Mitglied der Helmholtz-Gemeinschaft

Investigations of Degradation Phenomena in High Temperature Discharge Lamps using Thermo chemical Modelling

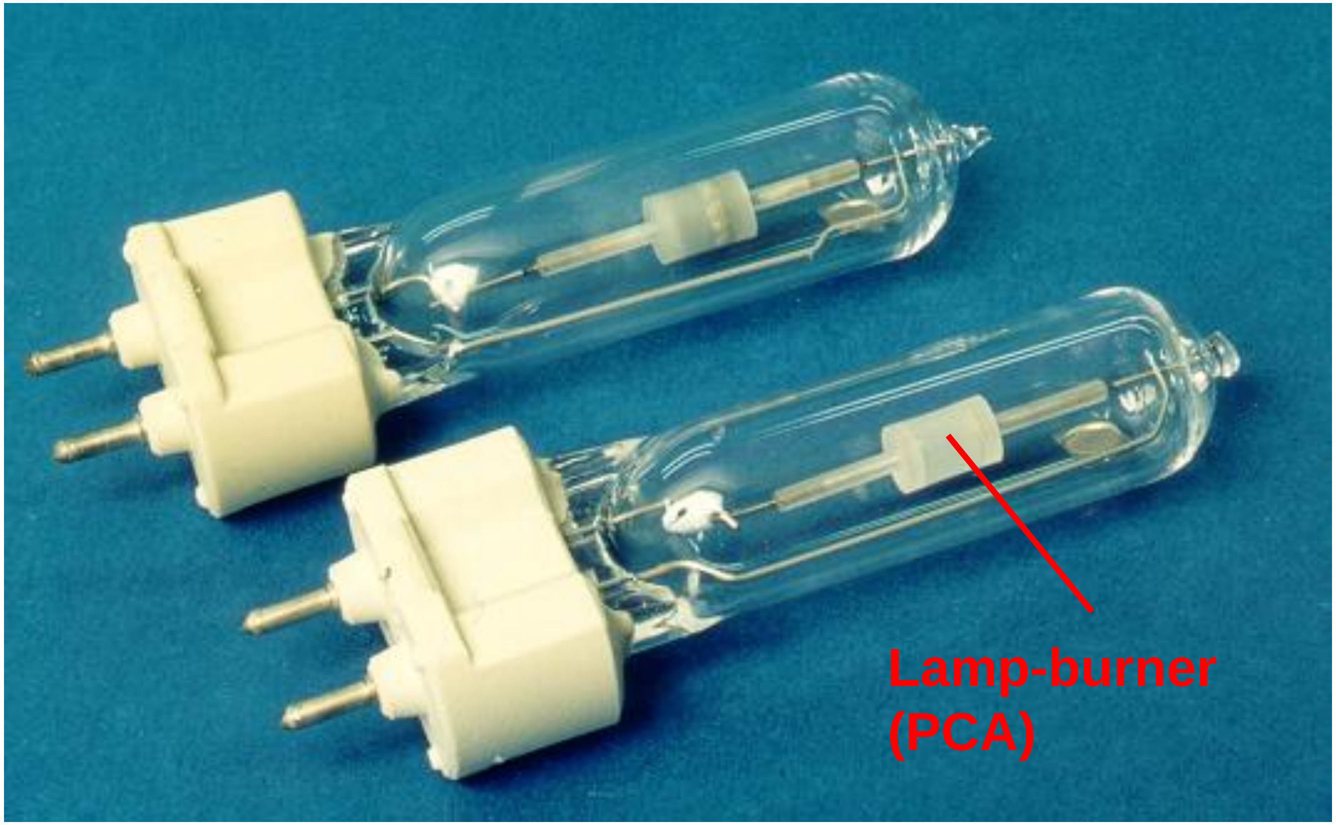
Torsten Markus and Sarah Fischer

Institute for Energy Research (IEF-2)
Forschungszentrum Jülich GmbH
52425 Jülich
T.Markus@fz-juelich.de

Content

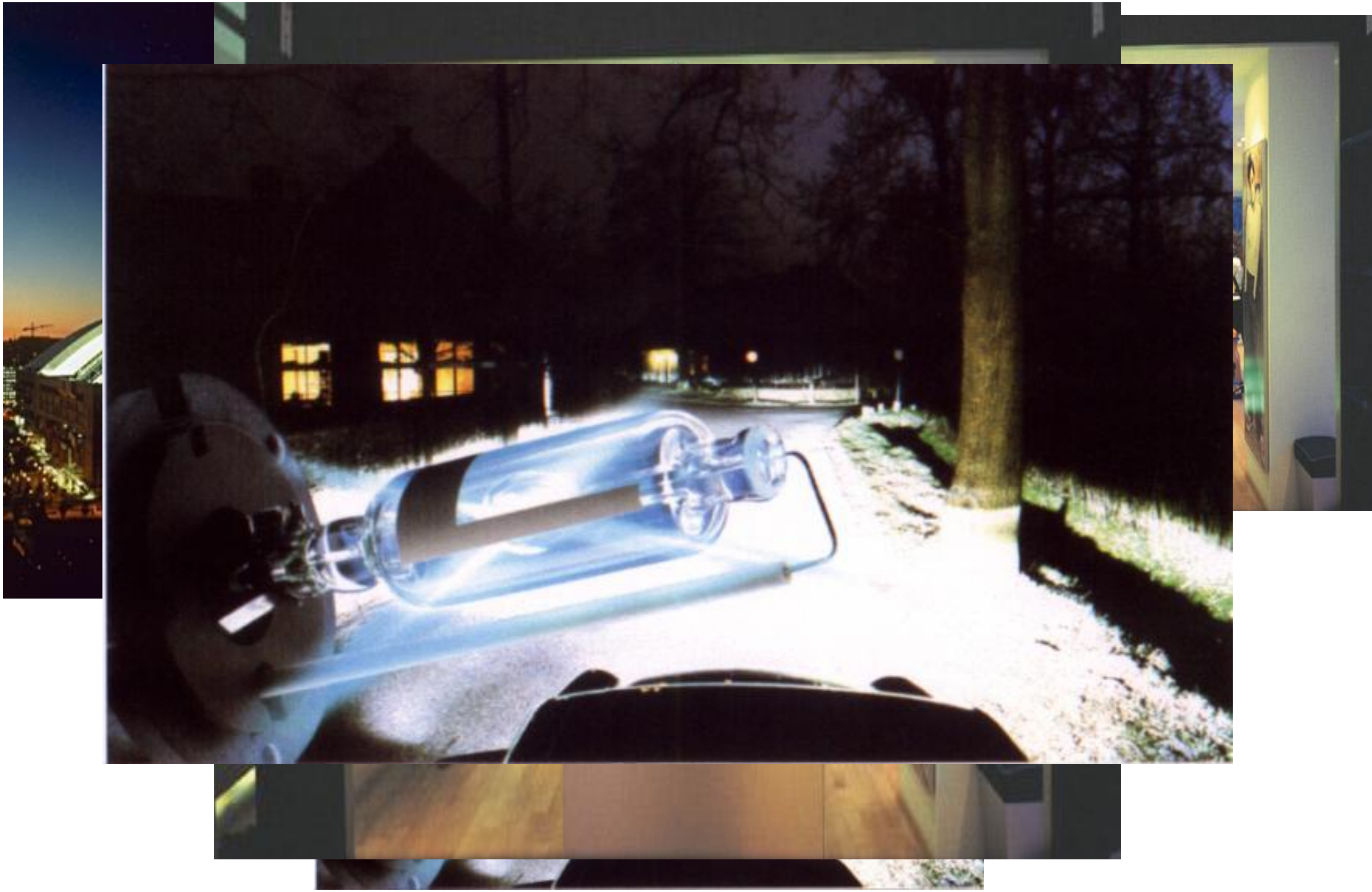
- Insight into Modern Light Sources
- Corrosion and Chemical Transport
- Calculation Design
- Results
- Conclusion

PCA-Lamps



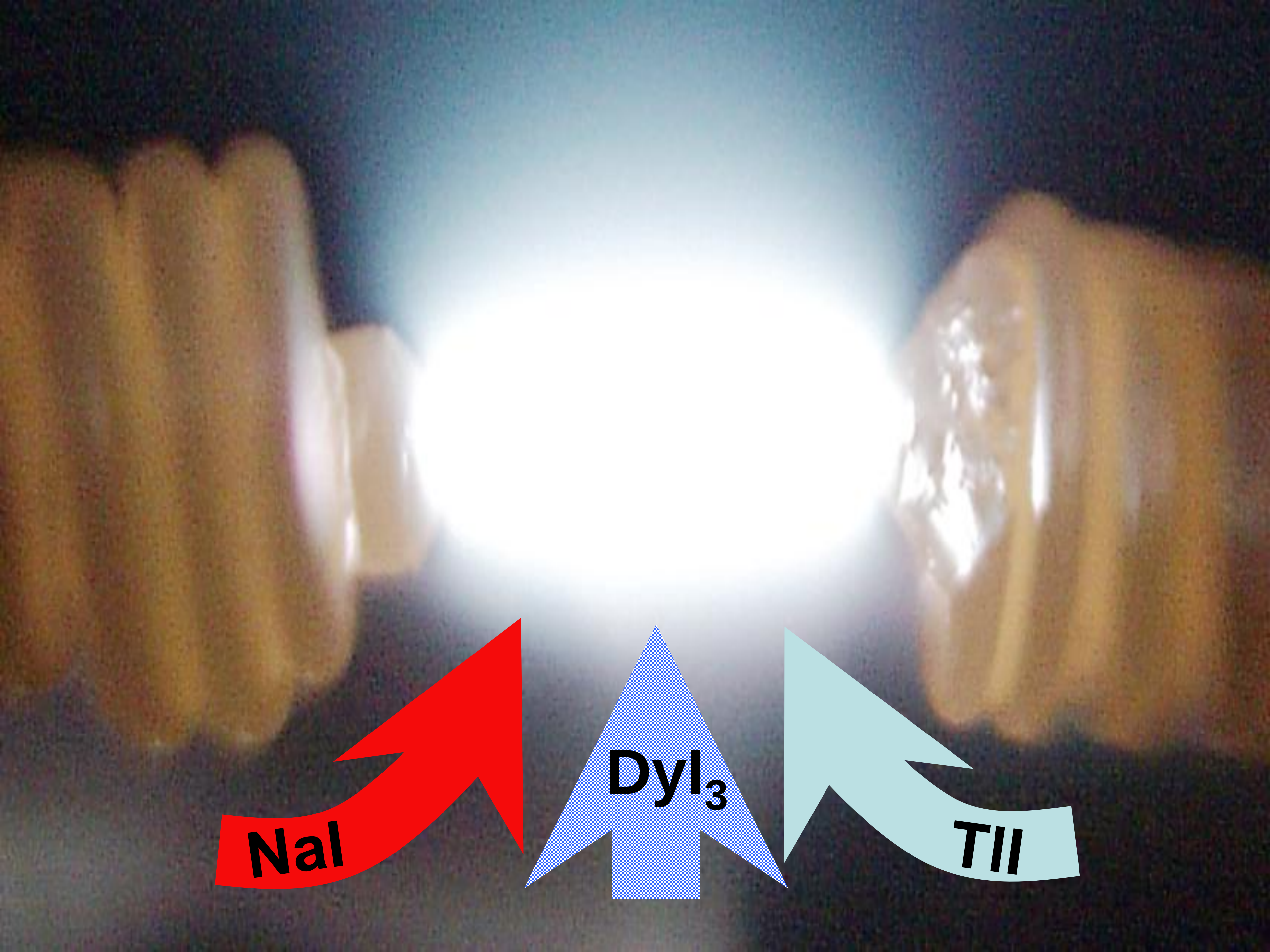
PCA = **P**oly **C**rystalline **A**lumina

