



Overview: The emf method as a source of experimental thermodynamic data

Herbert Ipser^{a,*}, Adolf Mikula^a, Iwao Katayama^b

^a University of Vienna, Department of Inorganic Chemistry / Materials Chemistry, A-1090 Wien, Austria

^b 1-2-31 Ankoji, Takatsuki, Osaka 569-1029, Japan¹

ARTICLE INFO

Article history:

Received 18 January 2010

Received in revised form

4 May 2010

Accepted 4 May 2010

Available online 23 May 2010

Keywords:

Review

Thermodynamics

Electromotive force

Experimental methods

emf measurements

ABSTRACT

The use of galvanic cells to determine the thermodynamic properties of metallic or ceramic materials from electromotive force (emf) measurements is described. Two basic types of the method are distinguished: those employing liquid electrolytes and those based on solid ion-conducting electrolytes. Liquid electrolytes can be aqueous solutions, but for thermodynamic measurements in metallic materials molten salt mixtures with the addition of the corresponding charge-carrying ion are mostly used. Solid electrolytes applied in the thermochemistry of alloys and ceramic materials are usually based on oxides (such as ZrO_2) as oxygen conductors, on β - or β' -alumina as sodium ion conductors (with the possibility to exchange sodium ions by other cations), or on fluorides (such as CaF_2) as fluoride conductors. For all these cases, typical cell arrangements and corresponding examples from the literature are given.

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1. Introduction

In general, there are three groups of experimental methods to determine thermodynamic properties, i.e., calorimetry, vapor pressure measurements, and emf (electromotive force) measurements. Various extensive reviews on these methods have been published in the past [1–6].

Calorimetry is a very convenient method to determine enthalpy values rather precisely, and it is the only method which allows obtaining integral thermodynamic quantities, e.g., enthalpies of formation, enthalpies of mixing, enthalpies of solution, etc., in a direct way. Although it is possible to arrive at integral Gibbs energy values by clever designing of calorimetric experiments (see, for example, Morishita and co-workers [7,8]), it is usually necessary to employ other experimental methods for the determination of Gibbs energies, i.e., the various types of vapor pressure and emf methods. In the vapor pressure methods, one usually tries to measure the partial pressures of individual components and to derive from them the thermodynamic activities and partial Gibbs energies. In the case where partial pressures can also be obtained as a function of temperature, this provides a way to calculate partial enthalpies and entropies, although these derived quantities are usually less accurate than the directly measured partial Gibbs energies. If all these partial quantities can be determined over

a corresponding composition range in binary or higher-order systems, integral thermodynamic properties may be obtained by means of Gibbs–Duhem integrations.

The other large group of methods to determine partial Gibbs energies is based on measuring the electromotive forces (emfs) of suitable galvanic cells, and their application for thermodynamic studies of metallic systems has been recently discussed in detail by Mikula [9,10]. A short description of the basic principles and requirements of emf methods was also given by Moser and Fitzner [11].

2. Principles of the emf method

The amount of work, other than the work for volume expansion, which is necessary in a galvanic cell for the transfer of one mole of a certain element in a valence state z from its pure state into a solution or compound is related to the transfer of a charge $z \cdot F$ by

$$\Delta G = -z \cdot F \cdot E, \quad (1)$$

where E is the electromotive force produced by the cell and F is the Faraday constant (96485 C mol^{-1}). Any meaningful thermodynamic investigation requires that the cell functions in a reversible way, i.e., that no external current is flowing. This is usually assured by the use of high-resistance (larger than $10^{10} \Omega$) measuring devices, resulting in the measurement of an open-circuit potential.

The main problems for a successful cell operation are:

- finding a suitable electrolyte; and
- the exact identification of the single reversible process occurring at each electrode.

* Corresponding author.

E-mail address: herbert.ipser@univie.ac.at (H. Ipser).

¹ Previously: Graduate School of Engineering, Osaka University, Japan.

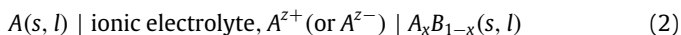
The corresponding electrolyte should provide purely ionic conductivity in the temperature range where it is used, i.e., one single ion should be responsible for establishing the potential. From a practical point of view, there are several additional requirements:

- the equilibrium potential at a given temperature should be established within a reasonable time;
- after temperature changes, the same equilibrium potential has to be established regardless of whether the temperature has been increased or lowered; and
- following polarization of the cell by a potential imposed from outside, again the same equilibrium potential has to be established.

In addition, there are a number of purely experimental requirements that have to be considered, especially in measurements at high temperatures:

- any reactions between electrodes and electrolyte as well as between electrodes and lead wires must be avoided;
- if lead wires of different materials are used it may be necessary to consider the corresponding thermo-emf;
- any temperature gradients in the cell should be avoided;
- reactions between crucible materials and electrodes or electrolyte should be excluded;
- concentration changes due to the vapor pressure of the electrodes must be taken into consideration;
- any direct exchange of matter between the two electrodes (e.g., via the gas phase) has to be excluded; and
- any electrical interference between the furnace in which the cell is heated and the cell itself should be avoided, either by a proper winding of the furnace or by a corresponding grounding.

