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 ($\Delta_{mix}H$, $\Delta_{mix}G$, $\Delta_{mix}S$). 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.

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 an secondary electron multiplier. From the temperature dependence of the measured ion intensities the partial pressure of the neutral molecules can be calculated as follows:

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

where:
- $p_i$ is the gas pressure
- $\sigma_i$ is the ionization cross section of species $i$
- $I_i$ is the ion intensity of the ion $i^+$ originating from neutral species $i$
- $T$ is the temperature

The thermodynamic activities of the components can be derived as:

$$a_i = \frac{p_i}{p_i^0} = \frac{I_i^0}{I_i^+}$$

where:
- $a_i$ is the partial pressure of species $i$ over the mixture (Li,LiSn)
- $I_i^+$ is the partial pressure of pure species $i$ (Li,LiSn)

It is possible to calculate activities of the second component in a binary system if the activity of one component is known. This method is based on the Gibbs-Duhem equation.

\[
\ln a_{Sn} = - \int_{x_{Li}=0}^{x_{Li}} \frac{x_{Li}}{x_{Sn}} \frac{1}{R} \frac{d\ln a_{Li}}{T} + \gamma_{Li} \gamma_{Sn}
\]

where:
- $x_i$ is the mole fraction of species $i$ ($Li,LiSn$)
- $R$ is the molar gas constant
- $\gamma_{Li}$ and $\gamma_{Sn}$ are the activity coefficients

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

$$\Delta_{ex}G = RT \ln a_{Li} + x_{Li} \ln y_{Li} + x_{Sn} \ln y_{Sn}$$

where:
- $R$ is the molar gas constant
- $y_{Li}$ is the activity coefficient of species $i$ ($Li,LiSn$)

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.

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- $y_{Li}$ is the activity coefficient of species $i$ ($Li,LiSn$)

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 ($\Delta_{ex}G$) 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.

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

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

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

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