Aplications for High Intensity Discharge Lamps

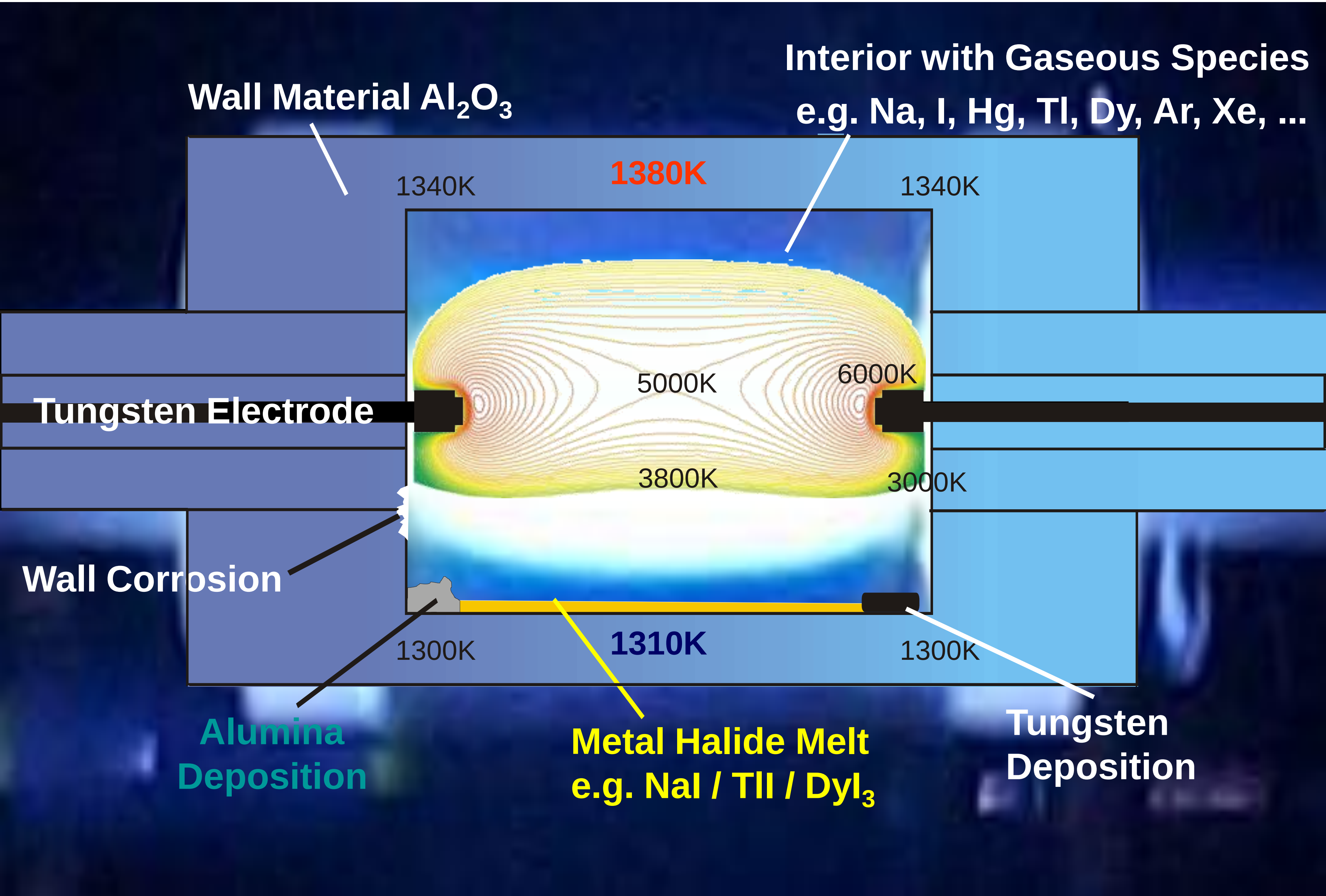


Halogen Light

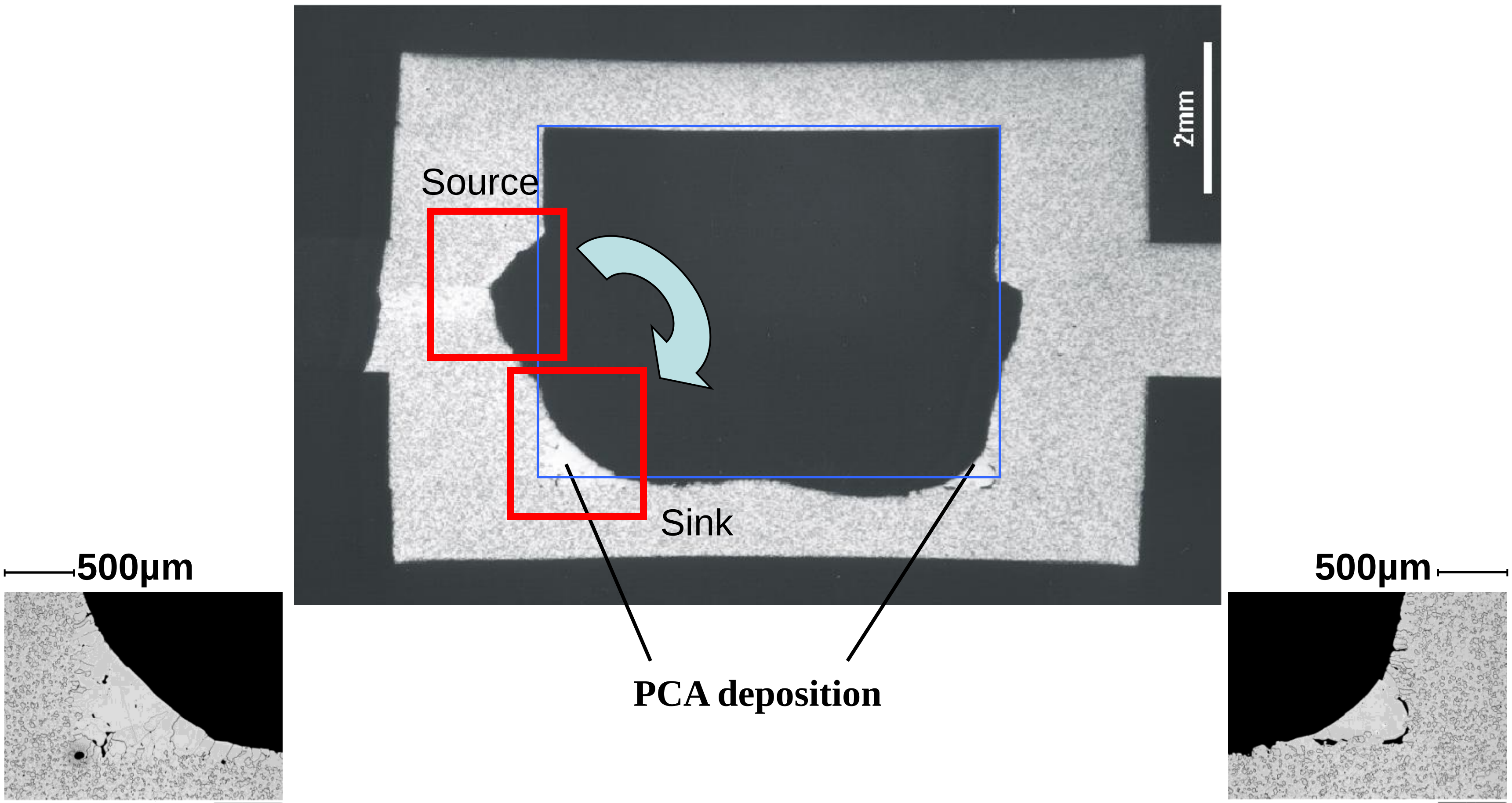
XENON LIGHT


NaI
DyI3
TlI

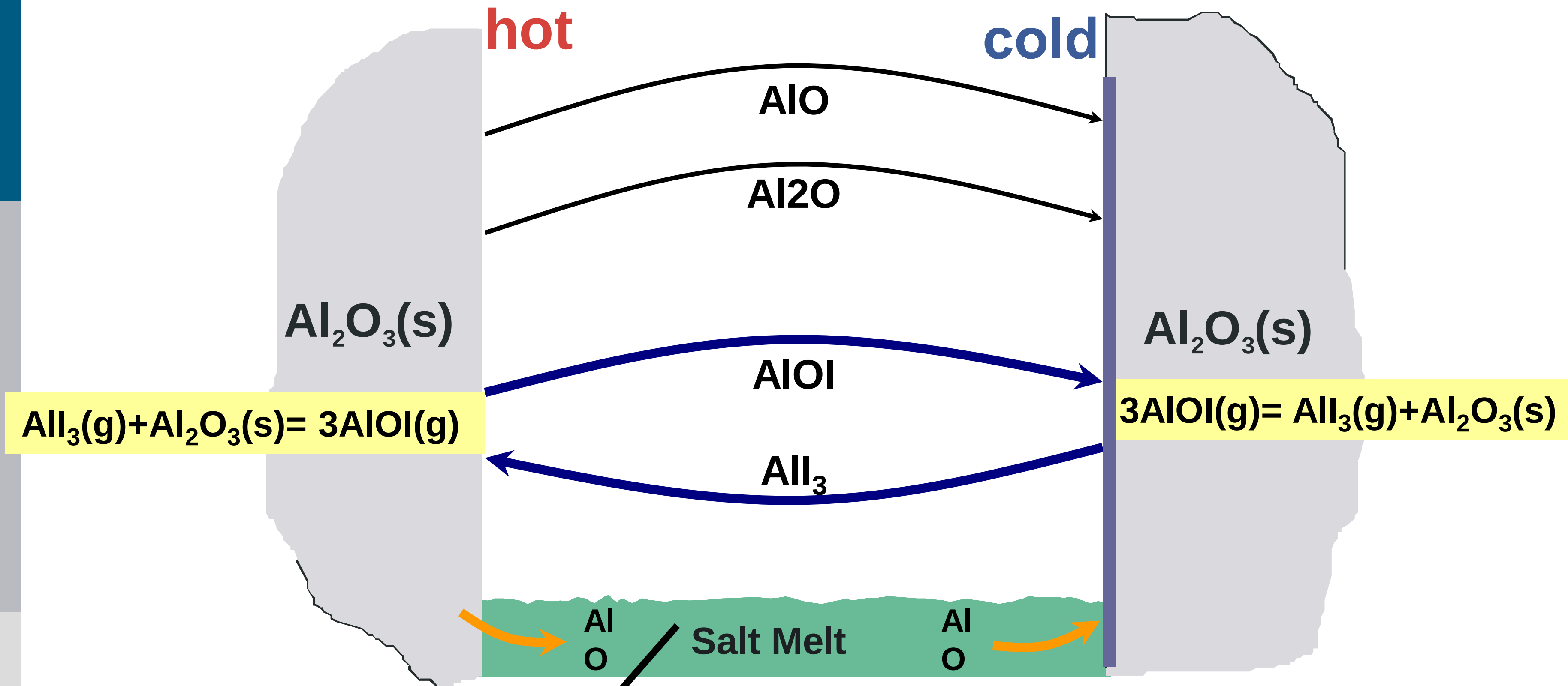
Schematic of a High Pressure Discharge Lamp



