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JÜLICH FORSCHUNGSZENTRUM

Experimental Determination of Thermochemical Properties

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Outline

- KEMS (Knudsen Effusion Mass Specktrometry)
  - Introduction and Example
- DTA (Differential Thermo Analysis)
  - Phase Diagram Determination
- DSC (Differential Scanning Calorimetry
- Modelling (Determination of Interaction Parameters)

KEMS – Introduction
(Knudsen Effusion MassSpectrometry)

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

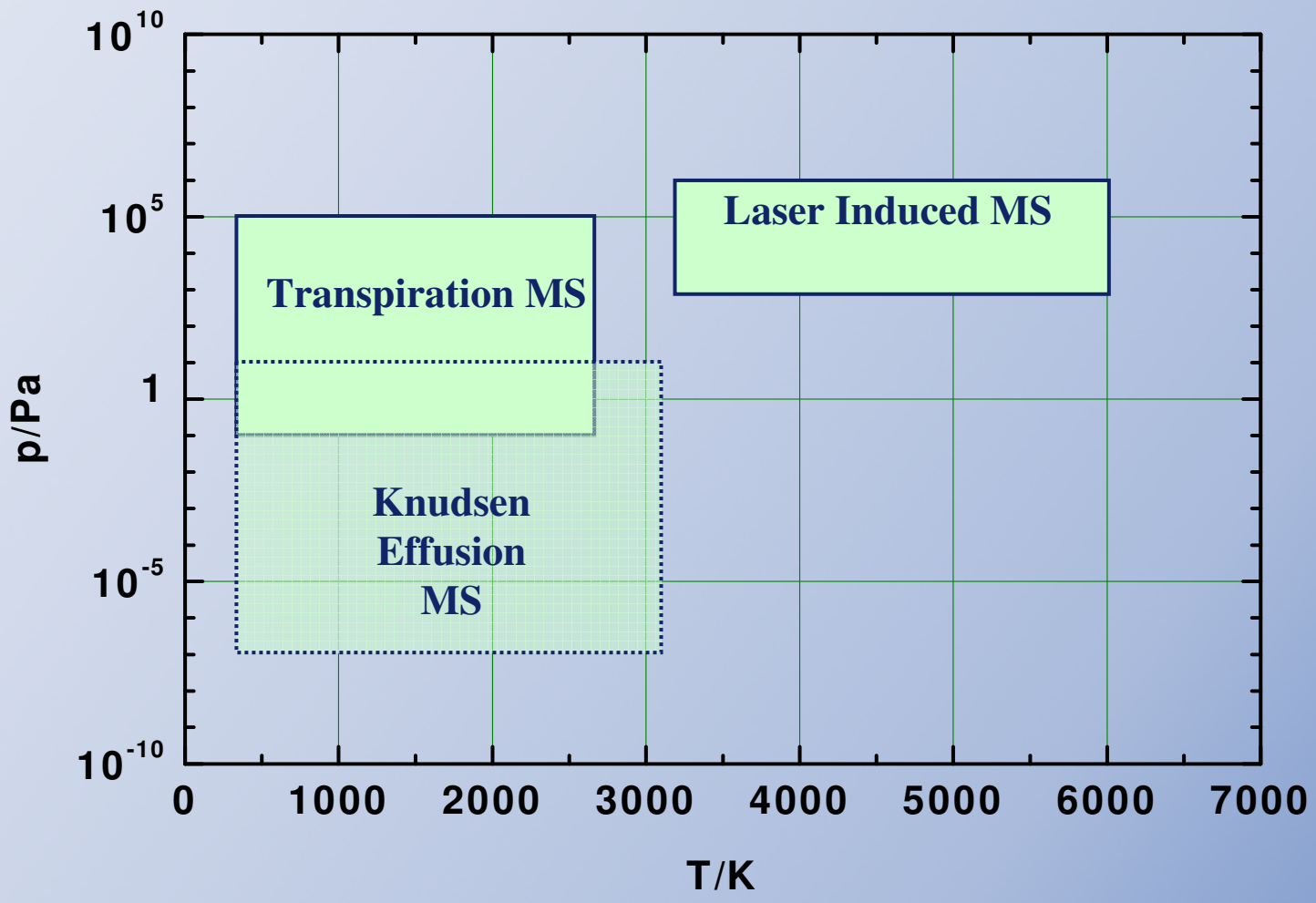
The *High Temperature Mass Spectrometry* is the most imortant method for the analysis of vapors over condensed phases

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

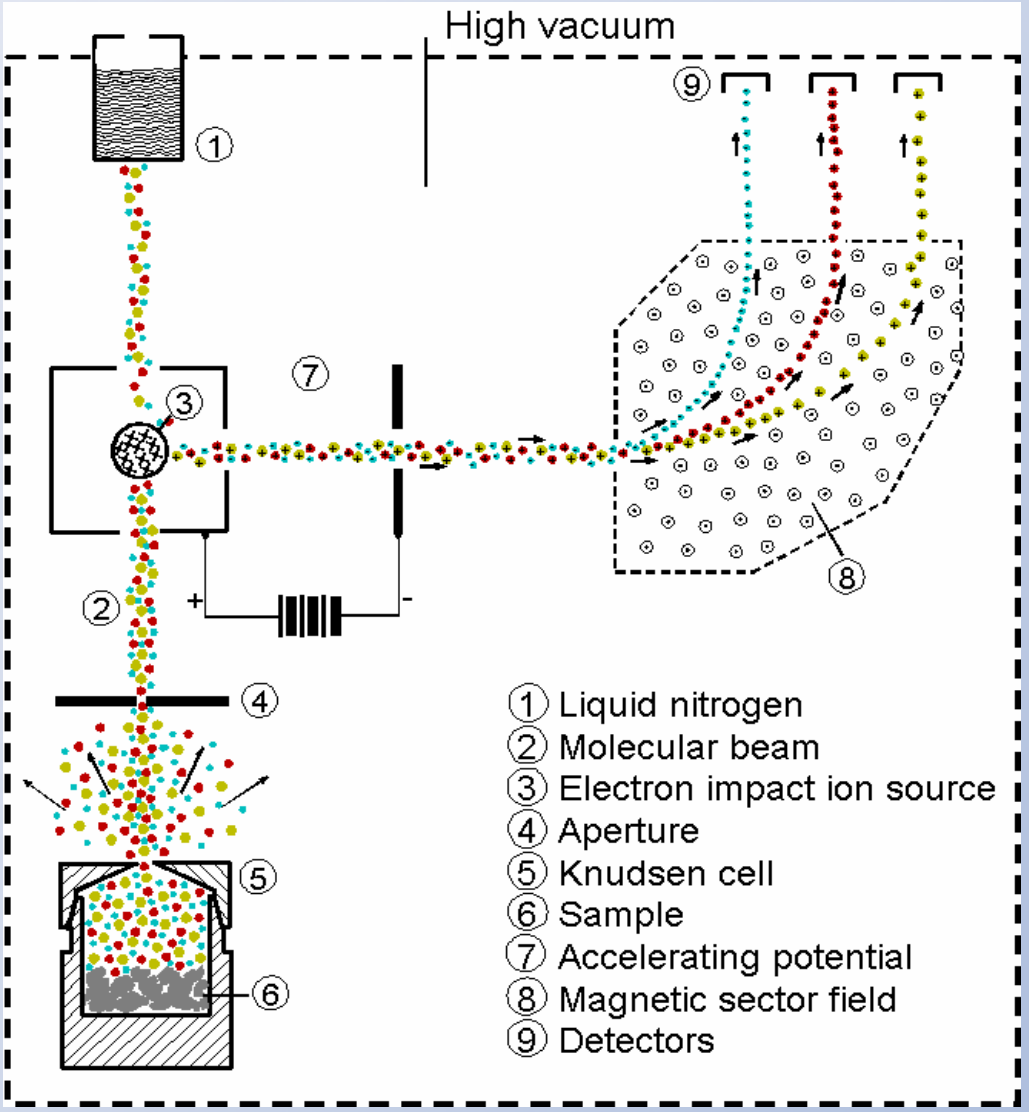
A special variant of this technique which is frequently used in inorganic gas phase chemistry, is the

Knudsen Effusion Masss Spectrometry (KEMS)

