Calorimetric investigations

in multi-component salt systems

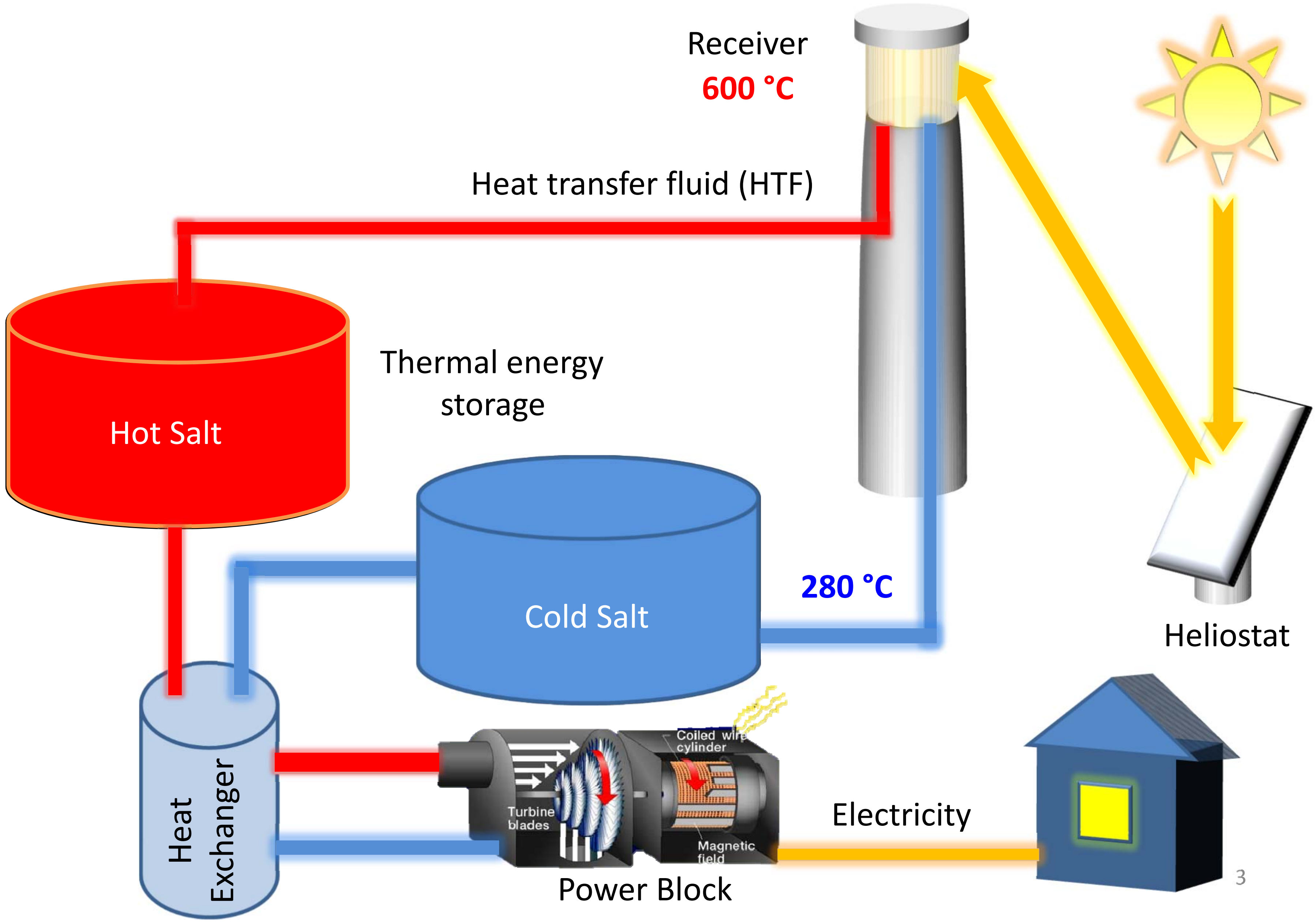
D. Sergeev[1], E. Yazhenskikh[1], N. Talukder[1], D. Kobertz[1], K. Hack[2], M. Müller[1]