Cross Section of a Corroded Discharge Vessel in Horizontal Burning Position (after 9000 h of operation)



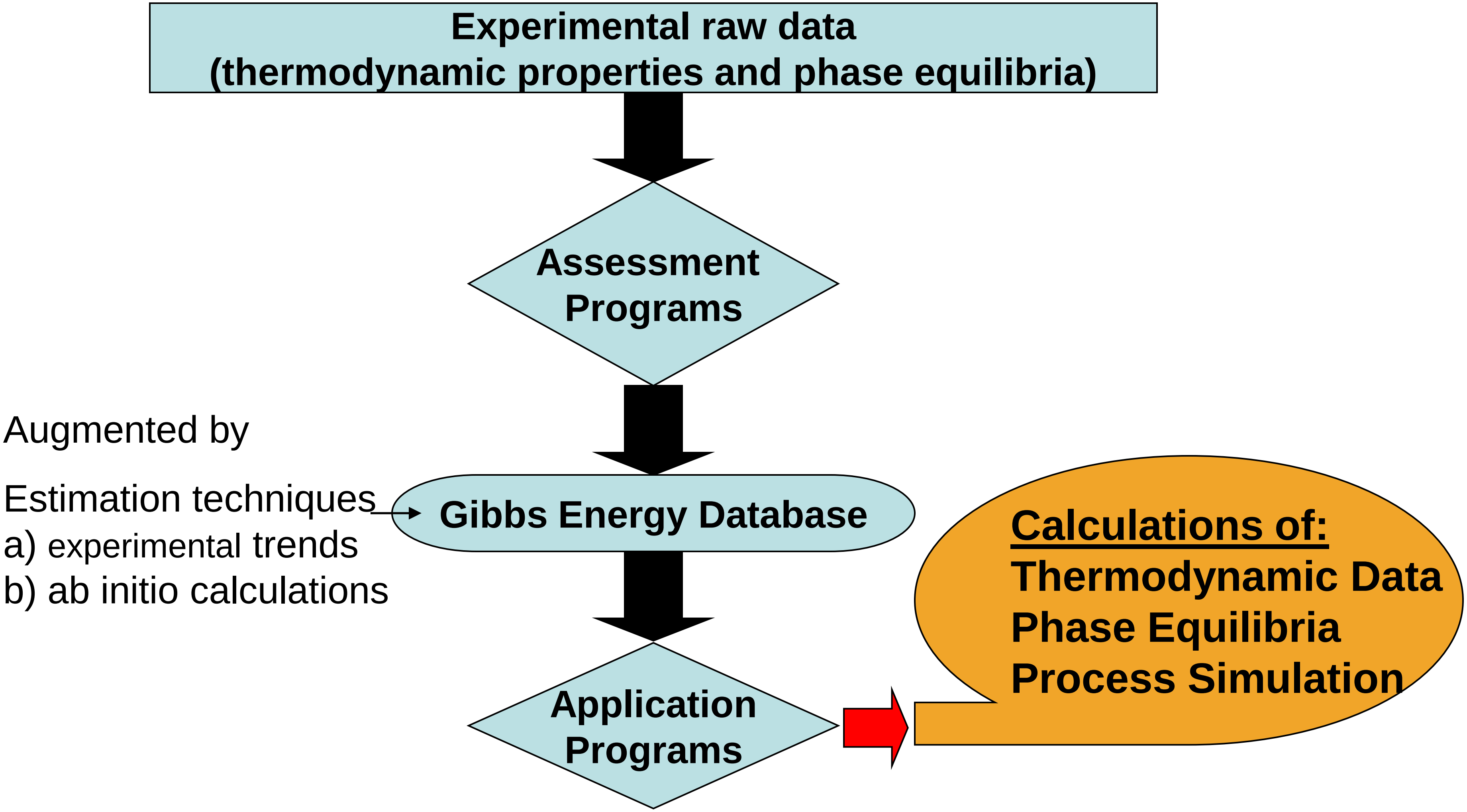
Explaination of Transport Phenomena



$3\ DyI_3(l) + 4\ Al_2O_3(s) = Dy_3Al_5O_{12}(s) + 3\ AlI_3(g)$

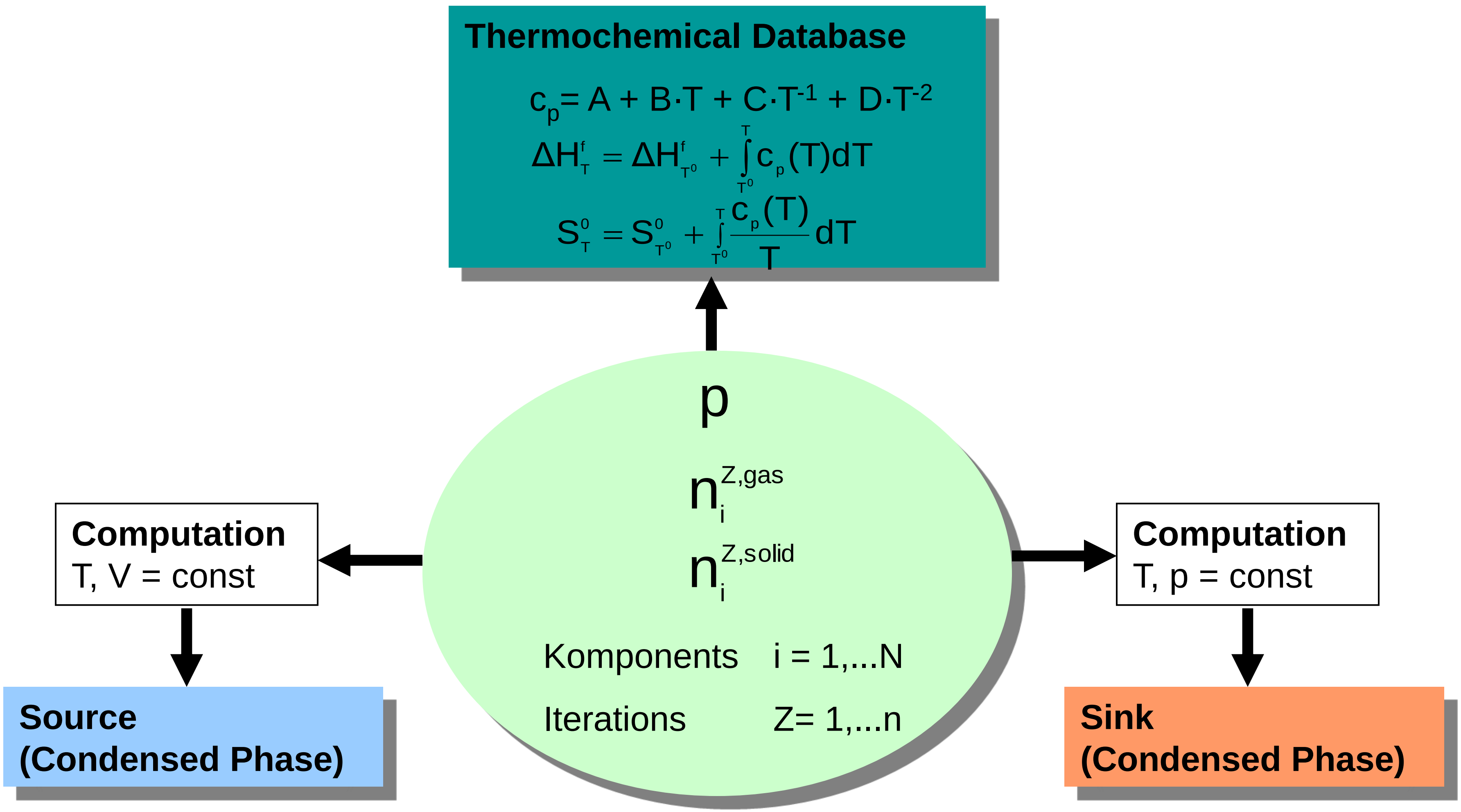
$DyI_3(g) + Al_2O_3(s) = DyAlO_3(s) + AlI_3(g)$