Temperatures and pressure ranges for KEMS, TMS, LVMS

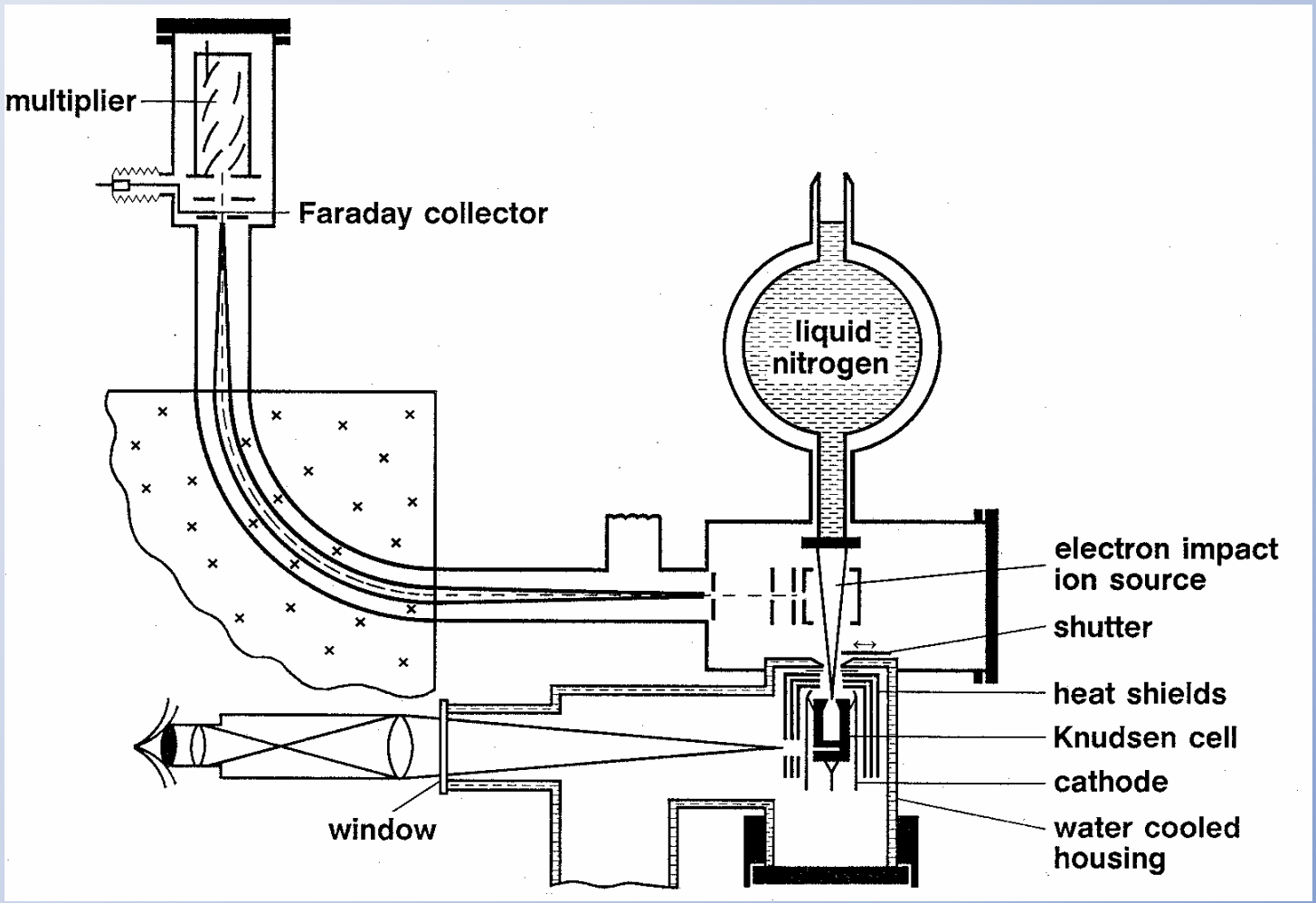


Principle of Knudsen Effusion Mass Spectrometry (KEMS)

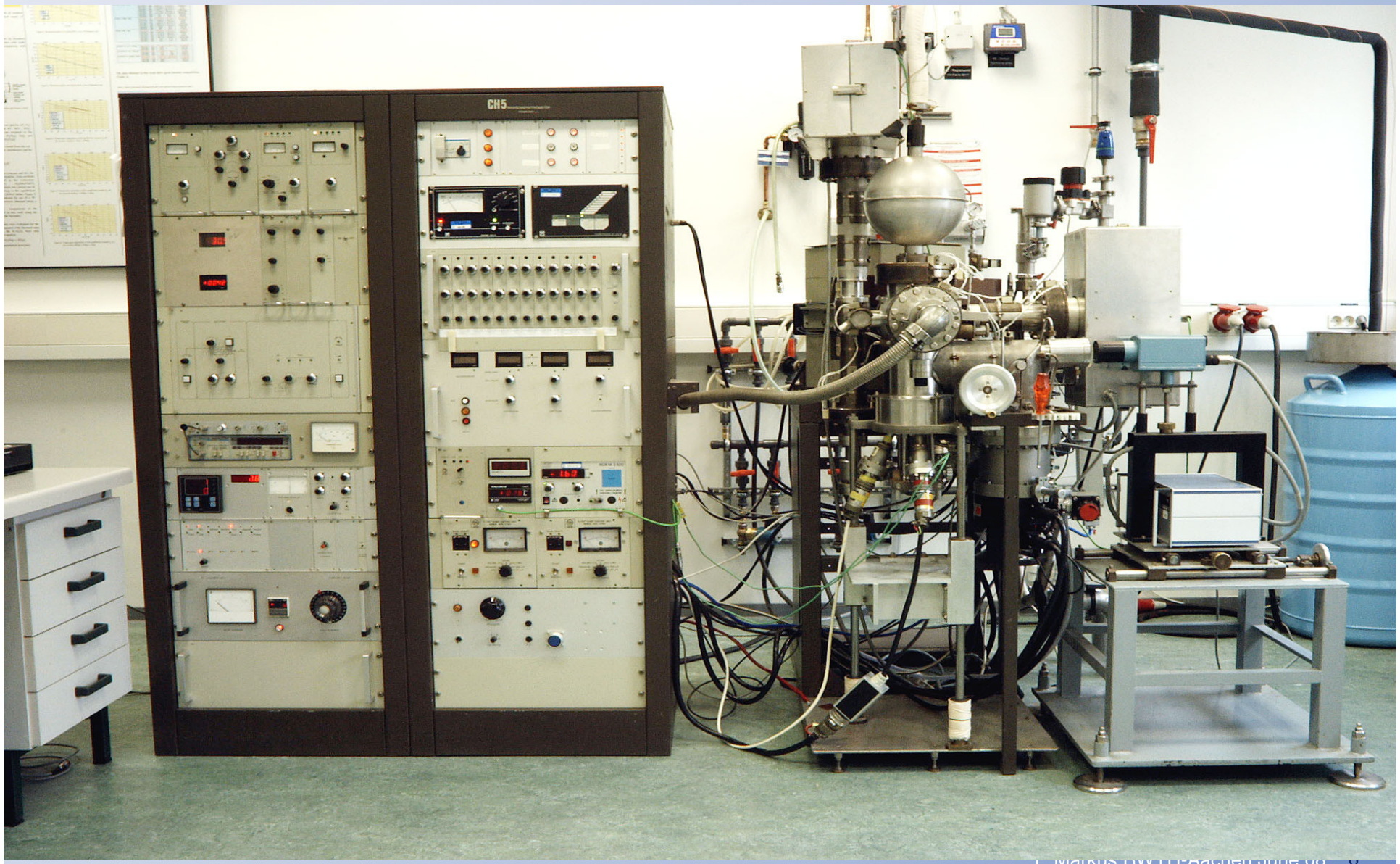


- Vaporisation studies up to 2800 K
- Identification of gaseous species
- Determination of partial pressures (10^{-8} ... 10 Pa)
- Evaluation of thermodynamic data of
  - gaseous species
  - condensed phases
- Elucidation of corrosion processes

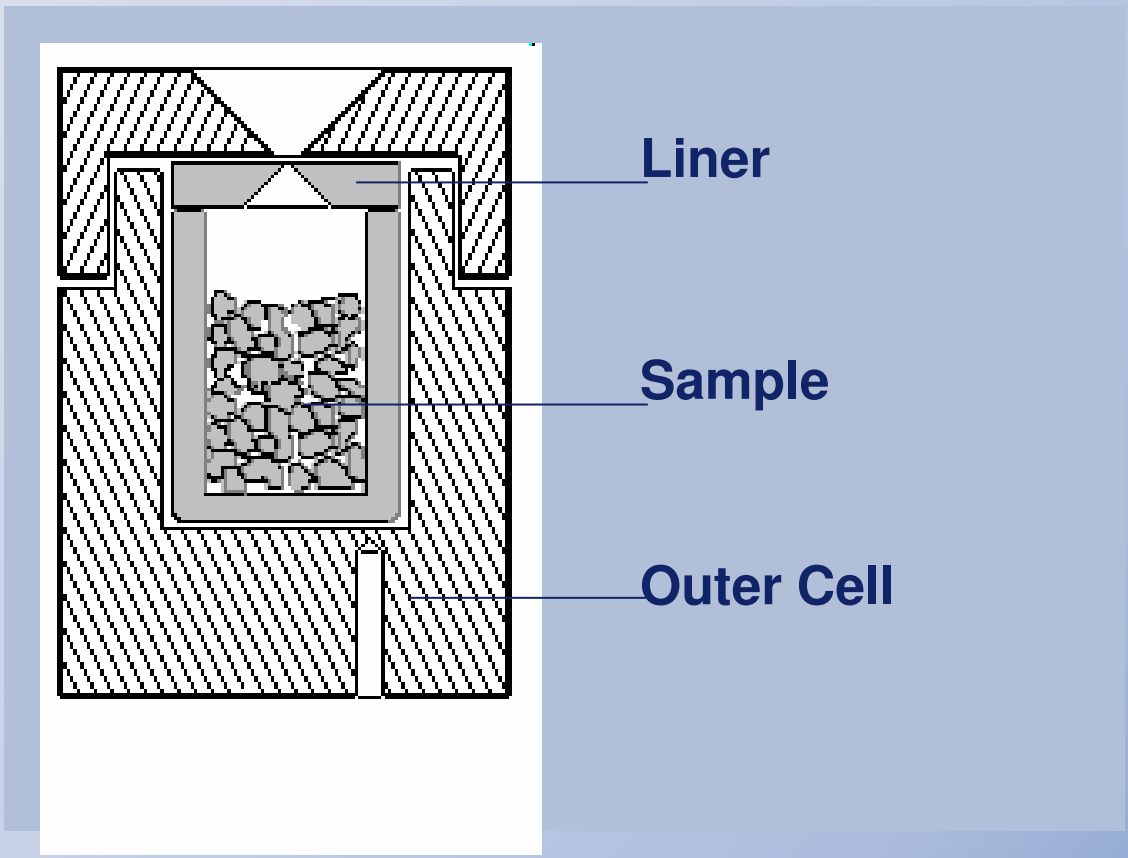
Schematic Representation of a Knudsen cell magnetic field mass spectrometer system



