Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft

Thermodynamic Data for Modeling of LTE Plasmas

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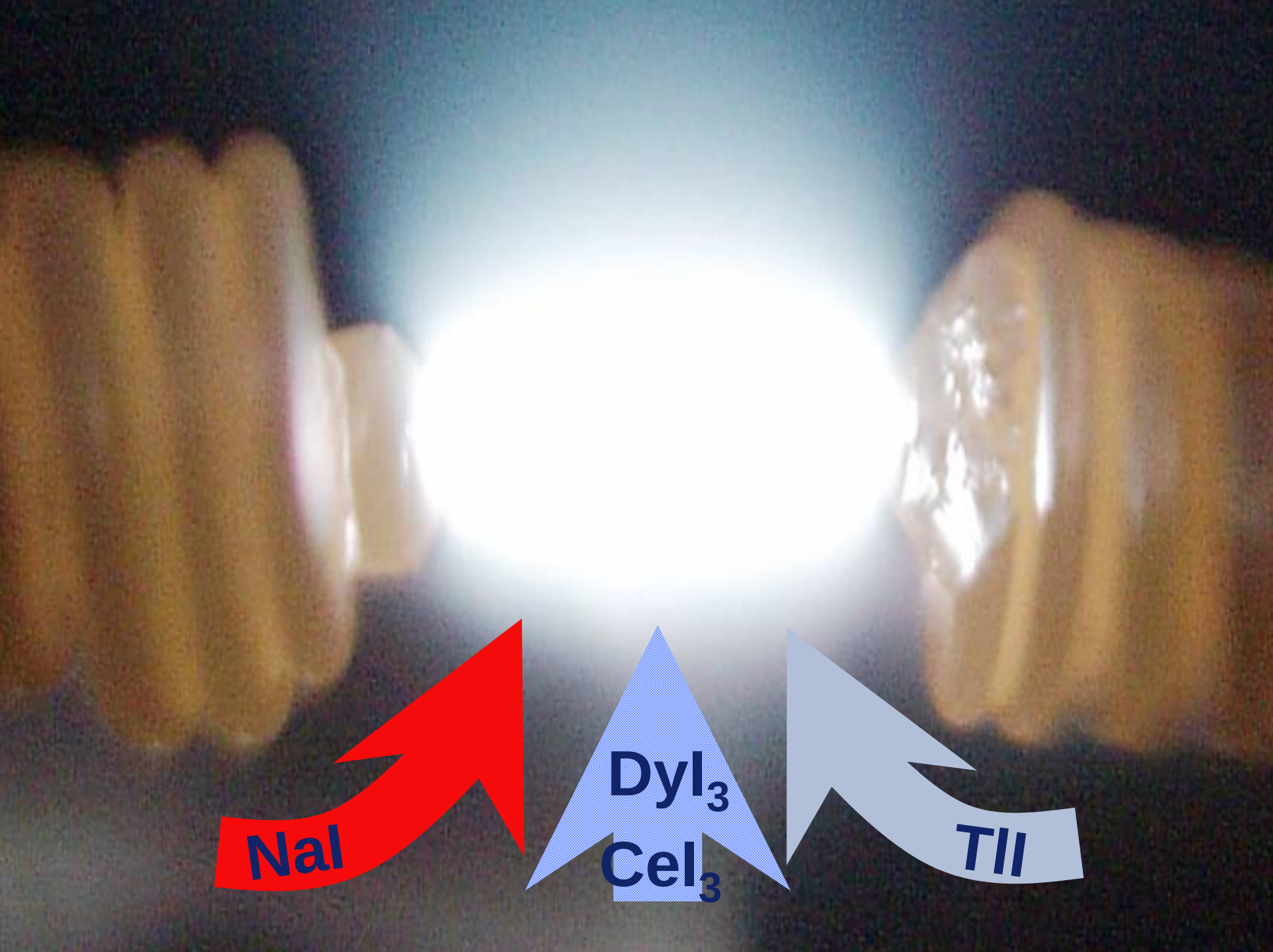
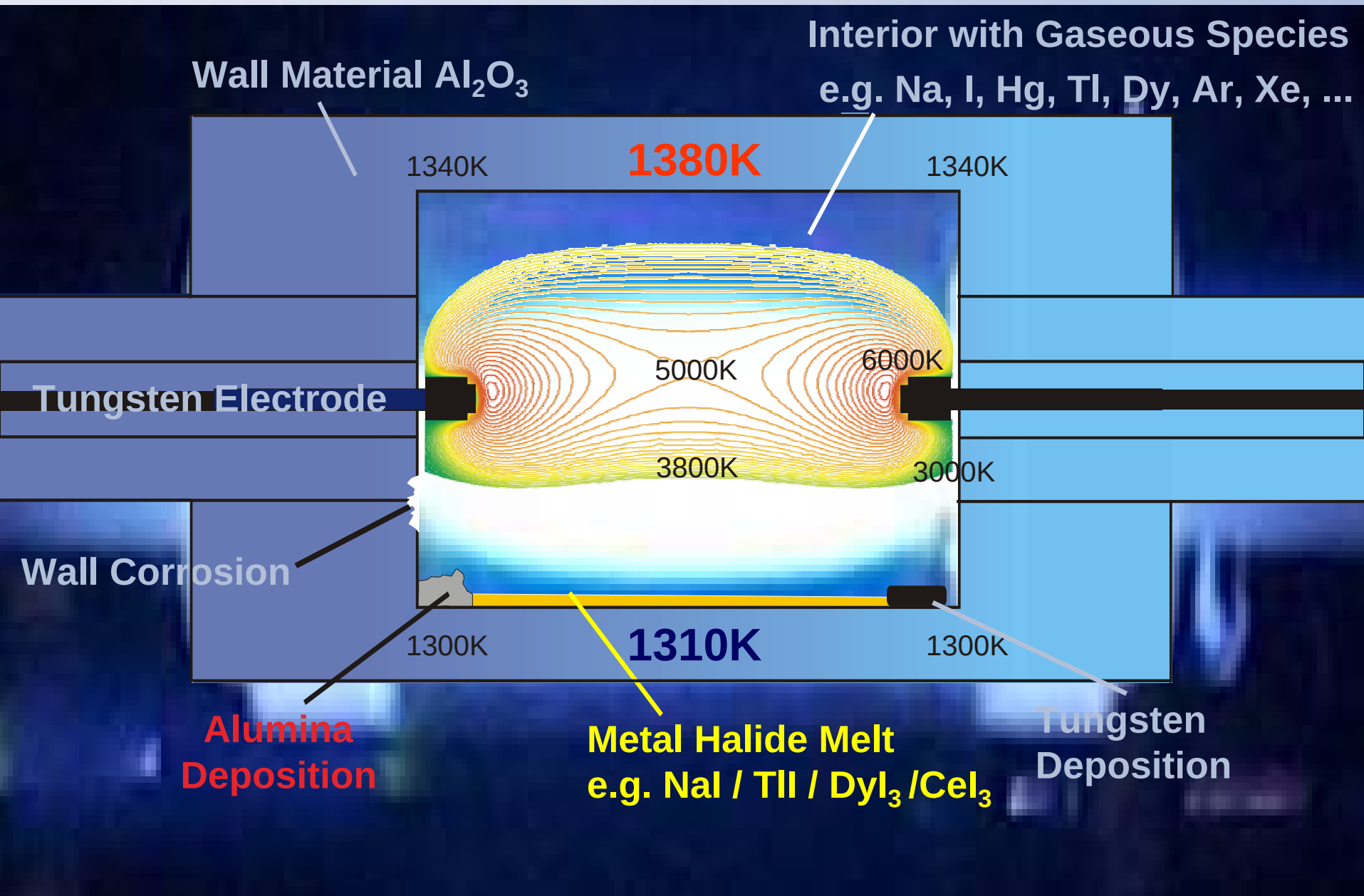
Outline

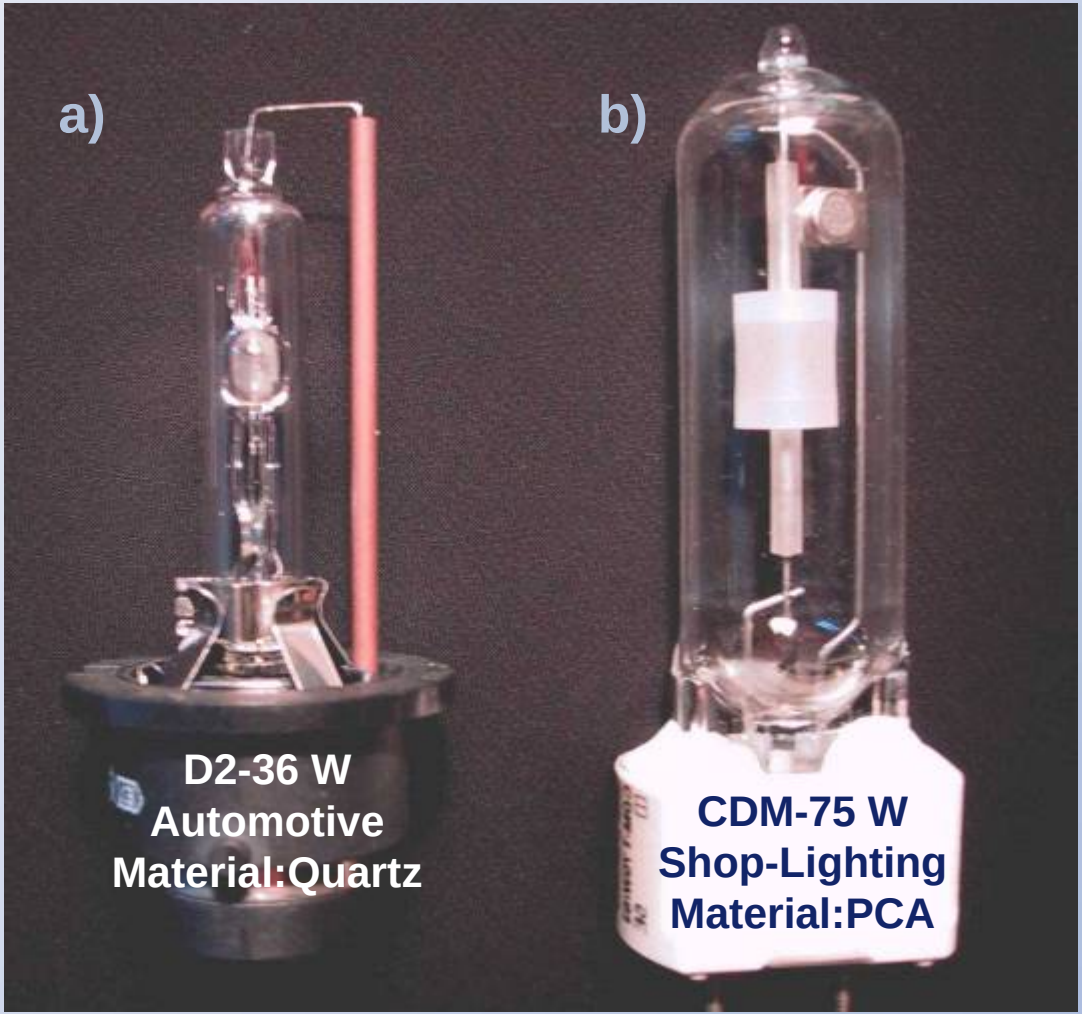
- **Motivation**
- **Computer based model calculations on the plasma (FIDAP)**
- **Determination of thermodynamic key data**
  - Vaporization studies with High Temperature Mass Spectrometry
  - Building up of thermodynamic database
- **Summary**


NaI
DyI3
CeI3
TlI

Schematic of a High Pressure Discharge Lamp

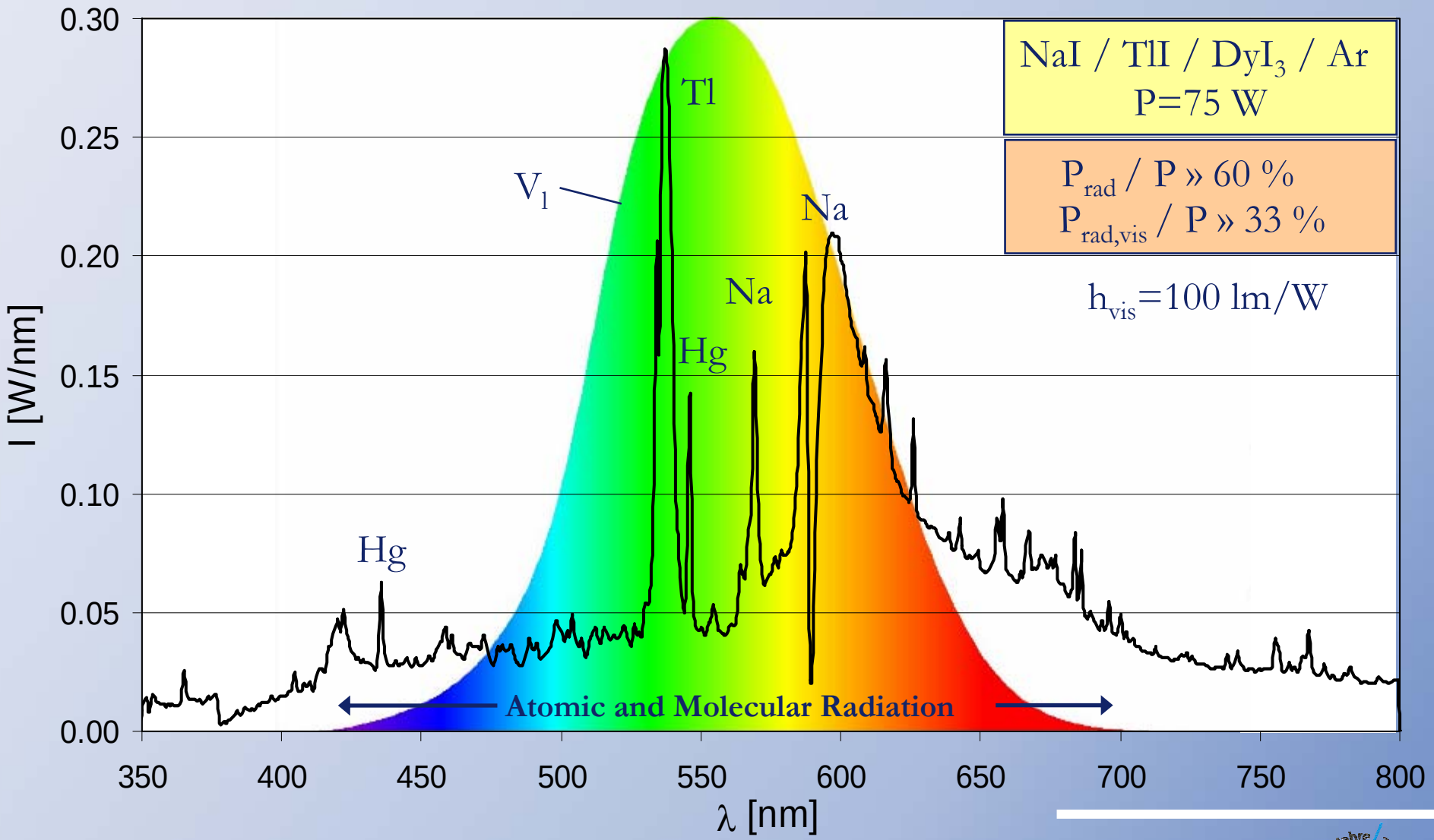


High Intensity Discharge Lamps



High Efficiency and excellent Colour Rendering

Spectrum of a Hg-containing CDM Lamp



Analysis and Modeling of LTE Plasma for High Pressure Discharge Lamps

a) Physical Analysis and Modeling of

- **plasma**
  → **energy balance, spectra, temperature, particle densities, electrical field strengths**

- **wall and electrodes**
  → **heat flux to components (thermal load), temperature distributions**

Stationary Energy Balance of High Pressure Discharge Lamps

Power density:

$$\sigma\vec{E}^2 = U_{rad} - \vec{\nabla}\cdot(\kappa\vec{\nabla}T) + \rho c_p \vec{v}\cdot\vec{\nabla}T$$

Electrical field:

$$\vec{\nabla}\cdot\vec{j} = 0 \quad , \quad \vec{j} = \sigma\vec{E}$$

Momentum:

$$\rho(\vec{v}\cdot\vec{\nabla})\vec{v} = \rho\vec{g} - \vec{\nabla}p_{total} + \vec{\nabla}\cdot\underline{\underline{\tau}}$$

$$\tau_{ij} = \eta\left(\frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j} - \frac{2}{3}\delta_{ij}(\vec{\nabla}\cdot\vec{v})\right)$$

