hochschule mannheim

Determination of Thermodynamic Data for Gaseous Phases using Knudsen Effusion Mass Spectrometry

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GTT Workshop 18.06.2019

Herzogenrath

Germany

Outline

- Method Knudsen Effusions Mass Spectrometry
- Determination of Thermodynamische Data & Use Cases
- KEMS Development
- Vapor Pressure Measurements in the System Al-Cr-Fe
- Conclusion

KEMS – Introduction
(Knudsen Effusion Mass Spectrometry)

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

Determination of Thermodynamic Data with Knudsen Effusion Mass Spectrometry

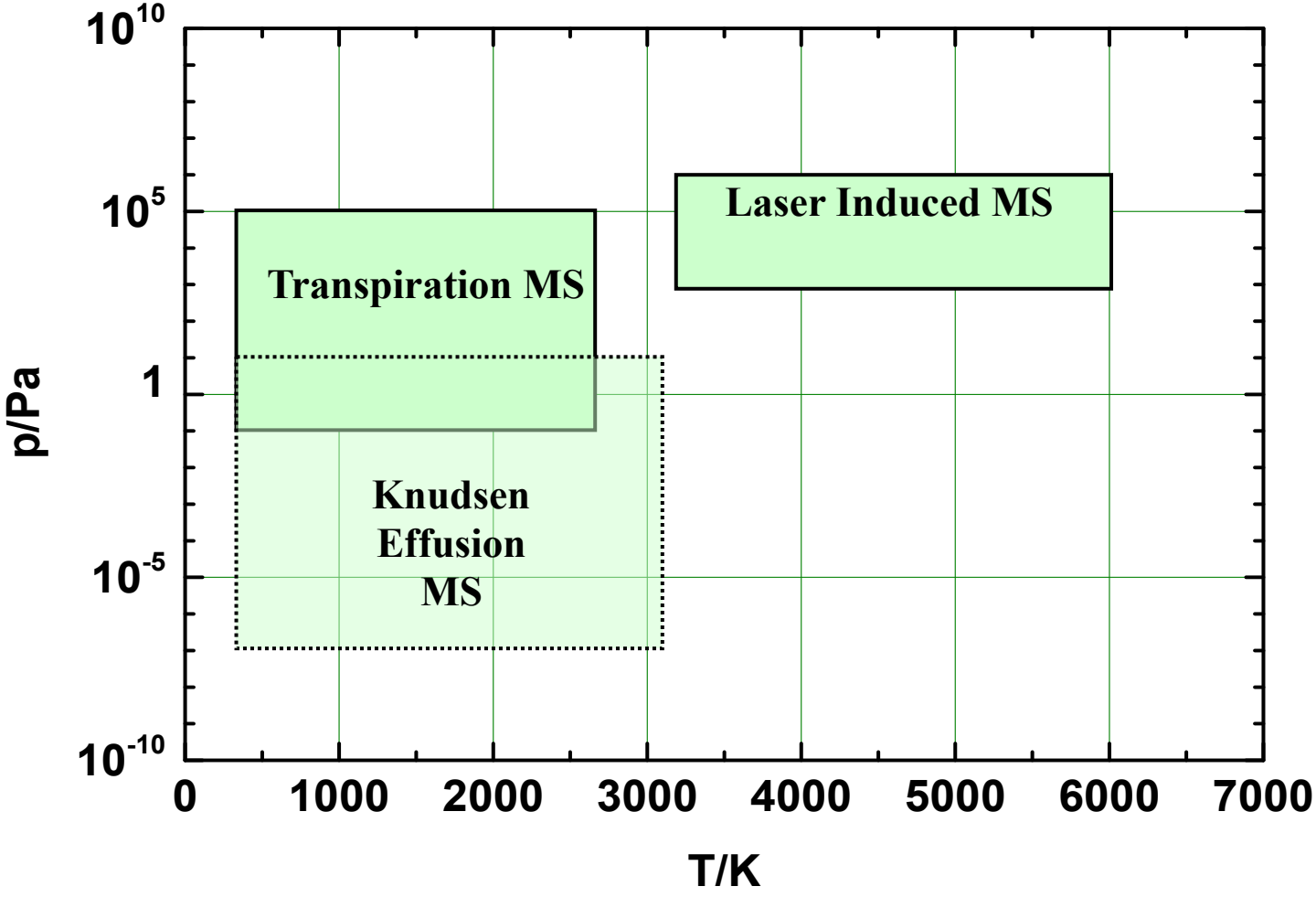
The *High Temperature Mass Spectrometry* is the most imortant method for the analysis of vapors over condensed phases

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 Masss Spectrometry (KEMS)

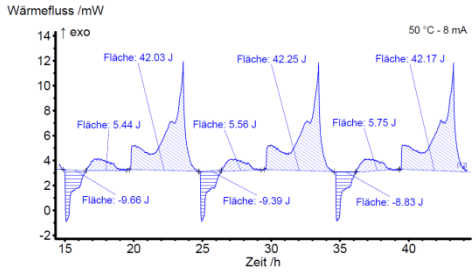
Temperatures and pressure ranges for KEMS, TMS, LVMS

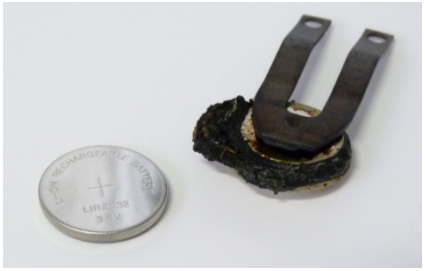


USE Cases

Lithium-Ionen Batteries

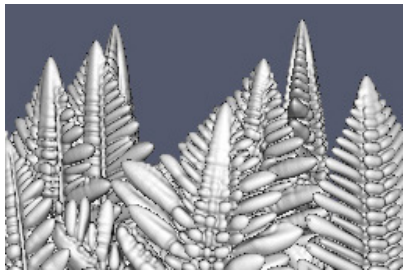
- cell capacity, cell voltage
- thermal & chemical stability
- thermal behavior during cycling





Metallurgy

- vapor pressures
- thermodynamic activities
- Enthalpies and entropies of formation



http://www.access.rwth-aachen.de/node/801

Chemische Industrie

- determination of chemical reactions and processes
- identification of gaseous species and their vaor pressures (REACH)
- determination of mixing enthalpies and -entropies

→ **For Computer Simmulations Materials Properties of High Quality are needed**

Introduction: Knudsen Effusion Method

- Partial pressure:

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

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*

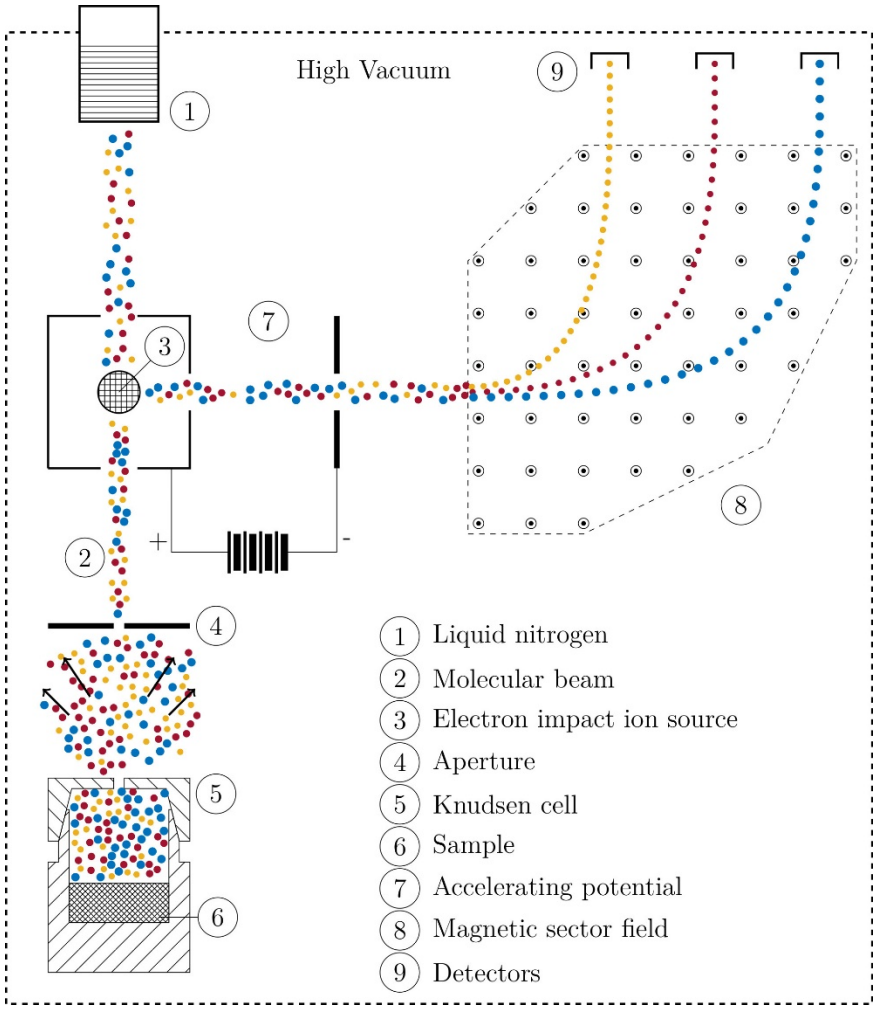
Thermodynamic activity:

$$a_i = \frac{p_i}{p^\circ_i} = \frac{I_{i^+}}{I^\circ_{i^+}}$$

P_i	*partial pressure of species I over the mixture (i=Li,Sn)*
p°_i	*partial pressure of pure species I (I=Li,Sn) over the pure components*

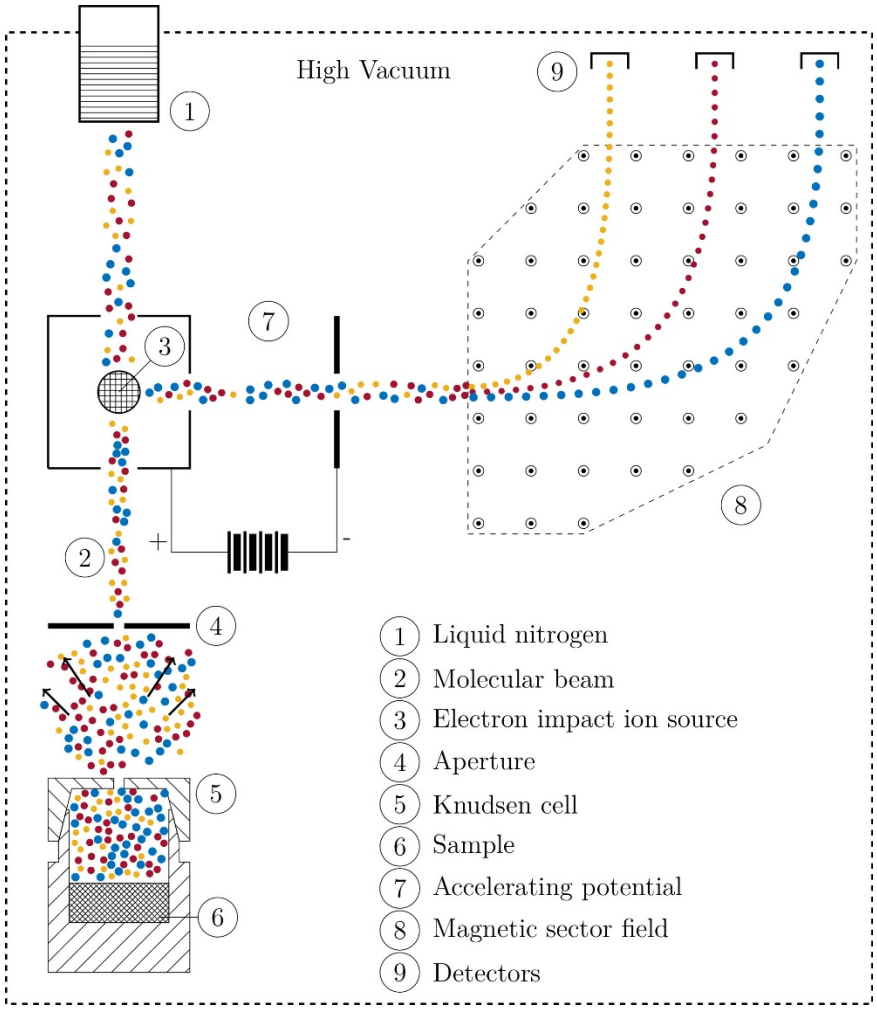
→ Thermodynamic Data:

- Thermodynamic activity
- Chemical potential
- $\Delta_{mix}H$, $\Delta_{mix}G$, $\Delta_{mix}S$