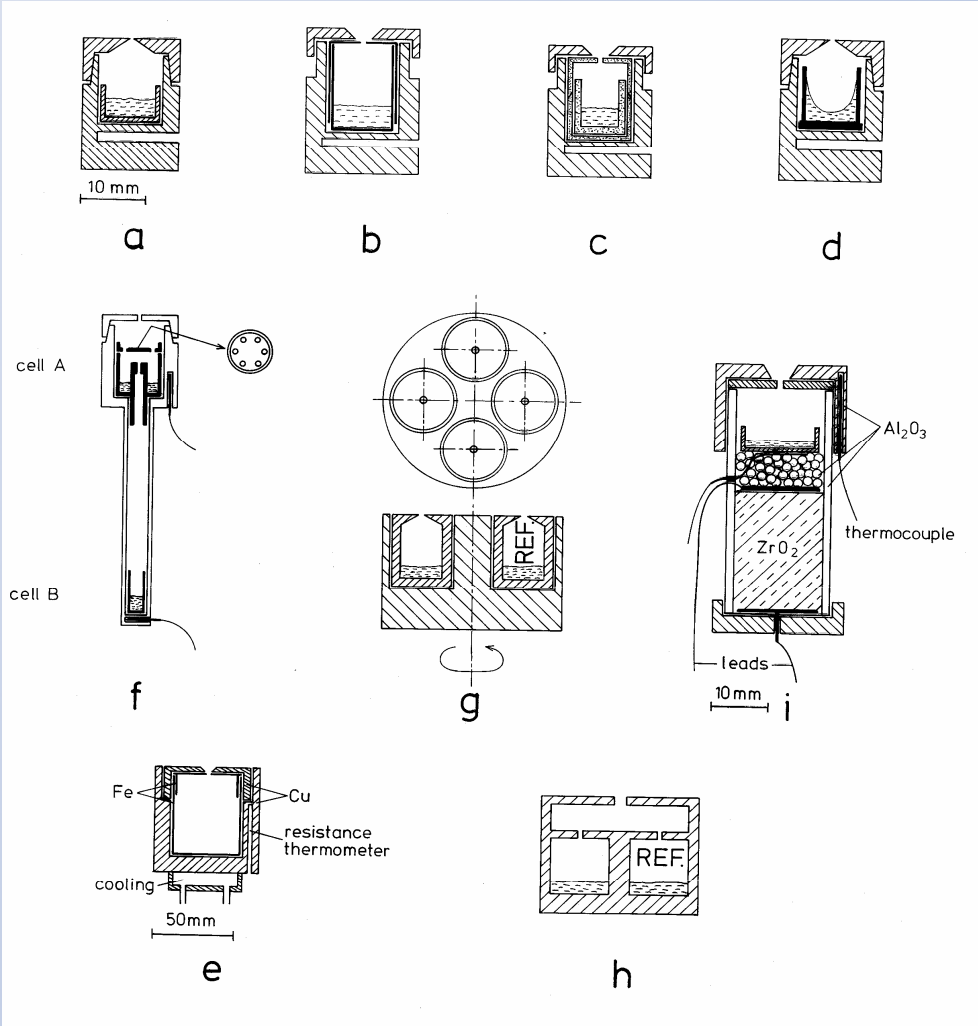
Mass Spectrometer Knudsen Cell System (CH 5)