From data assessment to an application calculation

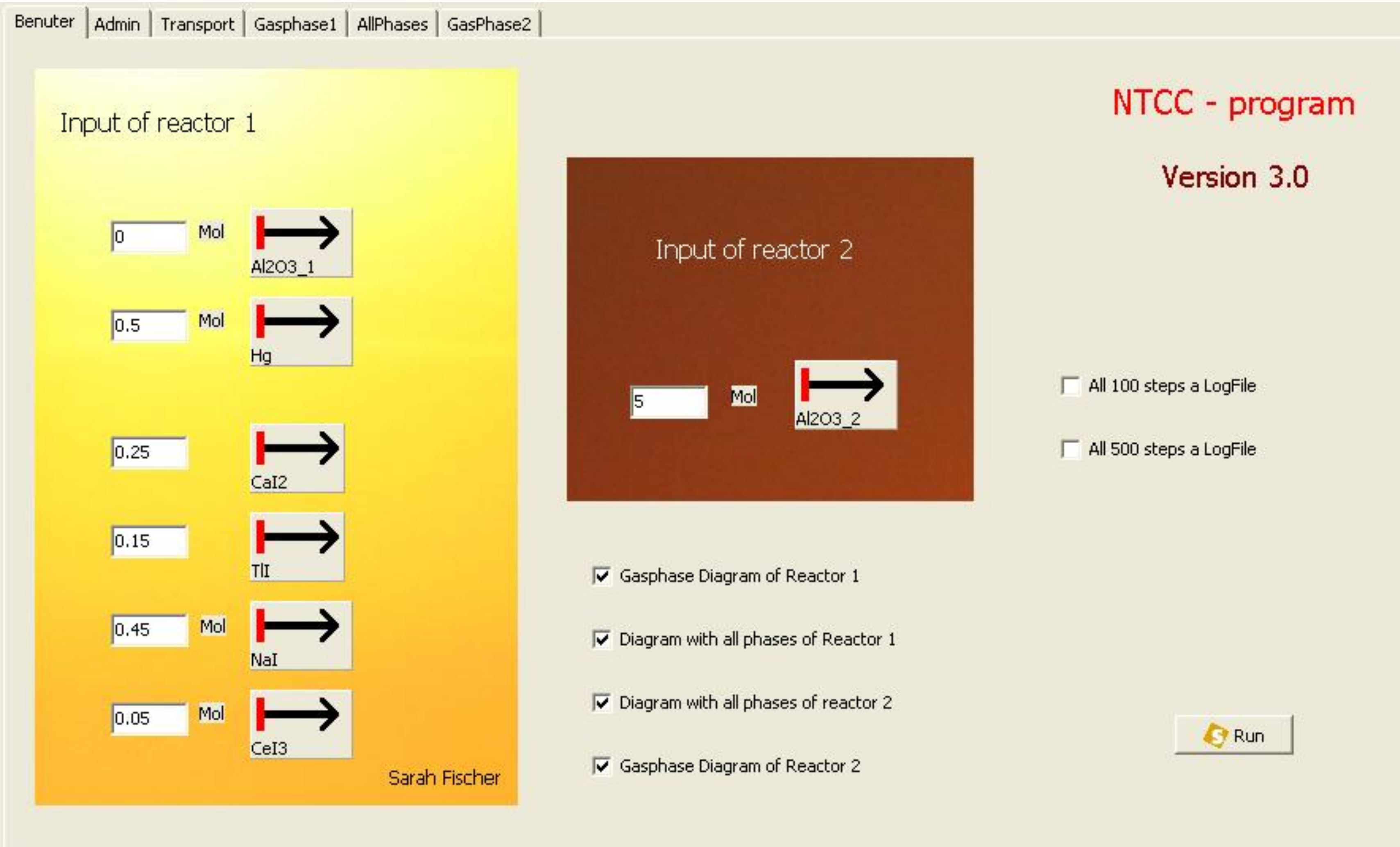


„Cooperative Transport Model"

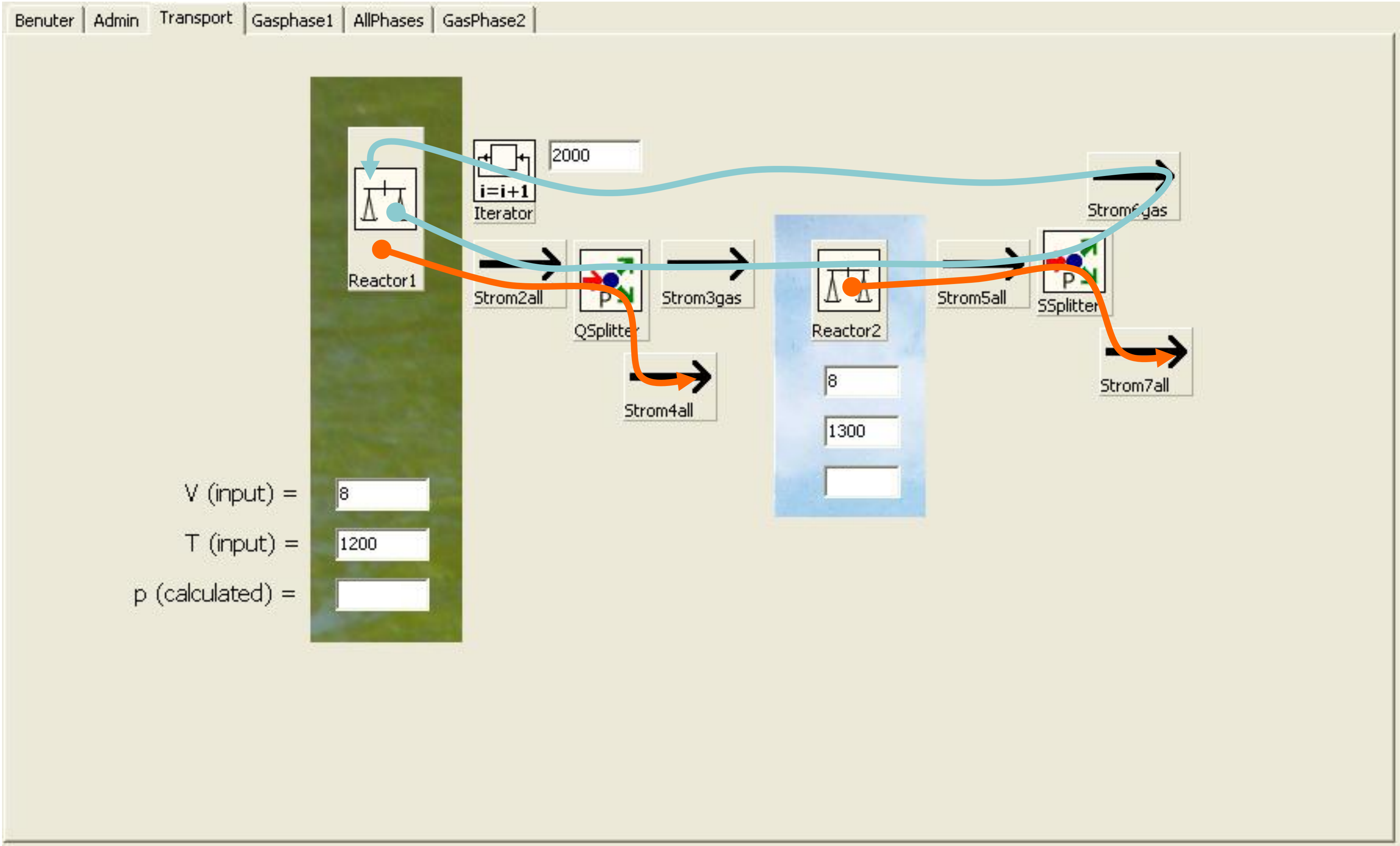
R. Gruehn, H.J. Schweitzer, Angew. Chem. 95, 80 (1983)