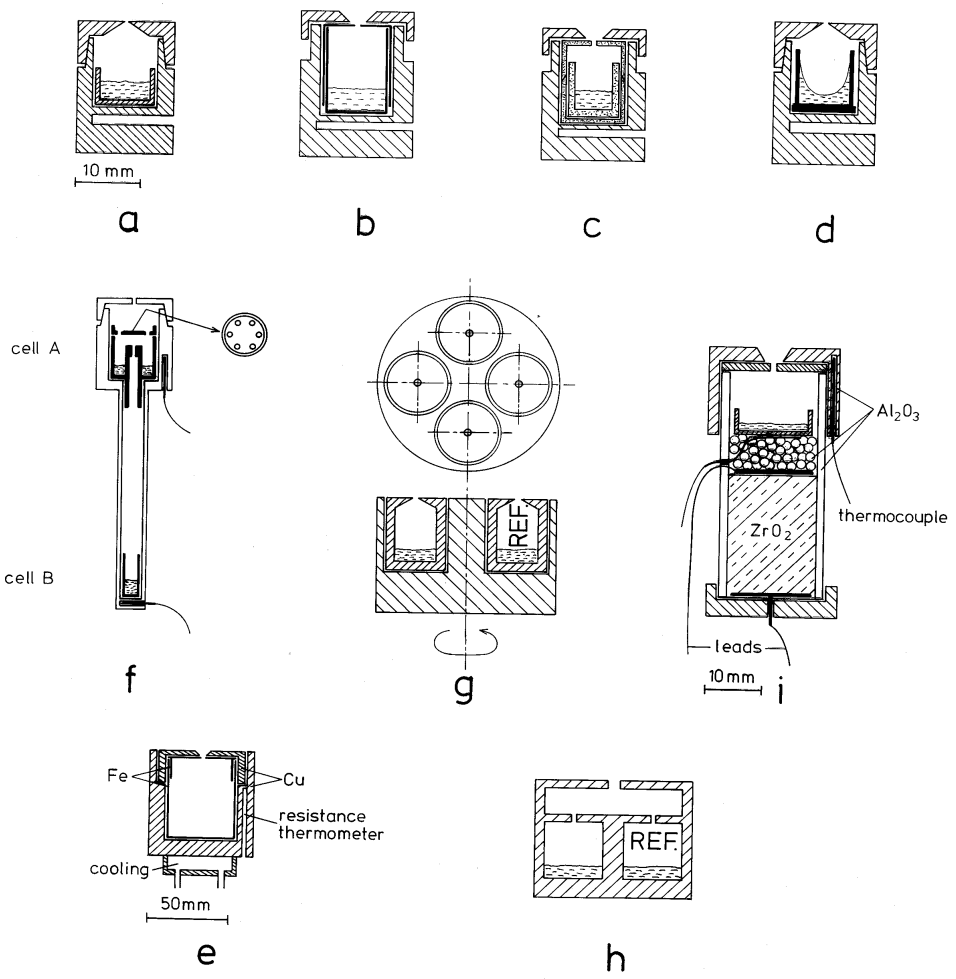


Introduction: Knudsen Effusion Method

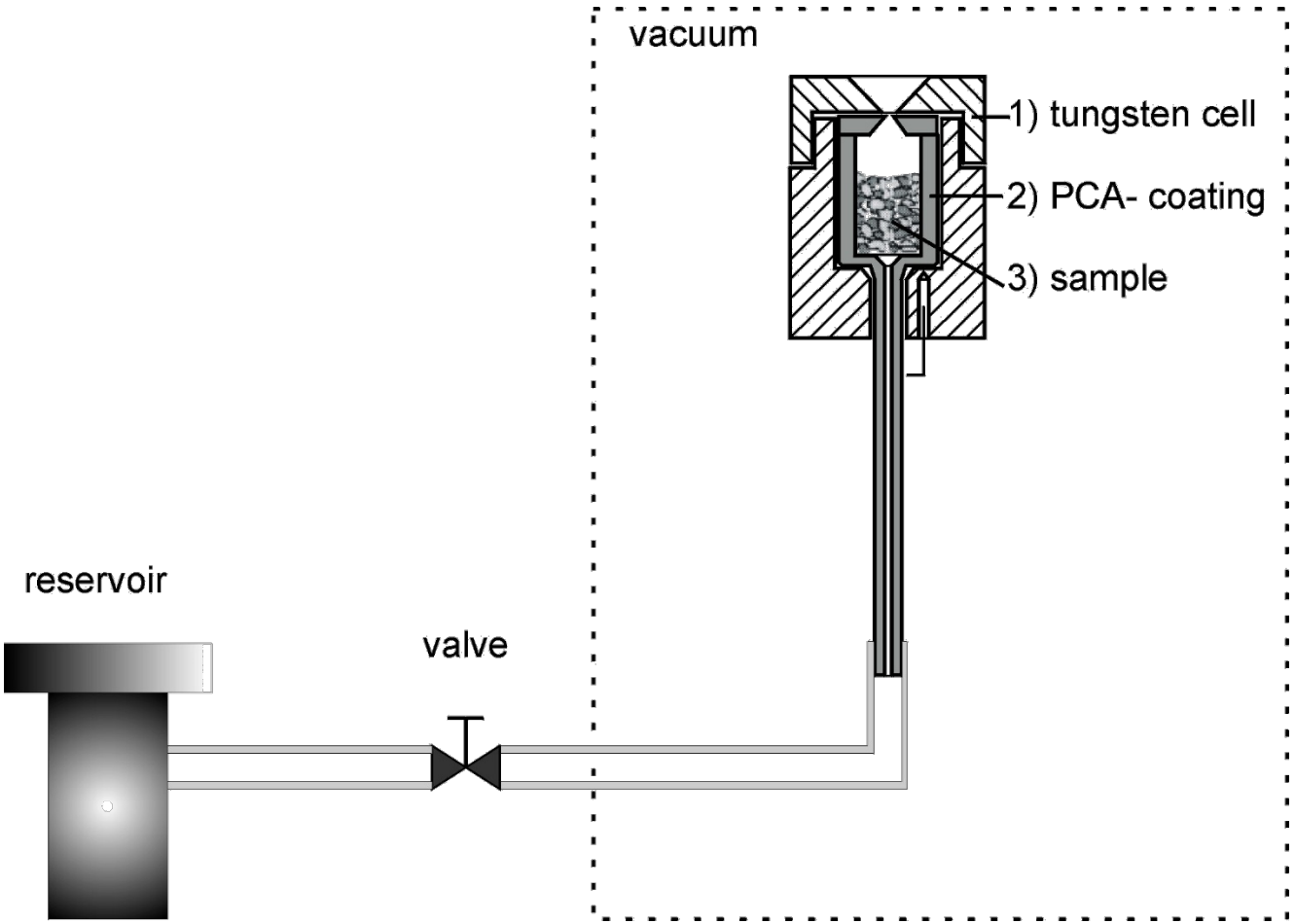
- Vaporisation studies up to 2800 K
- Identification of gaseous species
- Determination of partial pressures (10^{-8} ... 10 Pa)
- Evaluation of thermodynamic data of
  - gaseous species
  - condensed phases
- Elucidation of corrosion processes