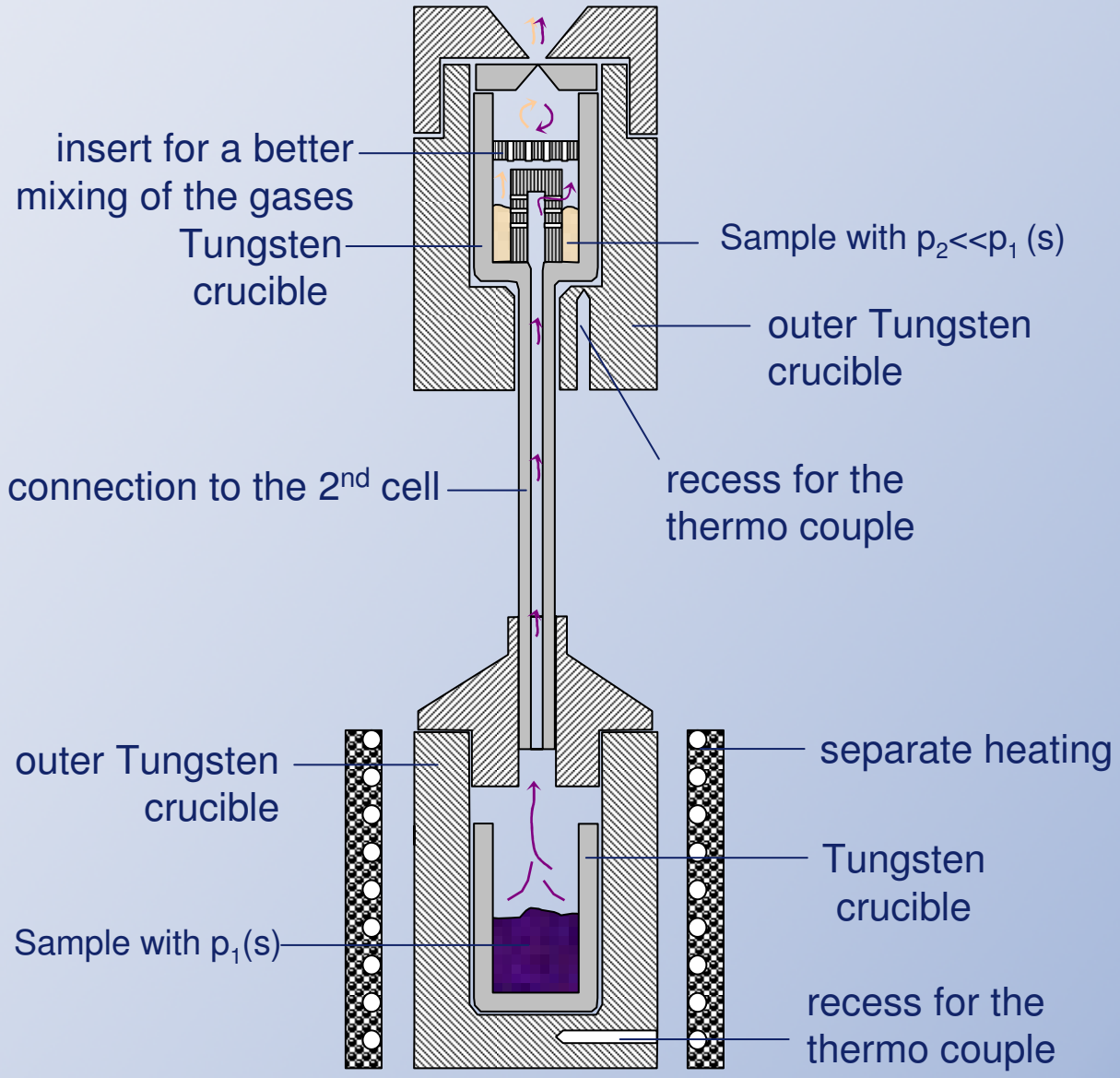
One Compartment Knudsen Cell

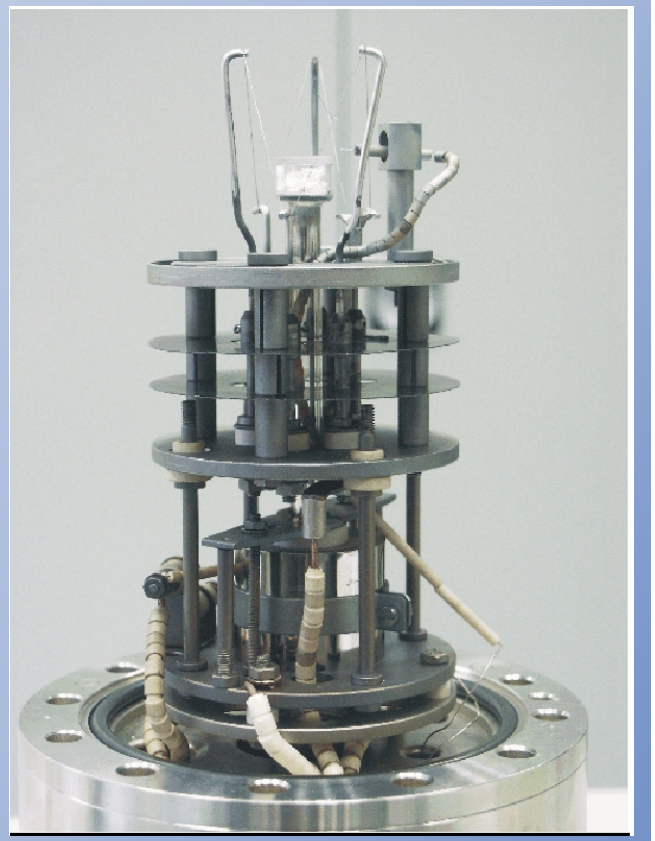


Different types of Knudsen Cells

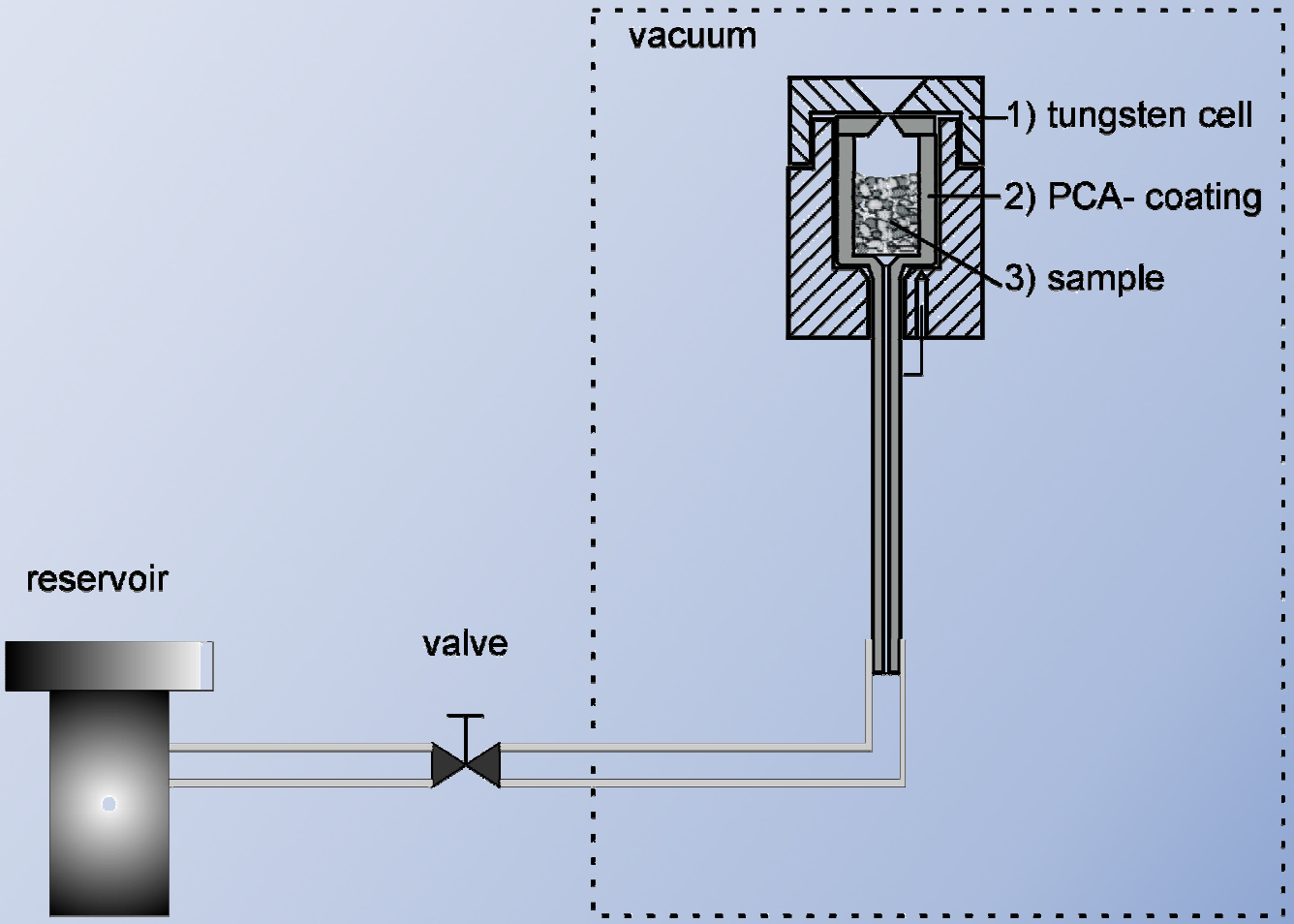


Functional principle of the two compartment Knudsen cell





Schematic representation of a Gas Inlet System



Determination of Thermodynamic Data
Example: ΔH; ΔS of DyI_3

1st step:

identification of species present in the mass spectrum

and

Assignment of fragments to their neutral precursor
=> fragmentation coefficients

Identification of Gaseous Species
Assignment of Fragments to their neutral precursor

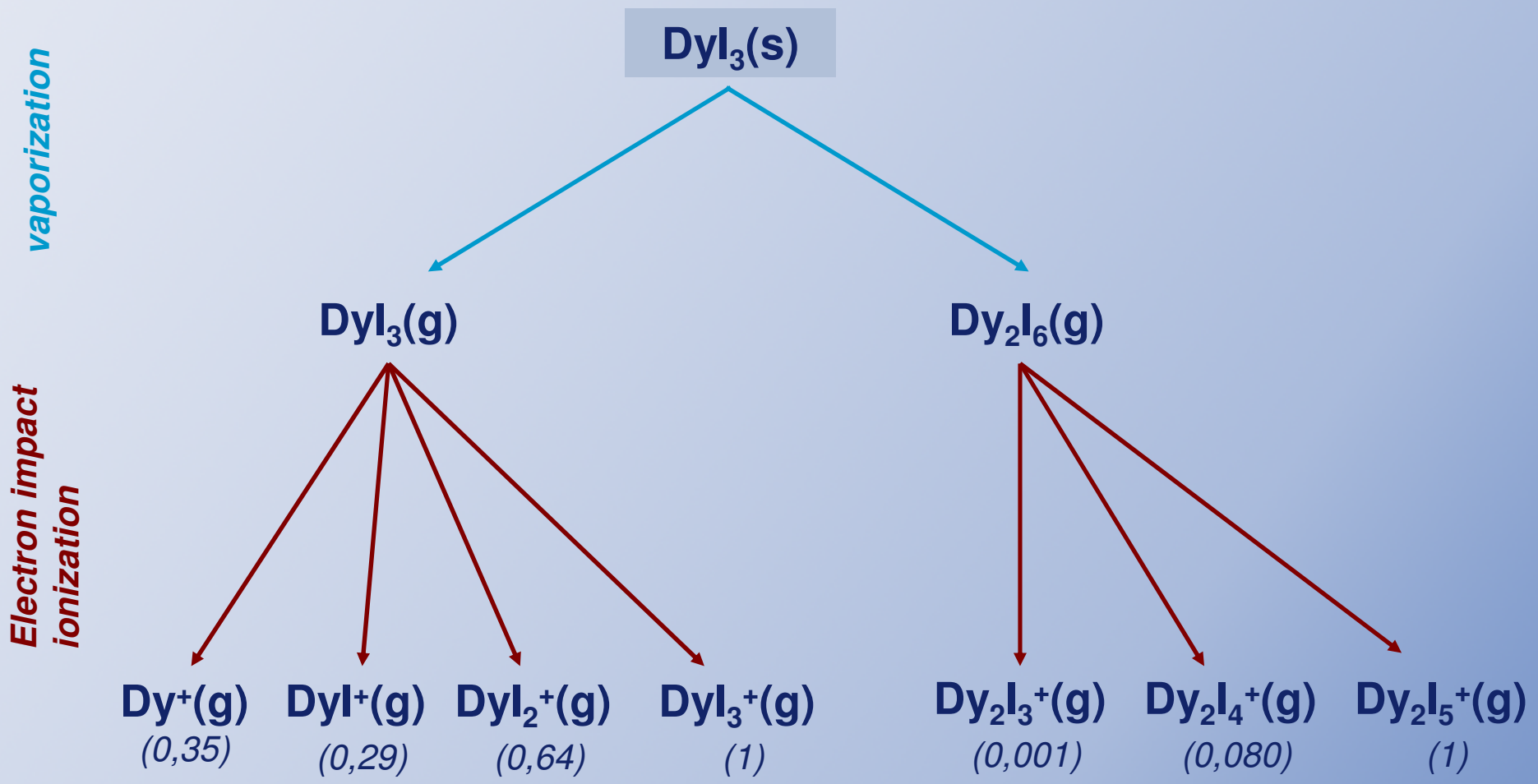
The temperature dependence of the ion intensities of the same neutral molecule generally show the same behaviour.

The appearance potential of the molecular ions formed by simple ionisation are generally smaller than those of fragments which come from the same neutral precursor. The appearance potential increase with increasing degree of fragmentation.

Fragmentation of a molecule is often indicated by the shape of the ionisation efficiency curve of the simple ionised ion

In comparison to molecular ions formed by simple ionisation the fragment ions have an additional kinetic energy contribution

Fragmentation



(fragmentation coefficient)

Determination of Thermodynamic Data
Example: ΔH^F of DyI_3

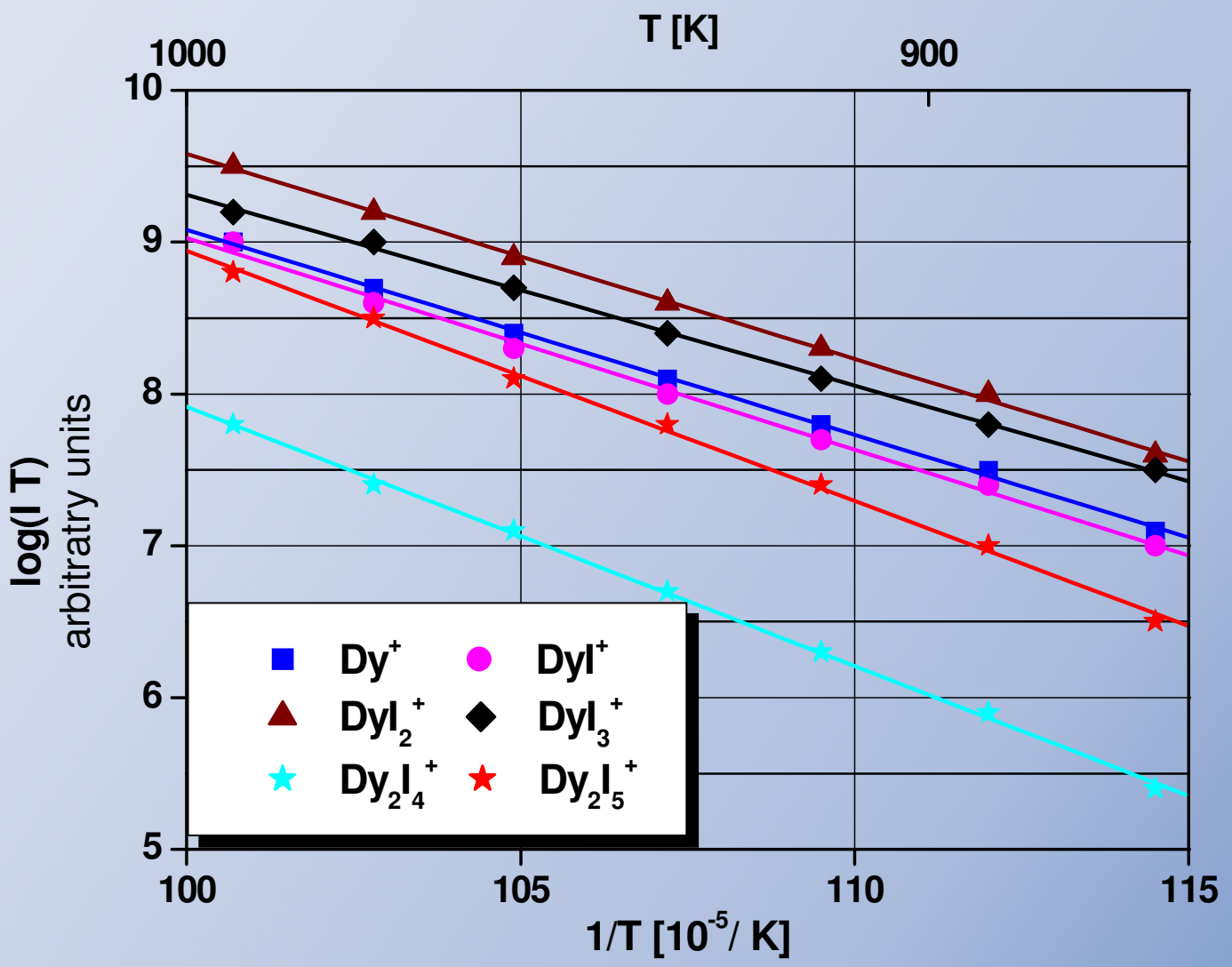
2nd step:

Measurement of the temperature dependence of ion intensities

and

Determination of partial pressures

Temperature Dependence of Ion Intensities for the Equilibrium Vaporization of $DyI_3(s)$



Experimental Determination of Partial Pressures p_i of Neutral Species i

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

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**
σ_i	**ionisation cross section of the neutral species i**
k	**pressure calibration constant**

Different Calibration Methods

1 vaporisation of a substance with a known vapor pressure

$$k = \gamma_i \sigma_i \frac{A_i}{100} \frac{p_i}{I_i^+ T}$$

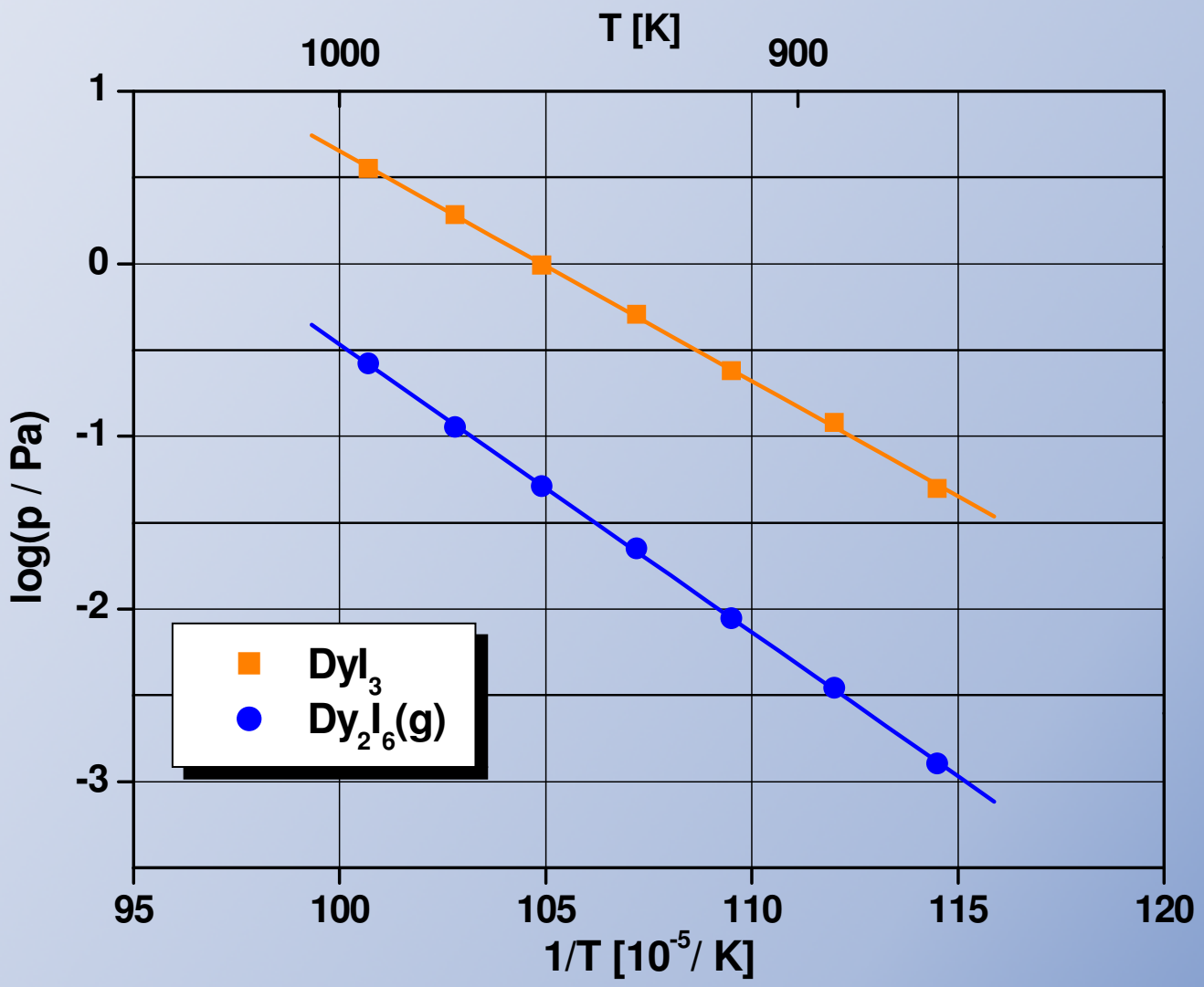
2 pressure dependent reaction taking place $X_2(g) \leftrightarrow 2X(g)$ $\quad K_p = \frac{p_X^2}{p_{X_2}}$

$$k = \frac{\sigma_X^2}{\sigma_{X_2}} \frac{I_{X_2}}{I_X^2} \frac{1}{T} k_p$$

3 calibration by using the mass loss

$$k = \frac{\sigma(i)}{I(i)T} \frac{1}{q \cdot c} \sqrt{\frac{2\pi RT}{M_i}} \frac{dm_i}{dt}$$

Temperature Dependence of the Partial Pressures for the Equilibrium Vaporization of $DyI_3(s)$



Determination of Thermodynamic Data Example: ΔH^F of DyI_3

3rd step:

Determination of Thermodynamic Data

Equilibrium Constant

$$DyI_3(s) \Leftrightarrow DyI_3(g)$$

$$K_p^0 = \prod_j \left(\frac{p_j}{p^0}\right)^{\nu_i} = \frac{p_{DyI_3(g)} \cdot p^0}{p^0 \cdot p_{DyI_3(s)}} = \frac{p_{DyI_3(g)}}{p^0}$$

with

$$p_{DyI_3(s)} = p^0$$

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

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

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

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

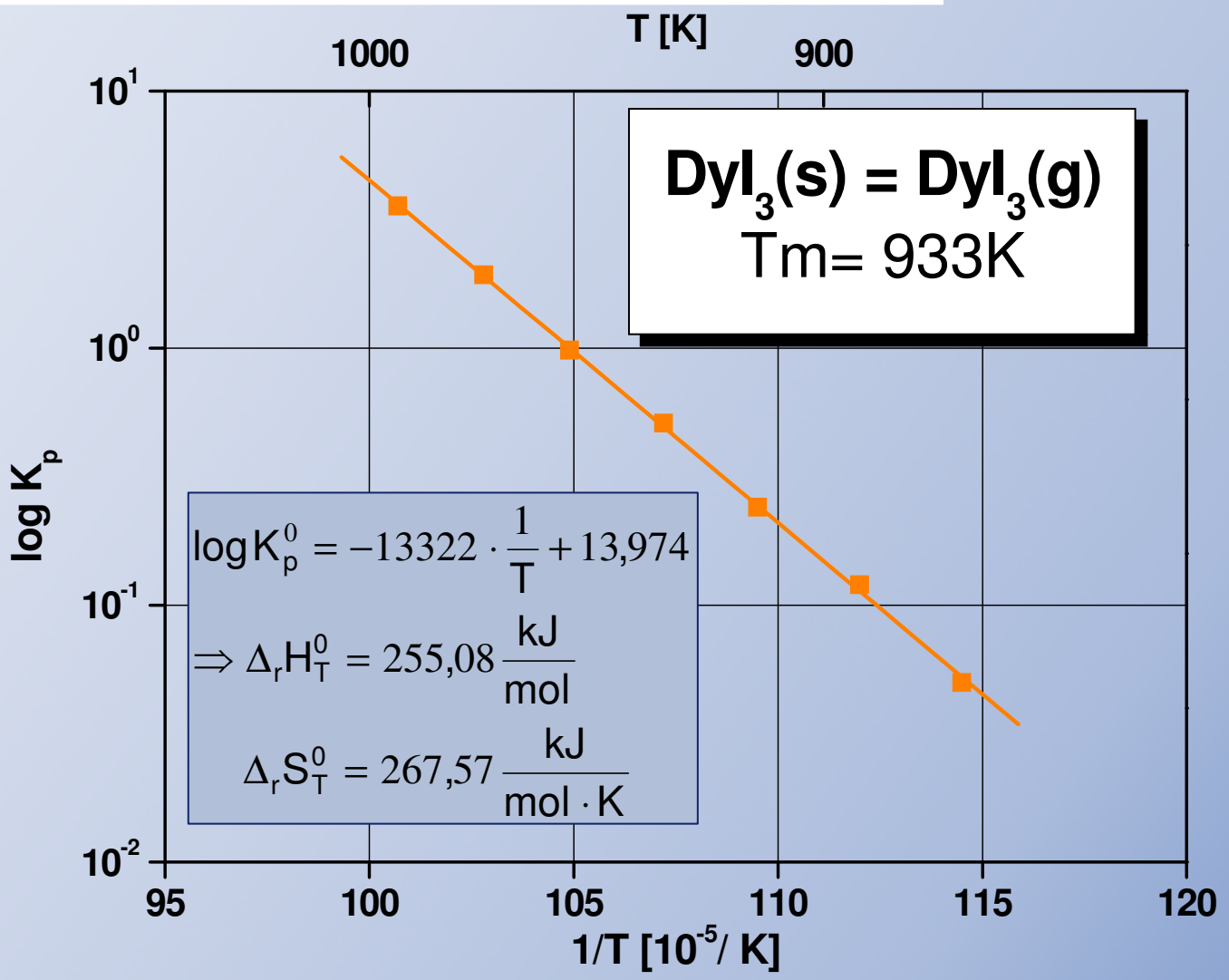
Determination of thermodynamic properties
2nd law method