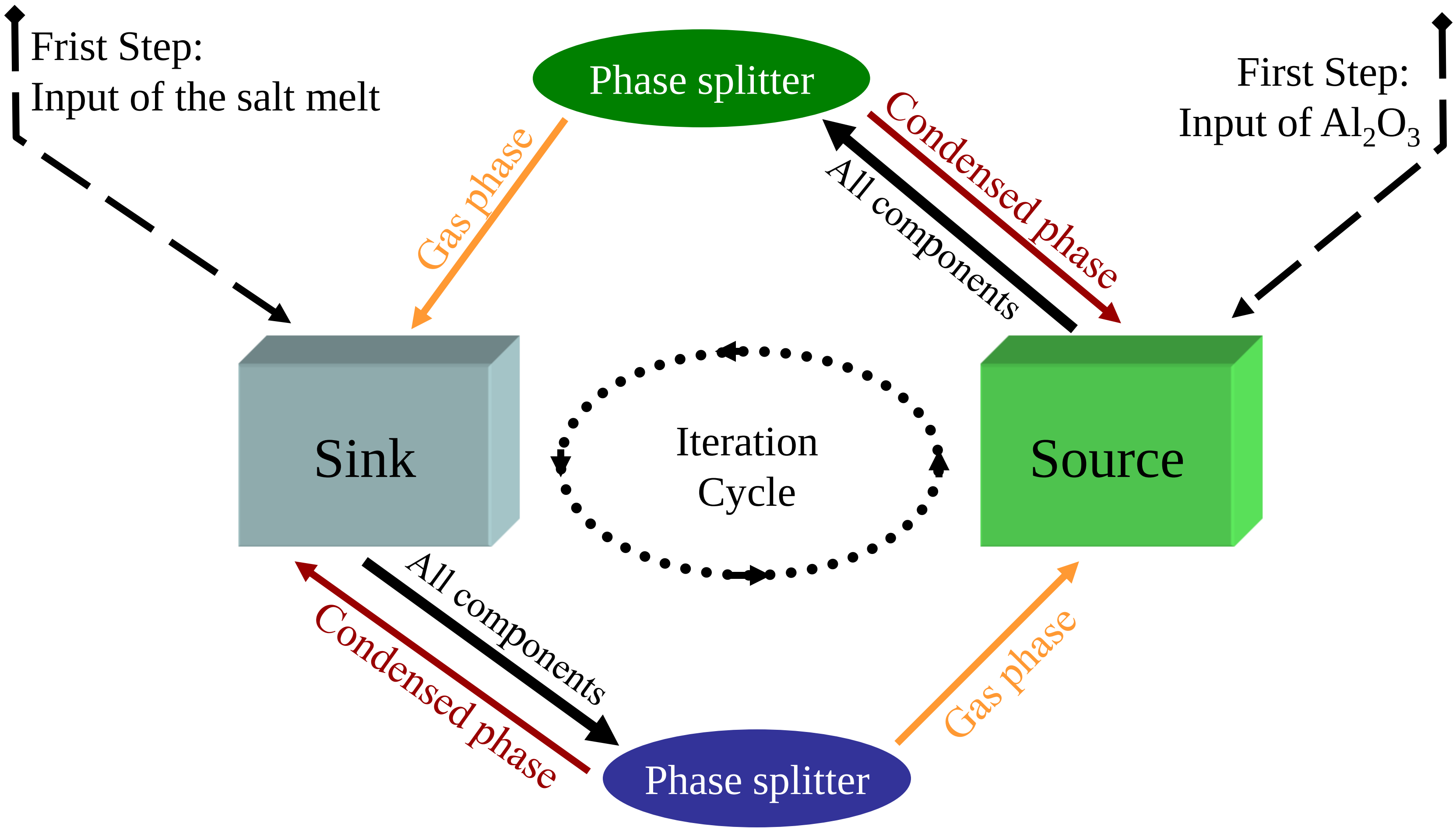
SimuSage Modelling



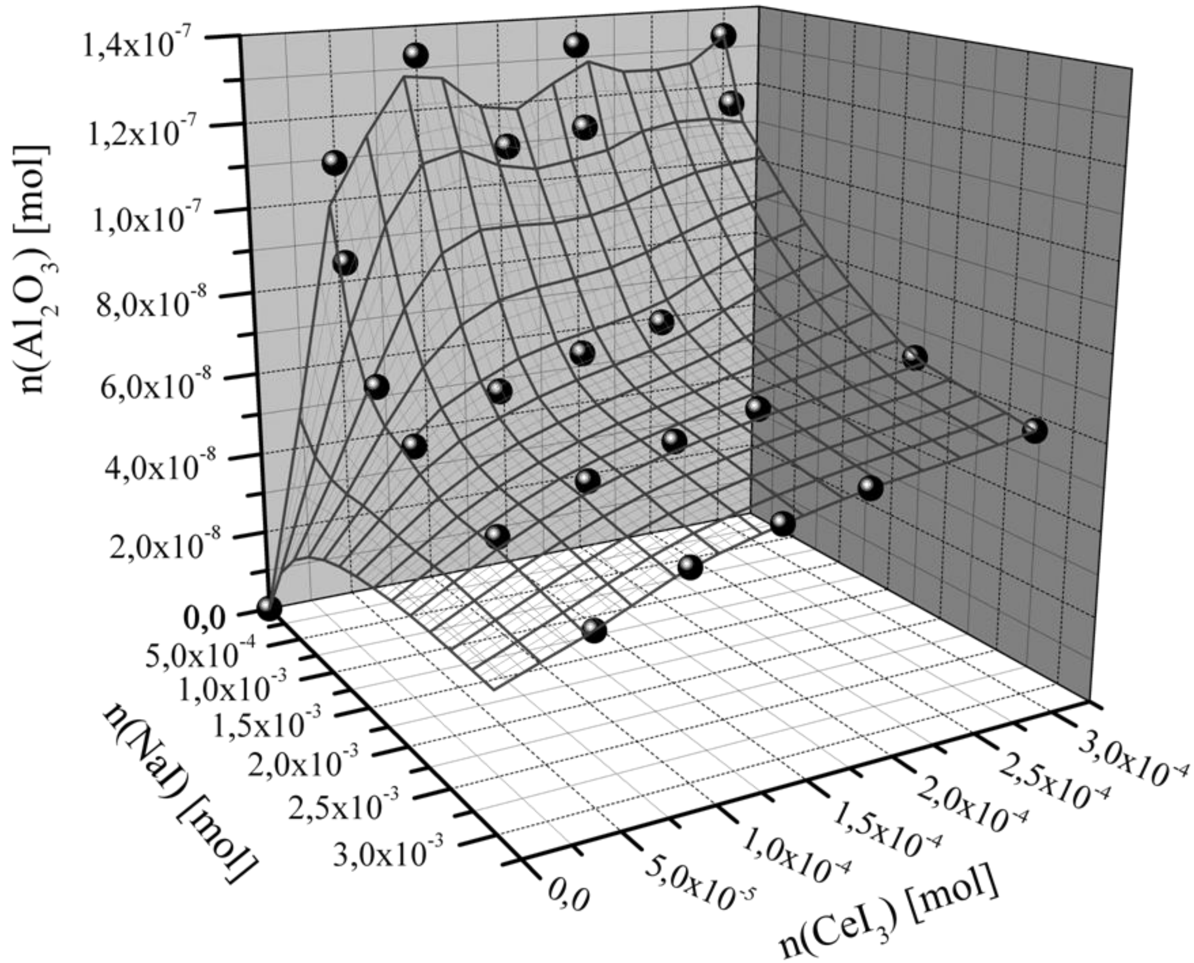
Equilibrium reactors



Scheme of the transport program



Example: NaI – CeI_3 – Mixture



T_{Sink} = 1200°C
T_{Source} = 1400°C
V = 0,0285 dm³

Comparison between experiments and simulations

NaI – CaI$_2$ - Mixture

	Composition NaI, CaI$_2$				
	75% NaI, 25% CaI$_2$		50% NaI, 50% CaI$_2$		25% NaI, 75% CaI$_2$
Simulation [mol Al_2O_3]:	$1{,}22 \cdot 10^{-9}$	<	$2{,}55 \cdot 10^{-9}$	<	$7{,}16 \cdot 10^{-9}$
Experimental certification:					

→ Agreement for NaI – CaI$_2$ – Mixture

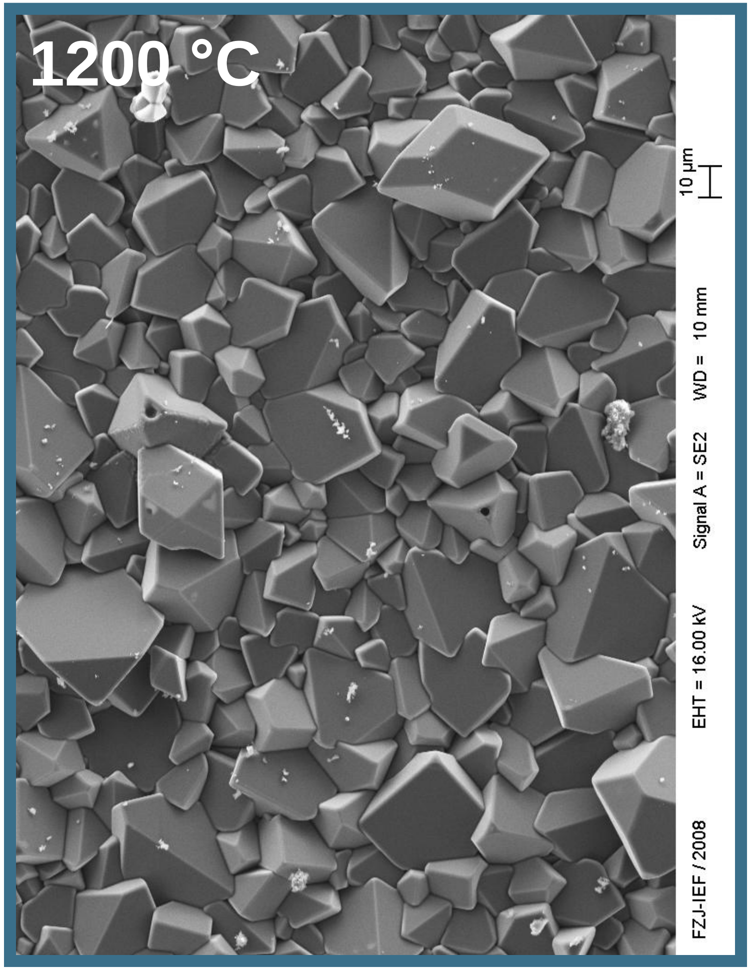
Comparison between experiments and simulations

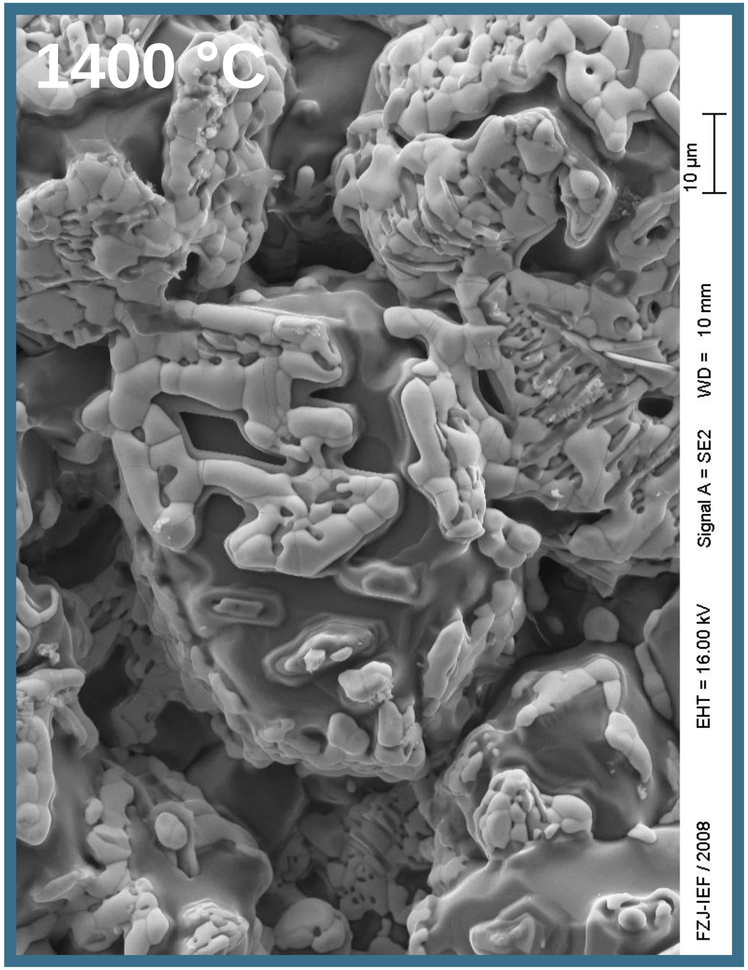
CaI_2 – CeI_3 - Mixture

	Composition CaI_2, CeI_3		
	90,48%, 9,52%		87,1%, 12,9%
Simulation [mol Al_2O_3]:	$5{,}08 \cdot 10^{-8}$	<	$5{,}58 \cdot 10^{-8}$
Experimental certification:		≈	