[1] – Forschungszentrum Jülich, IEK-2

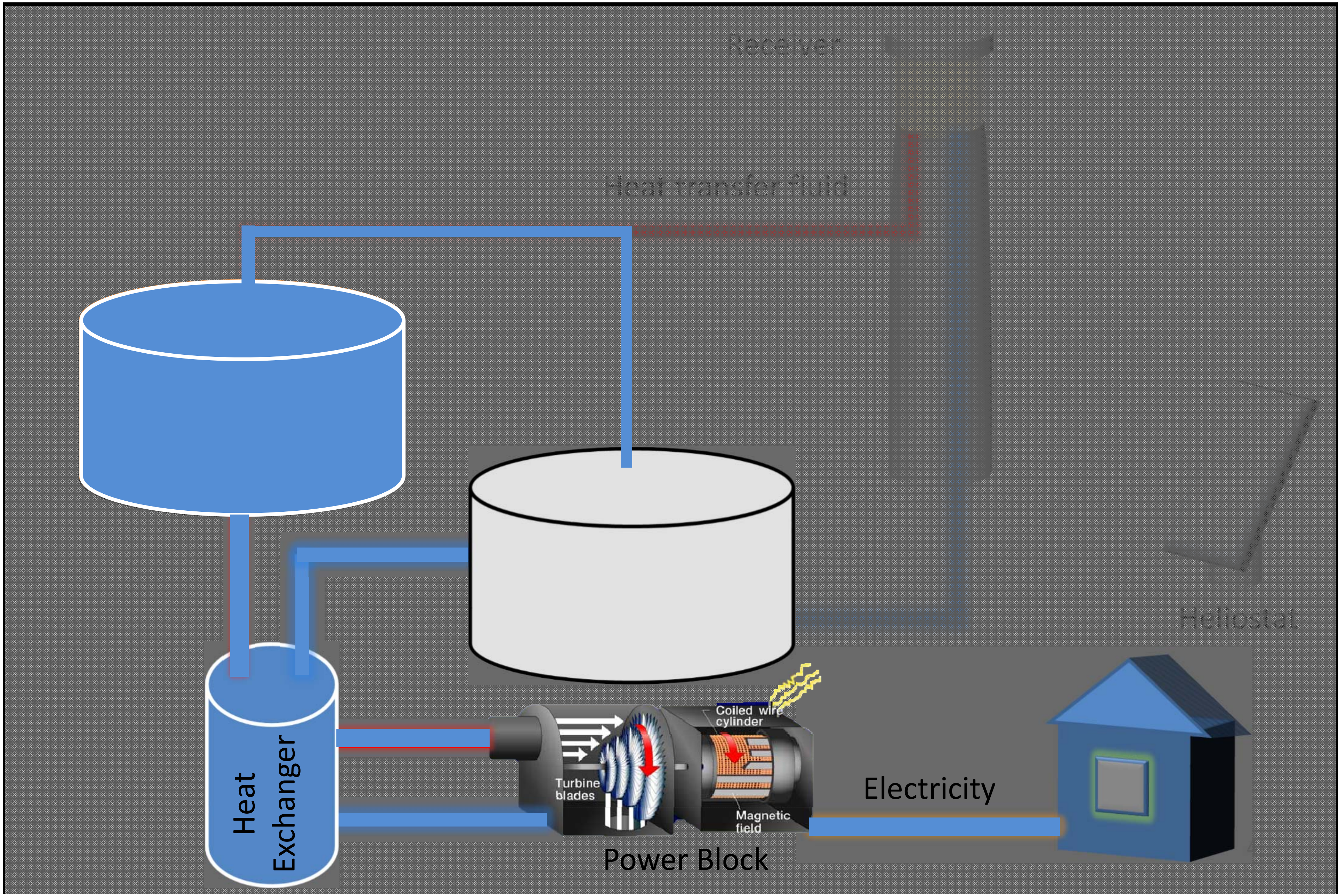
[2] - GTT-Technologies

Sensible Thermal Energy Storage

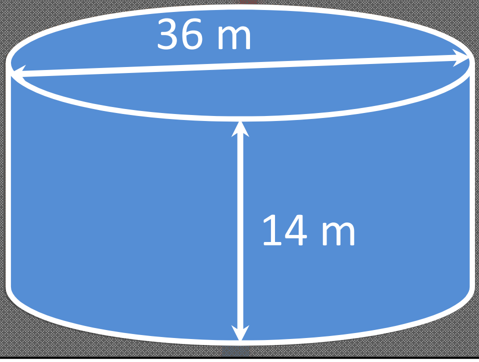
Scheme of Solar Power Plant



Scheme of Solar Power Plant



Thermal Energy Storage



28 500 kg
40%KNO_3-60%$NaNO_3$

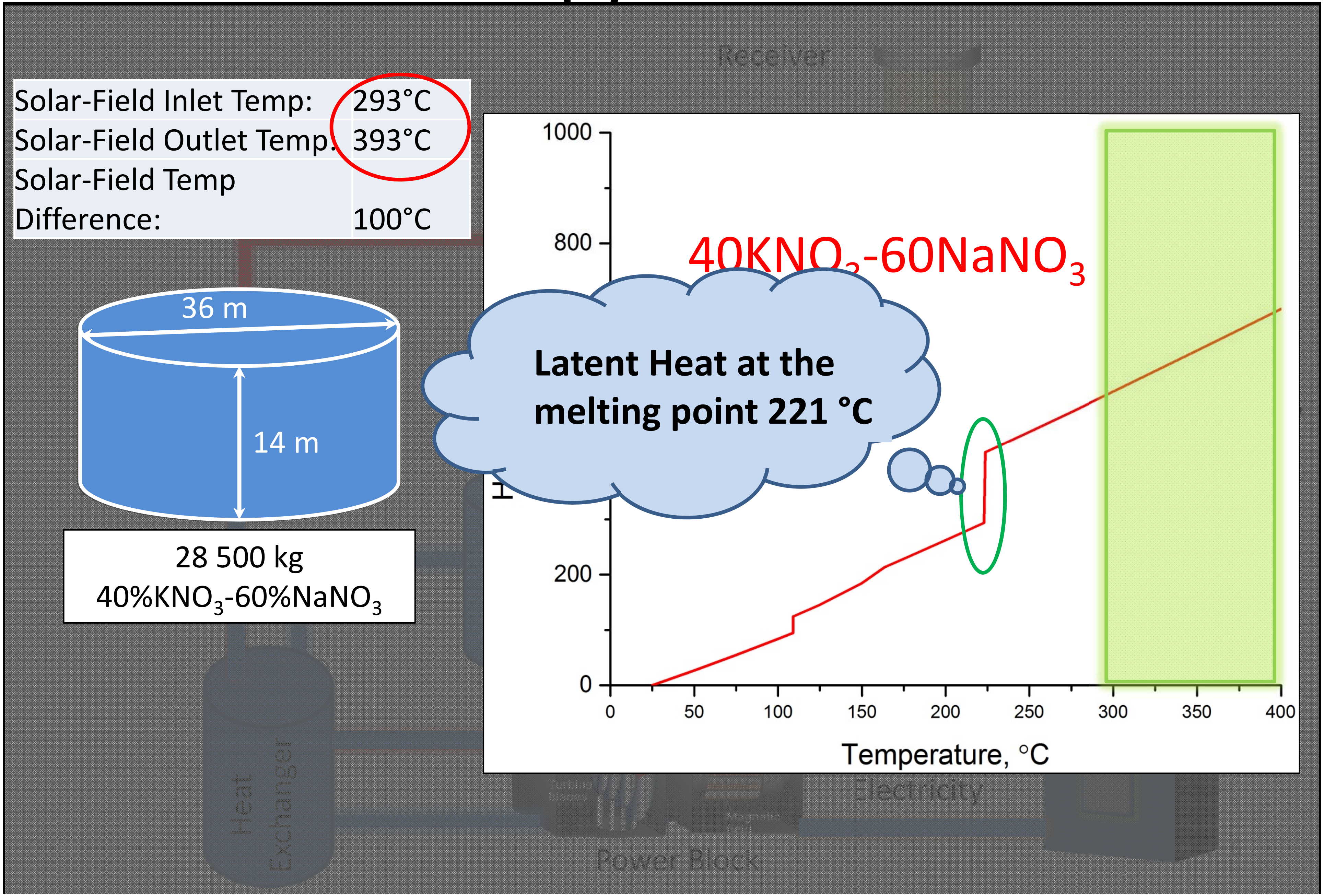
Project Name:	Extresol-3 (EX-3)
Country:	Spain
Start Year:	2012

Solar-Field Inlet Temp:	293°C
Solar-Field Outlet Temp:	393°C
Solar-Field Temp Difference:	100°C

Storage Type:	2-tank indirect
Storage Capacity:	7.5 hour(s)
Thermal Storage Description:	28,500 tons of molten salt. 60% sodium nitrate, 40% potassium nitrate. 1,010 MWh. Tanks are 14 m high and 36 m in diameter.

