Thermodynamic Properties of Al Cr Fe Alloys
Experimental Investigation by
Knudsen Effusion Mass Spectrometry

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TOFA-Meeting
Porto, Portugal
12.09.-17.09. 2010
Outline

- Knudsen Effusion Mass Spectrometry
  - Principle of the Method
  - Determination of Thermodynamic Data

- Experimental Results
  - Intermetallics / Alloys
    (Al-Fe)
    (Fe-Cr)
    (Al-Cr-Fe)

*Determinations of thermodynamic activities and enthalpies of mixing*
For chemical- and materials research elucidation of the vaporisation of materials is important

All materials vaporise if the temperature is sufficiently high

Thermodynamic data can be obtained from the partial pressures of the evaporating species (also for the condensed phase)

Knowledge of thermodynamic data is important to understand the chemical and thermodynamic behaviour like for example the interplay of substances during chemical reactions
The *High Temperature Mass Spectrometry* is the most important method for the analysis of vapors over condensed phases.

The *Thermodynamic Data* result from the measured temperature dependence of the *Partial Pressures* of the identified *Gaseous Species*.

A special variant of this technique which is frequently used in inorganic gas phase chemistry, is the *Knudsen Effusion Mass Spectrometry (KEMS)*.
Temperatures and pressure ranges for KEMS, TMS, LVMS

Graph showing:
- Transpiration MS
- Laser Induced MS
- Knudsen Effusion MS

Axes:
- T/K (Temperature in Kelvin)
- p/Pa (Pressure in Pascals)

Legend:
- Transpiration MS
- Laser Induced MS
- Knudsen Effusion MS
Principle of Knudsen Effusion Mass Spectrometry (KEMS)

- Vaporisation studies up to 2800 K
- Identification of gaseous species
- Determination of partial pressures (10^{-8} ... 10 \text{ Pa})
- Evaluation of thermodynamic data of
  - gaseous species
  - condensed phases
- Elucidation of corrosion processes
Schematic Representation of a Knudsen cell magnetic field mass spectrometer system
Mass Spectrometer Knudsen Cell System (CH 5)
Experimental Determination of Partial Pressures $p_i$ of Neutral Species $i$

$$p_i = k \frac{1}{\sigma_i} T \sum_j \frac{100}{\gamma_{i,j} A_{i,j}} I_{i,j}^+ = k \frac{1}{\sigma_i} \frac{I_{i}^+ T}{\gamma_i A_i}$$

- $T$: temperature
- $I_{i,j}^+$: intensities of to the neutral species $i$ related ions $j$
- $A_{i,j}$: isotopic abundance
- $\gamma_{i,j}$: multiplier gains
- $\sigma_i$: ionisation cross section of the neutral species $i$
- $k$: pressure calibration constant
Determination of Thermodynamic Properties

\[ \Delta_r G_T^0 = \Delta_r H_T^0 - T \Delta_r S_T^0 \]

Gibbs free reaction energy \hspace{0.5cm} \text{reaction enthalpy} \hspace{0.5cm} \text{reaction entropy}

\[ \Delta_r G_T^0 = -RT \ln K_p^0 \]

\[ K_p^0 = \prod_j \left( \frac{p_j}{p_j^0} \right)^{v_j} \text{ \textit{from meas.}} \]

\[ \ln K_p^0 = -\frac{\Delta_r H_T^0}{RT} + \frac{\Delta_r S_T^0}{R} \]

\[ \Delta_r H_T^0 = -T \left( R \cdot \ln K_p^0 - \Delta_r S_T^0 \right) \]

\[ \Delta_r S_T^0 = -\frac{\Delta_r G_T^0 - \Delta_r H_T^0}{T} \]

\[ \Delta_r H_{298}^0 = -T \left[ R \cdot \ln K_p^0 + \Delta_r \left( \frac{G_T^0 - H_{298}^0}{T} \right) \right] \]
Thermodynamic Properties of A and B in Alloys \{xA + (1-x)B\}

**Activities:**

According to definition:

\[
a(i) = \frac{p(i)}{p^\circ(i)} = \frac{I(i^+)}{I^\circ(i^+)} \quad (i = A, B)
\]