Under such circumstances the potential E of a given cell



is related to the partial Gibbs energy or the thermodynamic activity, respectively, of A by

$$\Delta \bar{G}_A = -zFE = RT \cdot \ln a_A, \quad (3)$$

where R is the gas constant, T the absolute temperature, and a_A is the thermodynamic activity of A in the alloy $A_x B_{1-x}$. If the emf of the cell can be measured as a function of temperature, the other partial properties of A can be derived:

$$\Delta \bar{S}_A = zF \left(\frac{\partial E}{\partial T} \right) \quad (4)$$

$$\Delta \bar{H}_A = zF \left[T \cdot \left(\frac{\partial E}{\partial T} \right) - E \right]. \quad (5)$$

Two types of electrolyte are used in thermodynamic measurements: liquid electrolytes and solid electrolytes, each with characteristic advantages and disadvantages. In the following sections, the two groups are described in detail, and typical examples as well as new developments will be discussed.

3. Liquid electrolytes

Since diffusion in liquids is generally much faster than in solids, liquid electrolytes have the advantage that the establishment of a stable emf is usually achieved in shorter times than with solid electrolytes. This considerably reduces the necessary equilibration times after changing the temperature and even makes a continuous variation of the temperature possible without loss of reproducibility. This can be easily proved by comparing the experimental values obtained from heating and from cooling cycles.

These liquid electrolytes can be water based, with the ion responsible for establishing the corresponding potential as a solute. However, such aqueous electrolytes are usually only used for determining the thermodynamic properties of various electrolytes and their mixtures in aqueous solutions. In many such cases, special ion-selective electrodes (ISEs) are employed for the emf measurements. As typical examples from recent years, there can be mentioned the thermodynamic studies of $\text{NaCl} + \text{CaCl}_2$ solutions by Galleguillos et al. [12], of $\text{RbCl} + \text{Rb}_2\text{SO}_4 + \text{CH}_3\text{OH}$ solutions by Jun et al. [13], or of $\text{KCl} + \text{K}_2\text{SO}_4$ solutions by Zhang et al. [14]. Solvation potentials of different metal chlorides in 1, 4-dioxane + water mixtures as well as other thermochemical parameters were obtained by emf measurements by Spah et al. [15]. A good review of the possible difficulties and error sources for emf measurements in aqueous solutions is given in the paper by Rard and Clegg [16] who discussed emf experiments to determine the activities of H_2SO_4 in aqueous solutions in a historical context.

There is one exception where aqueous solutions are employed for emf measurements in metallic systems, which is the so-called Touch Instant EMF Method (TIE method) [17]: here the emf is measured immediately ("in an instant") after making contact between electrodes and electrolyte before any polarization effects or displacement reactions can alter the equilibrium potential. Although this method has been highly controversial in the scientific community, it has been used, for example, for the determination of Ni activities in solid Ni–Te alloys by Kutsenok et al. [18] or of Cu activities in solid $\text{Cu}_x\text{Fe}_y\text{S}_{1-x-y}$ by Jalkanen [19]. Most recently, it was applied to determine the difference of Fe and Ni activities in austenitic and martensitic Fe–Ni alloys by Rostovtsev [20].

Nevertheless, it is non-aqueous electrolytes that are more or less exclusively used for emf measurements in metallic or ceramic systems, which has, of course, also to do with the much higher temperature ranges involved. Of these, liquid electrolytes based on polyvalent alcohols, in particular glycerol, have found some limited application and are being employed between room temperature and about 200 °C. Examples are the determination of Tl activities in the ternary systems In–Te–Tl [21] and Br–Se–Tl [22] by Babanly and co-workers, who used Tl^+ in glycerol solutions. An analogous procedure was employed by Gawel et al. to measure Tl activities in the pseudo-binary system $\text{CdTe–Tl}_2\text{Te}$ [23].

The standard liquid electrolytes for measurements at elevated temperatures are based on molten salts in which an ionic compound is dissolved containing the corresponding ion responsible for establishing the emf. The role of possible displacement reactions between electrodes and electrolyte was discussed in detail by Wagner and Werner [24], but it is usually assumed that they are negligible if the component whose partial Gibbs energy is to be measured is much less noble than the other alloying element(s). The lower-temperature limit of molten salt electrolytes is given by the melting temperature, and in many cases this temperature is further reduced by using eutectic mixtures of two (or even three) salts. The upper-temperature limit depends on the vapor pressures of the employed salts as well as on the increasing solubility of the different metals in the liquid salt mixture which may result in a noticeable contribution of electronic conduction. In addition, the contribution of electronic conductivity of the molten salt itself may become appreciable at higher temperatures. This has been studied in detail for eutectic mixtures of LiCl and KCl by Heus and Egan [25], who provided a method to estimate the influence of electronic conductivity depending on temperature and on the particular alloy system to be investigated.

An important aspect is the purification of the electrolyte prior to its use in order to make sure that it does not contain any traces of

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