http://www.nrel.gov/csp/solarpaces

Enthalpy Increment



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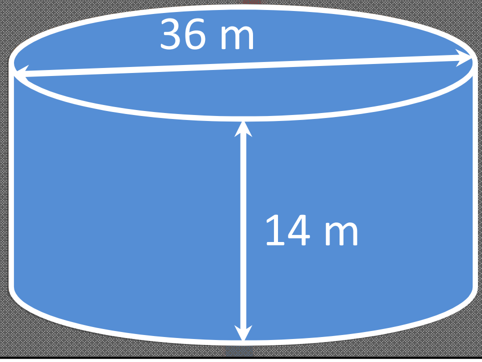

28 500 kg
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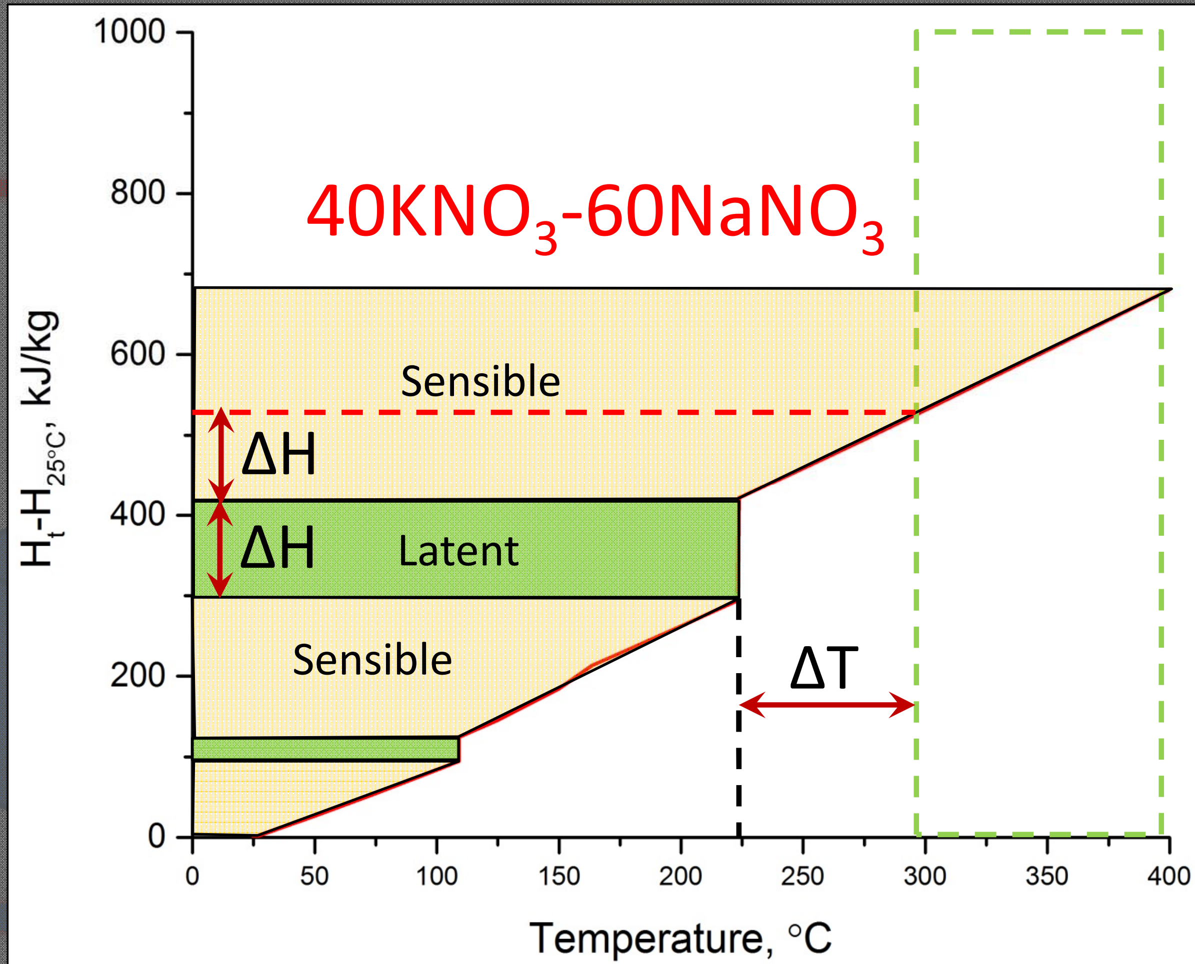
