

Determination of lithium activity in Li-Sn system by Knudsen Effusion Mass Spectrometry

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Introduction

Using the method of Knudsen Effusion Mass Spectrometry (KEMS) it is possible to determine thermodynamic activities and chemical potentials of the components of mixtures as well as partial and integral thermodynamic properties of mixing ($\Delta_{\text{mix}}H$, $\Delta_{\text{mix}}G$, $\Delta_{\text{mix}}S$). It is important to evaluate the KEMS set up accurately for Li-systems. This requires a validation by a limited number of experiments in well investigated systems. For this reason measurements within the Li-Sn system have been performed.

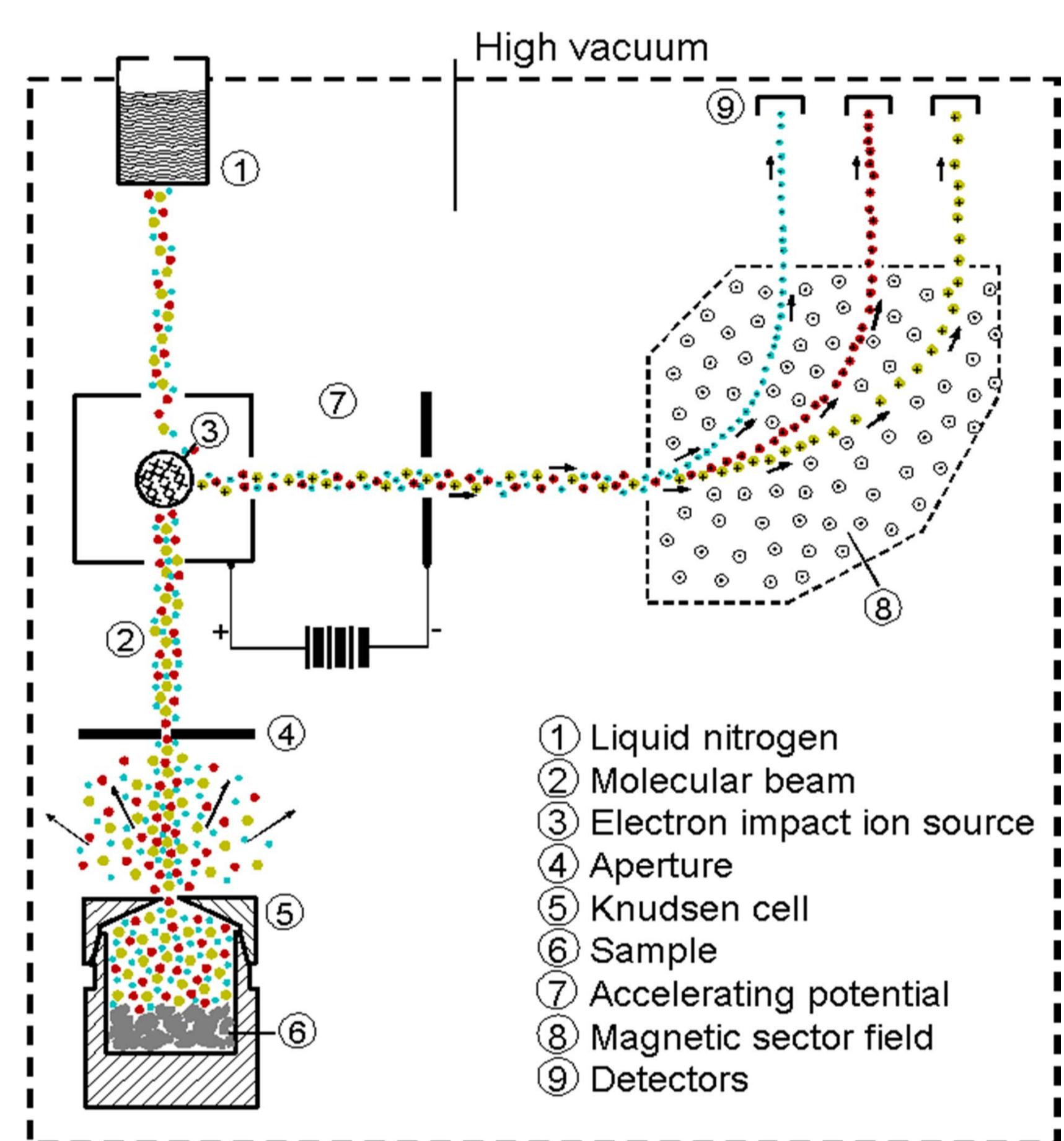


Fig.1: Schematic diagram of the Knudsen cell mass spectrometer system

Method

The method of KEMS allows a qualitative and quantitative analysis of the atoms and molecules present in the gaseous phase. Intensities of ions formed from the gaseous species over the condensed sample were measured by a secondary electron multiplier. From the temperature dependence of the measured ion intensities the partial pressure of the neutral molecules can be calculated as follows:

$$p_i = k \frac{1}{\sigma_i} I_i^+ T$$

i gas species
 k pressure calibration constant
 σ_i ionization cross section of species i
 I_i^+ ion intensity of the ion i^+ originating from neutral species i
 T temperature

The thermodynamic activities of the components can be derived as:

$$a_i = \frac{p_i}{p_i^\circ} = \frac{I_i^+}{I_i^+^\circ}$$

p_i partial pressure of species i over the mixture ($i=\text{Li}, \text{Sn}$)
 p_i° partial pressure of pure species i ($i=\text{Li}, \text{Sn}$) over the pure components

It is possible to calculate activities of the second component in a binary system, if the activity of one component is known. This method based on the Gibbs-Duhem equation. The activity of Sn in Li-Sn system cannot be directly measured by KEMS. Using the Gibbs-Duhem equation the activity of Sn can be determined as follows:

$$\ln a_{\text{Sn}} = - \int_{x_{\text{Li}}=0}^{x_{\text{Li}}} \frac{x_{\text{Li}}}{x_{\text{Sn}}} d \ln a_{\text{Li}}$$

x_i mole fraction of species i ($i=\text{Li}, \text{Sn}$)

The excess Gibbs-Energy ($\Delta_{\text{ex}}G$) can be calculated as follows:

$$\Delta_{\text{ex}}G = RT(x_{\text{Li}} \ln \gamma_{\text{Li}} + x_{\text{Sn}} \ln \gamma_{\text{Sn}})$$

R molar gas constant
 γ_i activity coefficient of species i ($i=\text{Li}, \text{Sn}$)

Results

Figure 2 shows the resulting temperature dependence of the activities of Li for selected compositions. The literature data for the compositions Li50Sn50 and Li10Sn90 are in good agreement with the results in this work. Figure 3 shows the activities of Sn by the Gibbs-Duhem Integration. The activities from the literature data (Barsoum and Tuller) were calculated. The results are reliable compared to literature data.