$$\Delta_r G_T^0 = -RT \ln K_p^0 \qquad \Delta_r G_T^0 = \Delta_r H_T^0 - T\Delta_r S_T^0$$

$$\Rightarrow \quad \ln K_p^0 = -\frac{\Delta_r H_T^0}{R} \cdot \frac{1}{T} + \frac{T\Delta_r S_T^0}{R}$$

$$= A \cdot \frac{1}{T} + B$$

Determination of ΔH and ΔS from Equilibrium Constant



Thermodynamic Data for the equilibrium vaporization of $DyI_3(s)$

	T_m	ΔH^0_{Tm}	ΔH^0_{298}	ΔH^0_{298}	ΔS^0_{298}	$k_p(T_m)$
	K	kJ mol^{-1}	kJ mol^{-1} 2nd law	kJ mol^{-1} 3rd law	kJ (kmol K)$^{-1}$	
I	920	260,5±2,7	279,4±2,8	278,0±0,9	201,9±3	$3{,}05 \cdot 10^{-6}$
II	920	325,6±4,4	352,9±4,3	356,5±1,0	250,7±5,24	$1{,}15 \cdot 10^{-7}$
II	920	-195,4±3,3	-205,4±3,3	-199,49±0,8	-153,0±3,0	$1{,}24 \cdot 10^{+4}$

I $DyI_3(s) \rightarrow DyI_3(g)$

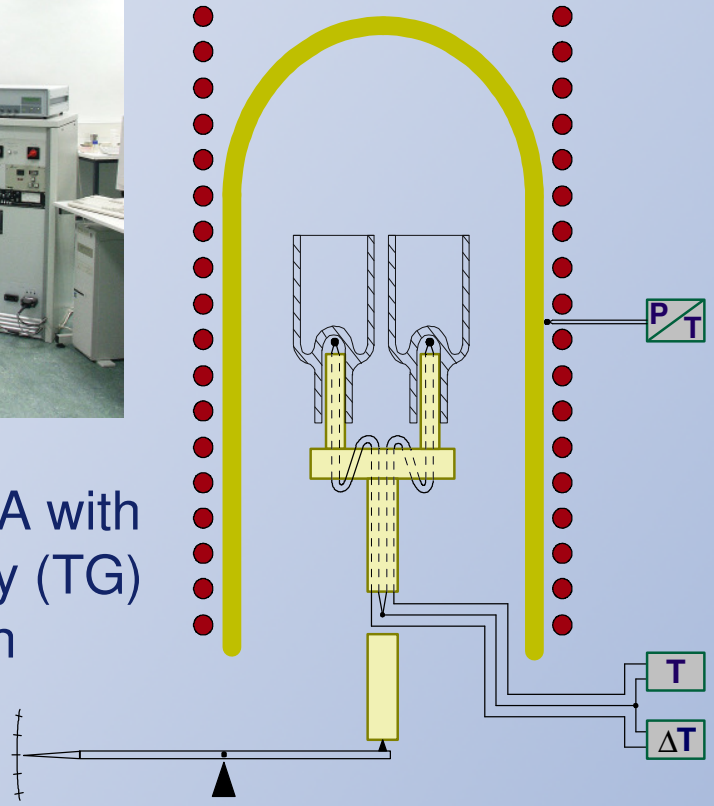
II $2DyI_3(s) \rightarrow Dy_2I_6(g)$

IV $2DyI_3(f) \rightarrow Dy_2I_6(g)$

Differential Thermal Analysis (DTA)

Simultaneous DTA with Thermogravimetry (TG)
STA 429, Netzsch

Principle of DTA



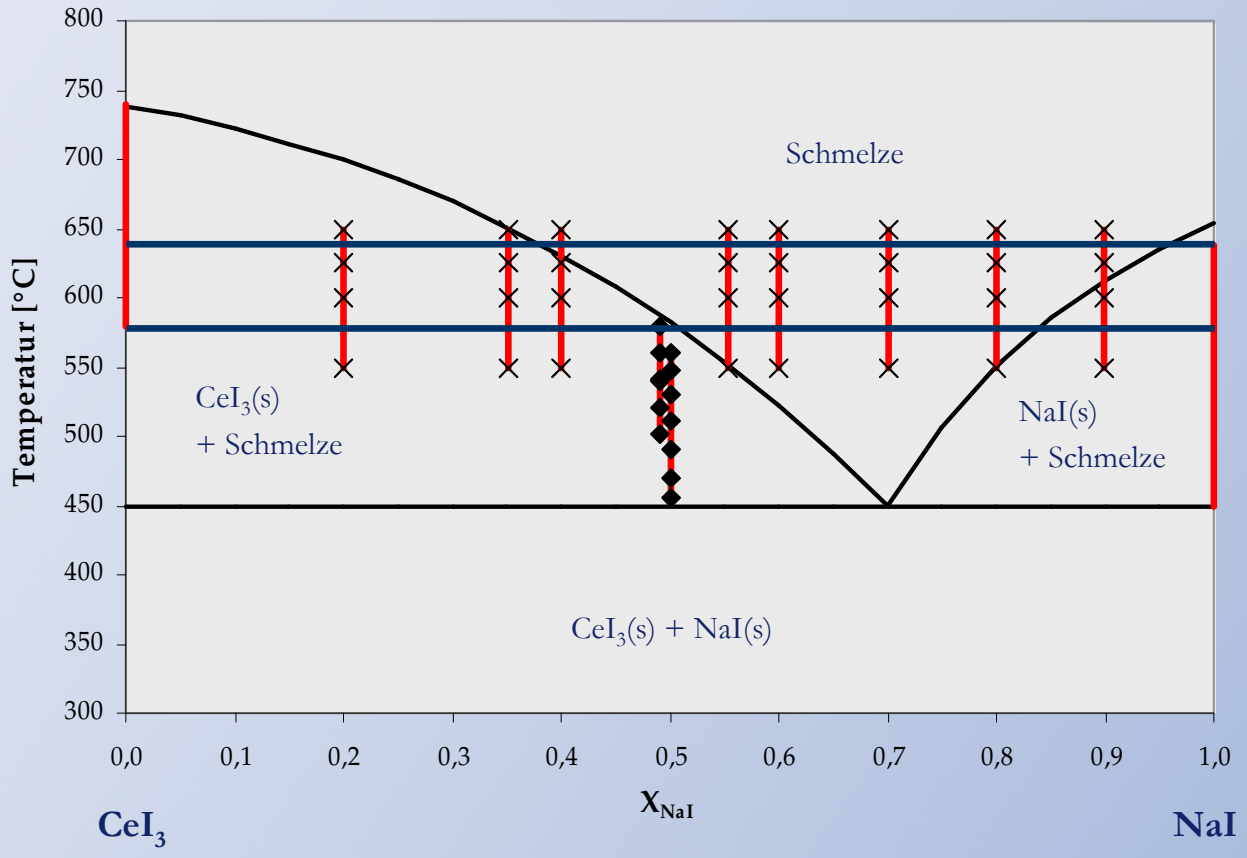
Measuring of Phase Transition Temperatures

Determination of the Quantity of Heat

Studies in different Atmospheres

Thermal Analysis from RT to 2800 K

Phase Diagram of NaI – CeI_3 determined by DTA and compositions and temperatures for KEMS measurements



Methoden:

1) $$a_i = \frac{p_{NaI}}{\overset{\circ}{p}_{NaI}} \qquad a_i = \frac{p_{CeI_3}}{\overset{\circ}{p}_{CeI_3}}$$

2) $$a(NaI) = \frac{[I^+(NaI)/I^+(NaI)_2]_{RS-NaI}}{[I^+(NaI)/I^+(NaI)_2]_{NaI/CeI_3}}$$

3) $$NaI(g) + CeI_3(s,l) \Leftrightarrow NaCeI_4(g)$$

$$a(CeI_3) = \left[\frac{I^+(NaI)}{I^+(NaCeI_4)}\right]_{ZPR} \cdot \frac{I^+(NaCeI_4)}{I^+(NaI)}$$

4) $$\ln a(CeI_3) = -\int_{x=0}^{1-x} \frac{x}{1-x}\, d\ln a(NaI)$$

Thermodynamic Properties of A and B in Mixtures {xA + (1-x)B}

Activities:

According to definition: $$a(i) = \frac{p(i)}{p^\circ(i)} = \frac{I(i^+)}{I^\circ(i^+)} \qquad (i = A, B)$$