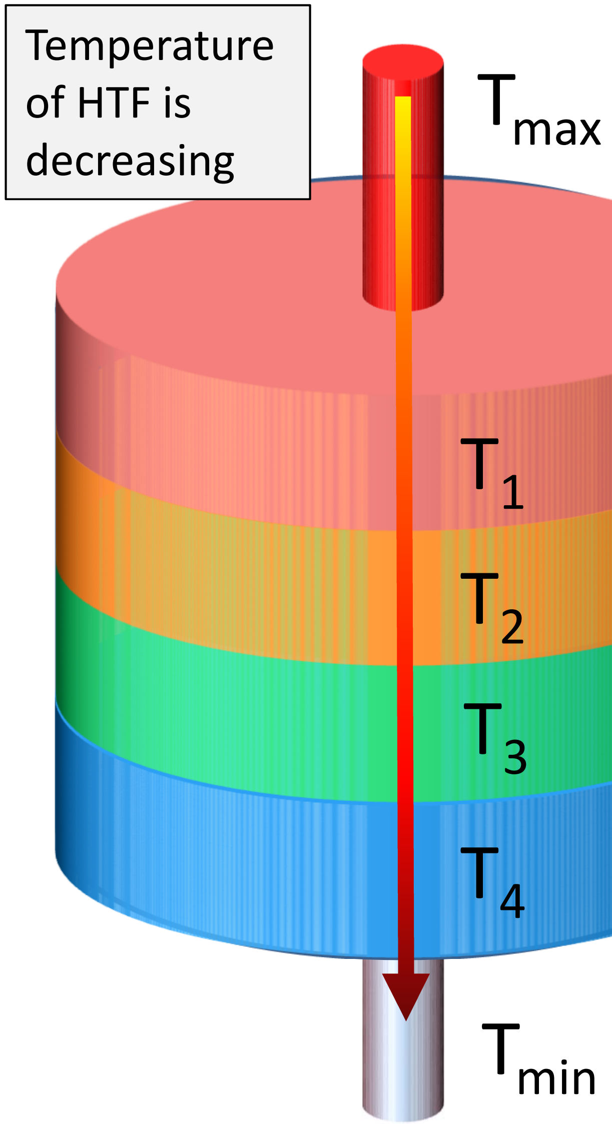
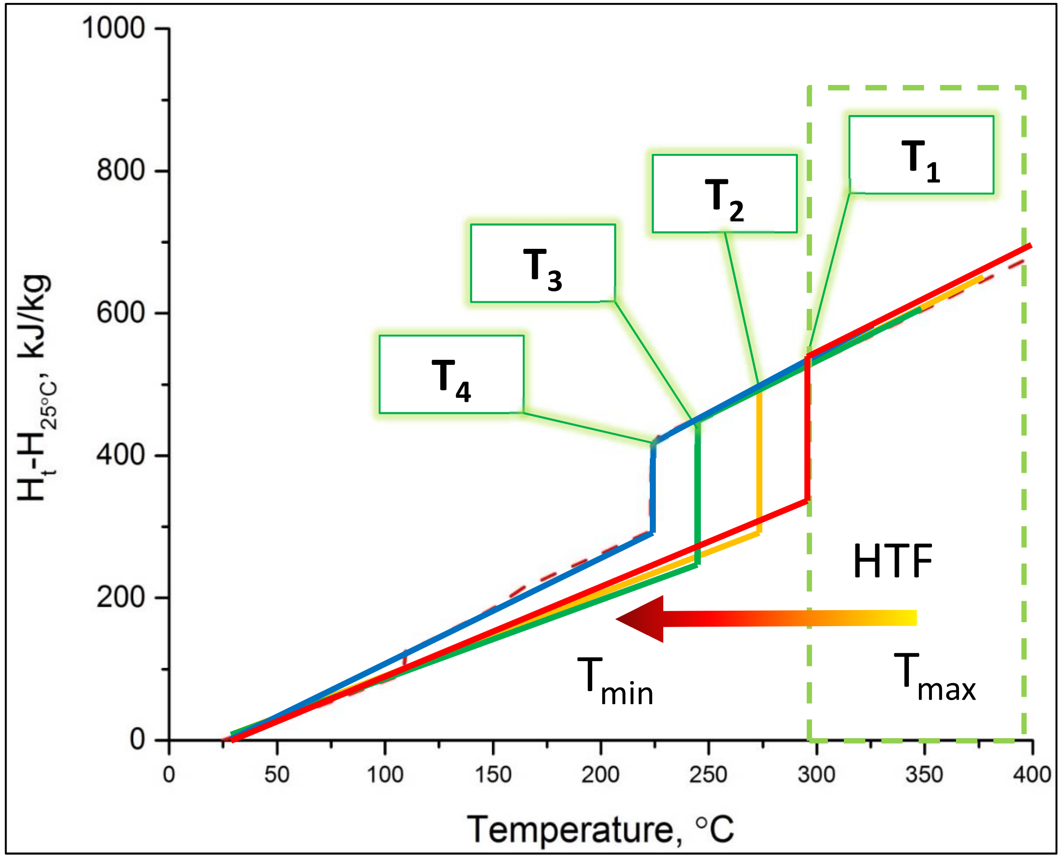
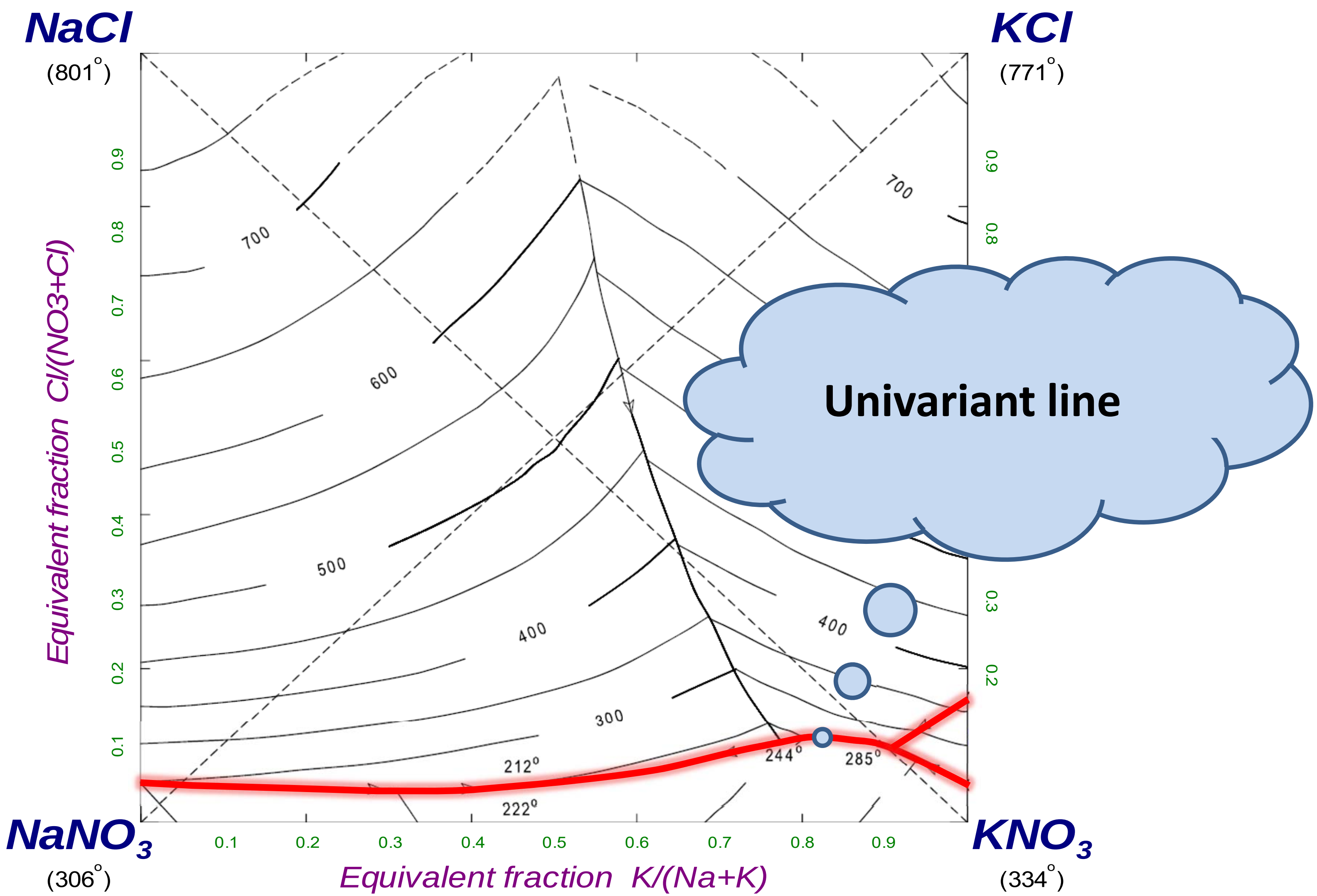


Cascaded Latent Heat Storage





Phase Diagram of the NaCl-KCl-$NaNO_3$-KNO_3 system



R.N. Nyankovskaya, *Izv. Sekt. Fiz.-Khim. Anal.*, 21 (1952) 259-270.