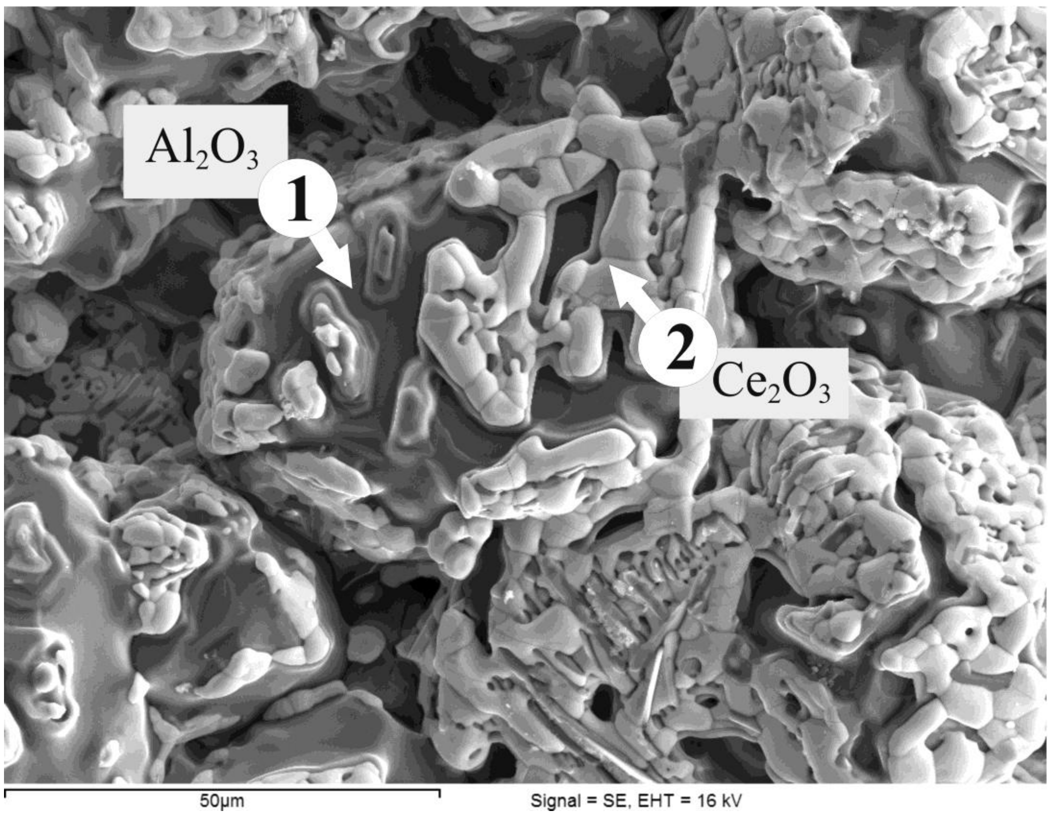
What causes this difference?

SEM – Analysis with 90,48% CaI_2 and 9,52% CeI_3



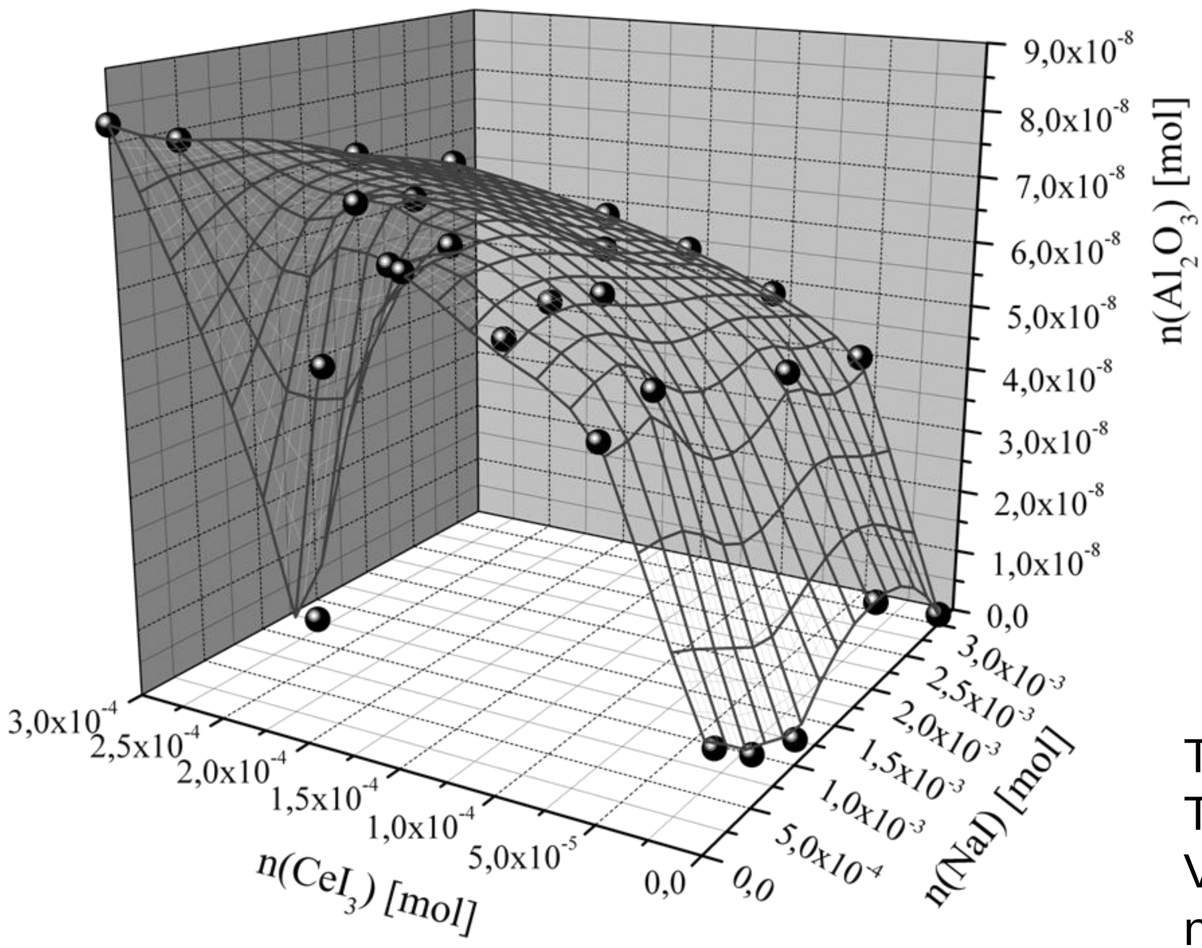


Formation of secondary phases



	Calculated Activity
Al_2O_3_ca(s)	1.0000E+00
CaI_2_l(liq)	9.4561E-01
Al_2O_3_cc(s2)	4.9718E-01
CaI_2_ci(s)	2.4571E-01
CeOI_ci(s)	1.1649E-01
CeI_3_l(liq)	5.4007E-02
Al_2O_3_l(liq)	3.5536E-02
$CeAlO_3$_ci(s)	2.0447E-02
$CeAl_{11}O_{18}$_ci(s)	1.3446E-02
CeI_3_ci(s)	1.1285E-02
$CeAlO_3$_l(liq)	5.4999E-03
$Ce_2Al_2O_6$_ci(s)	4.1199E-03
$CeAl_{11}O_{18}$_l(liq)	3.4167E-03
$CaAl_4O_7$_ci(s)	3.0990E-03
$CaAl_2O_4$_ci(s)	7.1260E-04
Al_l(liq)	6.7438E-04
Al_ci(s)	4.0705E-04
CaO_ci(s)	1.4573E-05
AlI_3_l(liq)	2.7872E-06
CeO_2_ci(s)	1.6025E-06
Al	9.3713E-07
Ce_2O_3_ci(s)	6.0181E-07

Example: NaI – CaI$_2$ – CeI$_3$ – Mixture



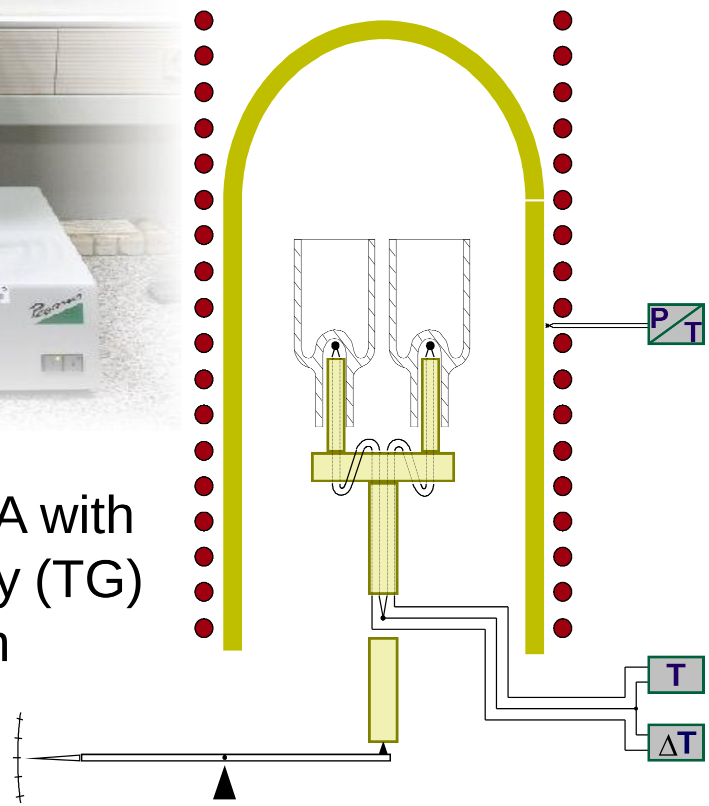
T_{Sink} = 1200°C
T_{Source} = 1400°C
V = 0,0285 dm³
n(CaI$_2$)=0,0008mol

Experimental Determination of Thermodynamic Data

Differential Thermal Analysis (DTA)