Continuity:

$$\vec{\nabla}\cdot(\rho\vec{v}) = 0$$

Equation of state:

$$p_{total} = \frac{\rho}{M_{carr}}RT$$

Boundary Conditions

zero flow velocity at inner wall: $\vec{v}\big|_{r=R} = 0$

electrical input power: $P = \int_V \sigma E^2 dV$

Wall and Electrodes

$$\vec{\nabla} \cdot (\lambda_{K,E} \vec{\nabla} T_{K,E}) = 0$$

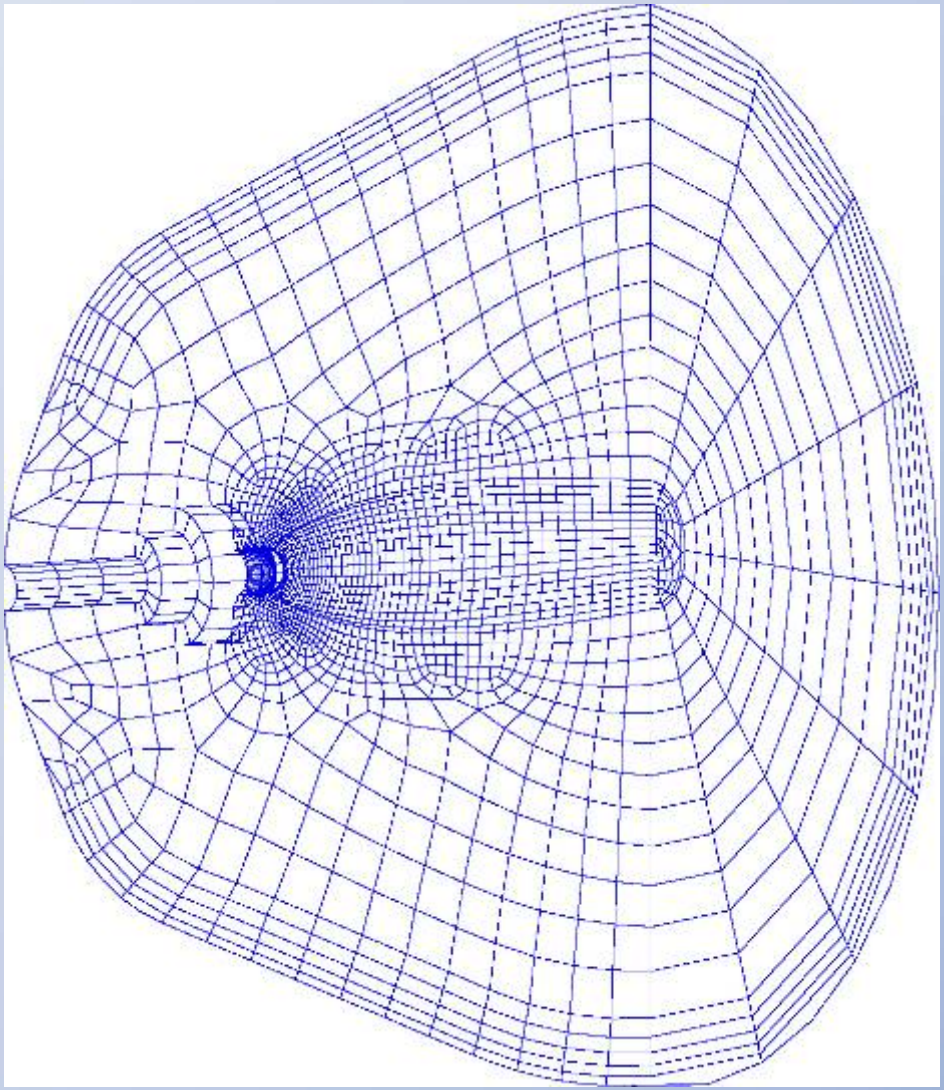
Outer Wall

$$q_{out} = \varepsilon(T_w)\sigma_{SB}(T_w{}^4 - T_{ref}^4) + h(T_w - T_{ref})$$

T_{ref}: ambient temperature

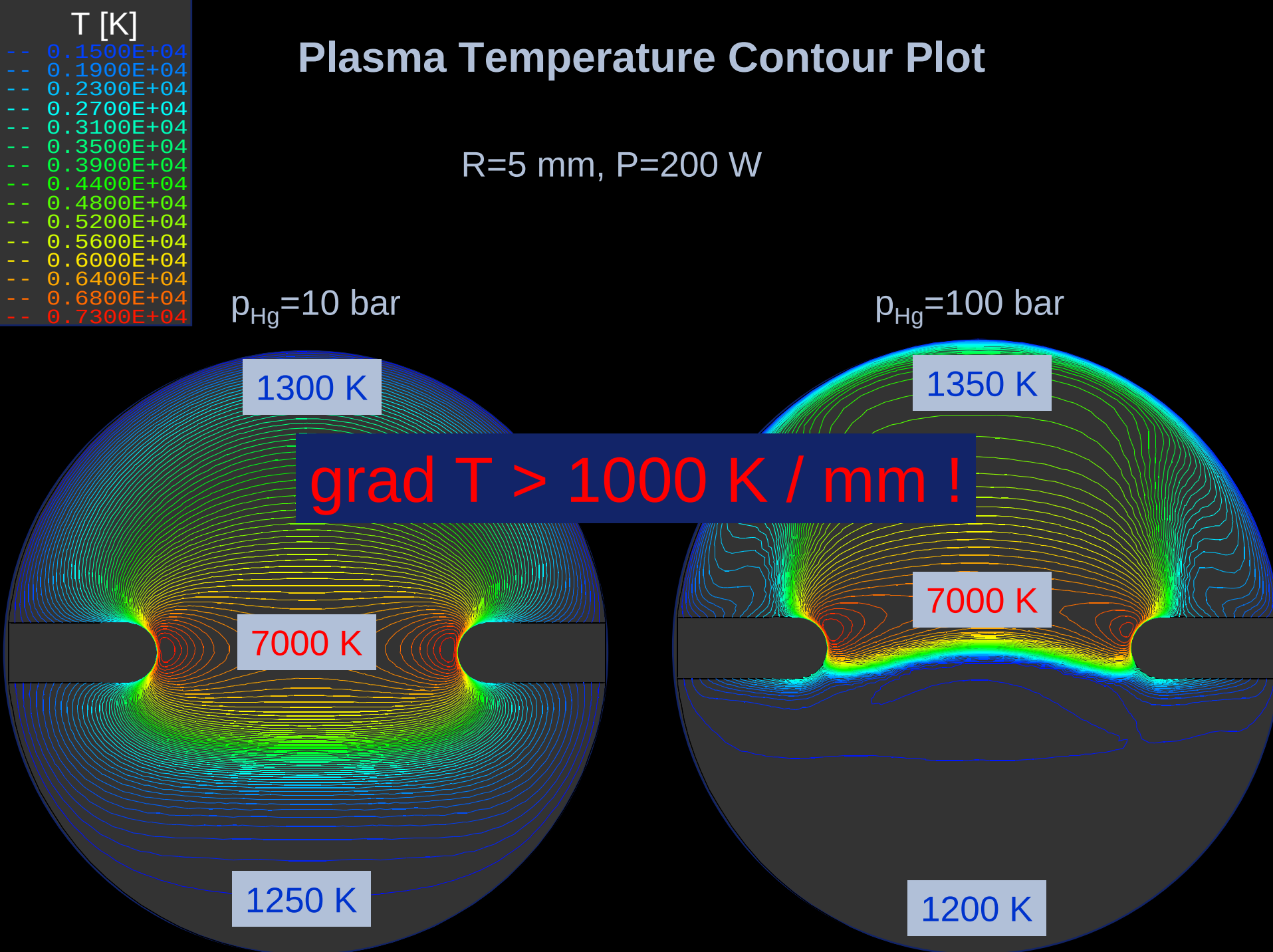
h : heat transfer coefficient (air, Ar ...)