Reciprocal $NaCl$-KCl-$NaNO_3$-KNO_3 System

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 51 (2015) 111–124

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Phase equilibria in the reciprocal $NaCl$–KCl–$NaNO_3$–KNO_3 system

D. Sergeev [a,*], E. Yazhenskikh [a], D. Kobertz [a], K. Hack [b], M. Müller [a]

[a] Forschungszentrum Jülich GmbH, IEK-2, D-52425, Germany
[b] GTT-Technologies, Kaiserstraße 100, D-52134 Herzogenrath, Germany

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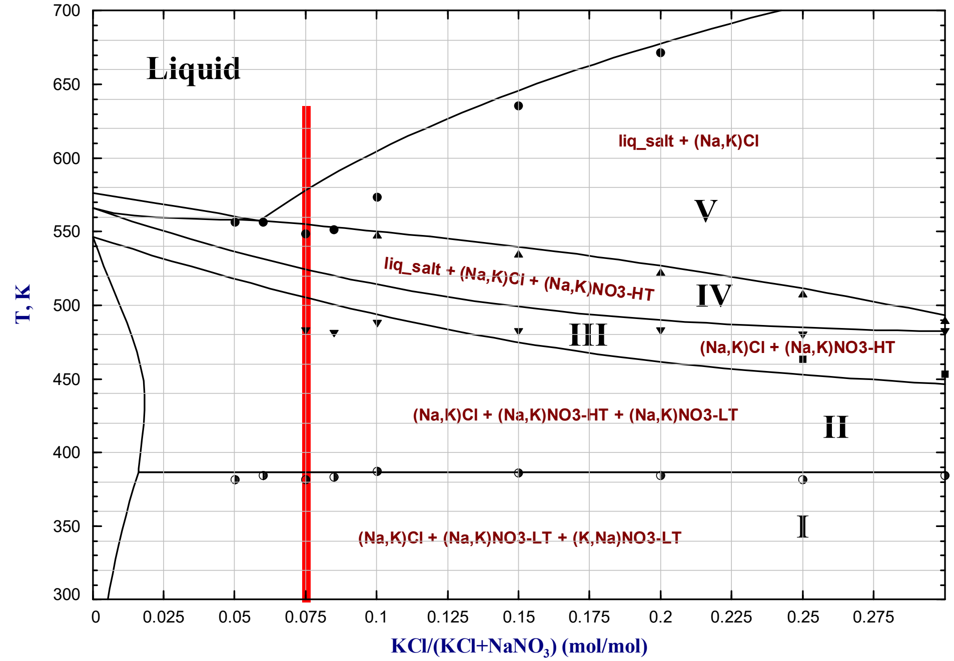
ABSTRACT

Differential thermal analysis of the various compositions in the KCl–$NaNO_3$ and $NaCl$–KNO_3 systems has been performed. Temperatures of phase transitions were obtained. The relative content of $NaCl$, KCl, $NaNO_3$, and KNO_3 compounds was determined by the use of X-ray diffraction analysis. These results together with the experimental data from literature were used for optimization of thermodynamic parameters for all available phases and compounds to obtain the Gibbs energy dataset which can be used for the calculation and prediction of the phase diagrams and other thermodynamic properties of these systems.

[1] R.N. Nyankovskaya, *Izv. Sekt. Fiz.-Khim. Anal.*, 21 (1952) 259-270.

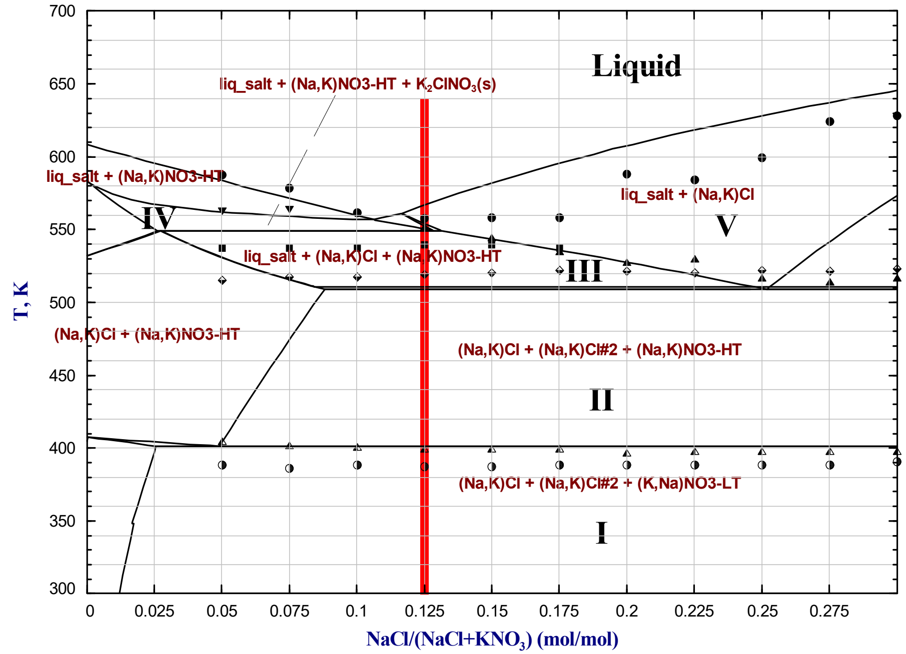
Diagonal sections of the $NaCl$-KCl-$NaNO_3$-KNO_3 system