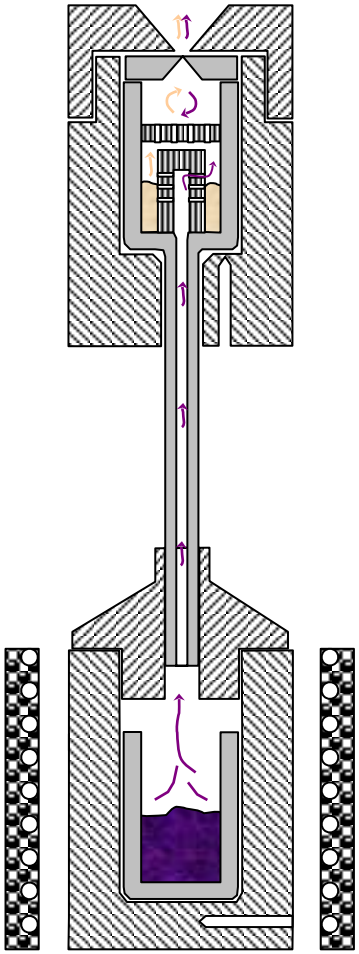
Different types of Knudsen Cells

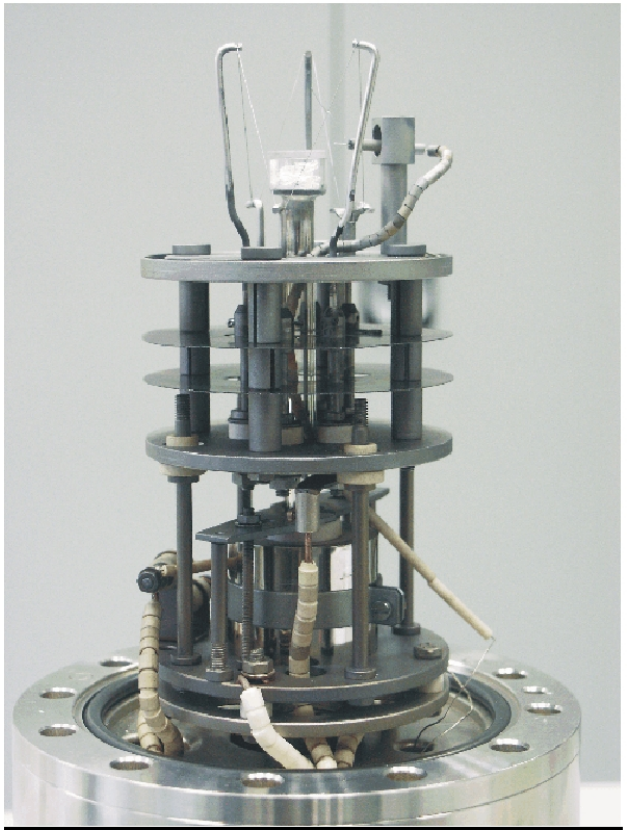


Schematic representation of a Gas Inlet System

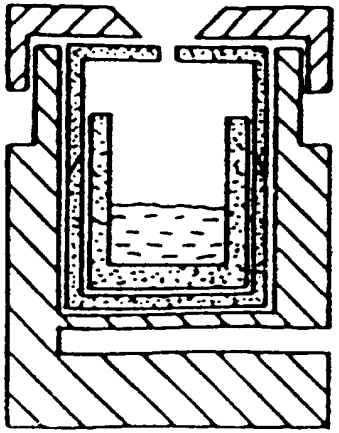


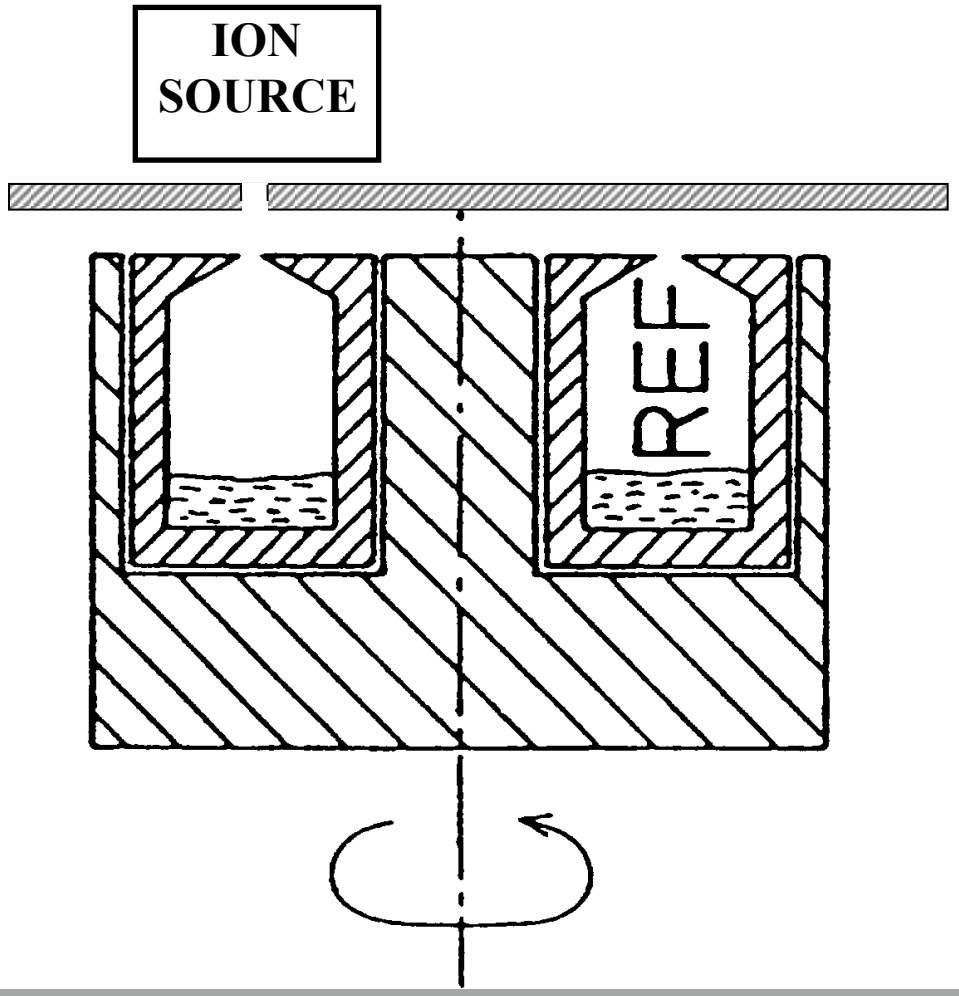
Schematic representation of a Douple Cell





Single and Double Knudsen Cells





Introduction: KEMS 4.0

Motivation

- KEMS was developed in the 50s
- Existing machines are laboratory prototypes or custom made
- Number of research groups is relatively limited and sinking due to age structure
- State of the Art is 90s or earlier

Development Goals

- Exceed state of the art
- New areas of application
- Developing new vacuum components and modules
- Developing an innovative control- and analyzing software

Project Partner:

- GHS Vakuumtechnik GmbH
- Supporting Partner Pfeiffer Vacuum GmbH

Gefördert durch:
Bundesministerium für Wirtschaft und Energie
aufgrund eines Beschlusses des Deutschen Bundestages

GHS VAKUUMTECHNIK GMBH

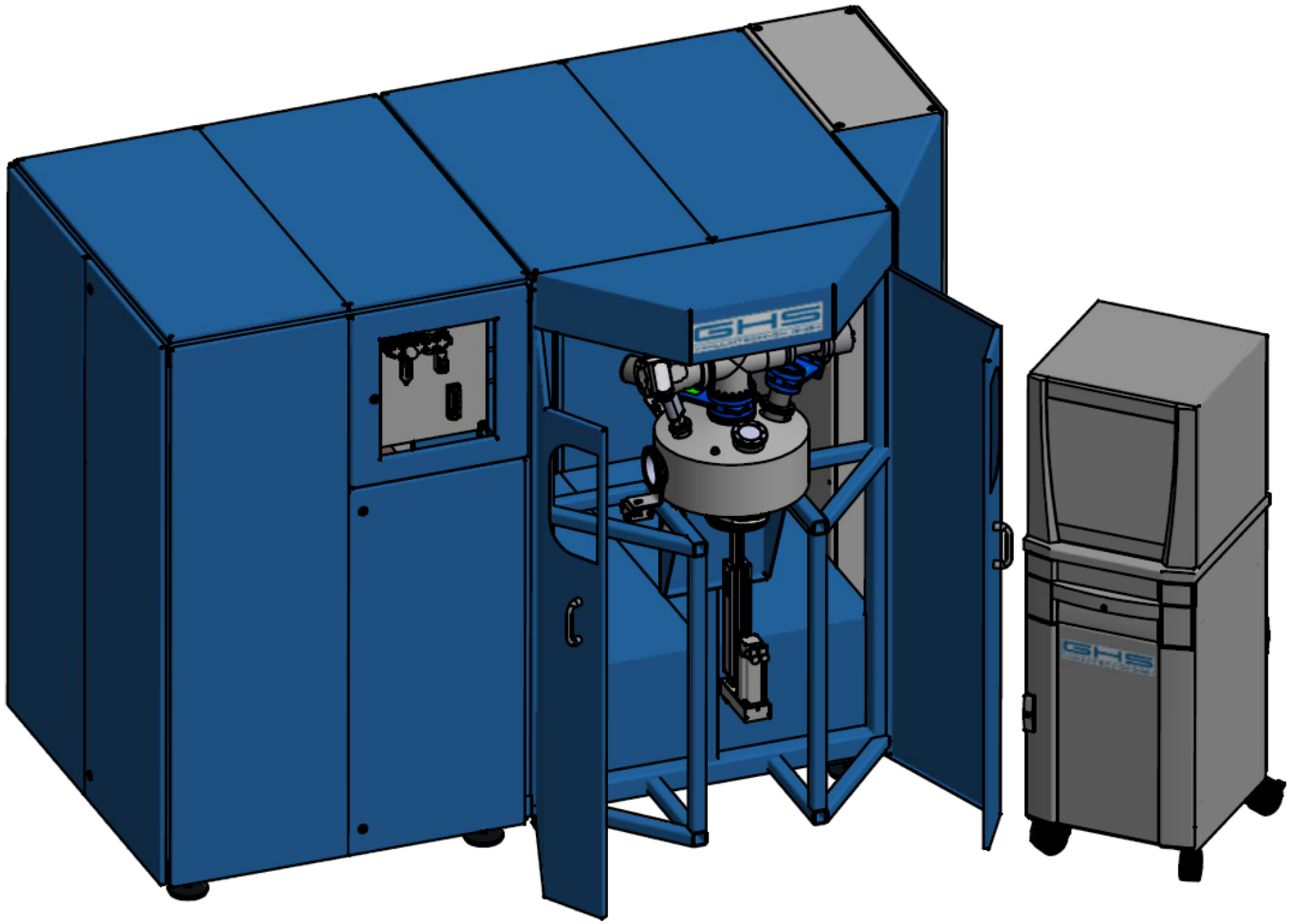
Supporting Partner:
PFEIFFER VACUUM

KEMS 4.0 – Development Goals

- Constant System Vacuum Pressure: $1 \cdot 10^{-9}$ mbar
- Sensitivity:
  - Min. Vapor pressure: $1 \cdot 10^{-12}$ mbar
  - Max. Vapor Pressure: 1 mbar
  - Temperature range: -80 °C bis 3000 °C