Lamp Grid used for Finite Element Code FIDAP



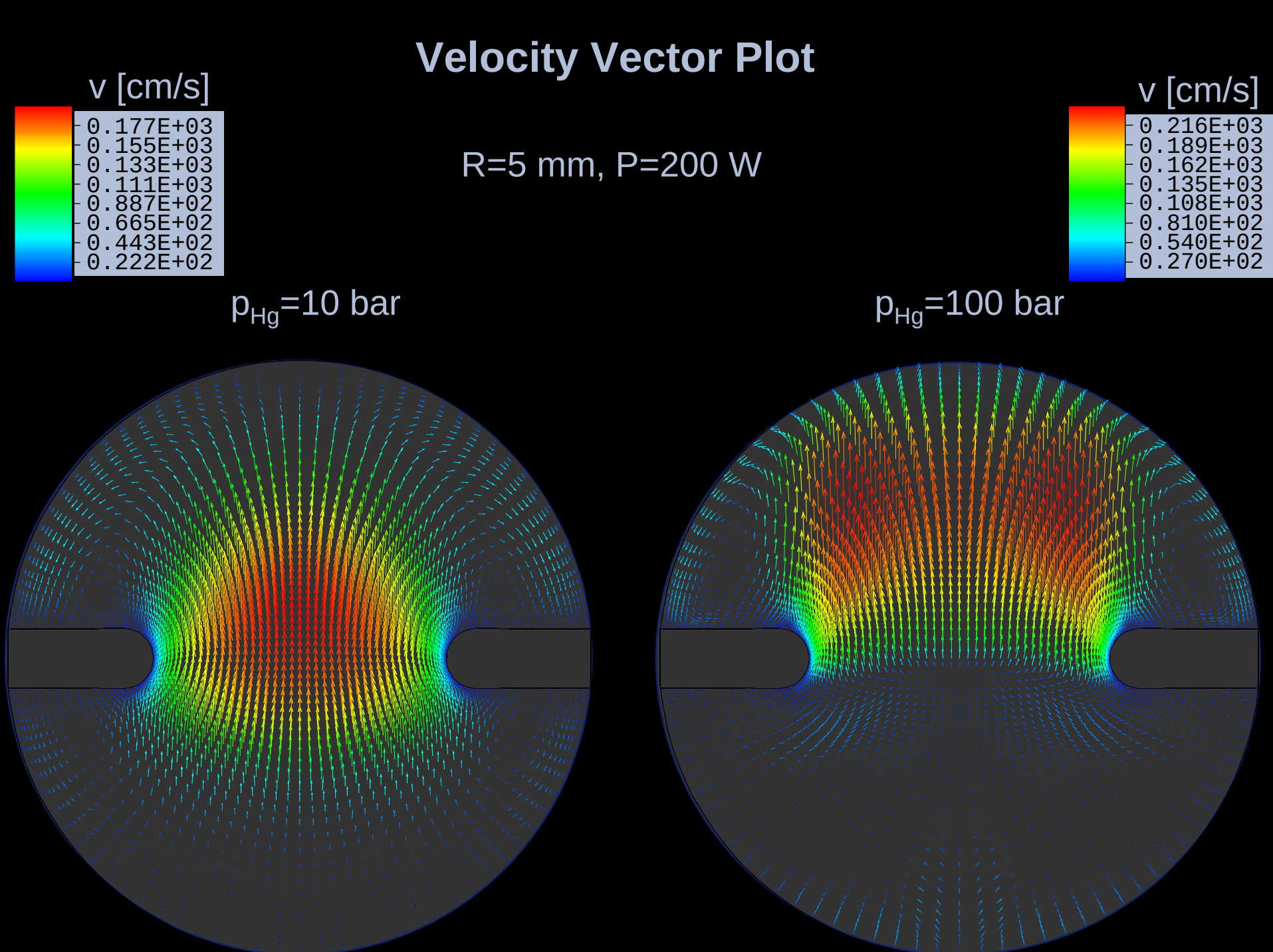
Plasma Temperature Contour Plot

R=5 mm, P=200 W

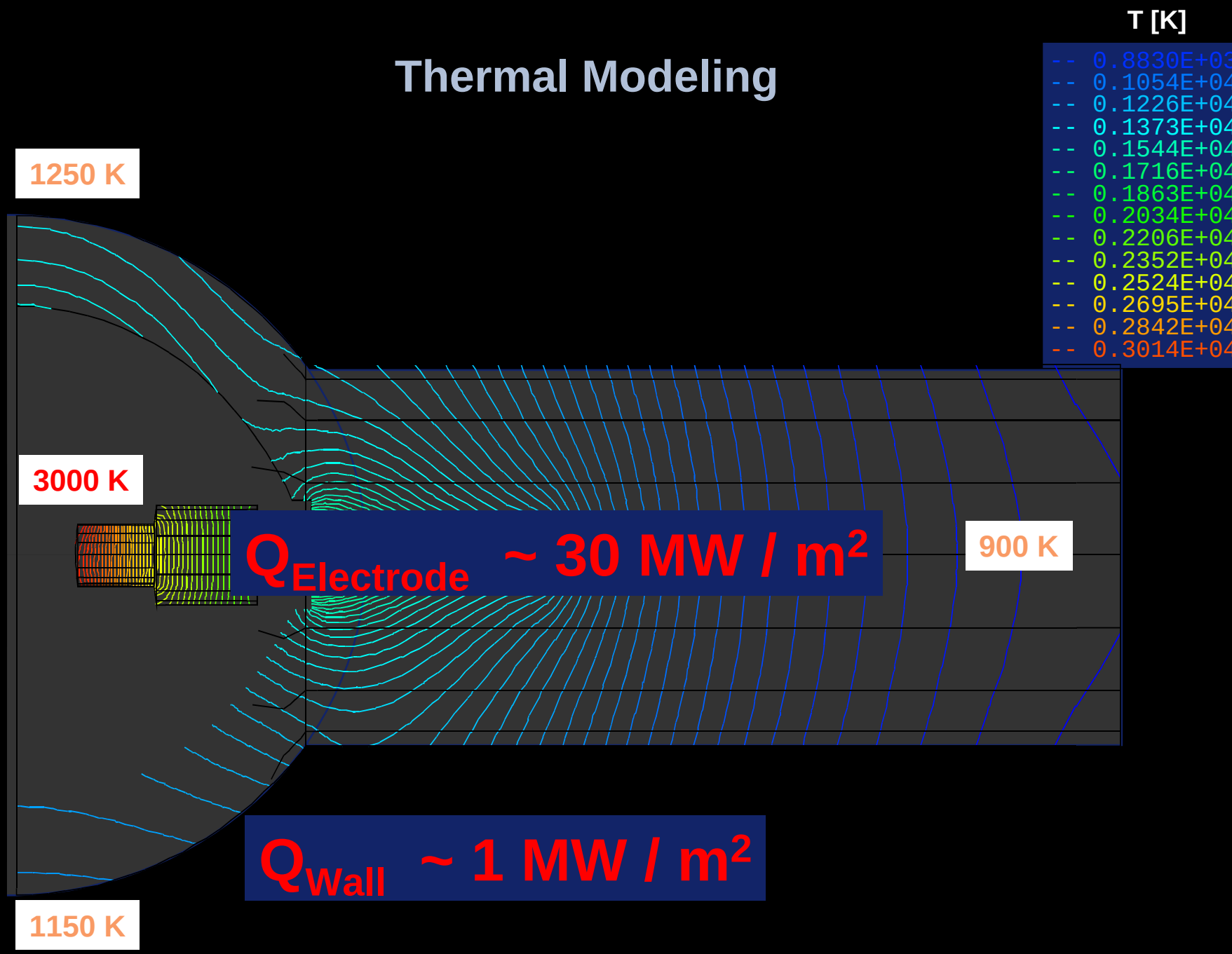


Velocity Vector Plot

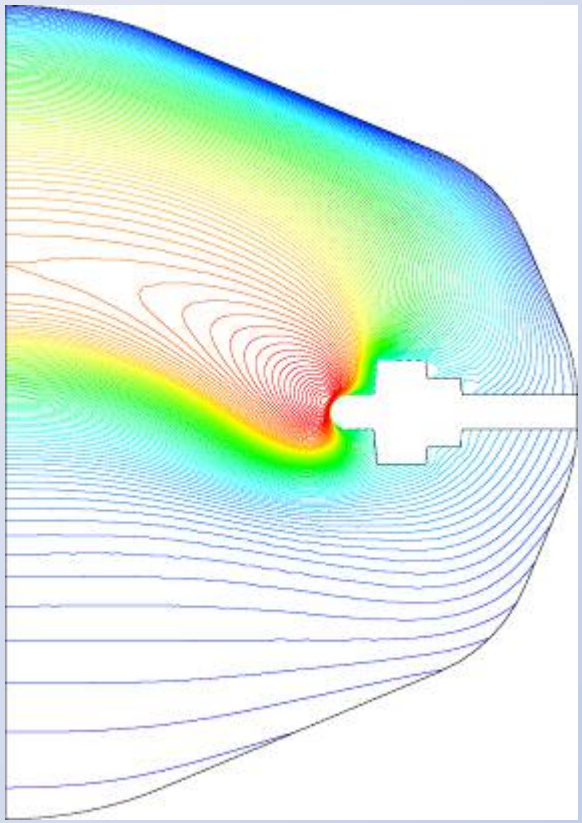
R=5 mm, P=200 W



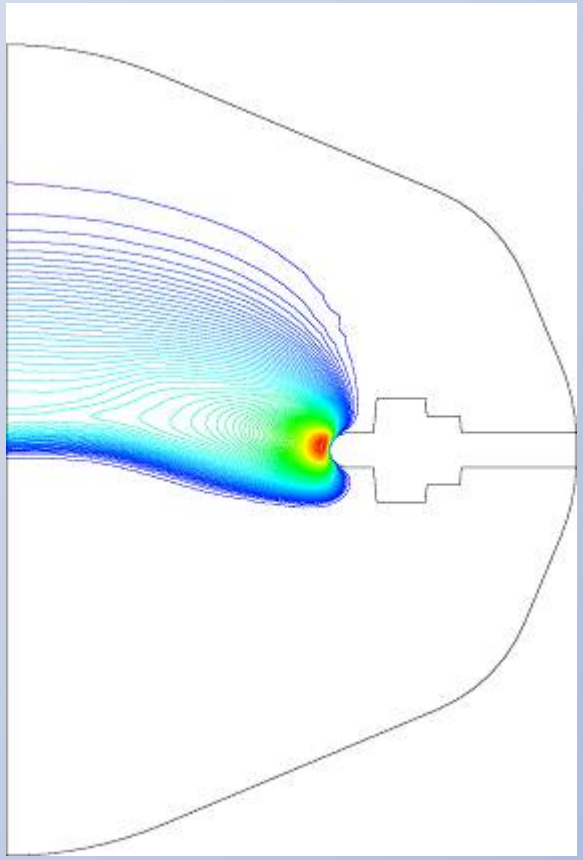
Thermal Modeling



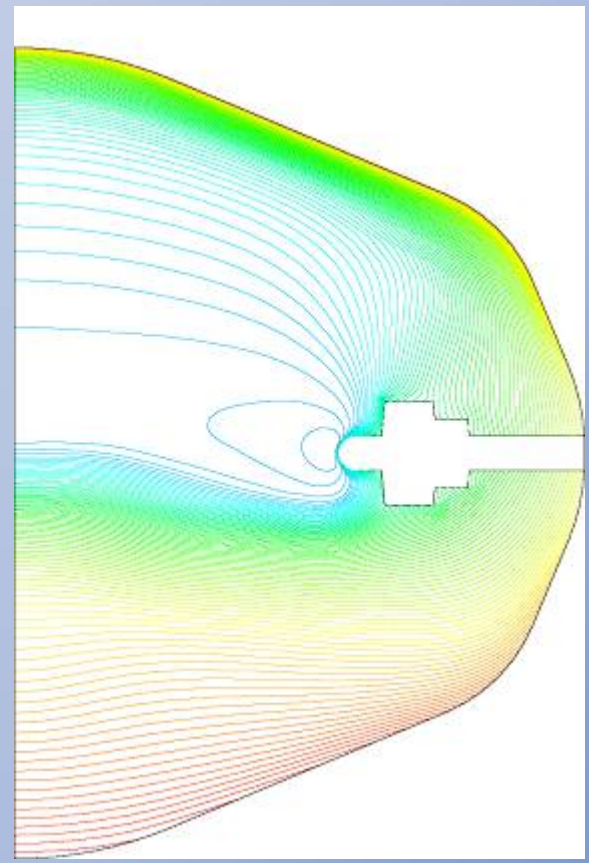
Plasma Temperature and Density Profiles



plasma temperature



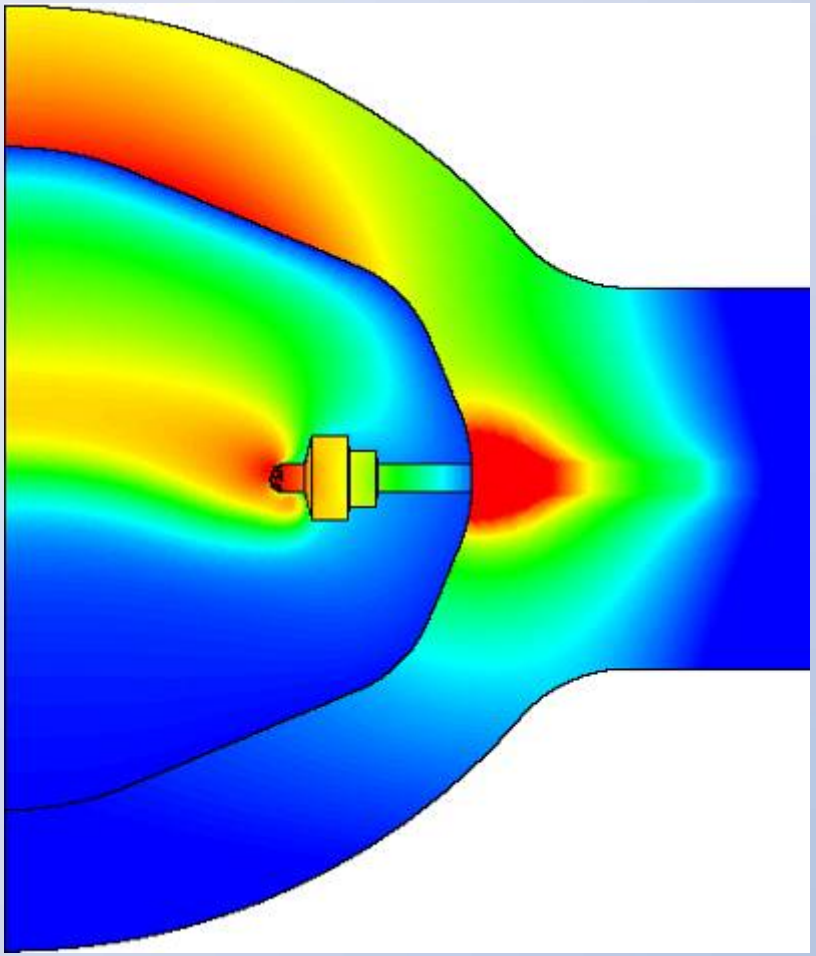
e^- density



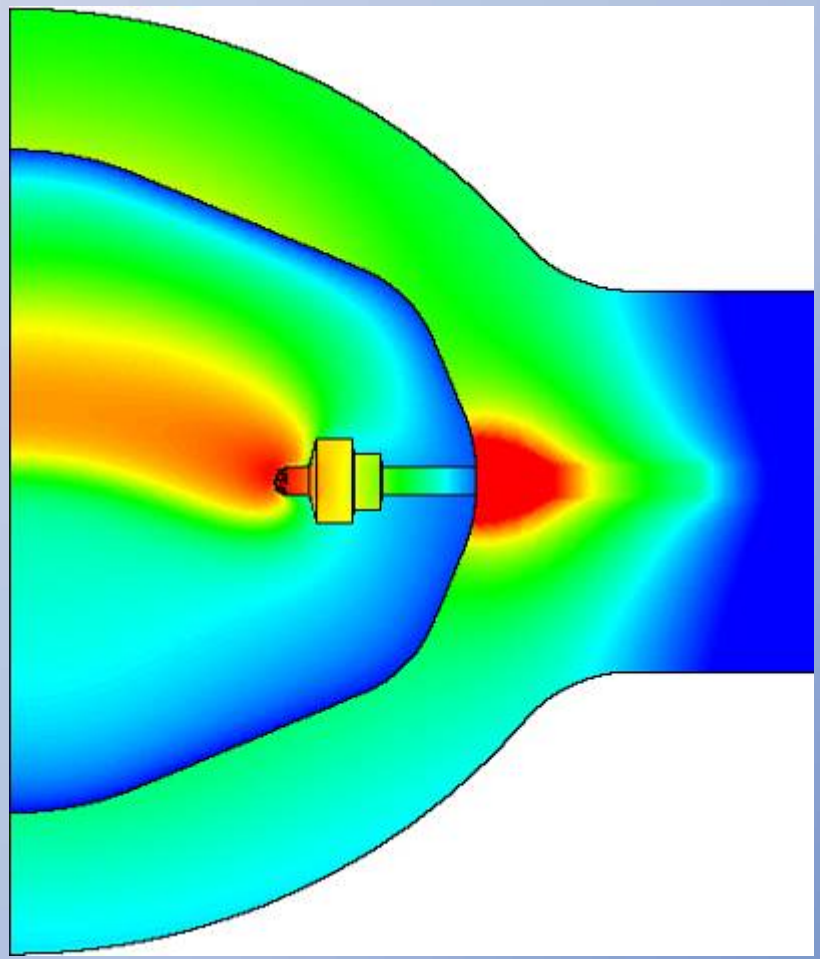
Hg density

Thermal Modeling of Wall and Electrode Temperatures

without



with radiation transport



Plasma Modeling Results

Input Data

- lamp and electrode geometry
- wall and electrode materials
- lamp filling
- electrical input power

- electrical conductivities (T)
- thermal conductivities (T)
- viscosities (T)
- specific heats (T)
- emissivities (T)
- particle densities (T)
- radiation emission (T)
  - atomic energy levels
  - transition probabilities
  - broadening constants

energy balance

Output Data

- plasma temperature $\vec{(r)}$
- particle densities $\vec{(r)}$
- radiation emission $\vec{(r)}$

- spectrum
- electrical field
- wall and electrode temperature distribution

Determination of partial pressures and key thermodynamic data

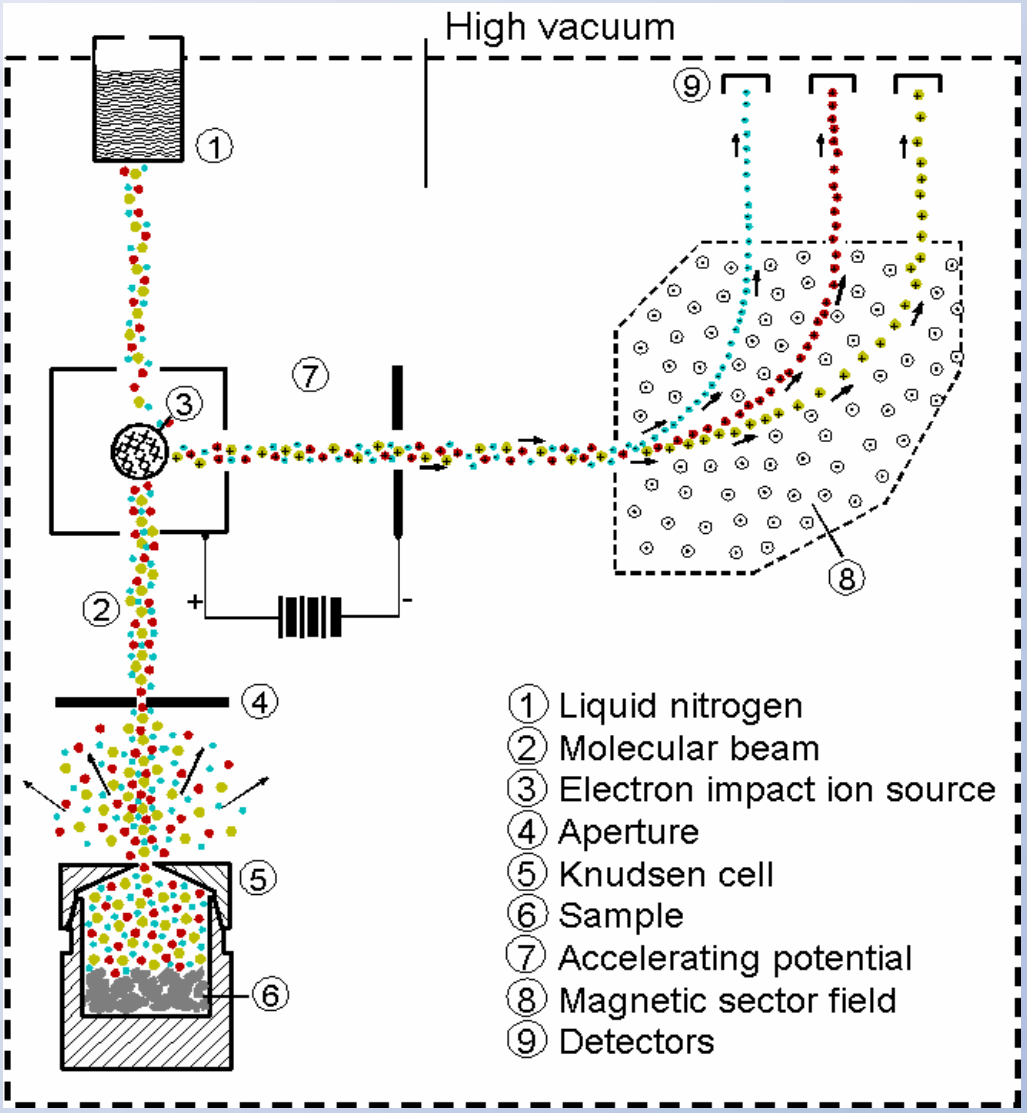
b) Thermochemical Analysis and Modeling of

- **gaseous and condensed phases**
  → determination of species and densities

- **chemical reactions and corrosion products**
  → lamp life, light technical and electrical stability

- **chemical transport**
  → e.g. tungsten transport to wall (blackening)

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**

High Temperature Mass Spectrometry - Introduction

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

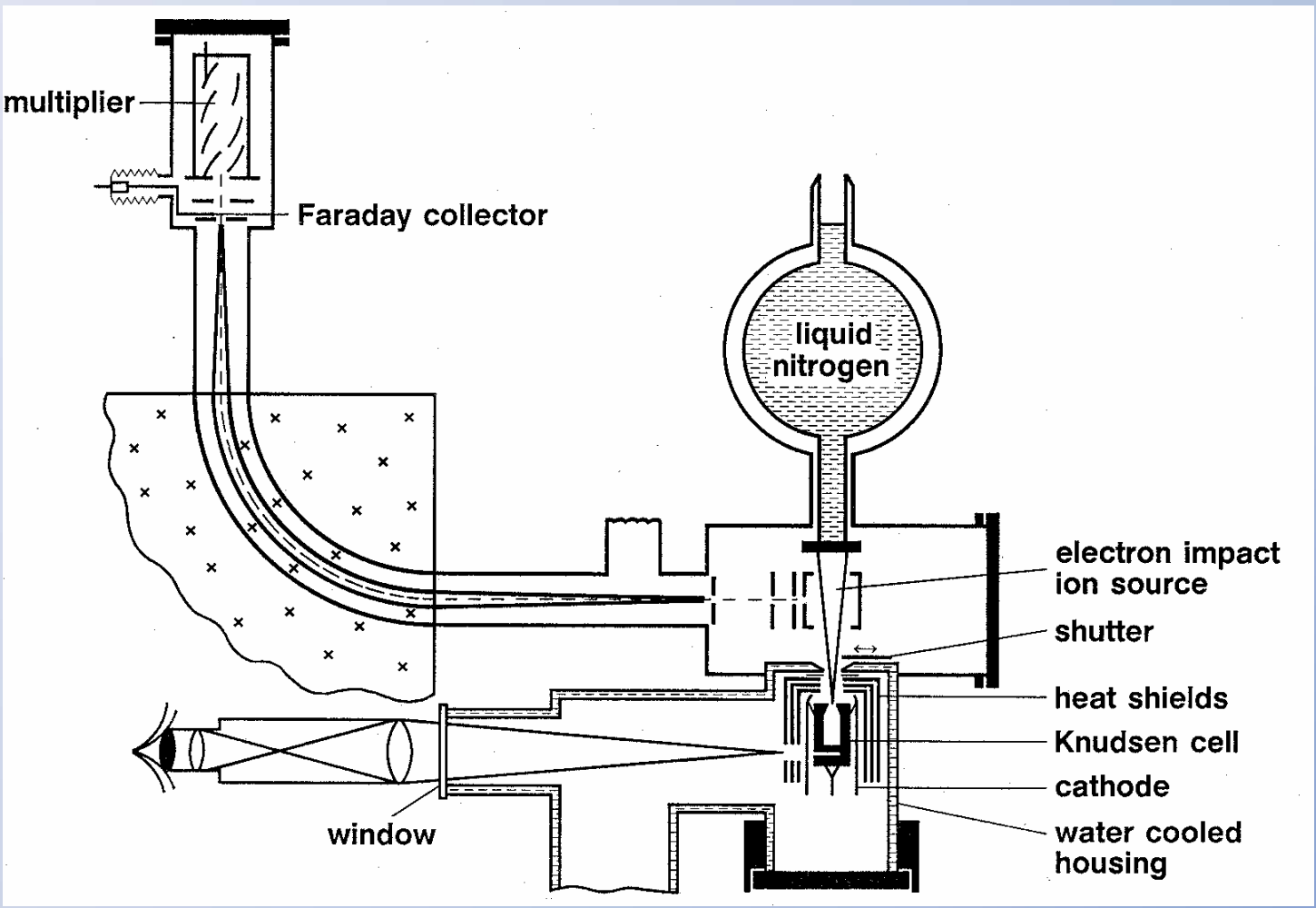
The *High Temperature Mass Spectrometry* is the most imortant method for the analysis of vapors over condensed phases