KCl-$NaNO_3$



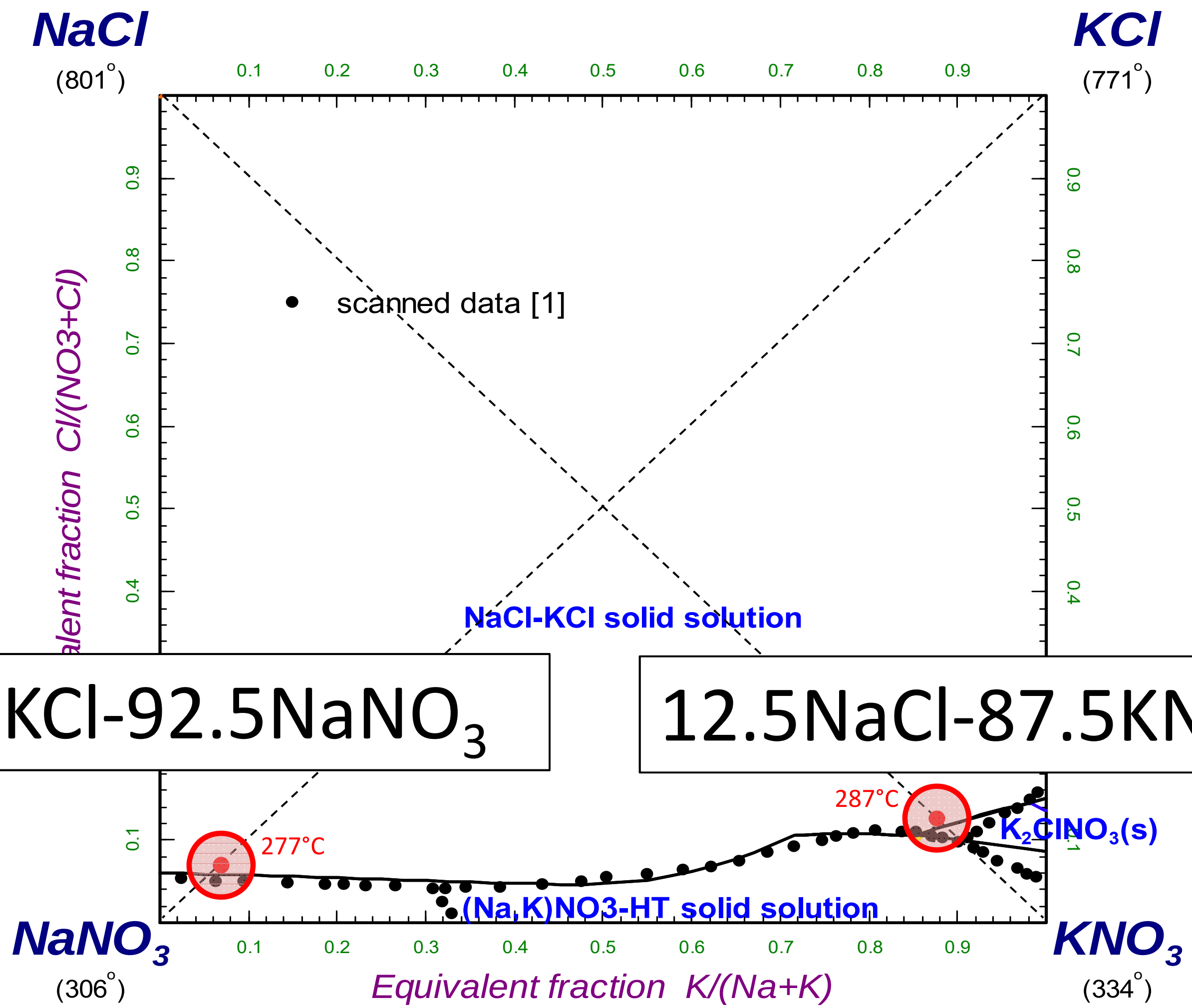
7.5KCl-92.5NaNO$_3$

$NaCl$-KNO_3



12.5NaCl-87.5KNO$_3$

Reciprocal NaCl-KCl-$NaNO_3$-KNO_3 system



7.5KCl-92.5$NaNO_3$

12.5NaCl-87.5KNO_3

What does a thermochemist do?