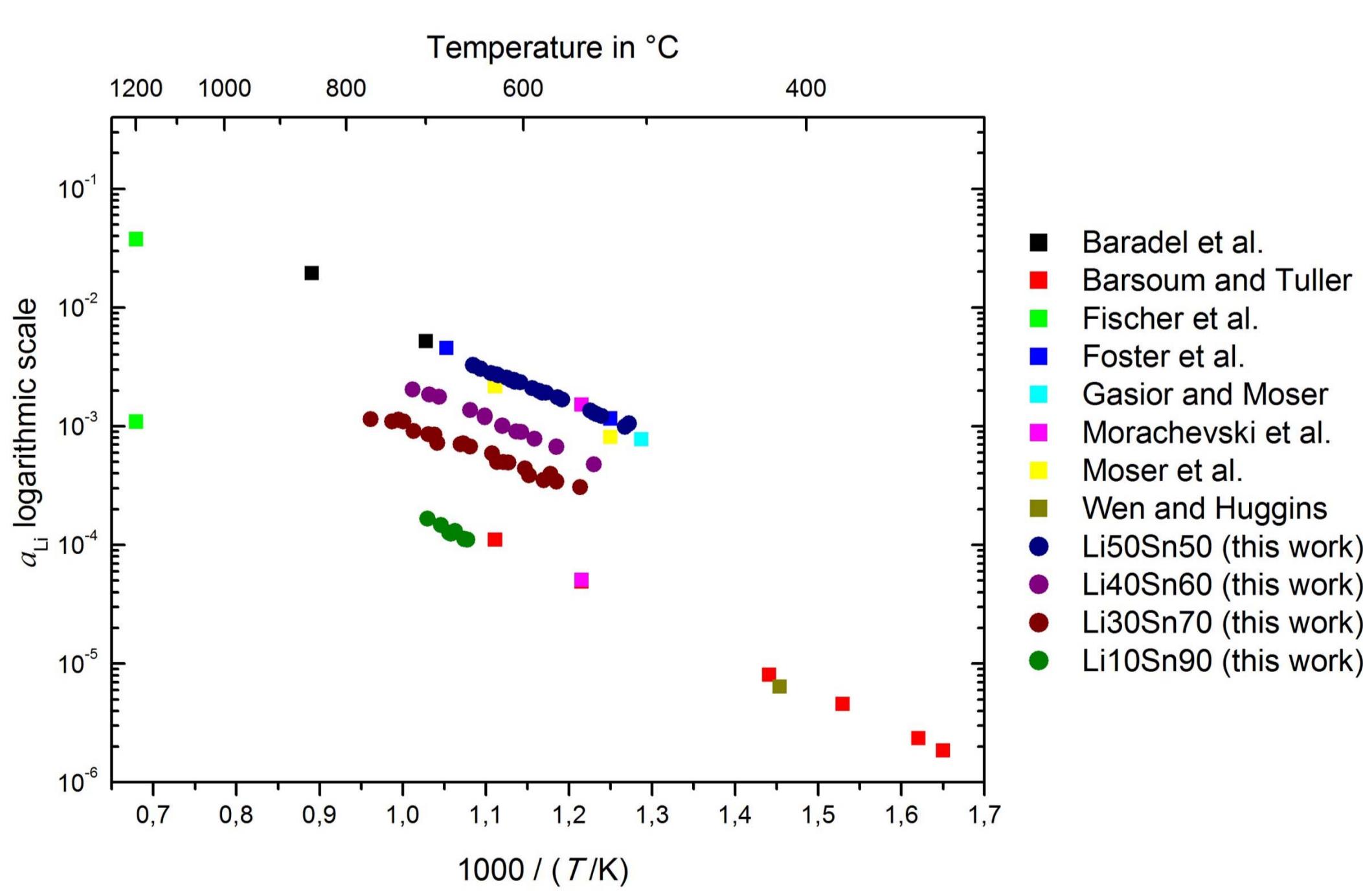


Fig.2: Thermodynamic activities of Li compared with literature data

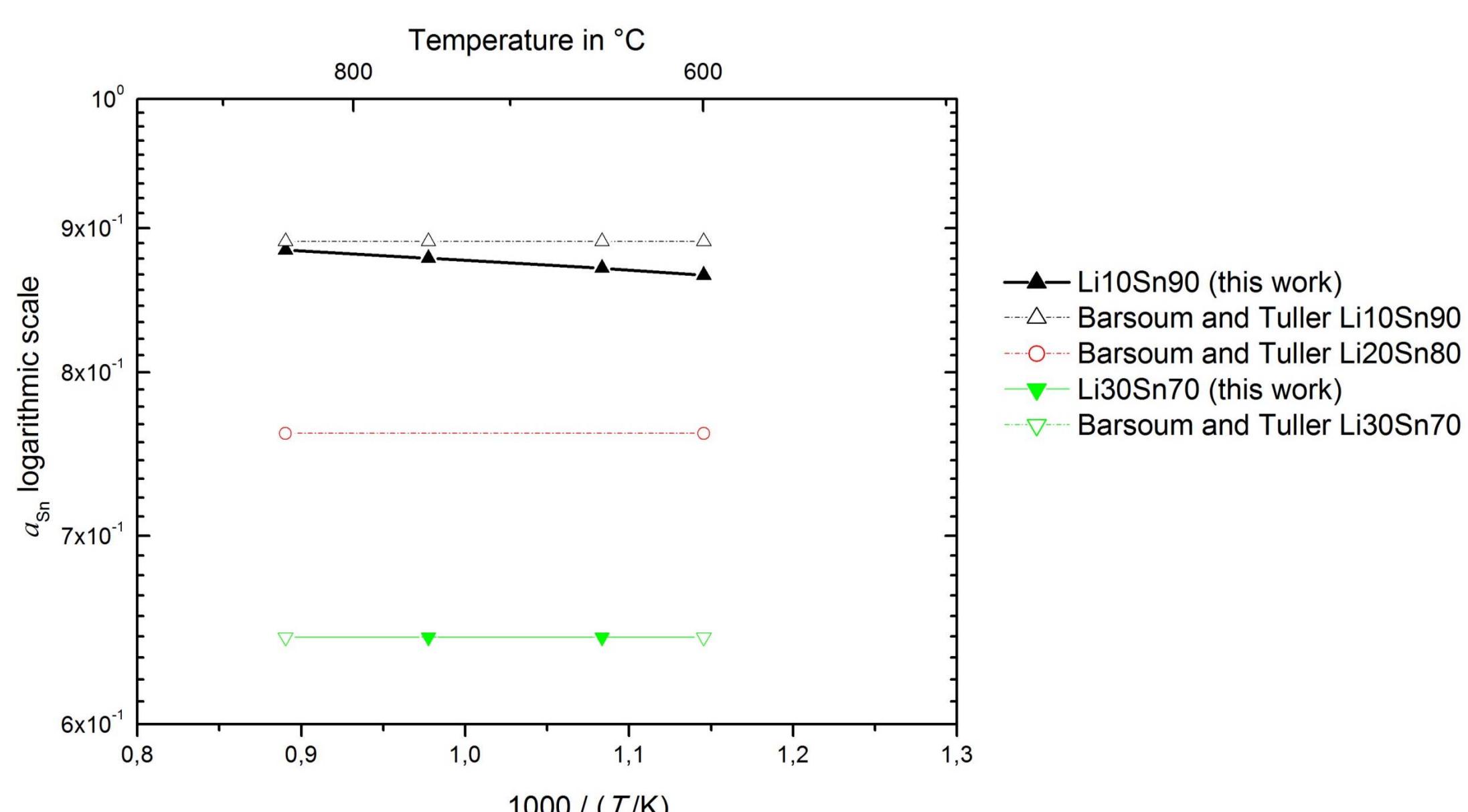


Fig.3: Thermodynamic activities of Sn compared with literature data

The data for the excess Gibbs-Energy ($\Delta_{\text{ex}}G$), computed from the literature data of Barsoum and Tuller, are in good agreement with the results in this work. Fig.4 shows the excess Gibbs-Energy ($\Delta_{\text{ex}}G$) at 900 K in dependence of the molar fraction of Li.