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

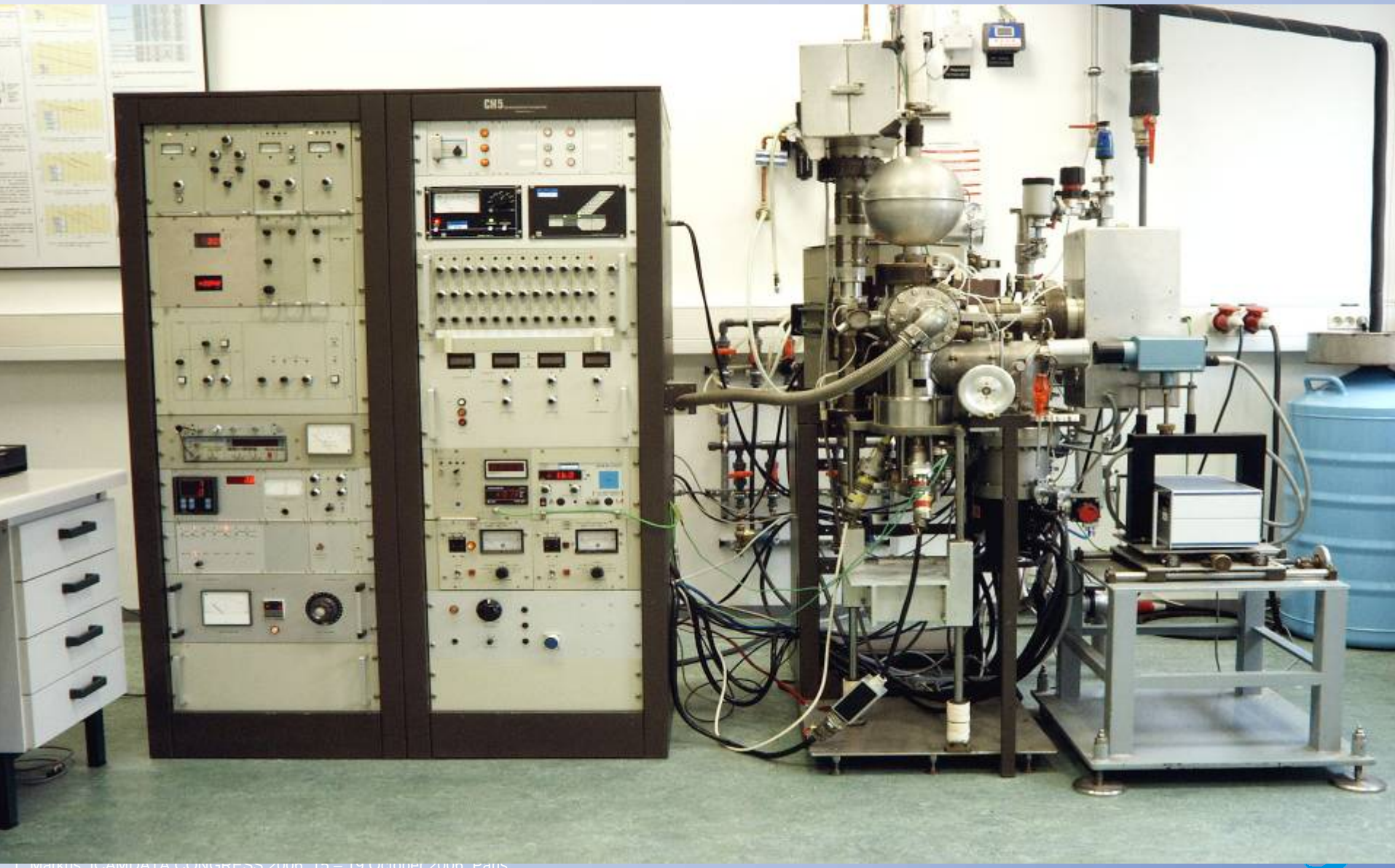
A special variant of this technique which is frequently used in inorganic gas phase chemistry, is the

Knudsen Effusion Masss Spectrometry (KEMS)

Schematic Representation of a Knudsen cell magnetic field mass spectrometer system



Mass Spectrometer Knudsen Cell System (CH 5)



Determination of Thermodynamic Data
Example: ΔH; ΔS of DyI_3

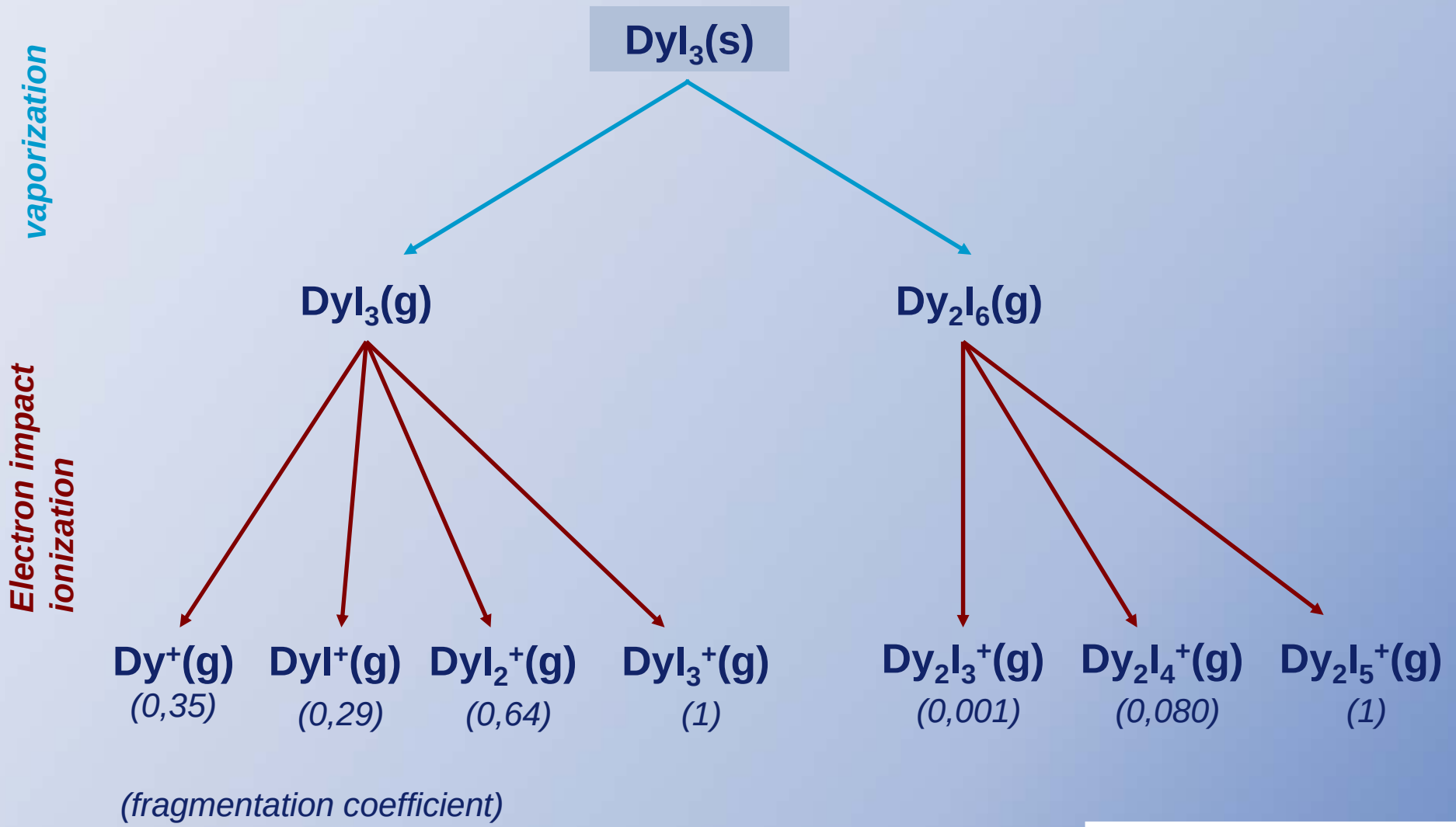
1st step:

identification of species present in the mass spectrum

and

Assignment of fragments to their neutral precursor
=> fragmentation coefficients

Fragmentation



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

Determination of Thermodynamic Data
Example: ΔH^F of DyI_3

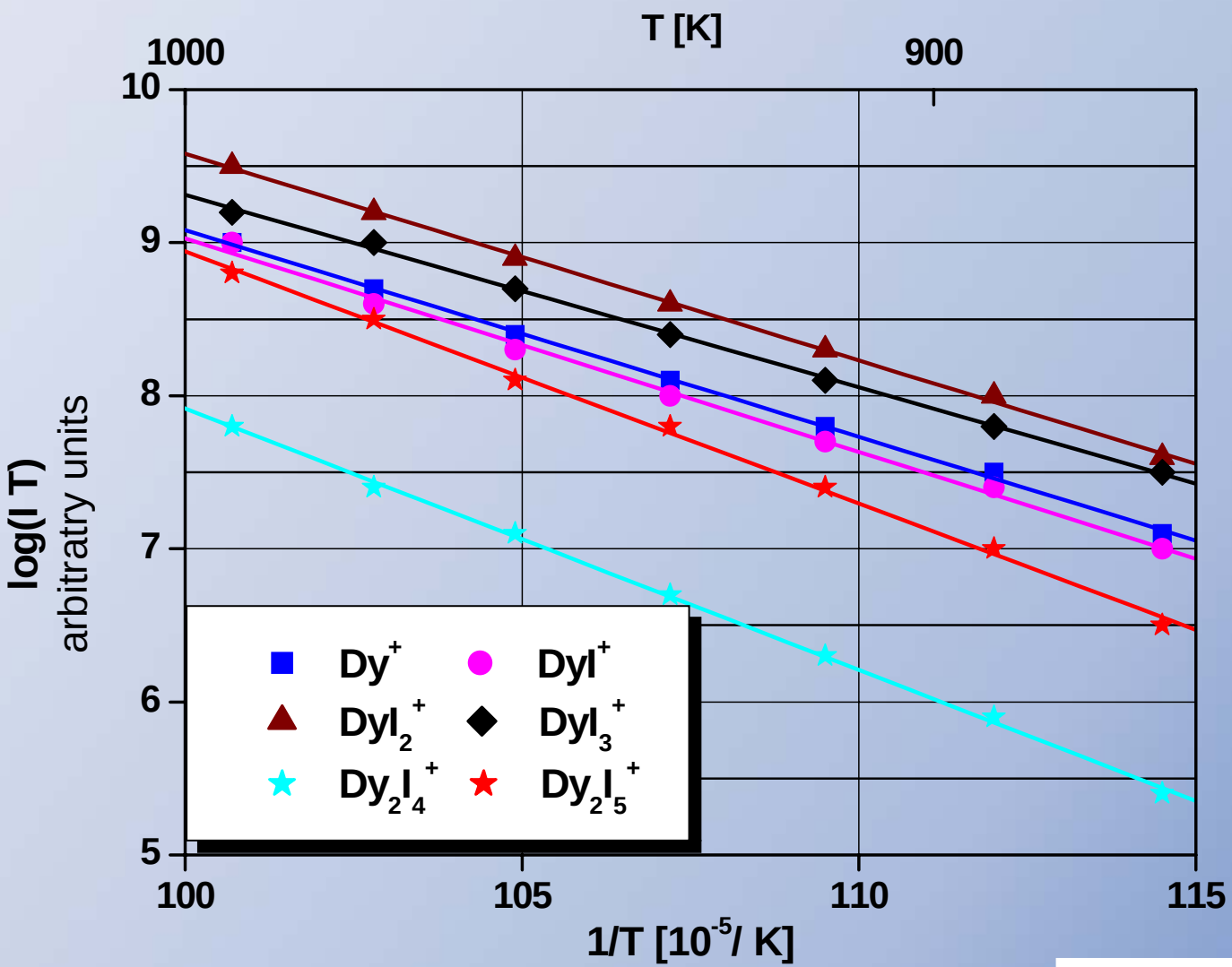
2nd step:

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

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

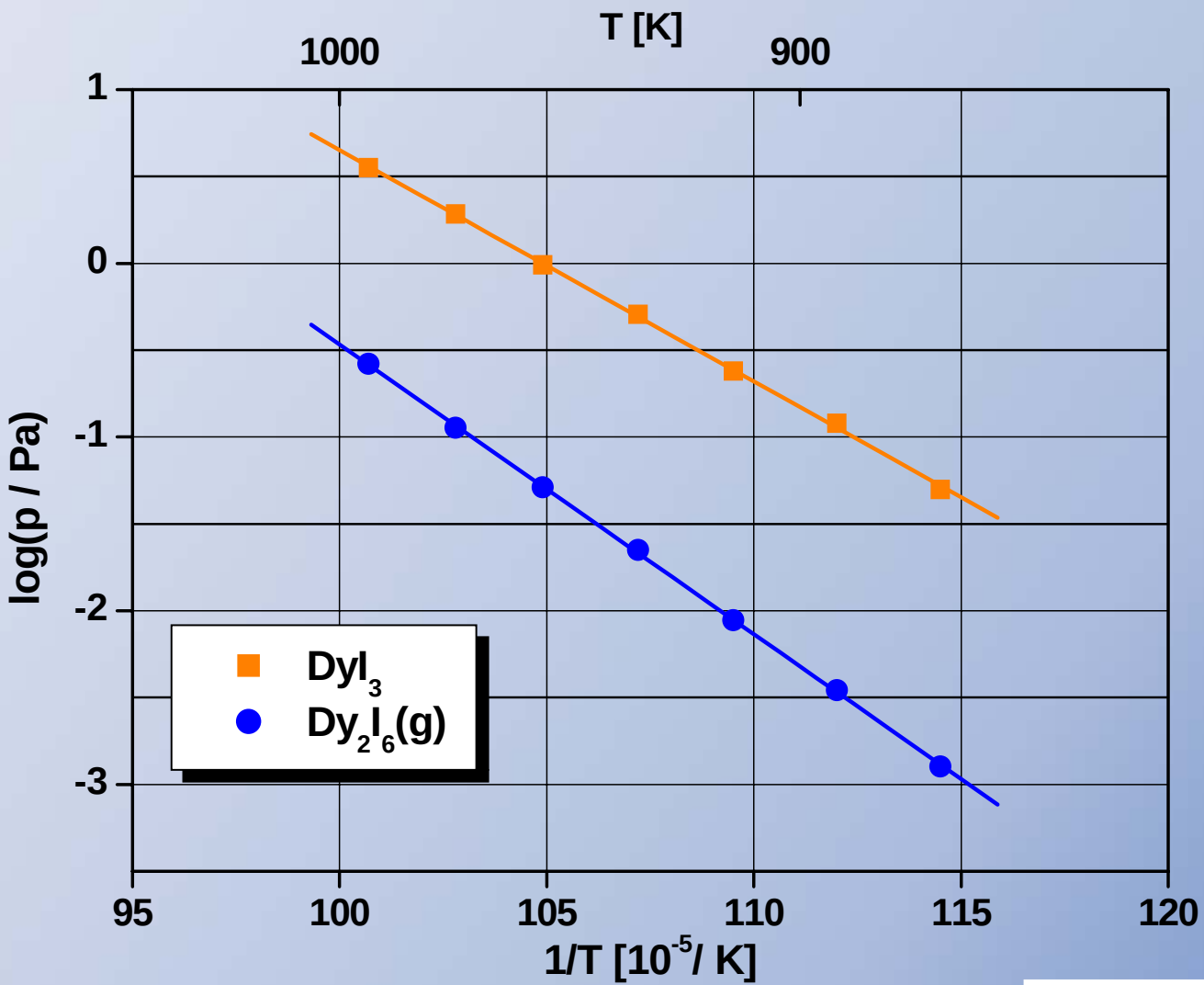
2 pressure dependent reaction taking place $X_2(g) \leftrightarrow 2X(g)$ $\quad K_p = \frac{p_X^2}{p_{X_2}}$