Simultaneous DTA with Thermogravimetry (TG)
STA 429, Netzsch

Principle of DTA



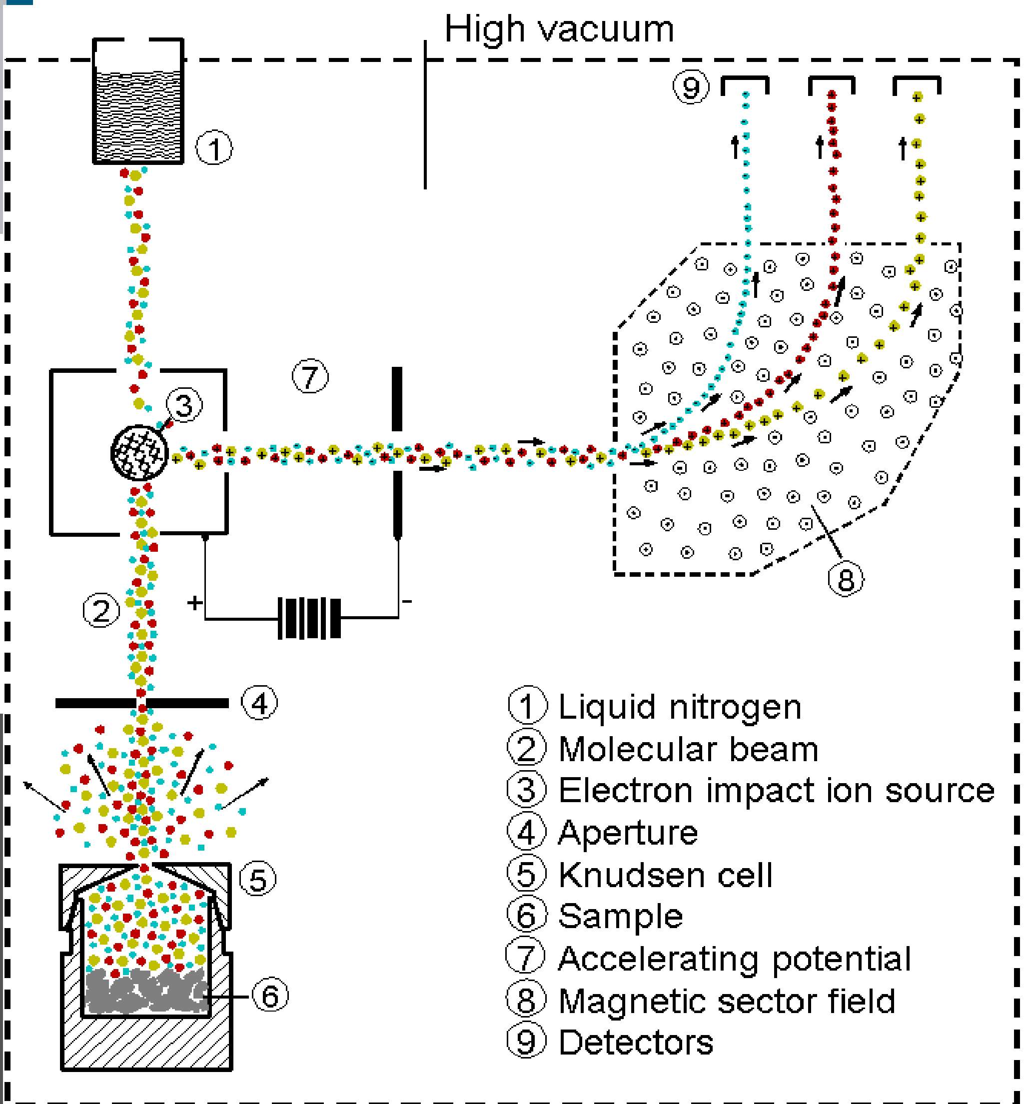
Measuring of Phase Transition Temperatures

Determination of the Quantity of Heat

Studies in different Atmospheres

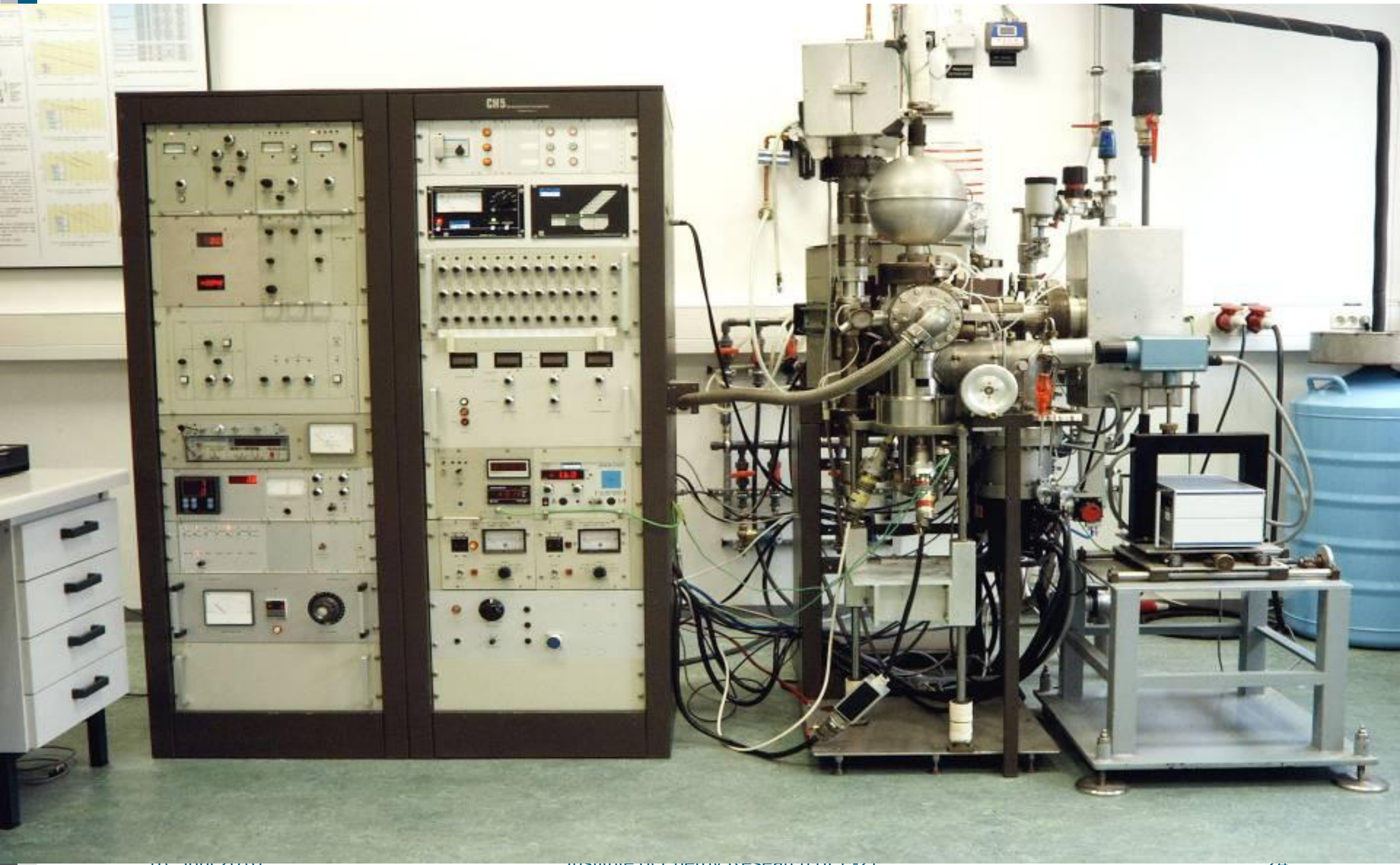
Thermal Analysis from RT to 2800 K

Principle of Knudsen Effusion Mass Spectrometry (KEMS)

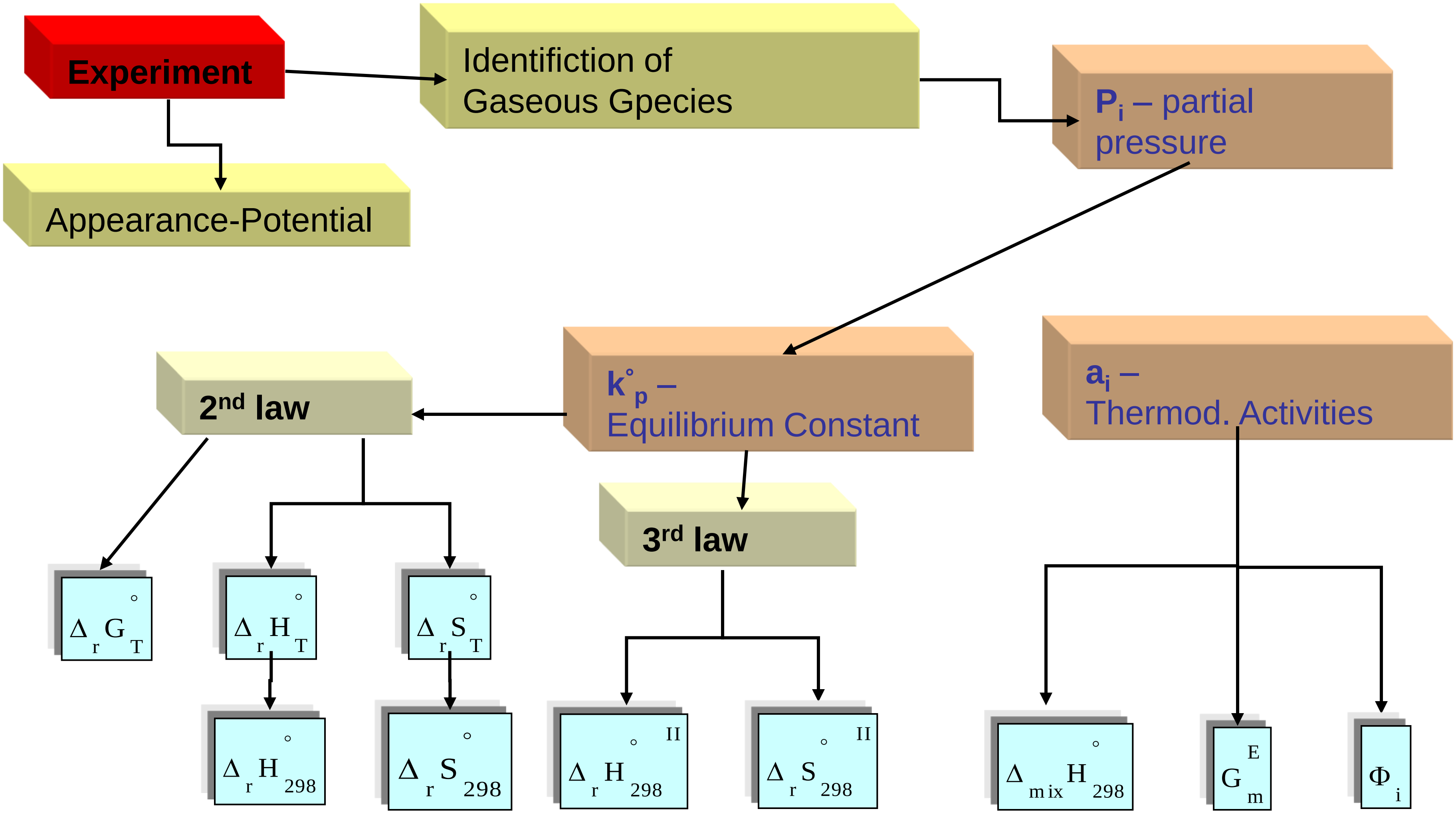


- **Vaporisation studies up to 2800 K**
- **Identification of gaseous species**
- **Determination of partial pressures (10^{-8} ... 10 Pa)**
- **Evaluation of thermodynamic data of**
  - **gaseous species**
  - **condensed phases**
- **Elucidation of corrosion processes**