What my friends think

What my chief thinks

What my parents think

What I really do

Sample Preparation

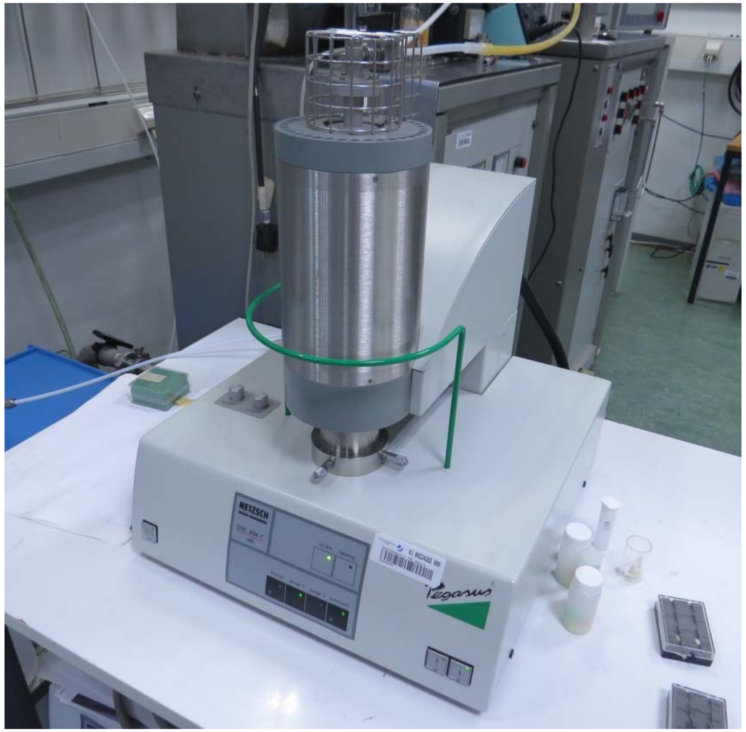
Glove box

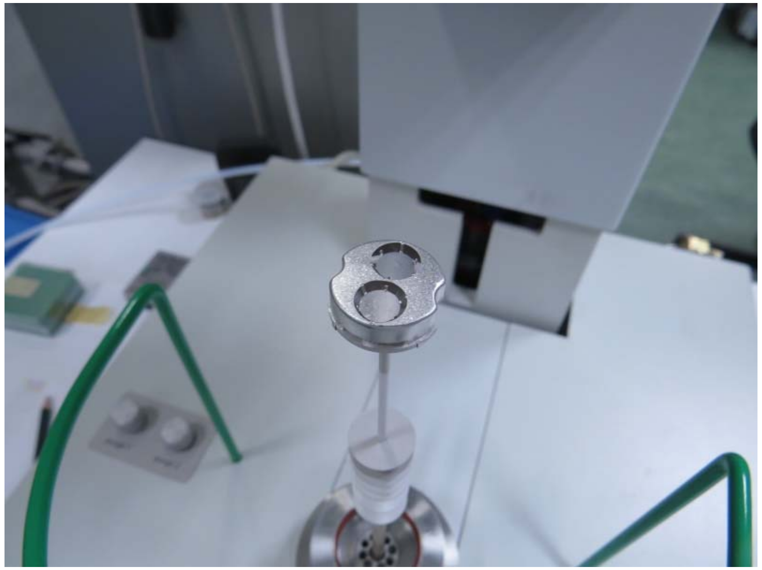
Vacuum seal

Closed glass containers

Differential Scanning Calorimetry

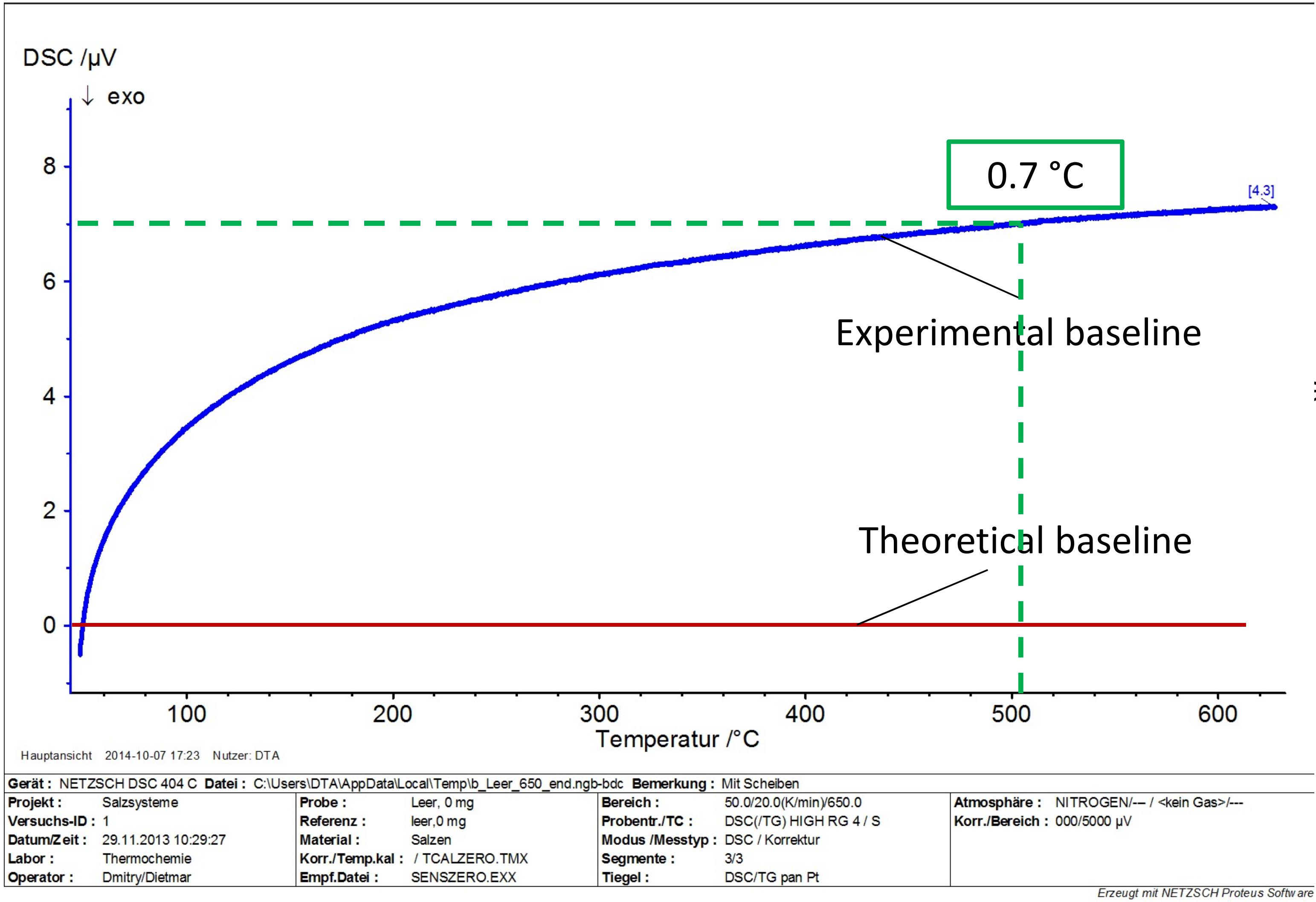
DSC 404C Netzsch





Sample holder

Differential Scanning Calorimetry



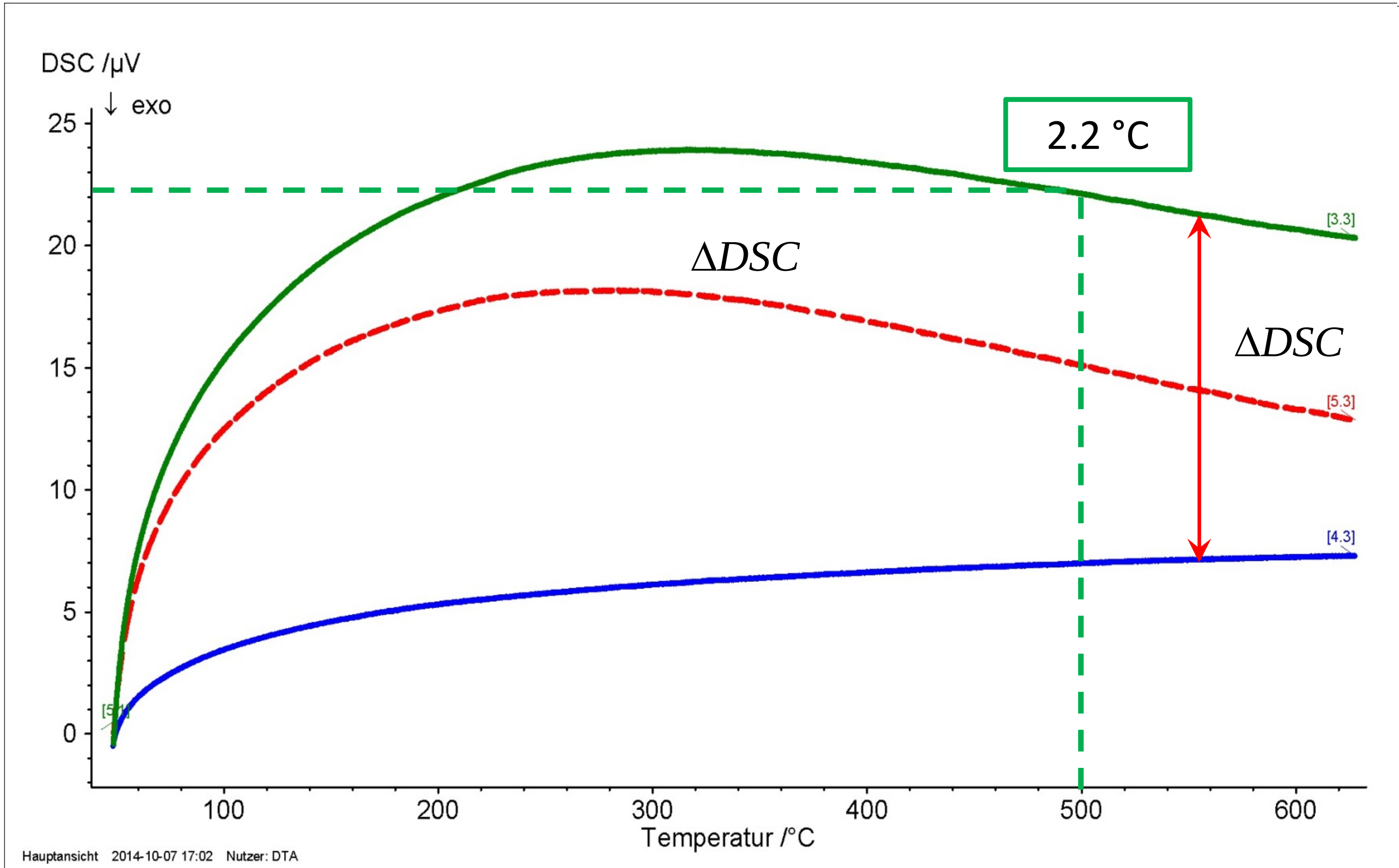
ater

heat

0 K/min

ΔT, µV

Differential Scanning Calorimetry



