Potential of Knudsen Effusion Mass Spectrometry (KEMS) for Thermo Chemical Studies in Materials Science

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Abstract

The key for establishing model calculations using ΔG minimization tools like FactSage, Pandat, MTData or Thermocalc is the knowledge of the thermodynamic data of molecules and compounds. This includes the partial pressures of gaseous species, the standard enthalpies and entropies of formation of gaseous and condensed phases as well as their enthalpies and entropies of mixing and the knowledge of phases and chemical compounds which are formed upon reactions.

The experimental determination of valuable thermodynamic data at elevated temperatures is a very important issue in Materials Science. The elucidation of vaporization processes with high temperature mass spectrometry is a possible approach.

Knudsen Effusion Mass Spectrometry enables the identification of gaseous species present above condensed phases and permits the determinability of their partial vapor pressures up to 200 Pa at measuring temperatures of up to 3000 K.

Introduction

For chemical- and materials research the elucidation of vaporization of materials is an important issue. All materials vaporize, if the temperature is sufficiently high. Generally their use is limited by the beginning of their vaporization. On the other hand thermodynamic data of the condensed phase can be obtained from the partial pressures of the evaporating species. The knowledge of the thermodynamic data of chemical substances is important to understand the chemical and thermodynamic behavior of materials like for example the interplay of substances during chemical reactions. The knowledge of the thermodynamic data helps to evaluate the reactions.

High temperature mass spectrometry is the most important method for the analysis of vapors over condensed phases in order to determine thermodynamic data. The first worth mentioning investigation in this field was carried out by [1]. [2] studied the free vaporization from carbon at very high temperatures and evaluated thermodynamic properties. During the years the high temperature mass spectrometric method gained wide acceptance. Many condensed phases were studied and their thermodynamic data have been determined using the possibilities and advantages of the method.

Corrosion, diffusion and vaporization processes which might be neglectable under moderate conditions become the limiting factors of materials which are applied to high temperatures. That is the reason, why the interest in knowledge and determination of thermodynamic properties of materials at high temperatures is recently increasing. The knowledge of the qualitative and quantitative composition of the gaseous phase is necessary for a complete description of the chemical system under those conditions. The technique of KEMS became the most powerful tool in this kind of investigation during the last decades. Review articles concerning the tasks of the method have been written by [3] and [4].

Principle of KEMS

Thermodynamic data result from the measured temperature dependence of the partial pressures of the identified gaseous species. Investigations by Knudsen effusion mass spectrometry generally mean the study of equilibrium reactions involving neutral molecules and/ or atoms.

Figure 1 shows the principle of a magnetic type sector field mass spectrometer with a Knudsen cell assembly. The cell can be heated up to temperatures of above 2500K by resistance heating (to about 1000K) and electron bombardment (for higher temperatures) The temperature is measured with an optical pyrometer or a thermocouple

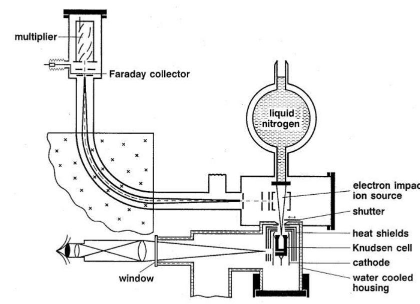

Fig. 1: Schematic representation of the Knudsen Cell Mass Spectrometer

Knudsen cells have an effusion orifice with a typical diameter of 0,1 to 1 mm. This ensures conditions for a molecular flow of the effusing species, so that the equilibrium in the cell is practically not disturbed. The molecular beam crosses the shutter valve and enters the electron impact ion source. Ions are formed by ionization. Fragmentation processes occur due to the electron bombardment in the ion source. The ions are accelerated by an electric field towards the magnet, where they are separated according to their mass to charge ratio. As detector systems a secondary electron multiplier and a Faraday cup are used.

The quantities which are measured in the course of a KEMS investigation are the ion intensities of species which effuse out of a Knudsen cell and the corresponding Knudsen cell temperatures. Partial pressures and thermochemical data are computed from these quantities for the identified vapor species.

Summary

The emphasis of the article lies on the technique and the application of the method of Knudsen effusion mass spectrometry. It covers the fundamentals of this technique as well as recent methodic developments. A detailed description will be given on the measurement of the temperature dependence of the partial pressures and the determination of thermodynamic data from these measurement properties. Examples of recently obtained results using this technique in different fields will be discussed.

References

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