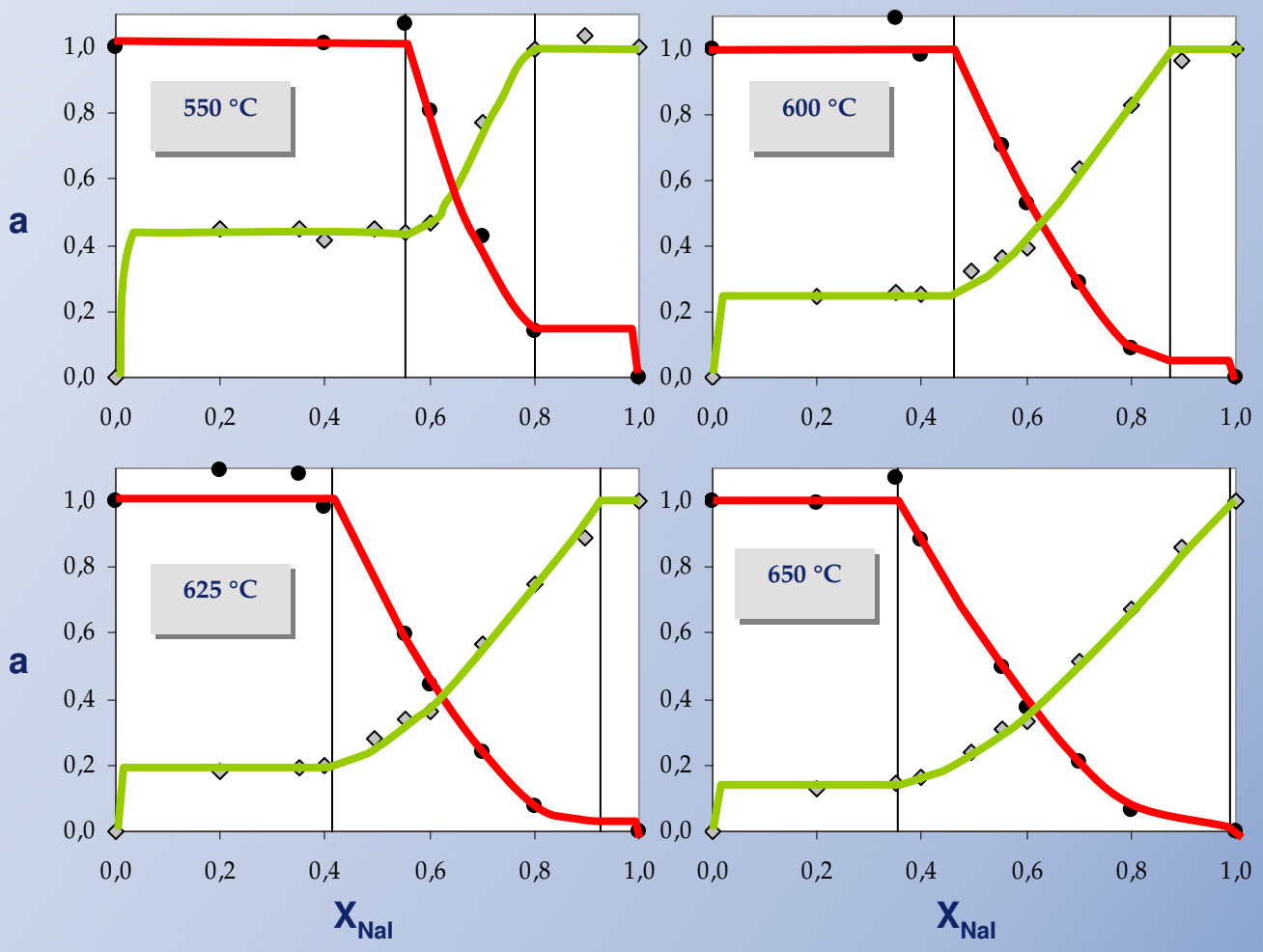
Ion Intensity Ratio integration Method (GD-IIR):

$$\ln f(A) = -\int_{x=1}^{x} (1-x)\ d\ln\left(\frac{x\ I(B^+)}{(1-x)\ I(A^+)}\right) \qquad a(A) = x\ f(A)$$

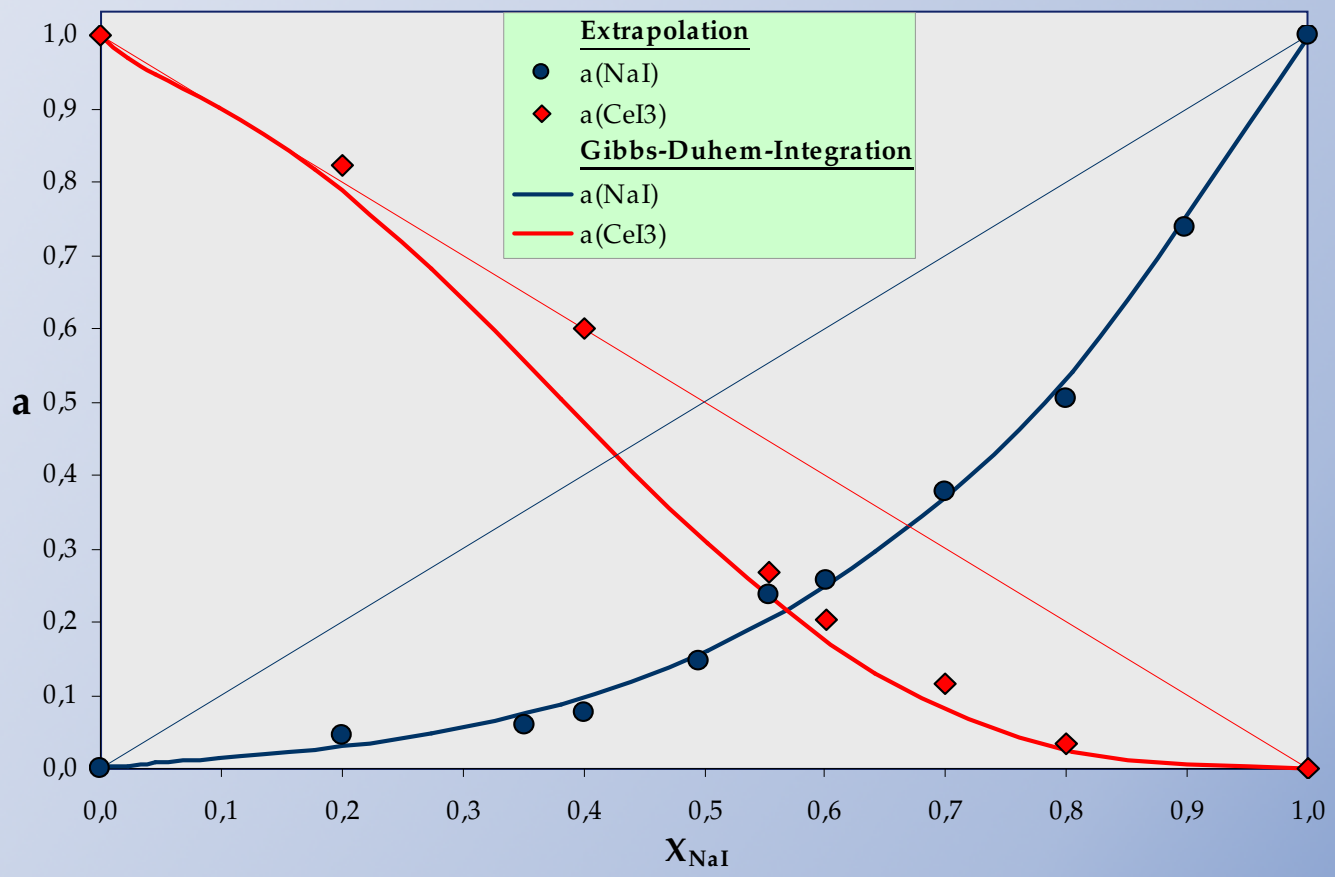
Enthalpies and Gibbs Energies:

$$\Delta_{mix} H(A) = R\ \frac{d\ \ln a(A)}{d(1/T)} \qquad G_m^E = RT\,[\,x_{MX_n} \ln \gamma_{MX_n} + (1 - x_{MX_n}) \ln \gamma_{M'X_m}\,]$$

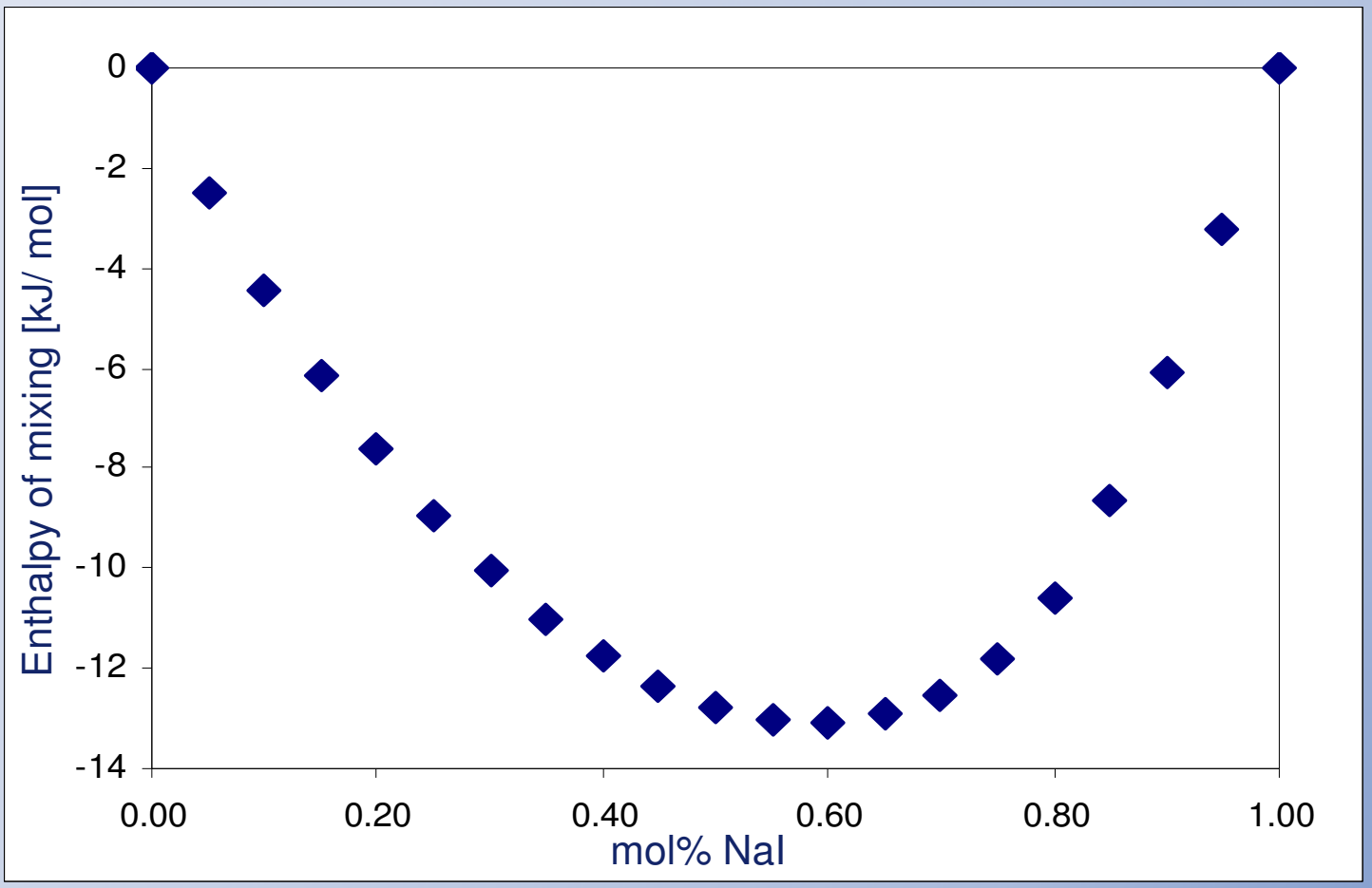
Temperature and Composition dependency of activity for the NaI – CeI$_3$ system