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

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

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

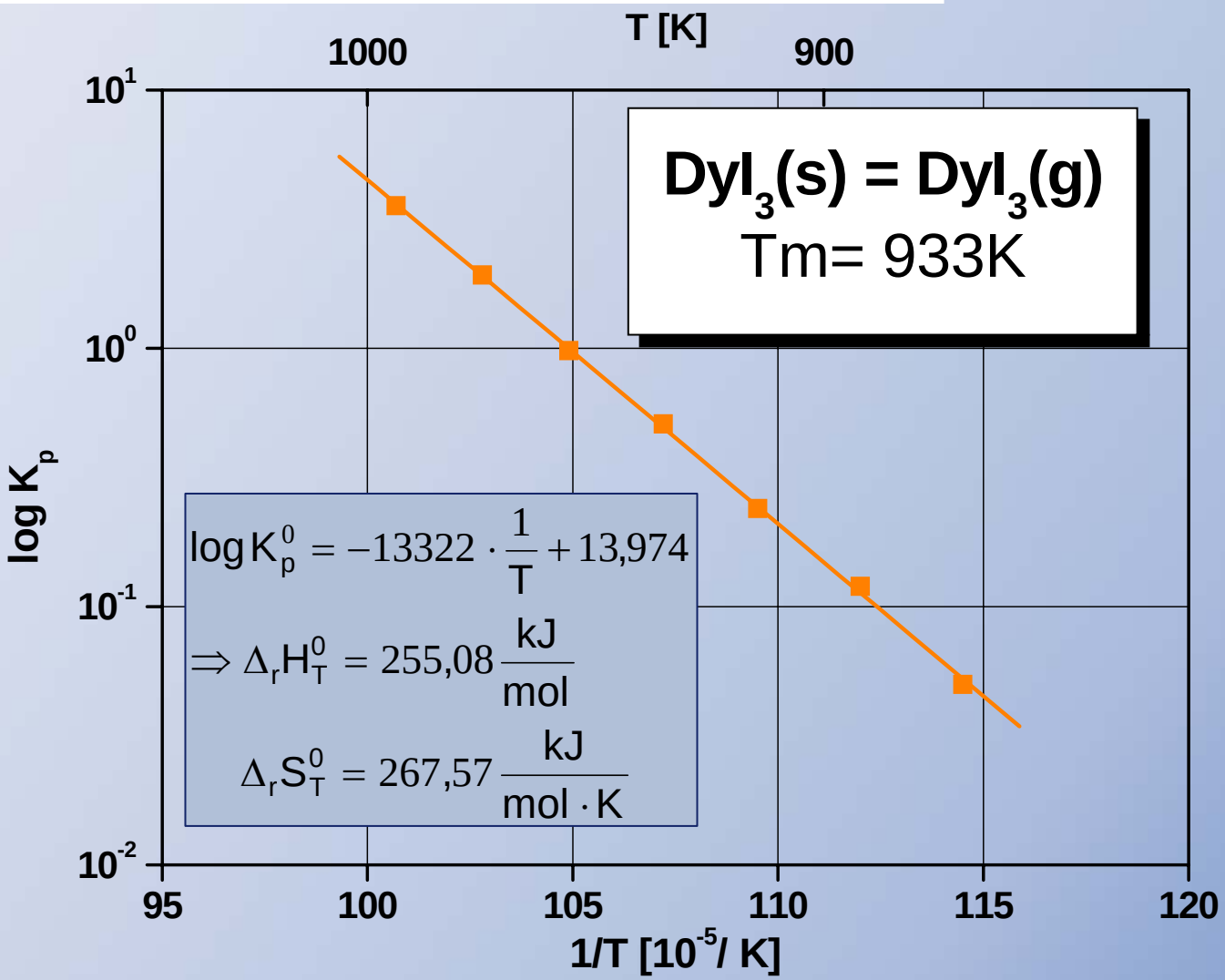
Determination of thermodynamic properties
2nd law method

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

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

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

Determination of ΔH and ΔS from Equilibrium Constant



Determination of thermodynamic properties
3rd law method

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

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

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

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

Free **E**nergy **F**unction (FEF)
from literature ex. JANAF tables

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

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

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

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

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

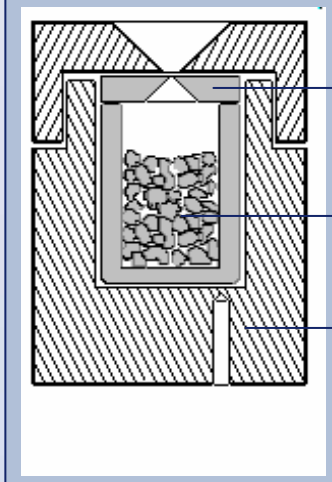
	T_m	ΔH^0_{Tm}	ΔH^0_{298}	ΔH^0_{298}	ΔS^0_{298}	$k_p(T_m)$
	K	kJ mol^{-1}	kJ mol^{-1} 2nd law	kJ mol^{-1} 3rd law	kJ (kmol K)$^{-1}$	
I	920	260,5±2,7	279,4±2,8	278,0±0,9	201,9±3	$3{,}05\cdot10^{-6}$
II	920	325,6±4,4	352,9±4,3	356,5±1,0	250,7±5,24	$1{,}15\cdot10^{-7}$
III	920	-195,4±3,3	-205,4±3,3	-199,49±0,8	-153,0±3,0	$1{,}24\cdot10^{+4}$

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

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

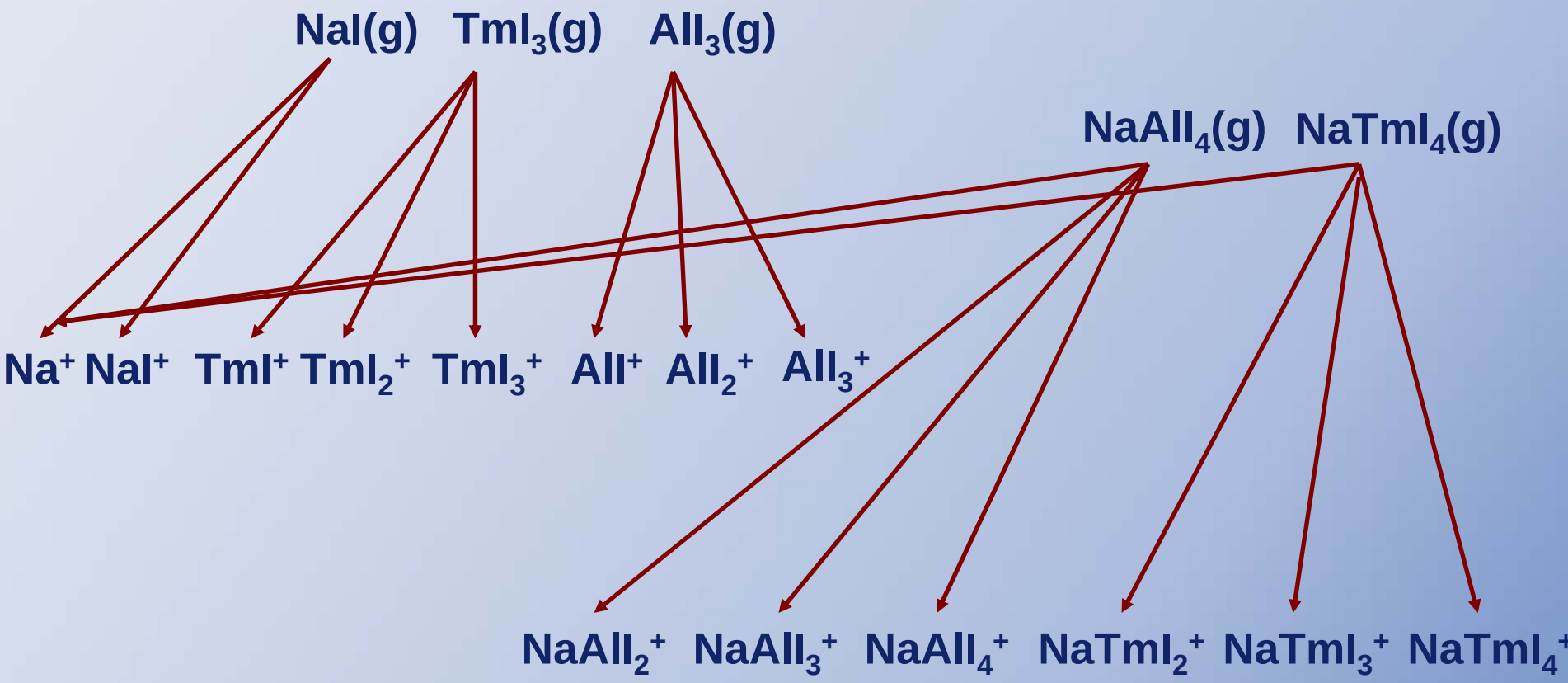
III $2DyI_3(s) \rightarrow Dy_2I_6(g)$

Example 2:
Determination of Thermodynamic Data for Corrosion

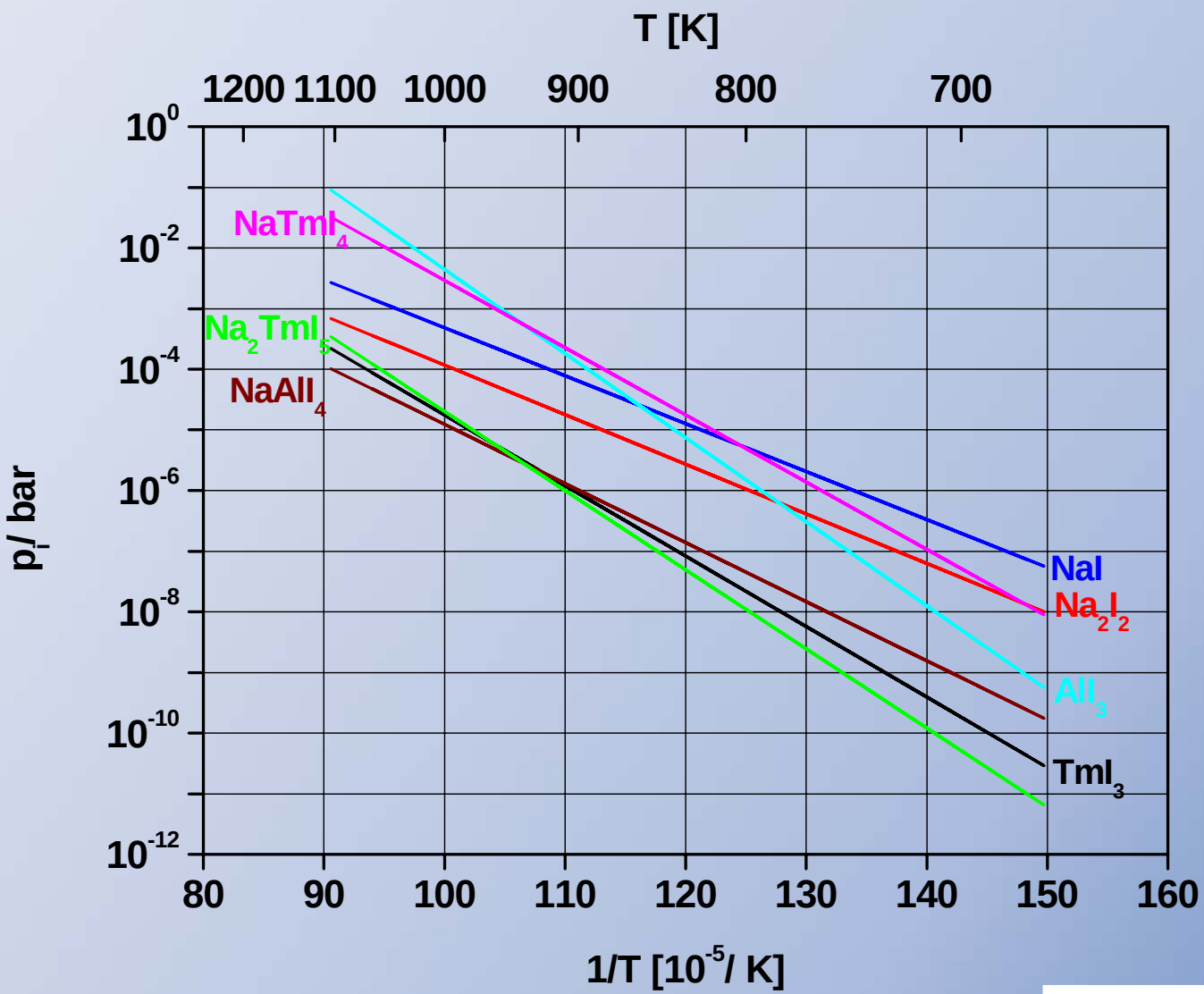


Reactands in Knudsen Cell	
$TmBr_3(s)+NaBr(s)+Al_2O_3(s)$	$TmI_3(s)+NaI(s)+Al_2O_3(s)$
T-Range	
744 - 1134 K	842 - 1103 K
Identified Ions in Mass Spectrum	
Na^+, $NaBr^+$, Na_2Br^+, $AlBr^+$, $AlBr_2^+$, $AlBr_3^+$, $TmBr^+$, $TmBr_2^+$, $TmBr_3^+$, ($Tm_2Br_5^+$) **$NaAlBr_3^+$, ($NaAlBr_4^+$) $NaTmBr_2^+$, $NaTmBr_3^+$, $NaTmBr_4^+$, $Na_2TmBr_4^+$**	Na^+, NaI^+, Na_2I^+, AlI^+, AlI_2^+, AlI_3^+, TmI^+, TmI_2^+, TmI_3^+, **$NaAlI_3^+$, $NaTmI_2^+$, $NaTmI_3^+$, $NaTmI_4^+$, $Na_2TmI_4^+$**