**Ion Intensity Ratio integration Method (GD-IIR):**

\[
\ln f(A) = - \int_{x=1}^{x} (1-x) \, \text{dln} \left( \frac{x I(B^+)}{(1-x) I(A^+)} \right) \quad a(A) = x \, f(A)
\]

**Enthalpies and Gibbs Energies:**

\[
\Delta_{\text{mix}} H(A) = R \frac{\text{d} \ln a(A)}{\text{d}(1/T)} \quad \Delta_{\text{mix}} G(A) = RT \ln a(A)
\]
Single and Double Knudsen Cells

ION SOURCE

TOFA 13.09.2010 Institute for Energy Research (IEF-2)
Metallic Shutter Valve

- Ion source chamber
- Knudsen cell chamber
- Silver gasket

Shutter Valve closed
Enthalpy of Sublimation for Ni(s) Measured at Different Days

(Mean temperatures are different: 1347 K - 1407 K)

\[ \Delta H_{\text{sub}}^{\text{Ni}} / (\text{kJ.mol}^{-1}) \]

Mean value recalc. to 1342 K: \( 419.8 \pm 1.9 \text{ kJ.mol}^{-1} \)

Lit. value for 1342 K: \( 416.3 \text{ kJ.mol}^{-1} \) (IVTANTHERMO)

Lit. value for 1342 K: \( 420.36 \text{ kJ.mol}^{-1} \) (IVTANTHERMO, DOS)

Lit. value for 1342 K: \( 422.58 \text{ kJ.mol}^{-1} \) (ChemSage, Thermocalc, SGPS)

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Institute for Energy Research (IEF-2)
Calibration Constant and sublimation Enthalpie measured for Fe

![Graph showing calibration constant and sublimation Enthalpy for Fe over time from 30.12.2008 to 04.05.2009.](image)

- Calibration constant (Fe)
- \( \Delta H_s \) (Fe)
Phase Diagram Fe-Al (SGTE) with sample compositions
Phase Diagram Cr-Fe (SGTE) with sample compositions
Phase Diagram Al-Cr-Fe (SGTE) with sample compositions
Sample compositions and temperature range of the investigated alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal composition [at. %]</th>
<th>T-Range of vaporization measurements [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>Cr</td>
</tr>
<tr>
<td>Ternary Al-Cr-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>te9</td>
<td>31</td>
<td>13</td>
</tr>
<tr>
<td>te8</td>
<td>20.5</td>
<td>24.4</td>
</tr>
<tr>
<td>te7</td>
<td>11</td>
<td>35</td>
</tr>
<tr>
<td>te6</td>
<td>35</td>
<td>21</td>
</tr>
<tr>
<td>te5</td>
<td>21</td>
<td>31</td>
</tr>
<tr>
<td>te4</td>
<td>26</td>
<td>19</td>
</tr>
<tr>
<td>te3</td>
<td>28.5</td>
<td>17</td>
</tr>
<tr>
<td>Binary Al-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bial1</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>bial2</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>bial3</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>bial5</td>
<td>65.2</td>
<td>-</td>
</tr>
<tr>
<td>Binary Cr-Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bicr1</td>
<td>-</td>
<td>48</td>
</tr>
<tr>
<td>bicr2</td>
<td>-</td>
<td>46</td>
</tr>
</tbody>
</table>
Activities of Al and Fe for two measured runs of the sample bial 5 (Al$_{65.2}$Fe$_{34.8}$)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{graph.png}
\caption{Activities of Al and Fe for two measured runs of the sample bial 5 (Al$_{65.2}$Fe$_{34.8}$).}
\end{figure}
Activities of Cr and Fe for two measured runs of the sample bicr1 ($\text{Cr}_{48}\text{Fe}_{52}$)

$T$ [K]

$\log(a_i) / T [\text{K}^{-1}]$
Phase Characterisation of binary Fe-Cr samples

### (Cr$_{45}$-Fe$_{55}$)

<table>
<thead>
<tr>
<th>at%</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.7</td>
<td>51.4</td>
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<tr>
<td>2</td>
<td>47.5</td>
<td>52.5</td>
</tr>
<tr>
<td>3</td>
<td>47.1</td>
<td>52.4</td>
</tr>
</tbody>
</table>