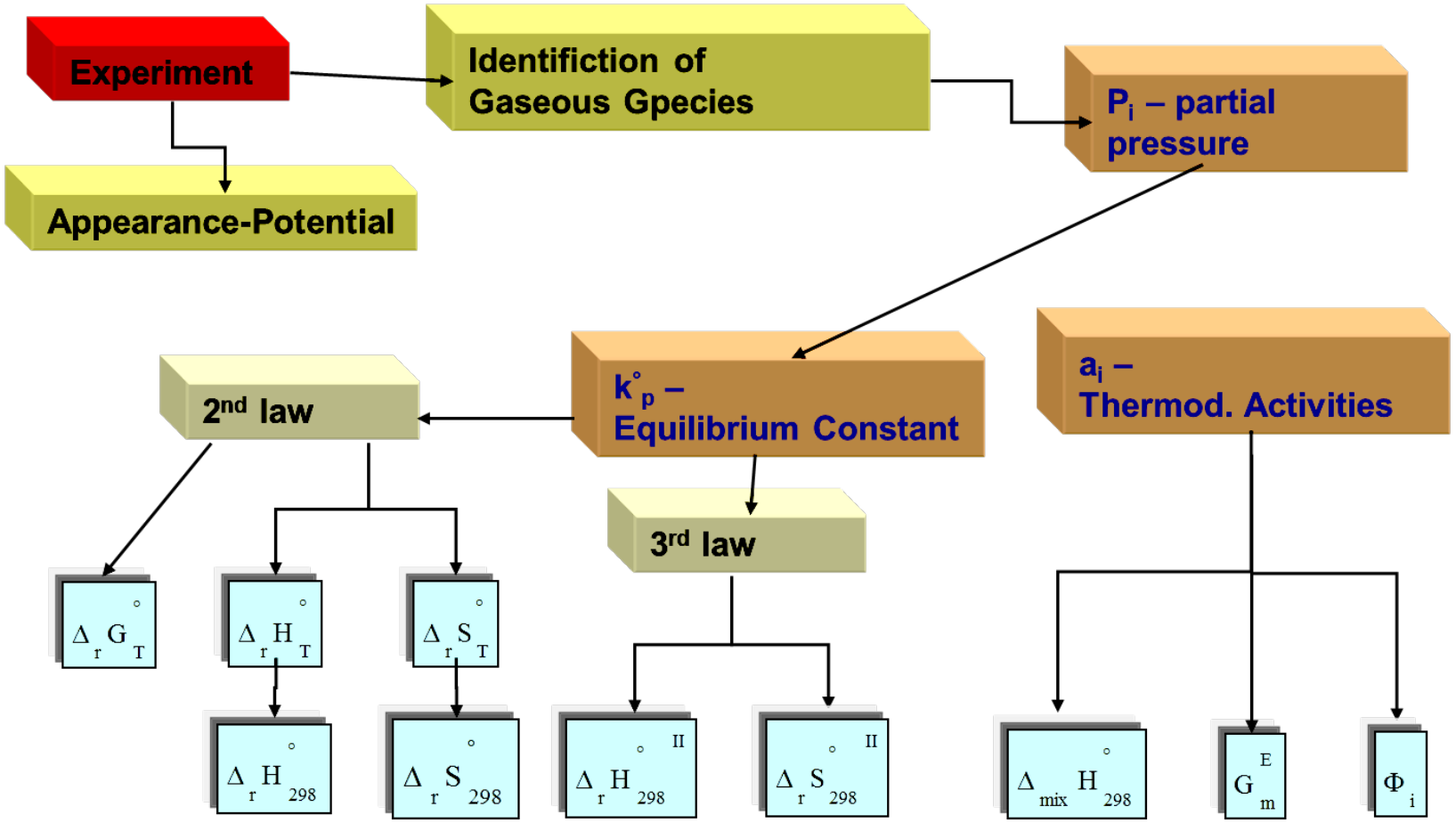
→ **Compact Size and user-friendly**
→ **New innovative control- and analyzing software**

KEMS 4.0 – Preliminary Impressions



- Construction is completed
- Production is going on

Potential of
Knudsen Effusion Mass Spectrometry



Determination of Thermodynamic Properties

$$\Delta_r G_T^0 = \Delta_r H_T^0 - T\Delta_r S_T^0$$

Gibbs free reaction energy — reaction enthalpy — reaction entropy

2nd law

$$\Delta_r G_T^0 = -RT \ln K_p^0$$

$$K_p^0 = \prod_j \left(\frac{p_j}{p^0} \right)^{\nu_j}$$ from meas.