activities at 750 °C



Enthalpy of mixing for the NaI-CeI$_3$ System



Thermodynamic Modeling Procedure

$$G = \sum_i \mu_i \nu_i = \sum_i \left(\mu_i^0(T) + RT \ln \frac{\nu_i}{\nu_0} \right) \nu_i = \min.$$

solve this problem and find $\nu_1 \ldots \nu_N$

input data needed:

$$\mu_i^0(T) = \underbrace{G_i^{m,0}(T) - H_i^{m,0}(T_{ref})}_{\text{Gibbs free energy related to enthalpie @ reference temperature } T_{ref}=298K} + \underbrace{\Delta H_f^{m,0}(T_{ref})}_{\text{formation enthalpy @ reference temperature } T_{ref}=298K}$$

This thermodynamic input data is taken from

- KEMS experiments
- calculations using $c_p(T)$ functions
- literature tables

Introduction to the Data Optimization procedure

The *aim is* to generate a consistent set of Gibbs energy parameters from a given set of experimental data using known Gibbs energy data from well established phases of a particular chemical system.

Typical experimental data include:

- **phase diagram data: transitions temperatures and pressures as well as amount and composition of the phases at equilibrium**
- **calorimetric data: enthalpies of formation or phase transformation, enthalpies of mixing, heat contents and heat capacity measurements**
- **partial Gibbs energy data: activities from vapor pressure or EMF measurements**
- **volumetric data: dilatometry, density measurements.**

The assessor has to use his best judgement on which of the known parameters should remain fixed, which set of parameters need refinement in the optimization and which new parameters have to be introduced, especially when assessing data for non-ideal solutions.

Overview of the data to be optimized in the NaI-CeI$_3$ system

Various experimental data on the binary NaI-CeI$_3$ system have been measured:

- phase diagram data (liquidus points, eutectic points)
- liquid-liquid enthalpy of mixing
- activity of NaI(liq) at different temperatures

OptiSage will be used to optimize the parameters for the liquid Gibbs energy model (XS terms). All other data ($G°$ of the pure stoichiometric solids, as well as the pure liquid components) will be taken from the FACT database (i.e. remain fixed).
A polynomial model for the Gibbs energy of the liquid will be used:
$G = (X_1 G°_1 + X_2 G°_2) + RT(X_1 \ln X_1 + X_2 \ln X_2) + G^E$

where $G^E = \Delta H - TS^E$

Using the binary excess terms:

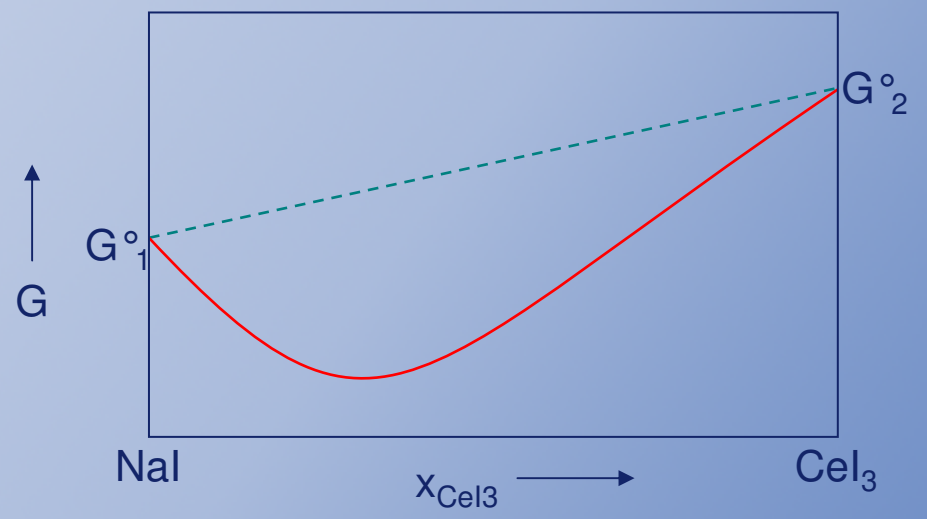
$\Delta H = X_1X_2 (A_1) + X_1^2X_2 (B_1)$

$S^E = X_1X_2 (A_3) + X_1^2X_2 (B_3)$

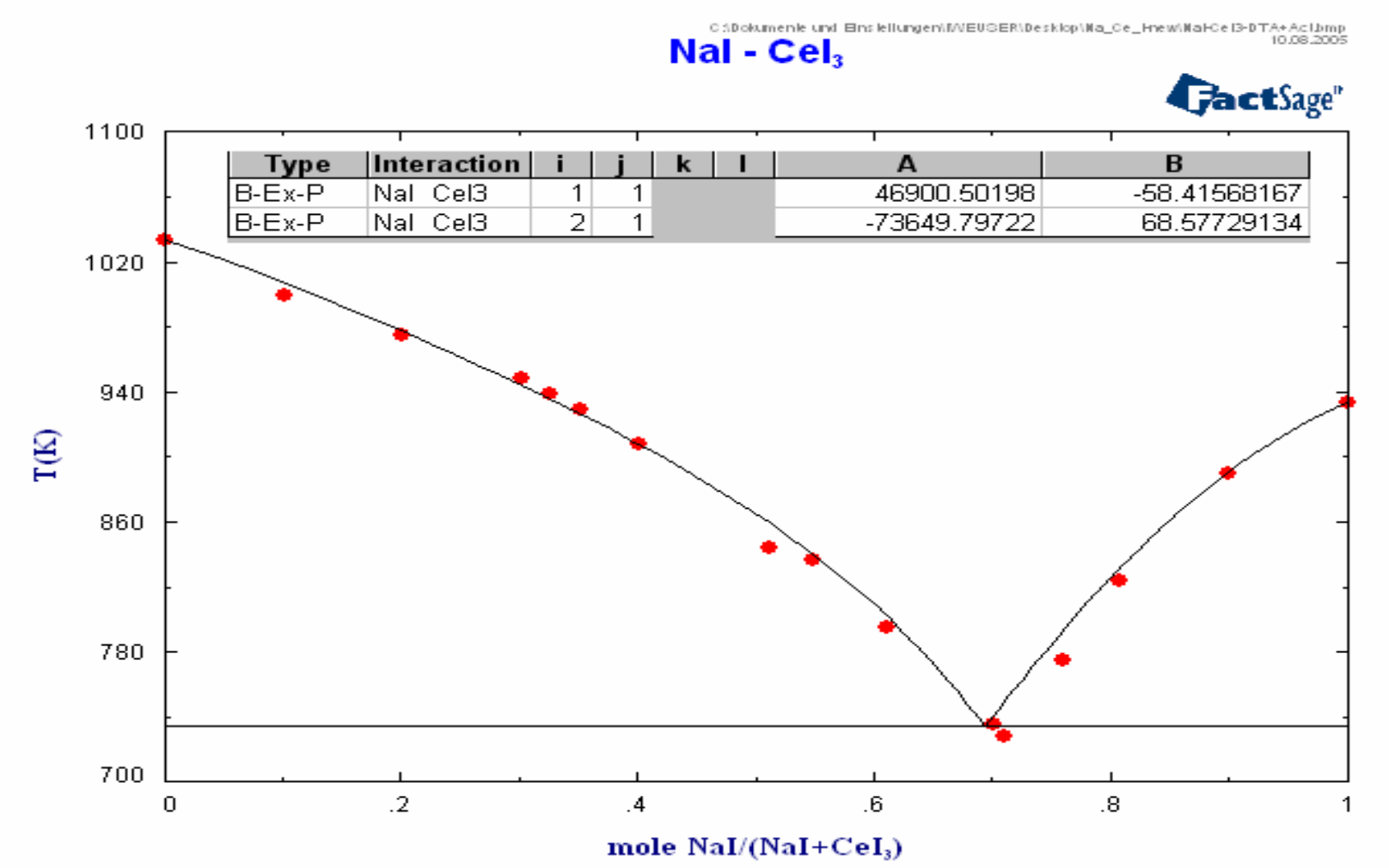
Hence:

$G^E = X_1X_2 (A_1 - A_3T) + X_1^2X_2 (B_1 - B_3T)$

Where A_1, A_3, B_1 and B_3 are the 4 parameters to be optimized.



Phase Diagram of the System NaI (calculated)



Type	Interaction	i	j	k	l	A	B
B-Ex-P	NaI CeI3	1	1			46900.50198	-58.41568167
B-Ex-P	NaI CeI3	2	1			-73649.79722	68.57729134

Binary Excess Polynomial:

$$G_m^E=(x_{NaI}^i)(x_{CeI3}^j)(A + B*T + C*T*\ln(T) + D*T^2 + E*T^3 + F*T^{-1})$$

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