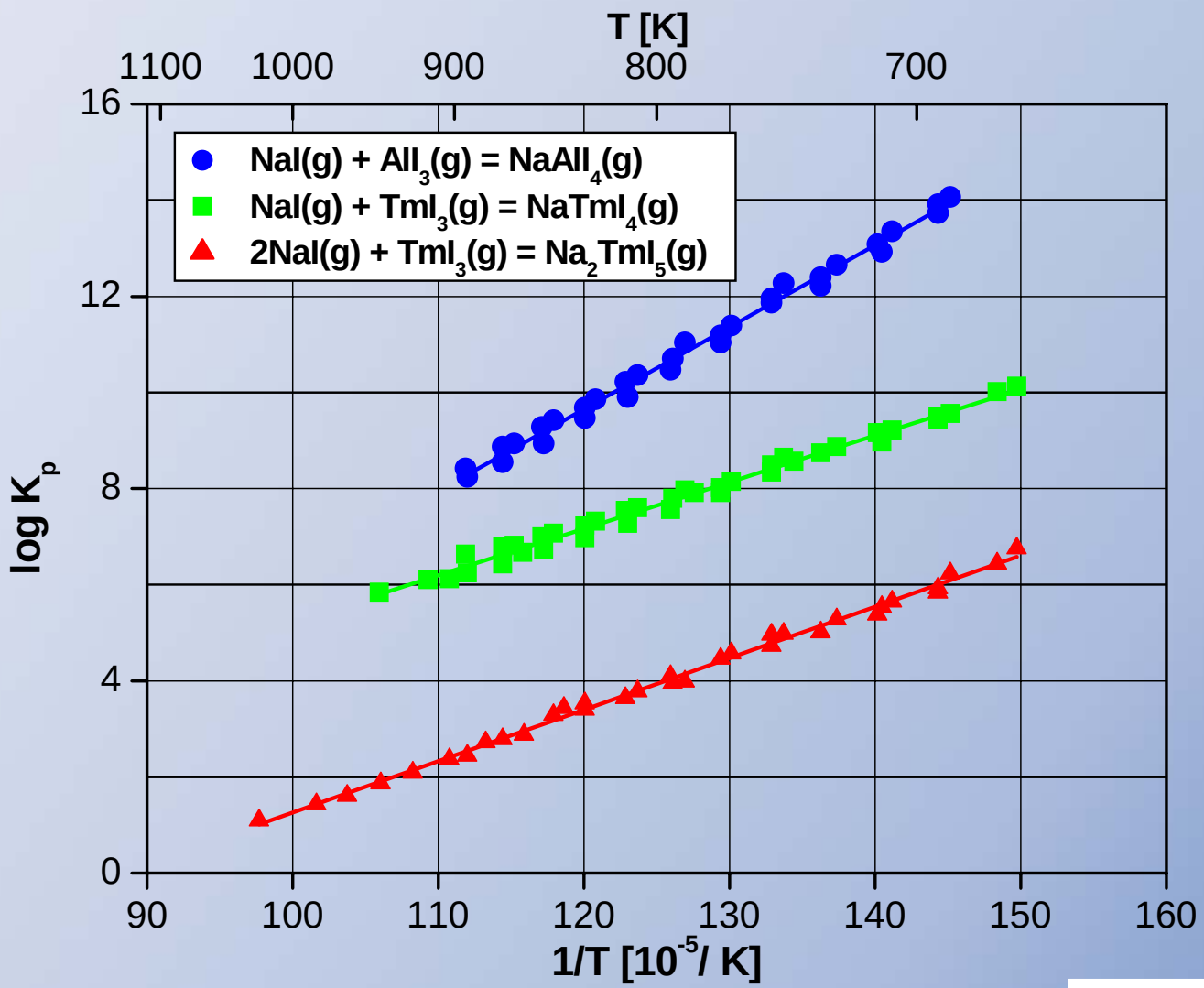
Fragmentation Pattern for the mixture NaI/ TmI_3 +Al_2O_3



Partial pressure over an equimolar mixture of $NaI/TmI_3/Al_2O_3$



Gaseous Equilibria over Al_2O_3/NaI/TmI_3 Mixture



Thermochemical Data of selected reactions in the $NaX/TmX_3/Al_2O_3$ (X=Br, I) systems

	T_m	ΔH^0_{Tm}	ΔH^0_{298}	ΔH^0_{298}	ΔS^0_{298}	$k_p(T_m)$
	K	kJ kmol^{-1}	kJ kmol^{-1} 2nd law	kJ kmol^{-1} 3rd law	kJ (kmol K)$^{-1}$	
I	806	-195,5±5,1	-202,1±5,1	-160,6±4,5	-183,2±5,7	$5{,}98\cdot10^{+3}$
II	787	-185,2±5,5	-191,5±5,5	-222,6±1,3	-93,5±8,3	$5{,}42\cdot10^{+07}$
II	789	-326,1±9,7	-338,8±9,7	-372,6±1,8	-236,3±13,3	$3{,}67\cdot10^{+10}$
IV	868	-226,7±15,0	-234,1±1,0	-183,6±1,6	-191,4±4,8	$2{,}31\cdot10^{+04}$
V	864	-228,1±6,8	-235,4±6,8	-242,9±0,3	-126,1±2,1	$3{,}93\cdot10^{+07}$
VI	866	-393,7±5,8	-408,5±5,8	-409,5±0,09	-281,6±5,0	$3{,}04\cdot10^{+10}$

I	$NaI(g) + AlI_3(g) \rightarrow NaAlI_4(g)$	*IV*	$NaBr(g) + AlBr_3(g) \rightarrow NaAlBr_4(g)$
II	$NaI(g) + TmI_3(g) \rightarrow NaTmI_4(g)$	*V*	$NaBr(g) + TmBr_3(g) \rightarrow NaTmBr_4(g)$
IV	$2NaI(g) + TmI_3(g) \rightarrow Na_2TmI_5(g)$	*VI*	$2NaBr(g) + TmBr_3(g) \rightarrow Na_2TmBr_5(g)$

Sytematic Investigations on binary and higher Order Metal Halide systems for thermodynamic database development

Measurements on the sytem NaI - CeI_3

Reactands in Knudsen Cell

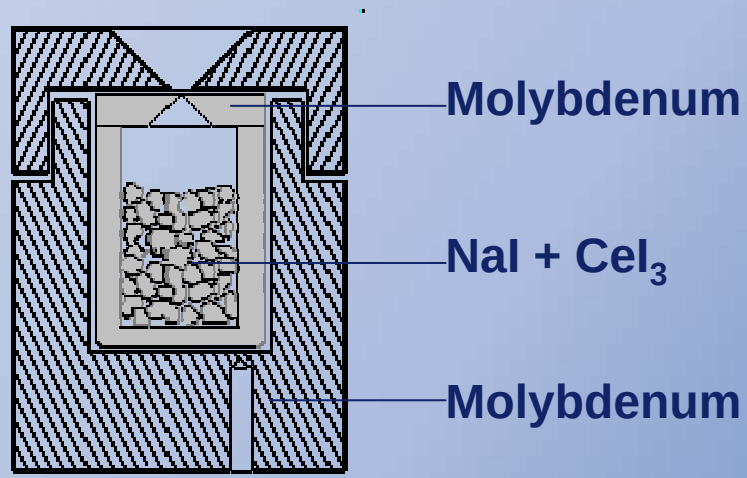
$NaI(l) + CeI_3(l)$

T-Range

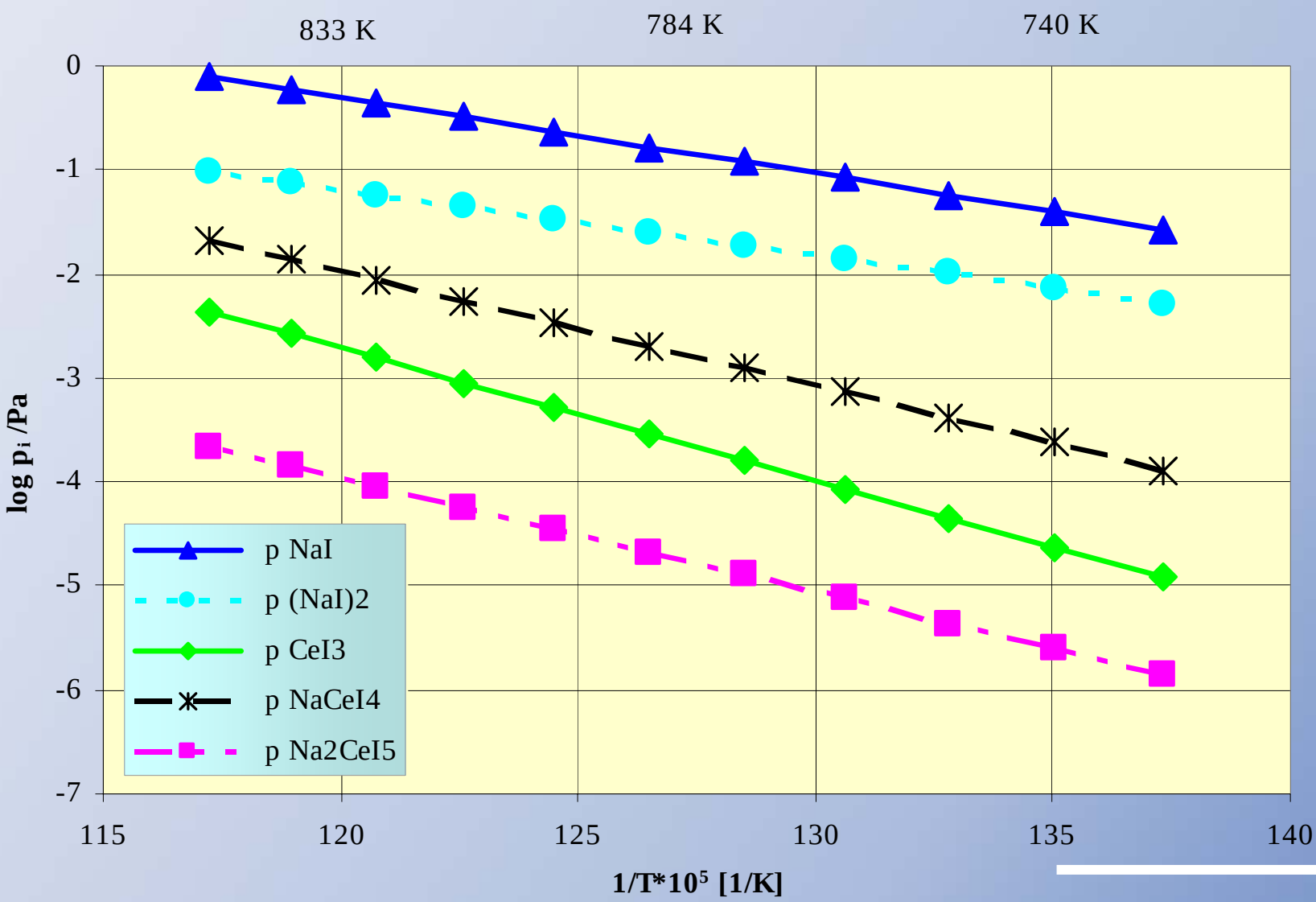
728 K – 923 K

Identified Ions in Mass Spectrum

Na^+, NaI^+, Na_2I^+, $(Na_2I_2^+)$
Ce^+, CeI^+, CeI_2^+, CeI_3^+
$(NaCeI^+)$, $NaCeI_2^+$, $NaCeI_3^+$,
$NaCeI_4^+$
$Na_2CeI_4^+$



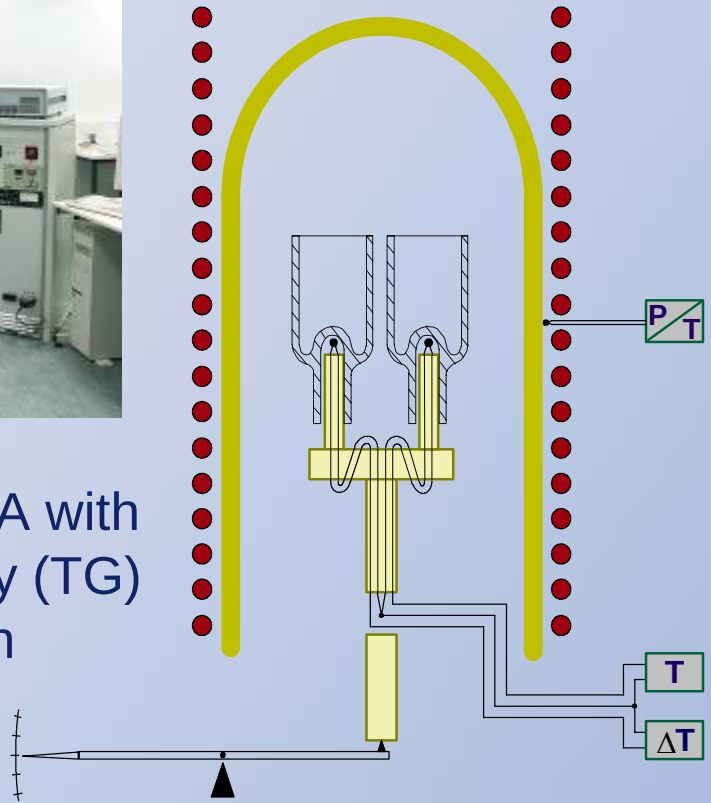
Partial pressures above a mixture of molten NaI-CeI_3 (50/50)



Differential Thermal Analysis (DTA)

Simultaneous DTA with Thermogravimetry (TG)
STA 429, Netzsch

Principle of DTA



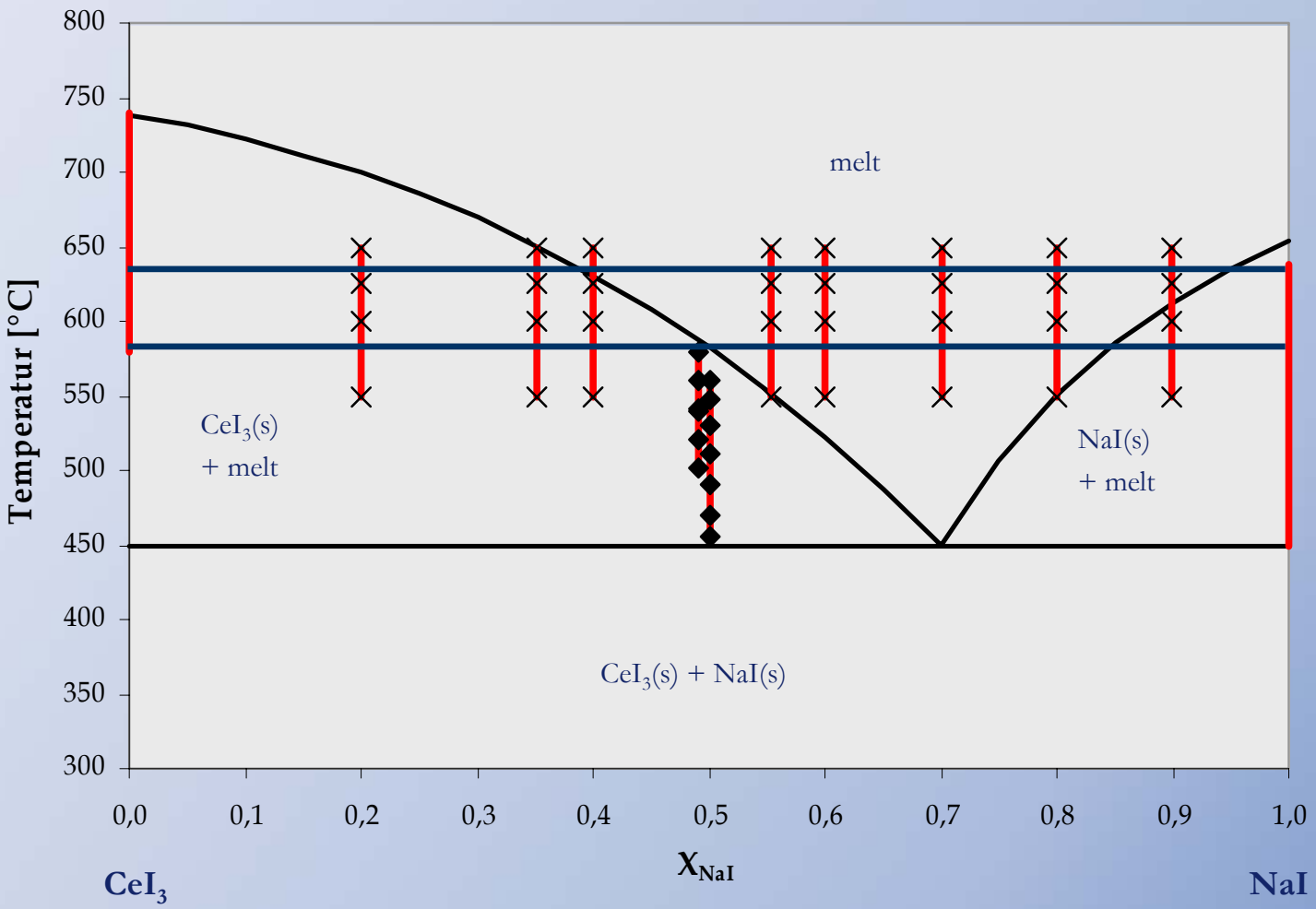
Measuring of Phase Transition Temperatures

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



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

Activities:

According to definition:

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

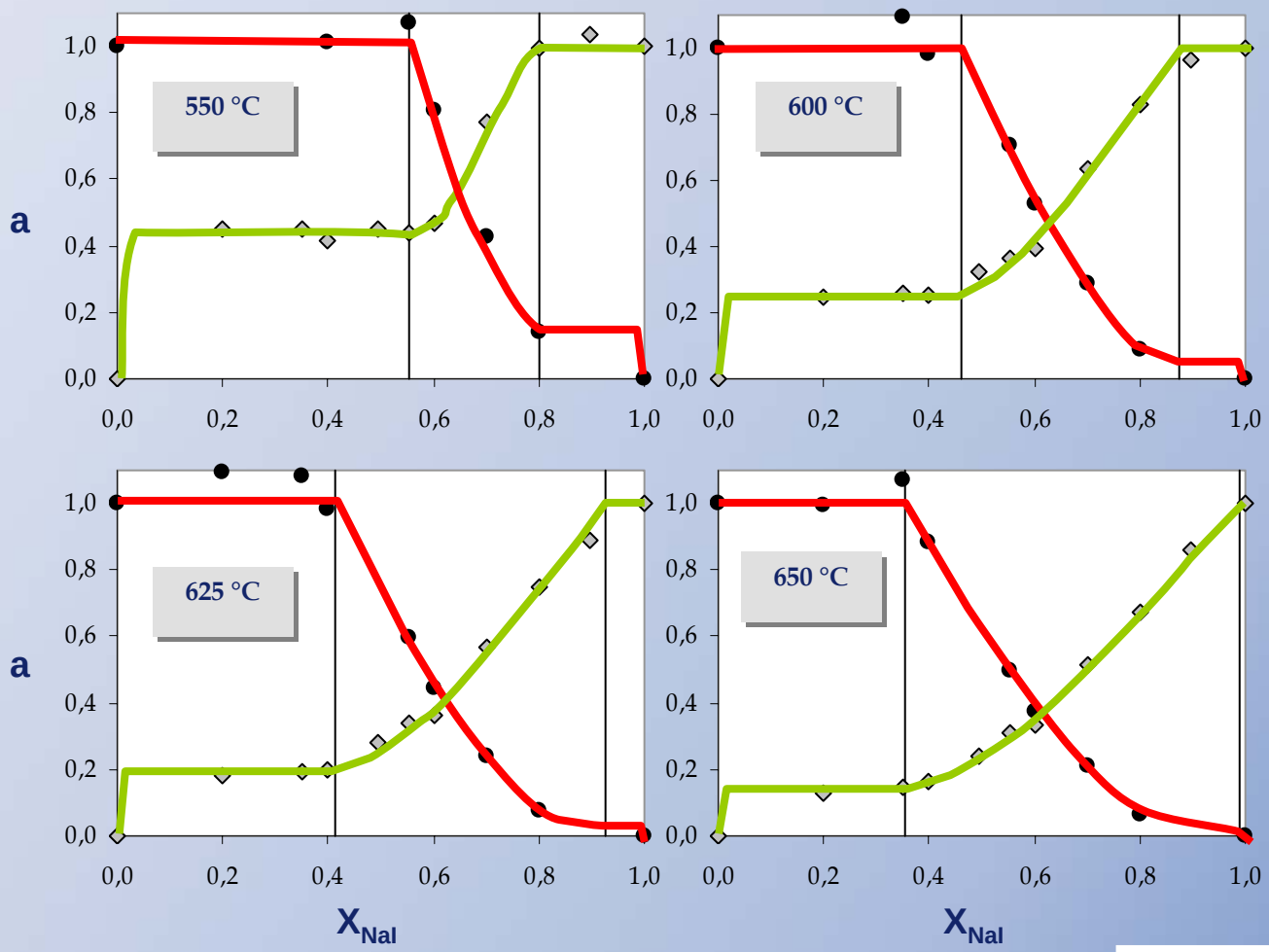
Ion Intensity Ratio integration Method (GD-IIR):

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

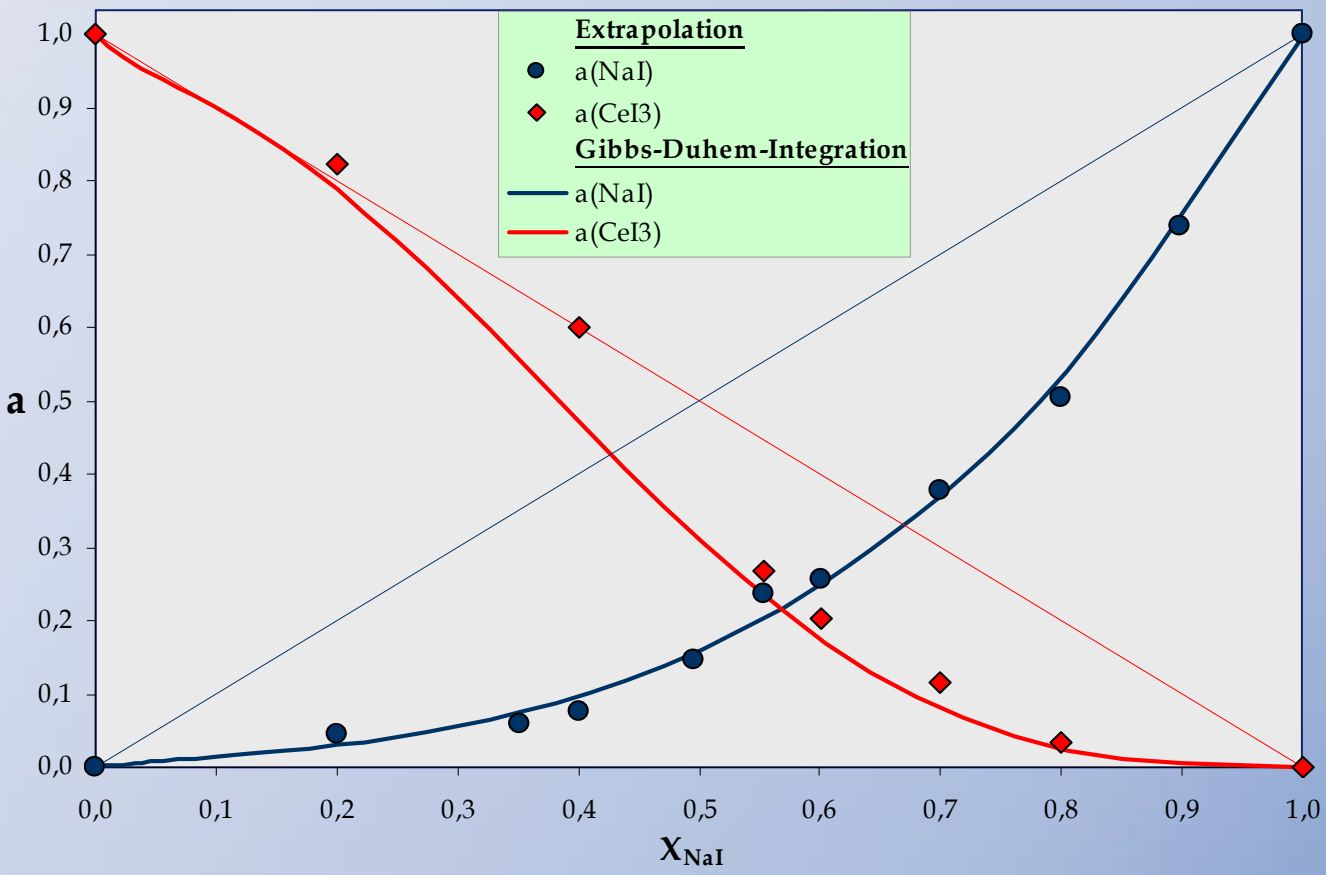
Enthalpies and Gibbs Energies:

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

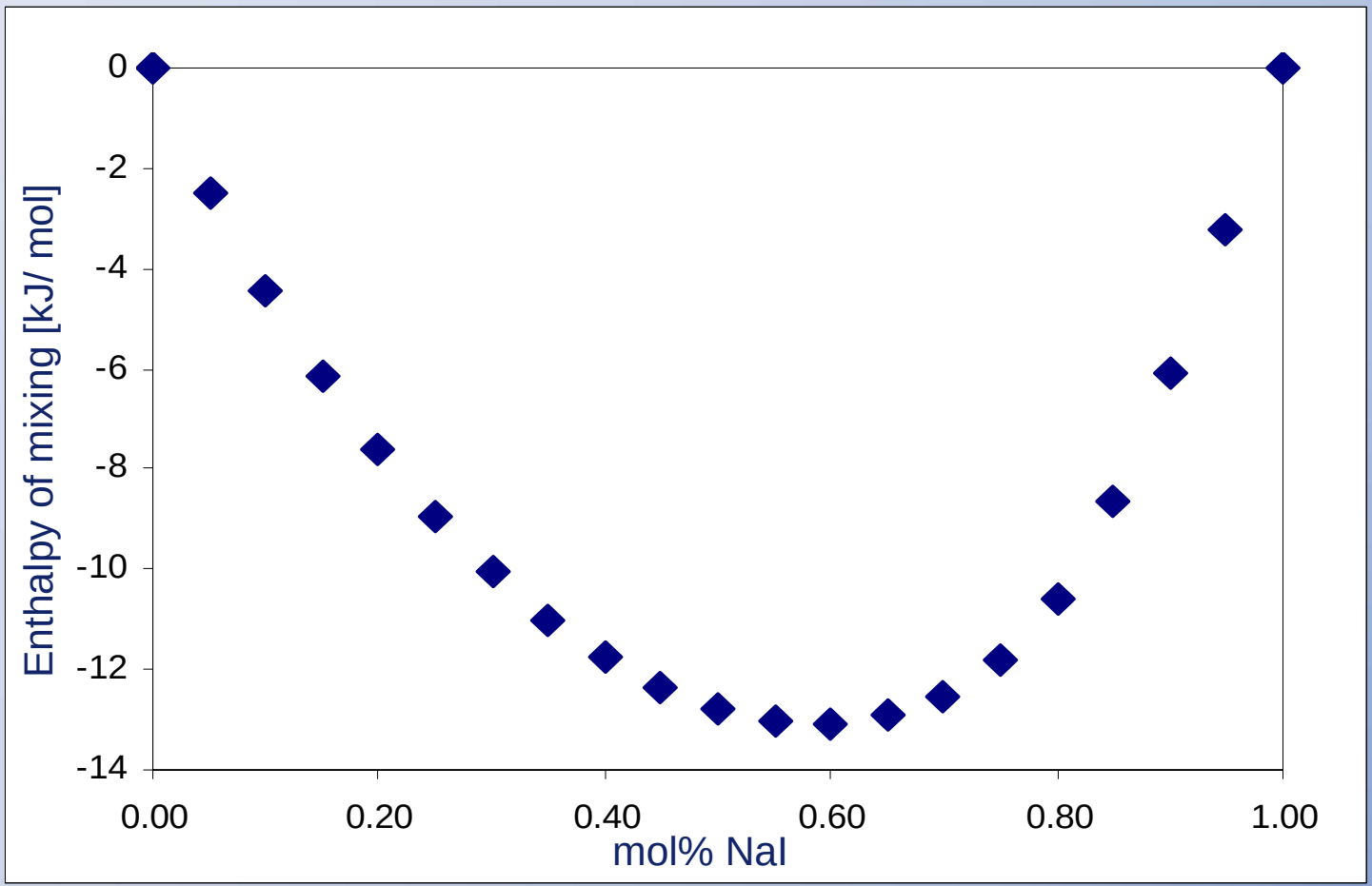
Temperature and Composition dependency of activity for the NaI – CeI_3 system



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:

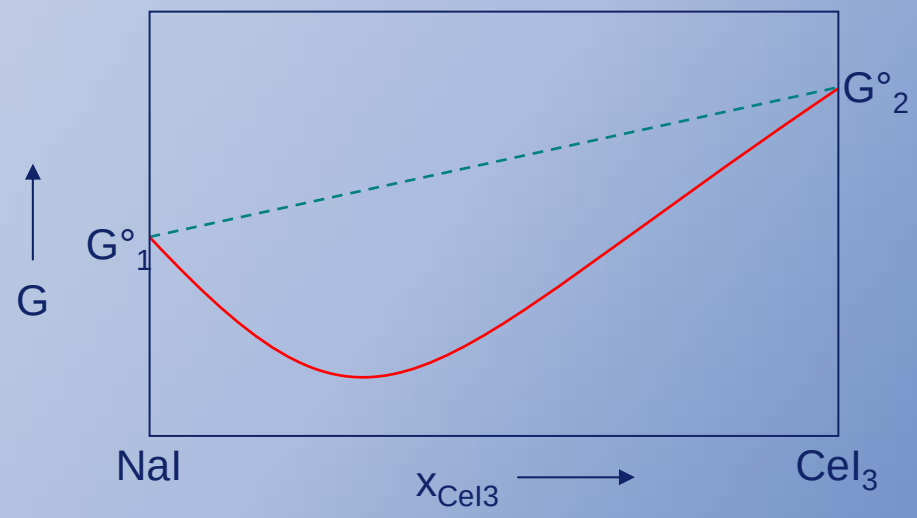
$$\Delta H = X_1X_2 (A_1) + X_1^2X_2 (B_1)$$

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

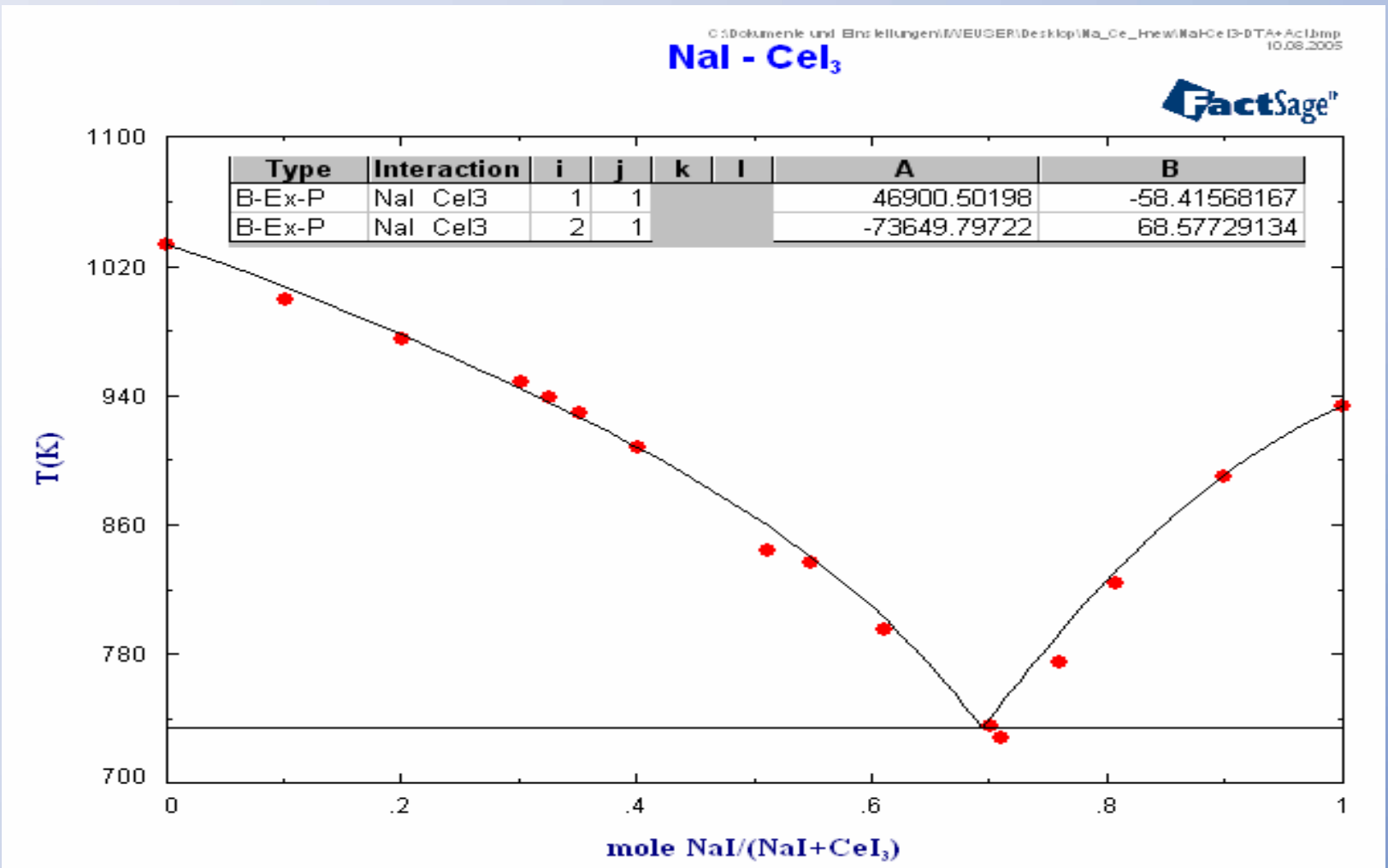
Hence:

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

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



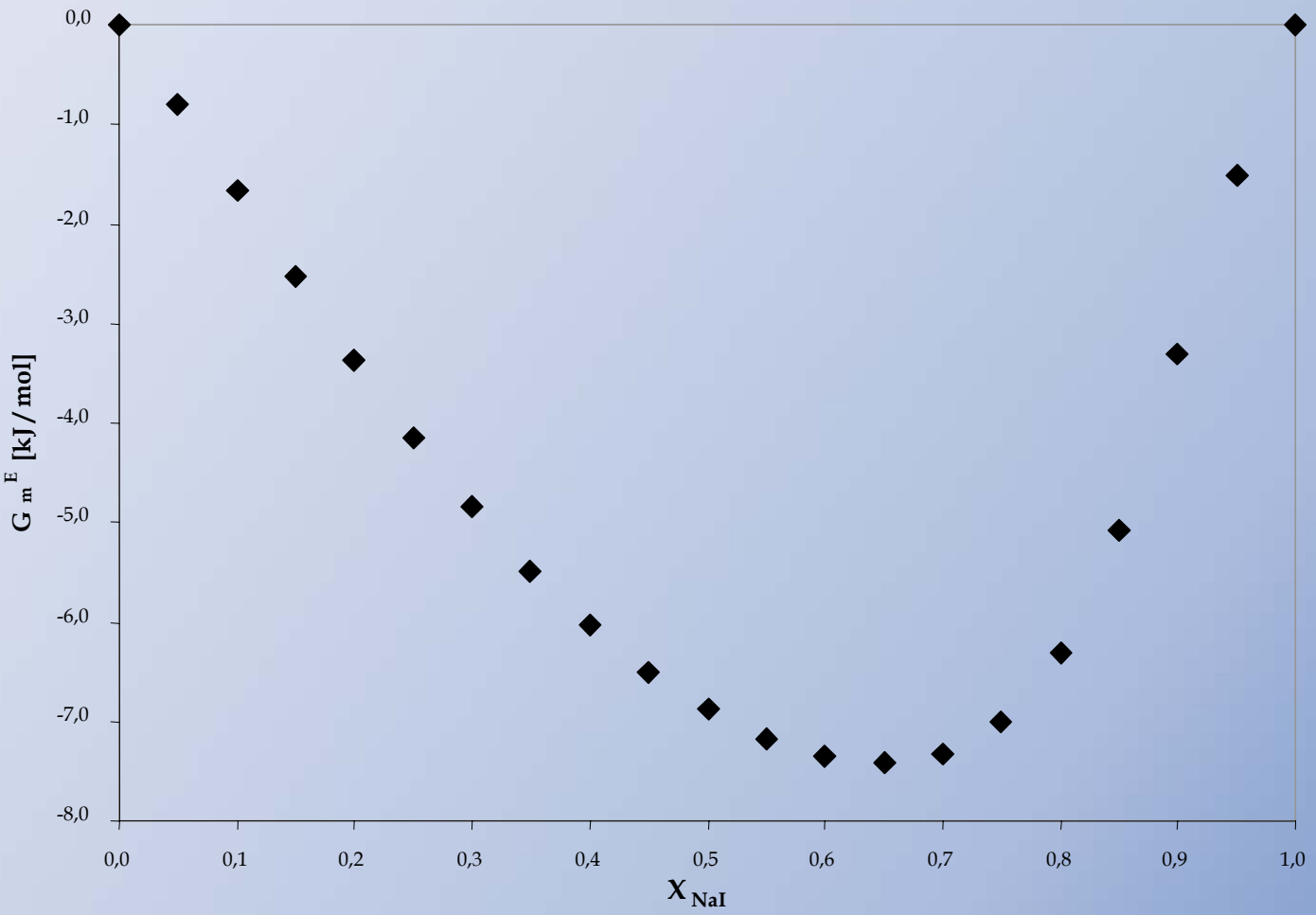
Phase Diagram of the System NaI–CeI$_3$ (calculated)



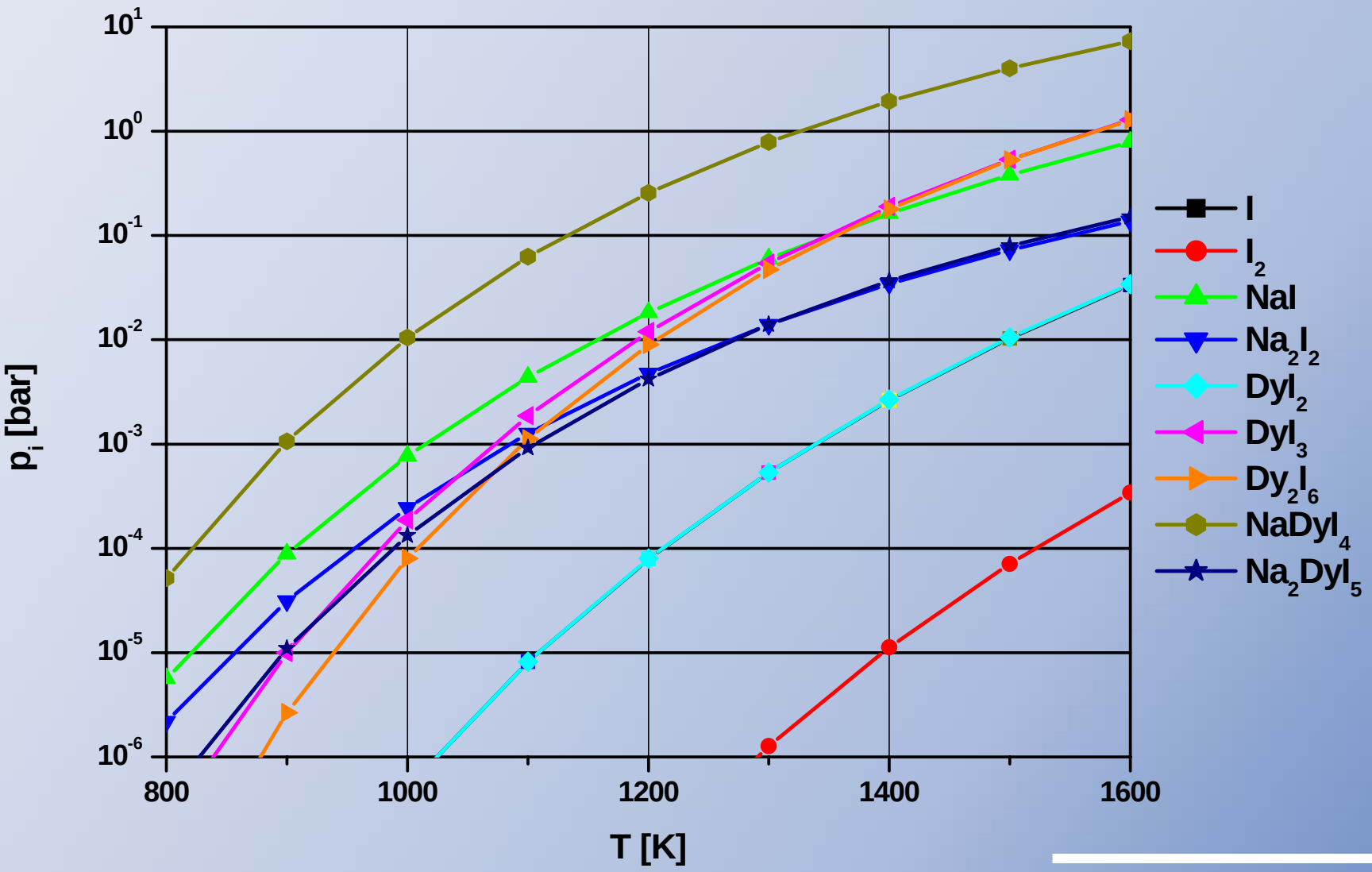
Binary Excess Polynomial:

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

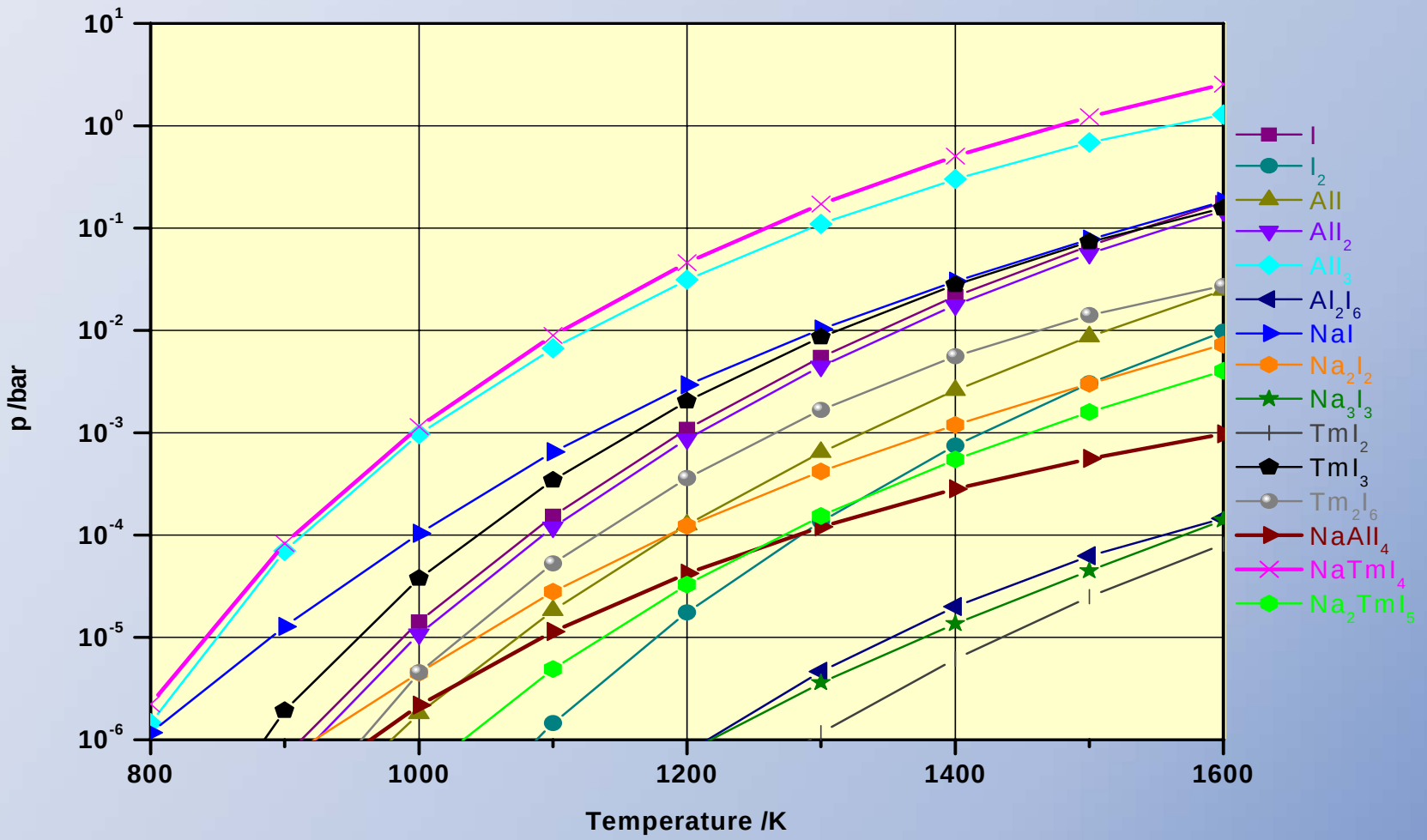
Integral Free Excess Enthalpy



Computed gas phase composition over an equimolar NaI/ DyI_3 mixture in a PCA Lamp

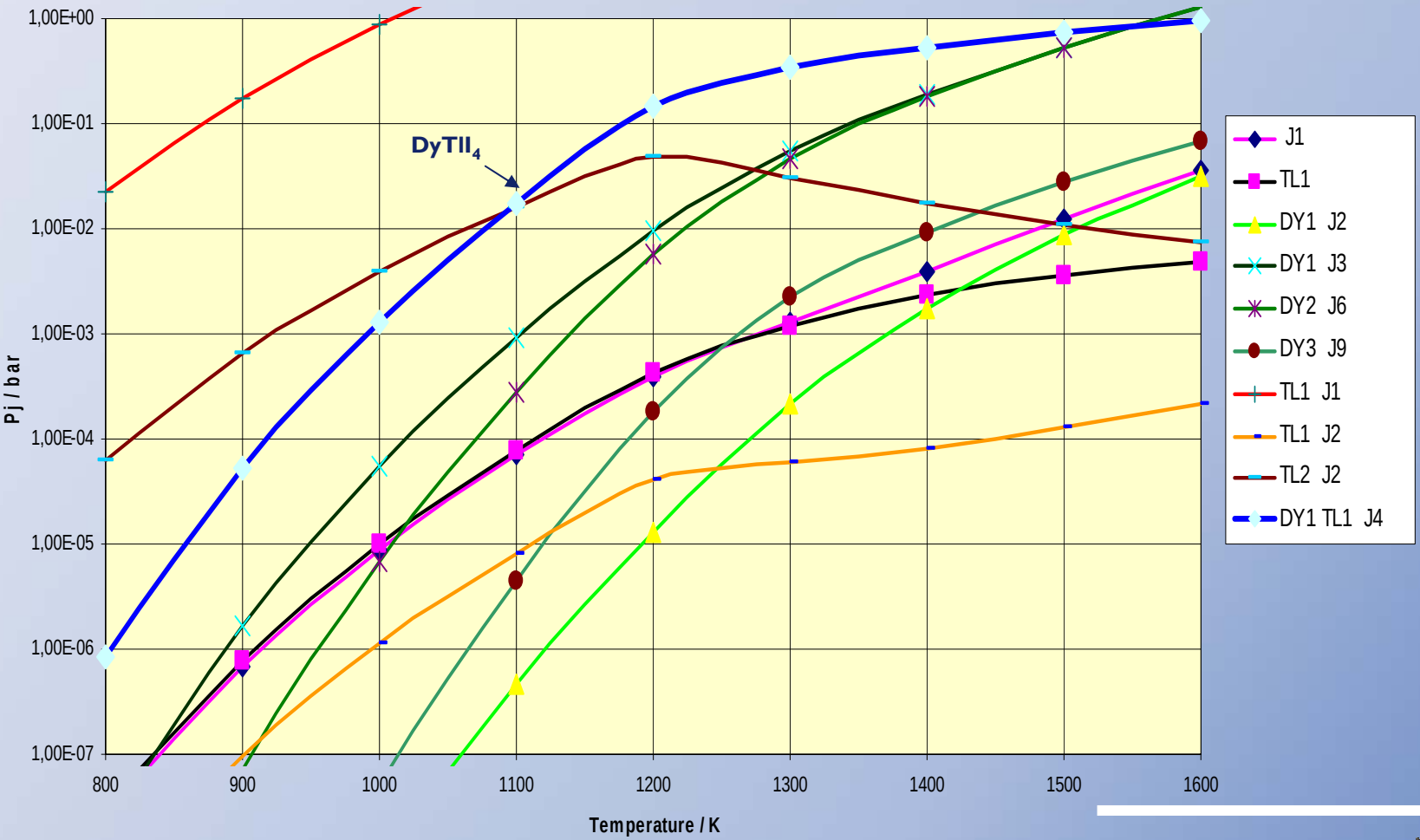


Computed gas phase composition over an equimolar NaI/ TmI_3 mixture in a PCA Lamp using FactSageTM



Berechnung der Gasphase über einer Mischung aus TlI und DyI_3

Filled amounts/MOL: 1.00E-03 DY1 J3 1.00E-03 TL1 J1



3. Summary / Conclusions

- Physical modeling of plasma
  → energy balance, temperature and density profiles, spectra

- Identification of (gaseous) species in discharge lamps and analysis of corrosion processes
  → KEMS measurements

- Determination of basic thermodynamic data
  → enthalpies and entropies of formation

- Thermochemical modeling by minimizing Gibbs free energy
  → simulation of partial pressures for complex systems

Predictive Lamp Model !

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