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

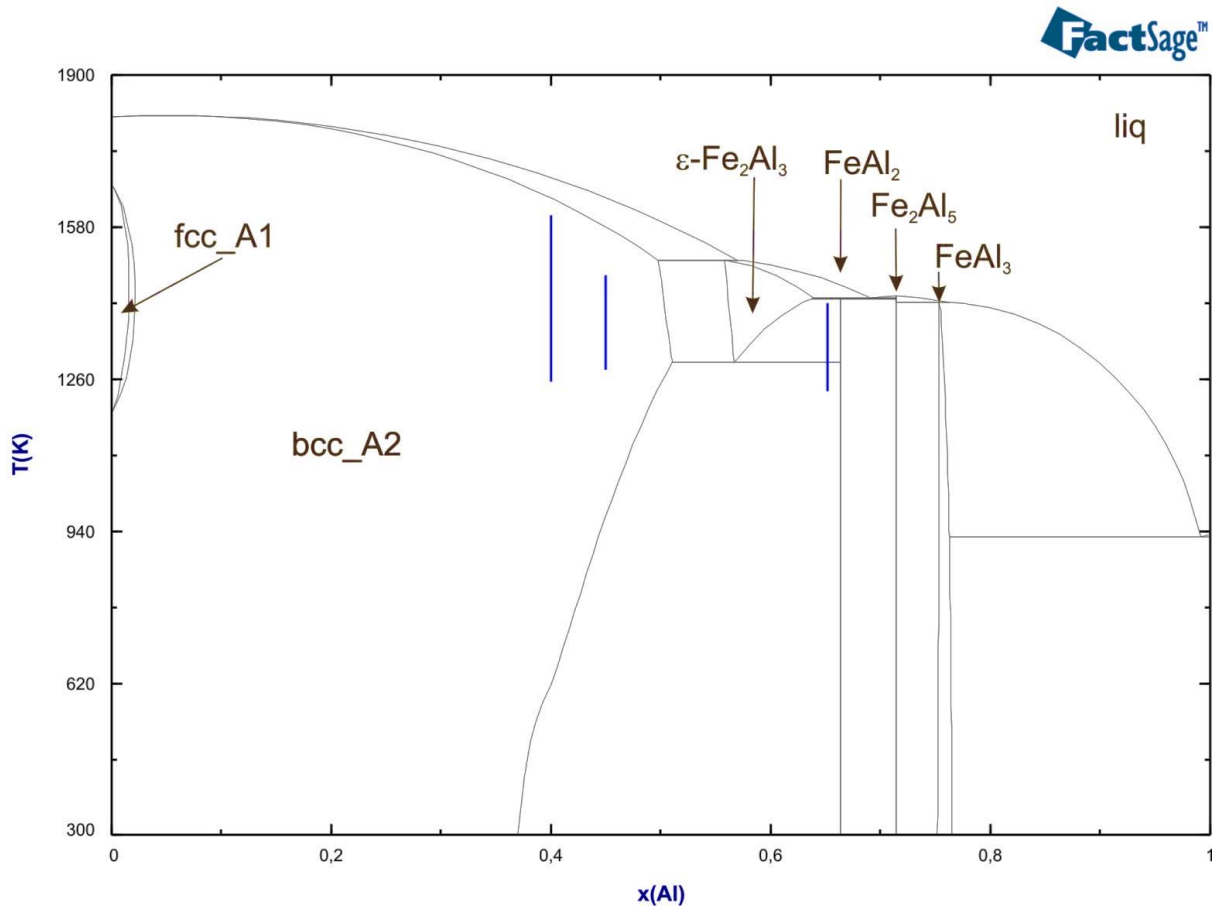
3rd law

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

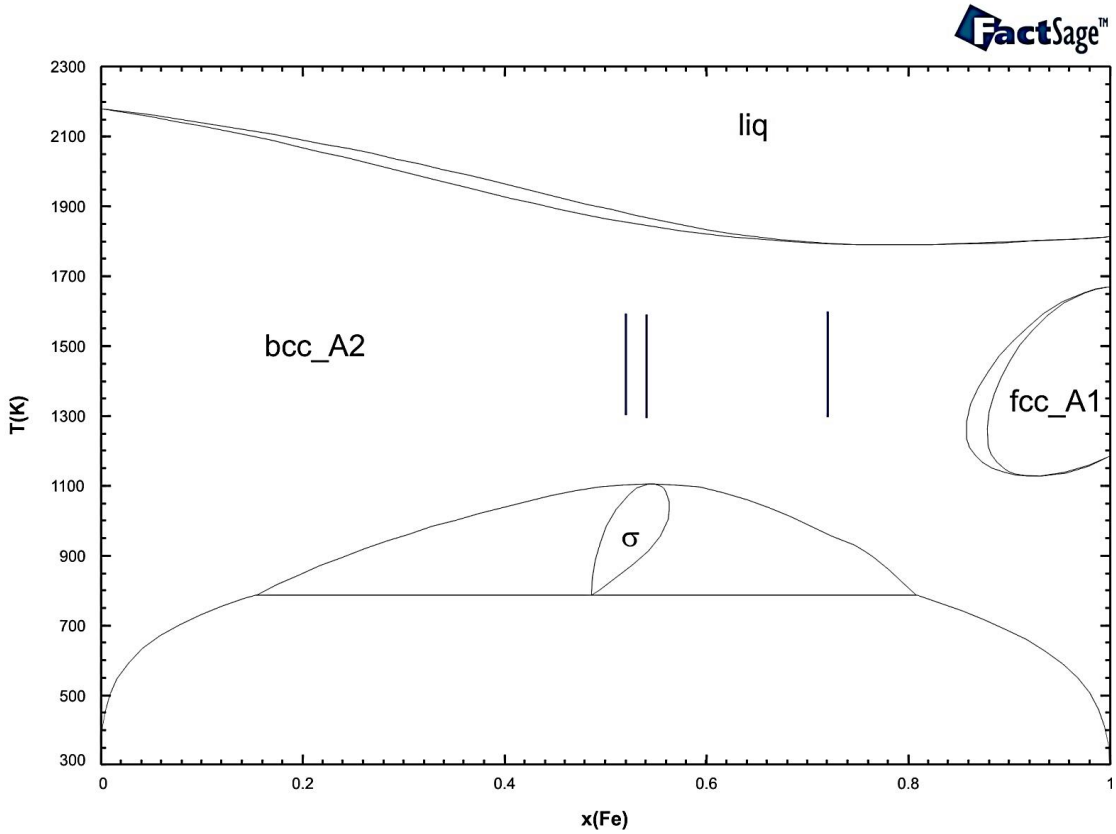
$$\Delta_r S_T^0 = -\frac{\left(\Delta_r G_T^0 - \Delta_r H_T^0\right)}{T}$$

$$\Delta_r H_{298}^0 = -T\left[R \cdot \ln K_p^0 + \Delta_r\left(\frac{G_T^0 - H_{298}^0}{T}\right)\right]$$

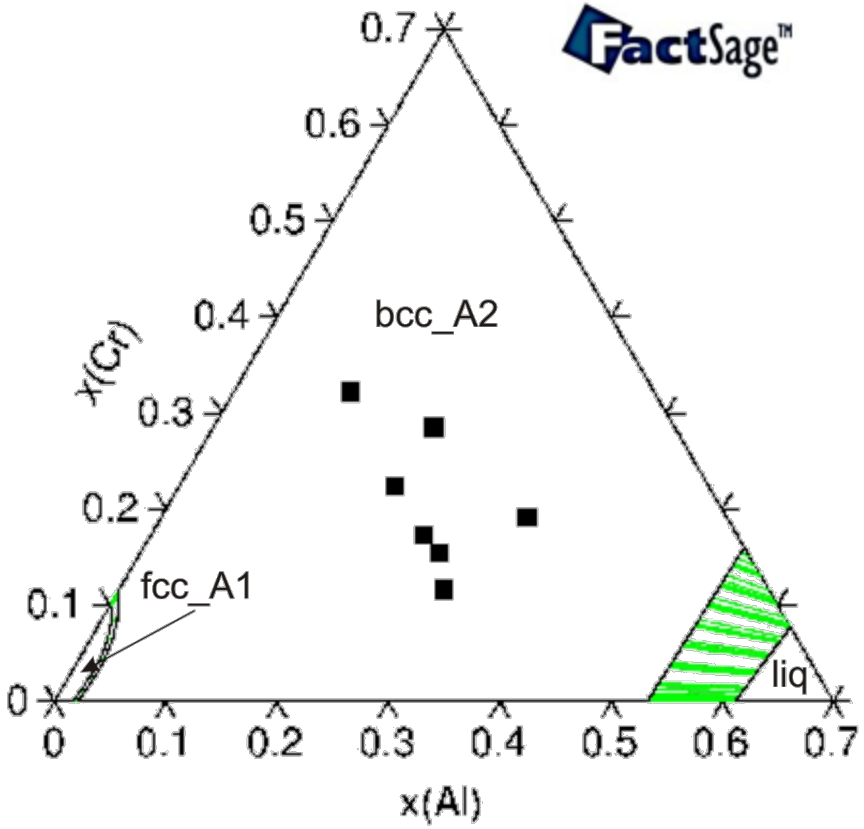
Phase Diagram Fe-Al (SGTE) with sample compositions