### (Cr$_{45}$-Fe$_{55}$)

<table>
<thead>
<tr>
<th>at%</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.5</td>
<td>54.5</td>
</tr>
<tr>
<td>2</td>
<td>46.2</td>
<td>53.8</td>
</tr>
<tr>
<td>3</td>
<td>45.9</td>
<td>54.1</td>
</tr>
</tbody>
</table>

### (Cr$_{28}$-Fe$_{72}$)

<table>
<thead>
<tr>
<th>at%</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.0</td>
<td>72.7</td>
</tr>
<tr>
<td>2</td>
<td>26.9</td>
<td>71.7</td>
</tr>
<tr>
<td>3</td>
<td>26.8</td>
<td>70.7</td>
</tr>
</tbody>
</table>
Partial pressures of Fe, Cr and Al over 57.5Fe-18Cr-24.5Al compared with the partial pressures of the pure components
Thermodynamic activities of Fe, Cr and Al in 57.5Fe-18Cr-24.5Al
Thermodynamic activities of Fe, Cr and Al in $\text{Al}_{0.26}\text{Cr}_{0.19}\text{Fe}_{0.55}$

![Graph showing thermodynamic activities of Fe, Cr, and Al in Al$_{0.26}$Cr$_{0.19}$Fe$_{0.55}$](image)

- $a(\text{Fe})$ Run1
- $a(\text{Cr})$ Run1
- $a(\text{Al})$ Run1
- $a(\text{Fe})$ Run2
- $a(\text{Cr})$ Run2
- $a(\text{Al})$ Run2

$T$ [K]

