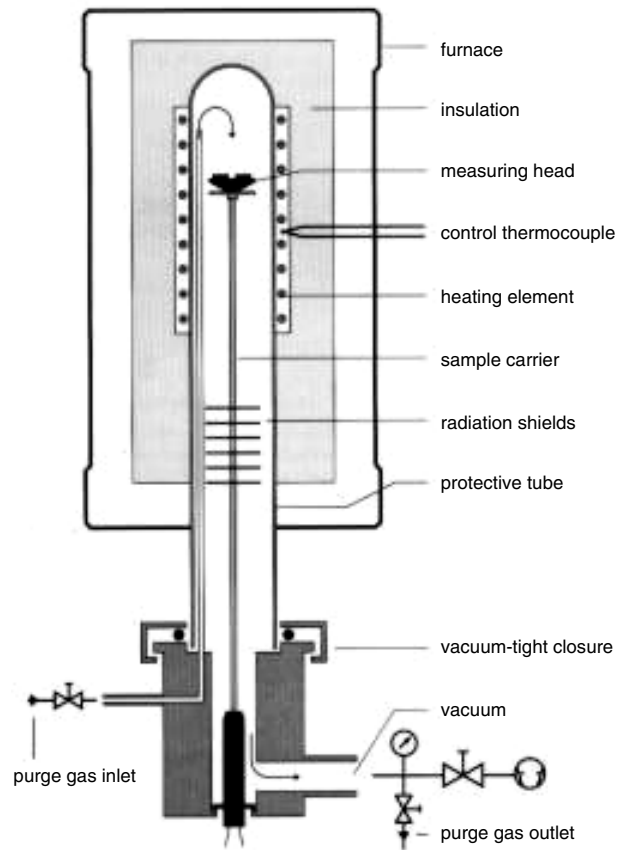


Figure 7. Schematic presentation of a DSC apparatus.

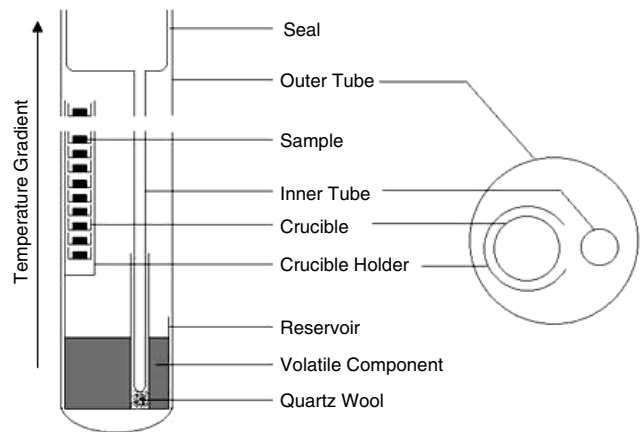


Figure 8. Apparatus for the isopiestic measurement.

components are equilibrated with the vapour of a volatile component in a temperature gradient (figure 8). The vapour pressure of the volatile component has to be three times higher than the vapour pressure of the non-volatile component. To keep the pressure constant, the mean free path of the gas is smaller than the length of the system, which is true except for very small pressures.

After the equilibrium state is reached, the whole system is quenched in water. The activity of the volatile component can be calculated from equation (6), and the Gibbs energy can be

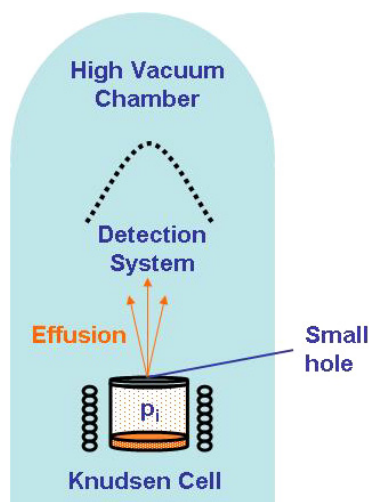


Figure 9. Scheme of the Knudsen measurement.

calculated from the activity values using equation (6):

$$a_i(T_s) = \frac{p_i(T_s)}{p_i^0(T_s)} = \frac{p_i^0(T_R)}{p_i^0(T_s)} \quad (6)$$

where T_s represents the temperature at the sample, T_R is the temperature in the reservoir, and p_i^0 is the pressure of the pure volatile component. The thermodynamic properties of the binary Pt–Zn system have been investigated using the isopiestic method by Chiang *et al* [25].

4.2. Knudsen effusion cell

The term ‘effusion method’ describes measurements that determine the vapour pressure depending on the effusion rate. These methods are indirect. The loss of mass is related to the vapour pressure according to equation (7). These methods are applicable to a vapour pressure of 10^{-4} – 10^{-10} , with certain modifications to 10^{-12} Pa:

$$p = \frac{m}{tAf} \cdot \sqrt{\frac{2\pi RT}{M}} \quad (7)$$

where m is the mass of the vapour, M is the molecular mass of the particles, t is the time of evaporation, A is the area where the vapour leaks out, f is the Clausing factor ($f = (0.98441 + 0.00466(L/R))/(1 + 0.46034(L/R))$, where L is the length of the hole and R is the radius of the hole). A schematic representation of the Knudsen cell is shown in figure 9. A recent investigation of the activity of the ternary Cu–In–Sn

system has been performed by Popovic and Bencze [26]. In many cases, a mass spectrometer is used as a detector.

5. Conclusion

Since more thermodynamic data are needed for metallurgical processes and for different types of calculations, this paper tries to encourage young scientists to start new experiments to measure thermodynamic properties.

Different methods, their advantages and disadvantages are presented, and some results of our own experiments are given. We hope that this paper will help young scientists to decide which experiment is useful to solve their problems and which type of experiment can be carried out successfully in their laboratory.

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