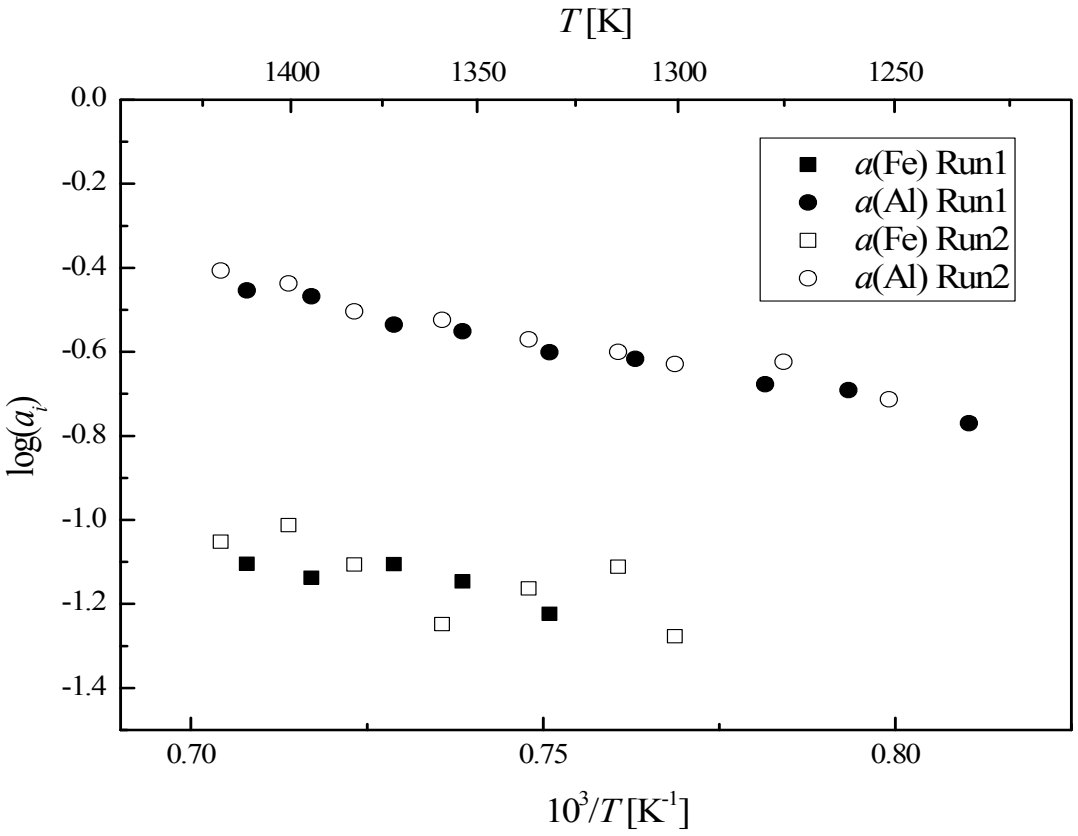
Phase Diagram Cr-Fe (SGTE) with sample compositions



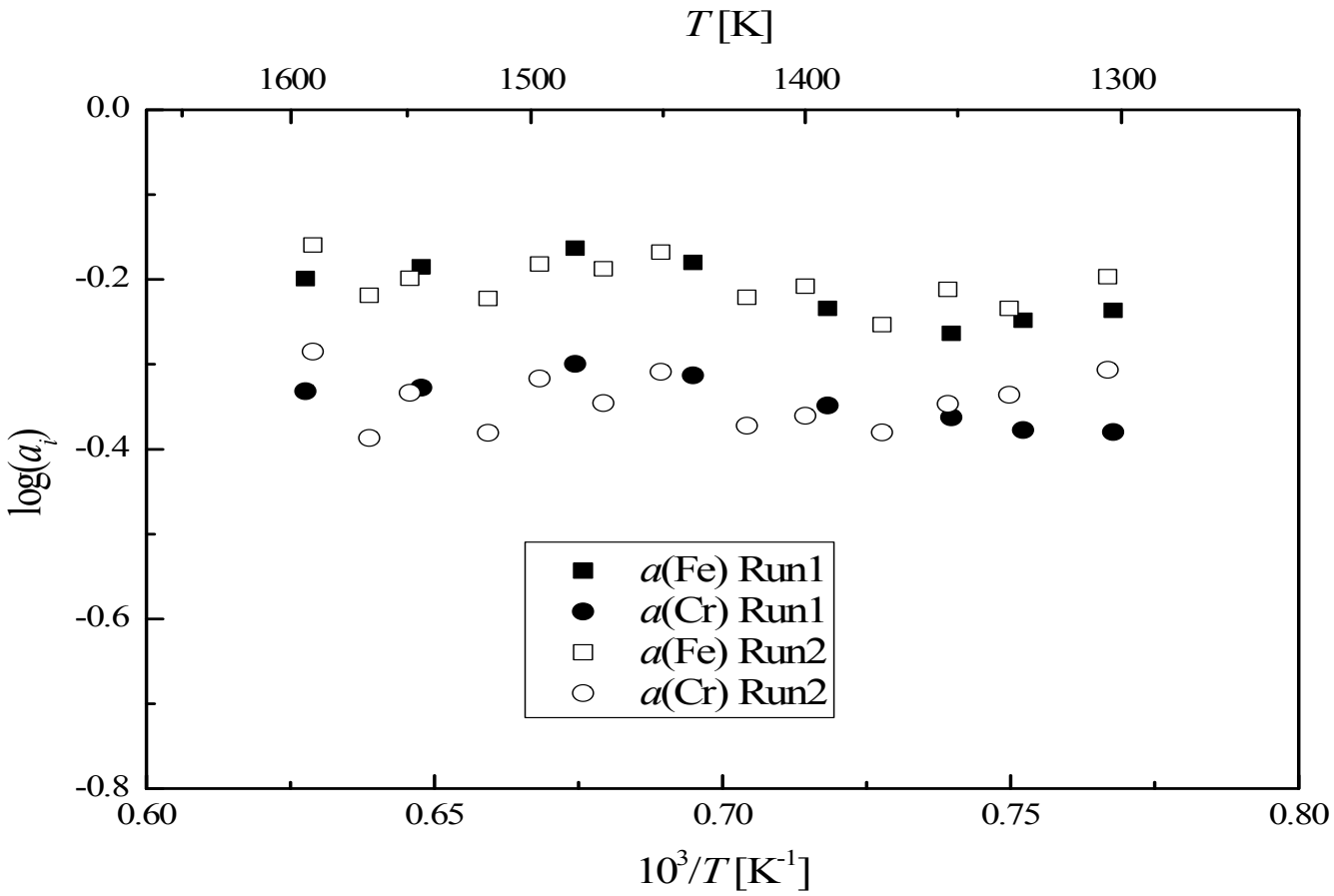
Phase Diagram Al-Cr-Fe (SGTE) with sample compositions



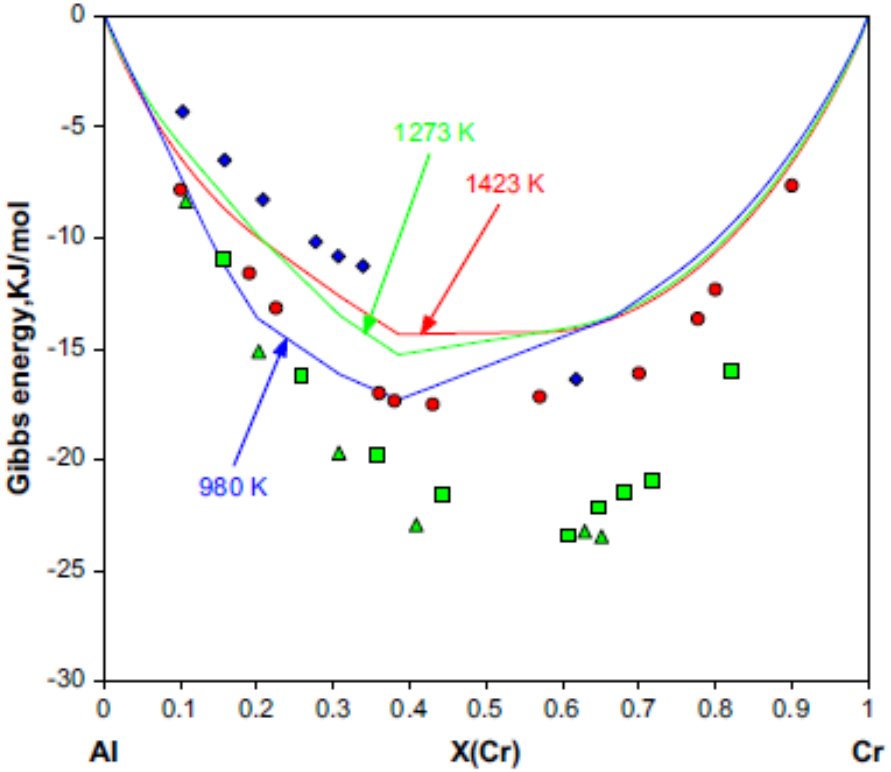
Activities of Al and Fe for two measured runs of the sample ($Al_{65.2}Fe_{34.8}$)