$10^3/T$ [K$^{-1}$]
### Parameters of the equation \( \log(a) = A/T + B \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition [at. %]</th>
<th>( \Delta T )</th>
<th>( T_m )</th>
<th>( \log(a_{Al}) = A/(T/K) + B )</th>
<th>( a_{Al} )</th>
<th>( \log(a_{Fe}) = A + B/(T/K) )</th>
<th>( a_{Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bial1</td>
<td>Al 45, Fe 55</td>
<td>1286-1477</td>
<td>1384</td>
<td>-4700 ± 207, 2.25 ± 0.15</td>
<td>0.059</td>
<td>26 ± 589, -0.78 ± 0.43</td>
<td>0.17</td>
</tr>
<tr>
<td>bial2</td>
<td>Al 45, Fe 55</td>
<td>1279-1468</td>
<td>1381</td>
<td>-4486 ± 176, 2.09 ± 0.13</td>
<td>0.059</td>
<td>-97 ± 388, -0.53 ± 0.28</td>
<td>0.25</td>
</tr>
<tr>
<td>bial3</td>
<td>Al 40, Fe 60</td>
<td>1254-1604</td>
<td>1426</td>
<td>-4069 ± 153, 1.60 ± 0.11</td>
<td>0.039</td>
<td>-1 ± 106, -0.46 ± 0.07</td>
<td>0.35</td>
</tr>
<tr>
<td>bial5</td>
<td>Al 65.2, Fe 34.8</td>
<td>1234-1420</td>
<td>1333</td>
<td>-3000 ± 148, 1.68 ± 0.11</td>
<td>0.029</td>
<td>-2633 ± 829, 0.79 ± 0.61</td>
<td>0.069</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition [at. %]</th>
<th>( \Delta T )</th>
<th>( T_m )</th>
<th>( \log(a_{Cr}) = A/(T/K) + B )</th>
<th>( a_{Cr} )</th>
<th>( \log(a_{Fe}) = A + B/(T/K) )</th>
<th>( a_{Fe} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>bicr1</td>
<td>Cr 48, Fe 52</td>
<td>1302-1593</td>
<td>1439</td>
<td>-200 ± 146, -0.20 ± 0.10</td>
<td>0.46</td>
<td>-387 ± 122, 0.06 ± 0.08</td>
<td>0.62</td>
</tr>
<tr>
<td>bicr2</td>
<td>Cr 46, Fe 54</td>
<td>1294-1589</td>
<td>1446</td>
<td>221 ± 70, -0.49 ± 0.05</td>
<td>0.46</td>
<td>-71 ± 113, -0.17 ± 0.08</td>
<td>0.60</td>
</tr>
<tr>
<td>bicr3</td>
<td>Cr 28, Fe 72</td>
<td>1296-1598</td>
<td>1446</td>
<td>473 ± 93, -0.80 ± 0.06</td>
<td>0.33</td>
<td>43 ± 97, -0.10 ± 0.07</td>
<td>0.85</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition [at. %]</th>
<th>( \Delta T )</th>
<th>( T_m )</th>
<th>( \log(a_{Al}) = A/(T/K) + B )</th>
<th>( a_{Al} )</th>
<th>( \log(a_{Cr}) = A + B/(T/K) )</th>
<th>( a_{Cr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>te9</td>
<td>Al 31, Cr 13, Fe 56</td>
<td>1304-1597</td>
<td>1444</td>
<td>-3656 ± 74, 1.22 ± 0.05</td>
<td>0.050</td>
<td>859 ± 112, -1.35 ± 0.08</td>
<td>0.18</td>
</tr>
<tr>
<td>te8</td>
<td>Al 20.5, Cr 24.4, Fe 55</td>
<td>1299-1599</td>
<td>1450</td>
<td>-3471 ± 173, 0.55 ± 0.12</td>
<td>0.014</td>
<td>822 ± 135, -1.15 ± 0.09</td>
<td>0.26</td>
</tr>
<tr>
<td>te7</td>
<td>Al 11, Cr 35, Fe 54</td>
<td>1305-1606</td>
<td>1455</td>
<td>-3845 ± 191, 0.28 ± 0.13</td>
<td>0.0042</td>
<td>518 ± 80, -0.77 ± 0.06</td>
<td>0.39</td>
</tr>
<tr>
<td>te6</td>
<td>Al 35, Cr 21, Fe 44</td>
<td>1319-1601</td>
<td>1461</td>
<td>-2191 ± 234, 0.38 ± 0.16</td>
<td>0.073</td>
<td>1570 ± 246, -1.75 ± 0.17</td>
<td>0.21</td>
</tr>
<tr>
<td>te5</td>
<td>Al 21, Cr 31, Fe 48</td>
<td>1318-1600</td>
<td>1459</td>
<td>-3798 ± 113, 0.74 ± 0.08</td>
<td>0.013</td>
<td>470 ± 97, -0.83 ± 0.07</td>
<td>0.31</td>
</tr>
<tr>
<td>te4</td>
<td>Al 26, Cr 19, Fe 55</td>
<td>1319-1608</td>
<td>1464</td>
<td>-3581 ± 79, 0.83 ± 0.05</td>
<td>0.023</td>
<td>666 ± 80, -1.09 ± 0.06</td>
<td>0.24</td>
</tr>
<tr>
<td>te3</td>
<td>Al 28.5, Cr 17, Fe 54.5</td>
<td>1309-1608</td>
<td>1463</td>
<td>-3284 ± 122, 0.79 ± 0.08</td>
<td>0.034</td>
<td>787 ± 128, -1.22 ± 0.09</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Summary

- The most noticeable fact on the alloying is, that adding Cr to binary Fe-Al has the effect of remarkably lower the Fe and Al activities.
- Arrhenius plots of the activities indicate the large dynamic range and the high precision of the vapour pressure measurements by KEMS.
- Two or three independent runs were carried out for each composition.
- Mean ‘slope’ and ‘intercept’ data of the \( \log(a_i) = A/(T/K) + B \) equation were calculated for each composition as well as partial molar and integral thermodynamic quantities.
- Vacancy dependent (true) integral enthalpies and entropies can only be determined by modelling.
Acknowledgement

We gratefully acknowledge financial support by the German Science Foundation Deutsche Forschungsgesellschaft (DFG)

Thank You for Your Attention