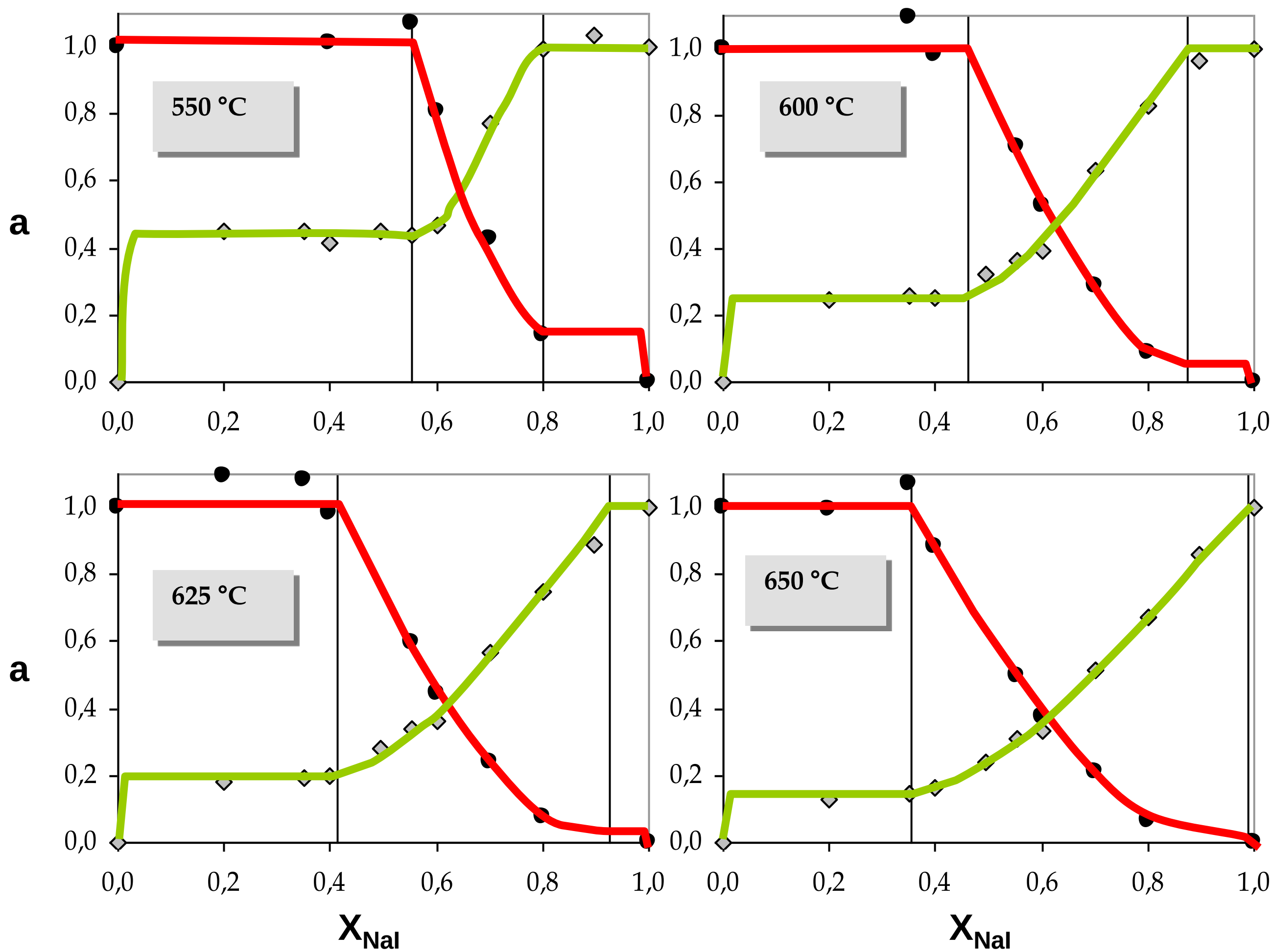
Mass Spectrometer Knudsen Cell System (CH 5)



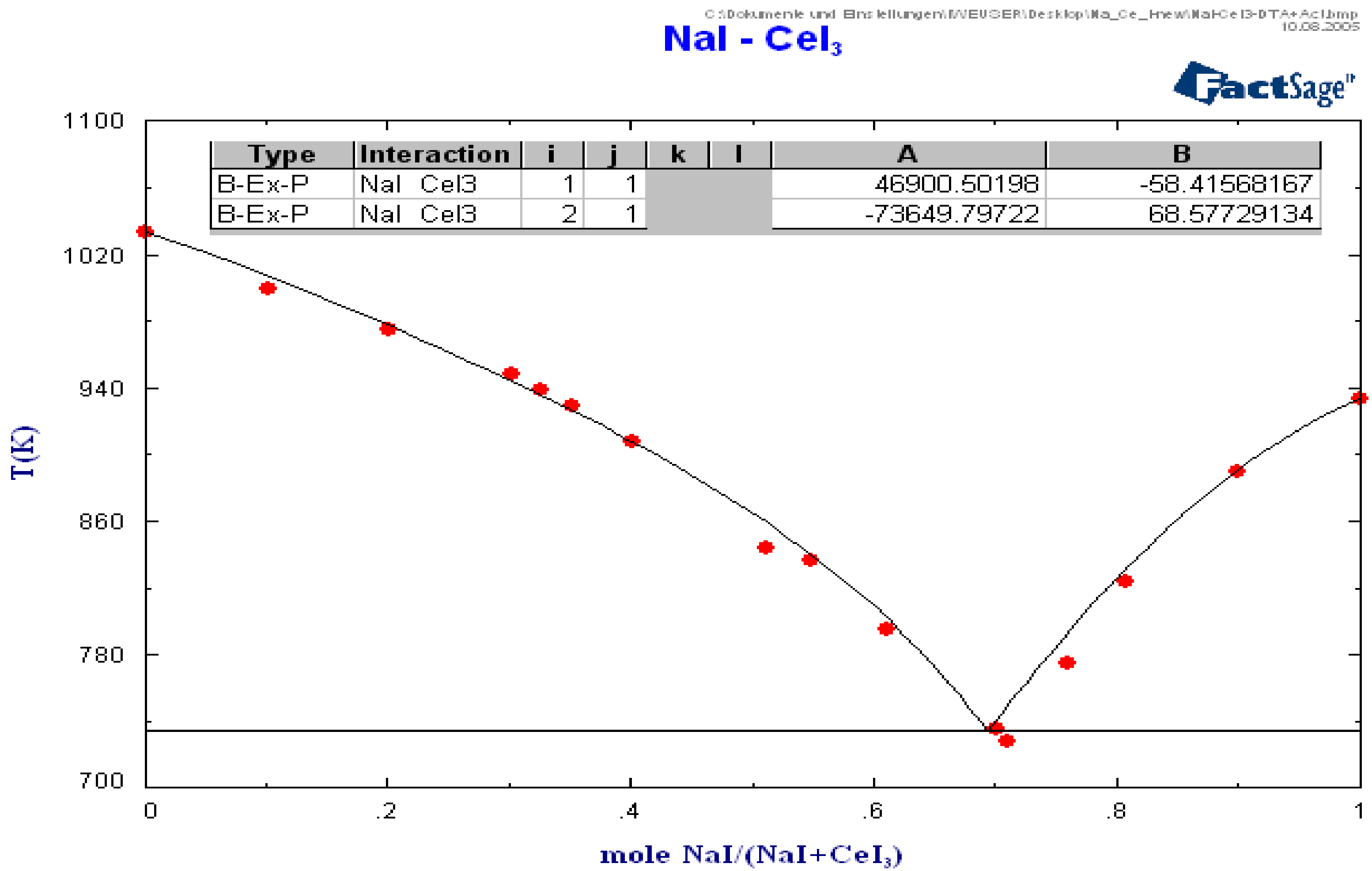
Potential of Knudsen Effusion Mass Spectrometry



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



Phase Diagram of the System NaI–Ce (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:

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

Overview of the data to be optimized in the $NaI\text{-}CeI_3$ system

Various experimental data on the binary $NaI\text{-}CeI_3$ 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:

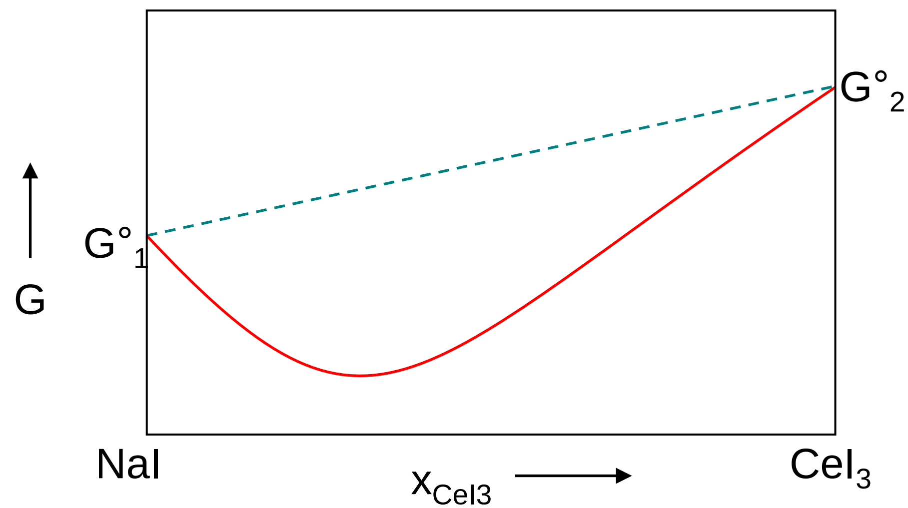
$\Delta H = X_1X_2 (A_1) + X_1^2X_2 (B_1)$

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

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.



Summary

- Corrosion- and rearrangement – effects of the wall material limit the life time of High-Energy-Discharge-Lamps
- Cooperative Transport Model was programmed with SimuSage
- Simulations of the corrosion speed of lamp relevant salt mixtures
- Comparison of the experiments and simulations show remarcable agreement