Activities of Cr and Fe for two measured runs of the sample ($Cr_{48}Fe_{52}$)

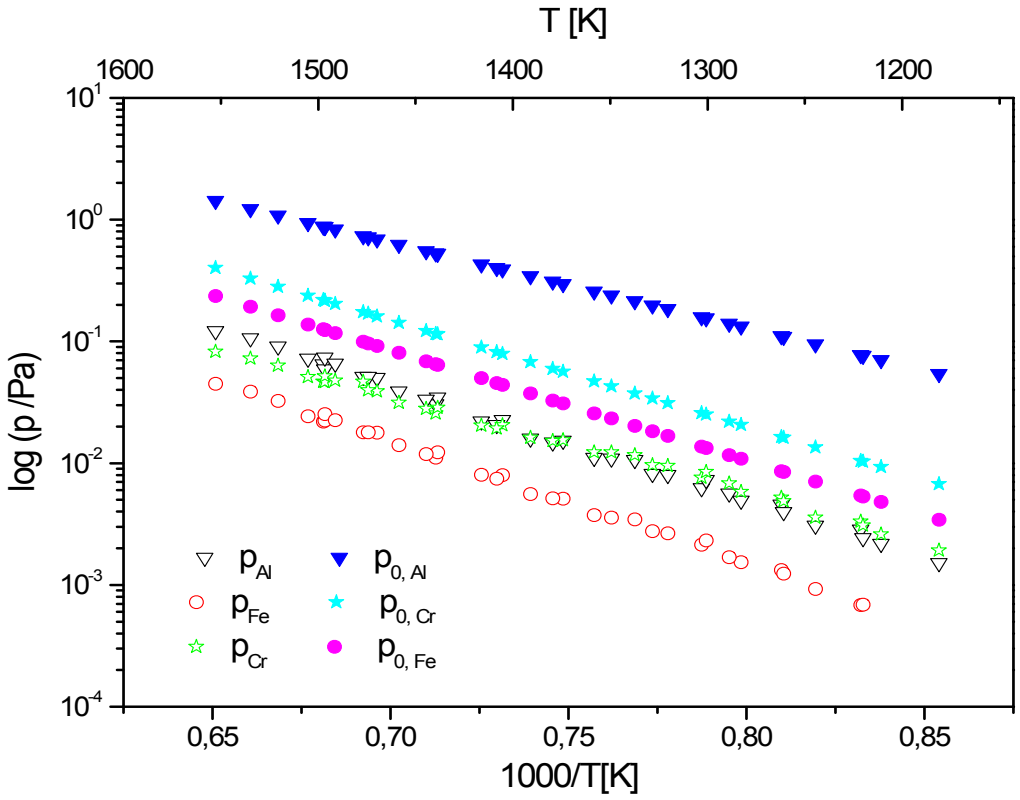


Calculated Gibbsenergy of bcc_A2 in Al-Cr. reference: Al(liquid) andCr(bcc_A2) @ 980K

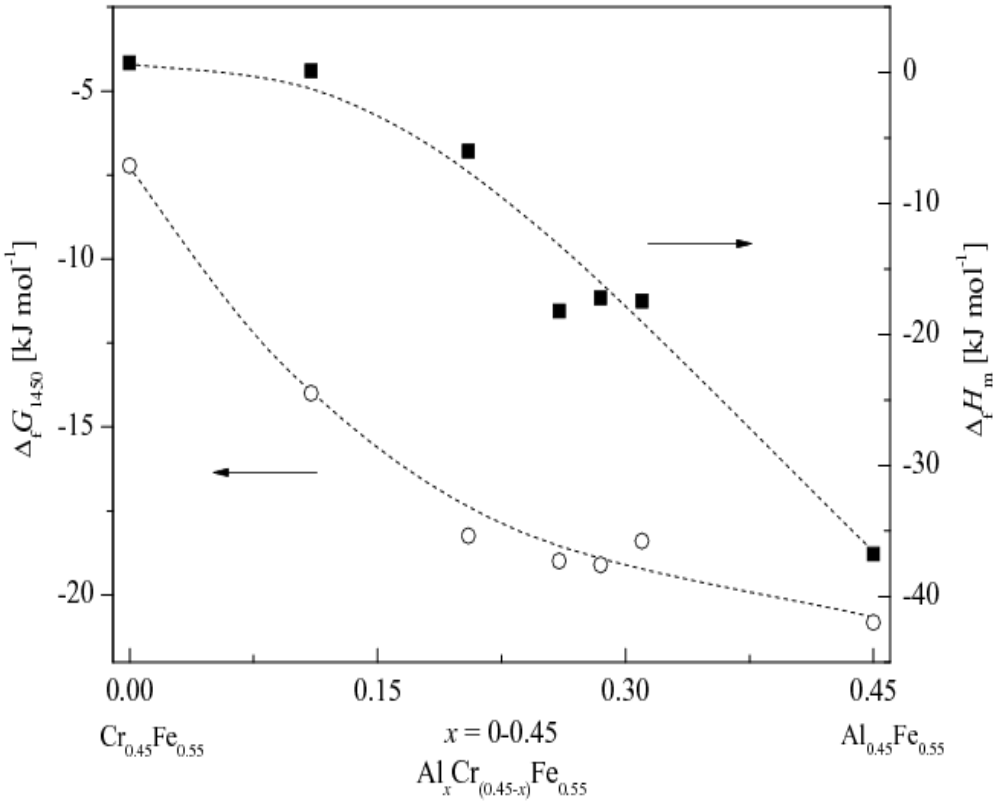


M. Jacobs, R. Schmid-Fetzer , T. Markus , V. Motalov , G. Borchardt , K.-H. Spitzer, Intermetallics 16 (2008) 995–1005

Partial pressures of Fe, Cr and Al over $Al_{24.5}$-Cr_{18}-$Fe_{57.5}$ compared with the partial pressures of the pure components



Mean integral molar enthalpies of formation as well as the mean integral Gibbs energies of formation as a function of composition, for section $Al_xCr_{(0.45-x)}Fe_{0.55}$ (x = 0 to 0.45)



Conclusions

•Thermodynamic activities of the components in the ternary Al-Cr-Fe alloys have been determined as primary data with high accuracy and precision. The reliability of the data is confirmed by their internal consistency on the one hand and by agreement with earlier published results on the binary systems on the other hand.

•The log (*a*) *vs* 1/*T* plots for Al, Cr, and Fe are substantially straight lines over the wide temperature ranges covered, which means that the partial and integral enthalpies and entropies of formation are nearly independent of temperature within this range.

•Reliable values have been obtained for the partial and integral enthalpies, entropies and Gibbs energies of formation. The integral molar enthalpy and Gibbs energy of formation for $Al_xCr_{(0.45-x)}Fe_{0.55}$ section (x = 0-0.45) depend on composition nonlinearly.

Acknowledgement

Institut für Angewandte Thermo- und Fluiddynamik

David Henriques
Jens Peter
Matthäus Wittek
Gert Thiel

Uzair Tahir
George Bourne
Jan Neunzling
Maximilian Länge

Tim Hartmann
Angela Hermann
Hans Giel
Christoph Huber

Gefördert durch:

Bundesministerium für Wirtschaft und Energie

aufgrund eines Beschlusses des Deutschen Bundestages

GHS VAKUUMTECHNIK GMBH

Supporting Partner:

PFEIFFER VACUUM

DFG Deutsche Forschungsgemeinschaft

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Thank you for your attention !!!