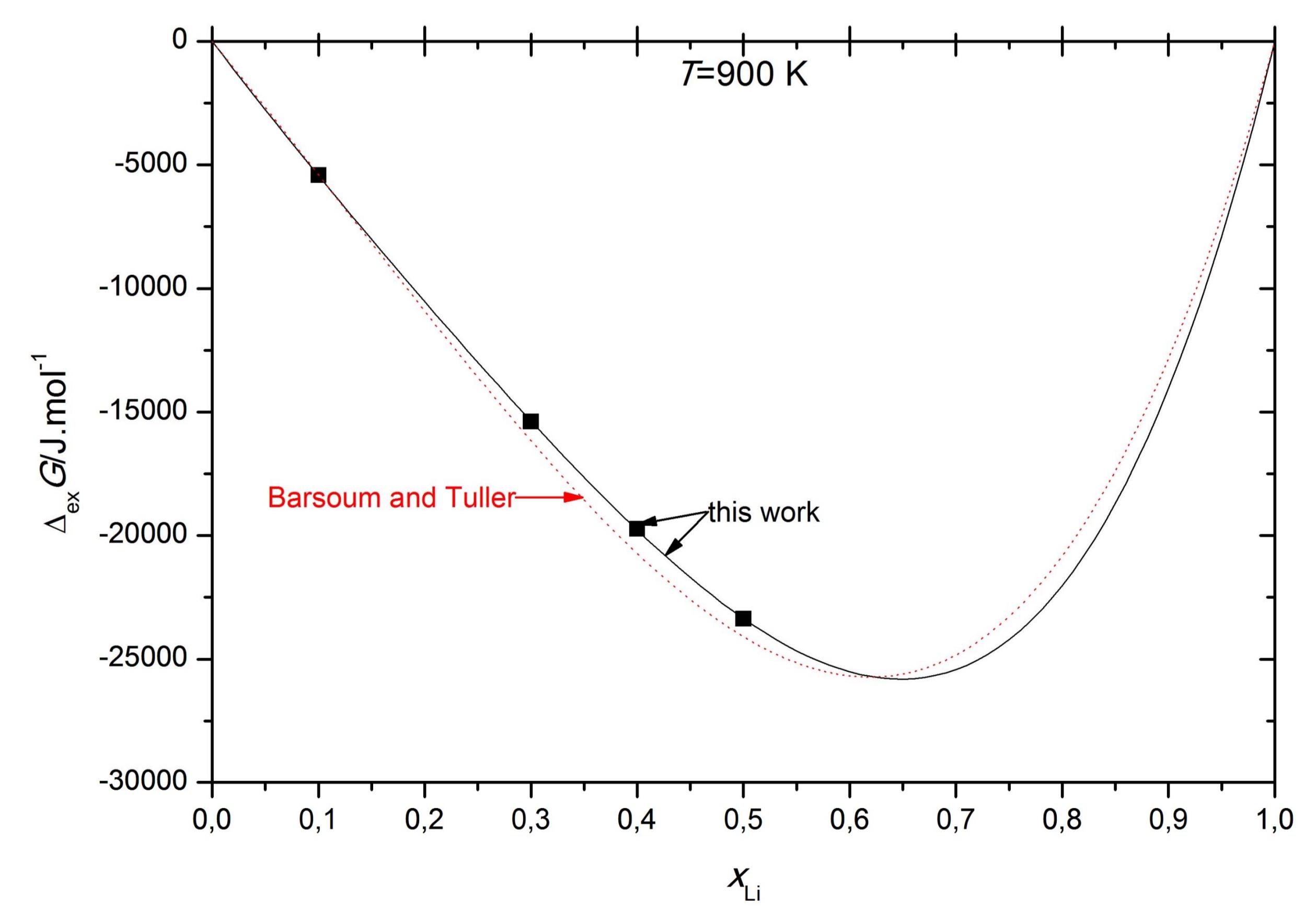


Fig.4: Calculated excess Gibbs-Energy ($\Delta_{\text{ex}}G$) at 900 K.

Conclusion

In this work KEMS measurements were done for the determination of thermodynamic activities in the binary system Li-Sn. The measured activities are in good agreement with the available literature data. The reliability of the computed excess Gibbs-Energy ($\Delta_{\text{ex}}G$) data could be demonstrated with the literature data obtained from Barsoum and Tuller.

The KEMS set up was adjusted in this work for Li-systems. It is possible to determine reliable thermodynamic data in Li-systems with the Knudsen Effusion Mass Spectrometry.