[#] Gerät	Datei	Datum	Versuchs-ID	Probe	Masse/mg	Segment	Bereich	Atmosphäre	Korr.
[3.3] DSC 404 C	r8_SapphirI_650_end.ngb-ddc	2013-11-29	1	Sapphir	55.89	3/3	50.0/20.0(K/min)/650.0	NITROGEN/--- / <kein Gas>/---	---
[4.3] DSC 404 C	b_Leer_650_end.ngb-bdc	2013-11-29	1	Leer	0	3/3	50.0/20.0(K/min)/650.0	NITROGEN/--- / <kein Gas>/---	---
[5.1] DSC 404 C	r7_Sapphir_650_end.ngb-ddc	2013-11-28	1	Sapphir	55.89	1/3	45.0/40.0(K/min)/50.0	NITROGEN/--- / <kein Gas>/---	020

er

eat

K/min

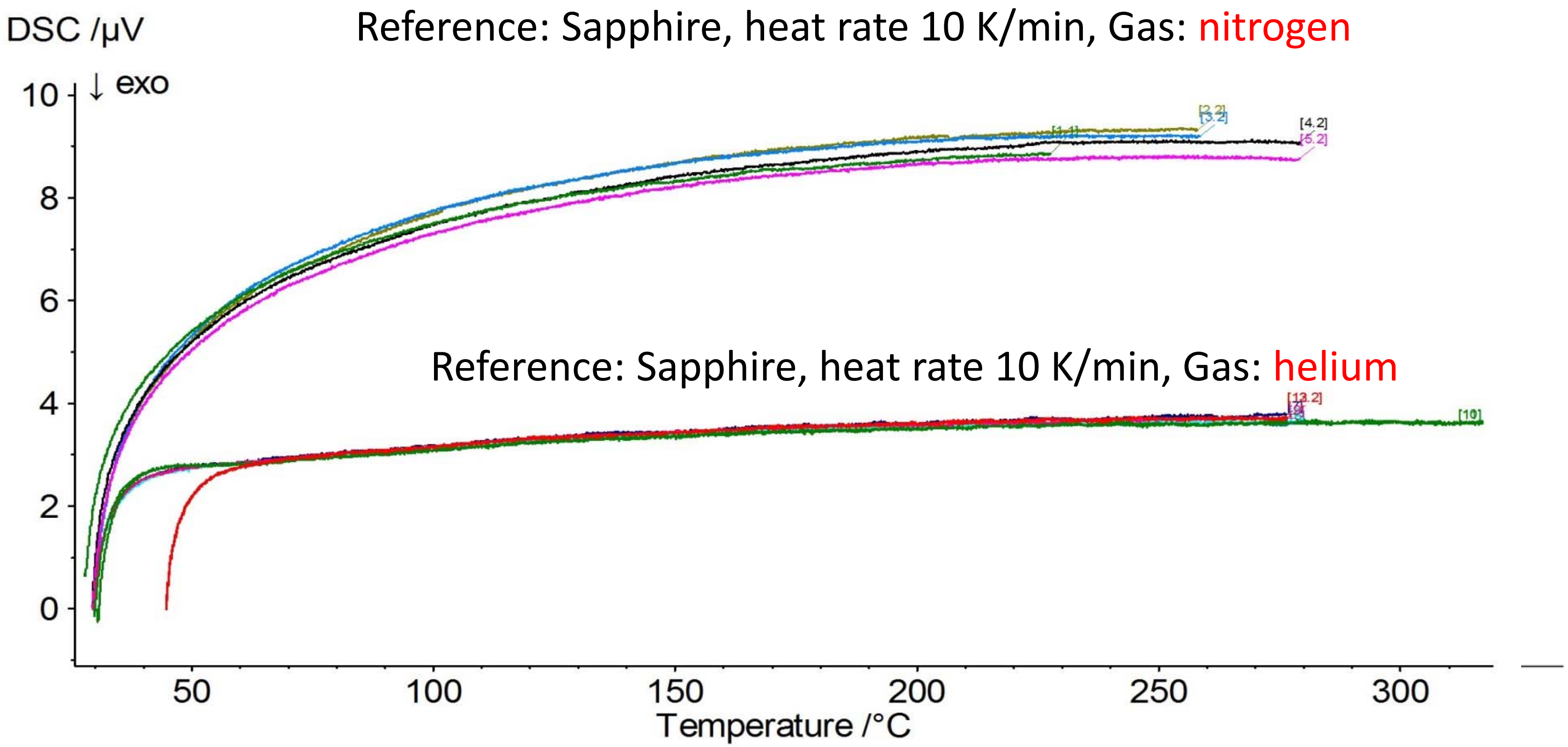
ΔT, µV

Heat Capacity

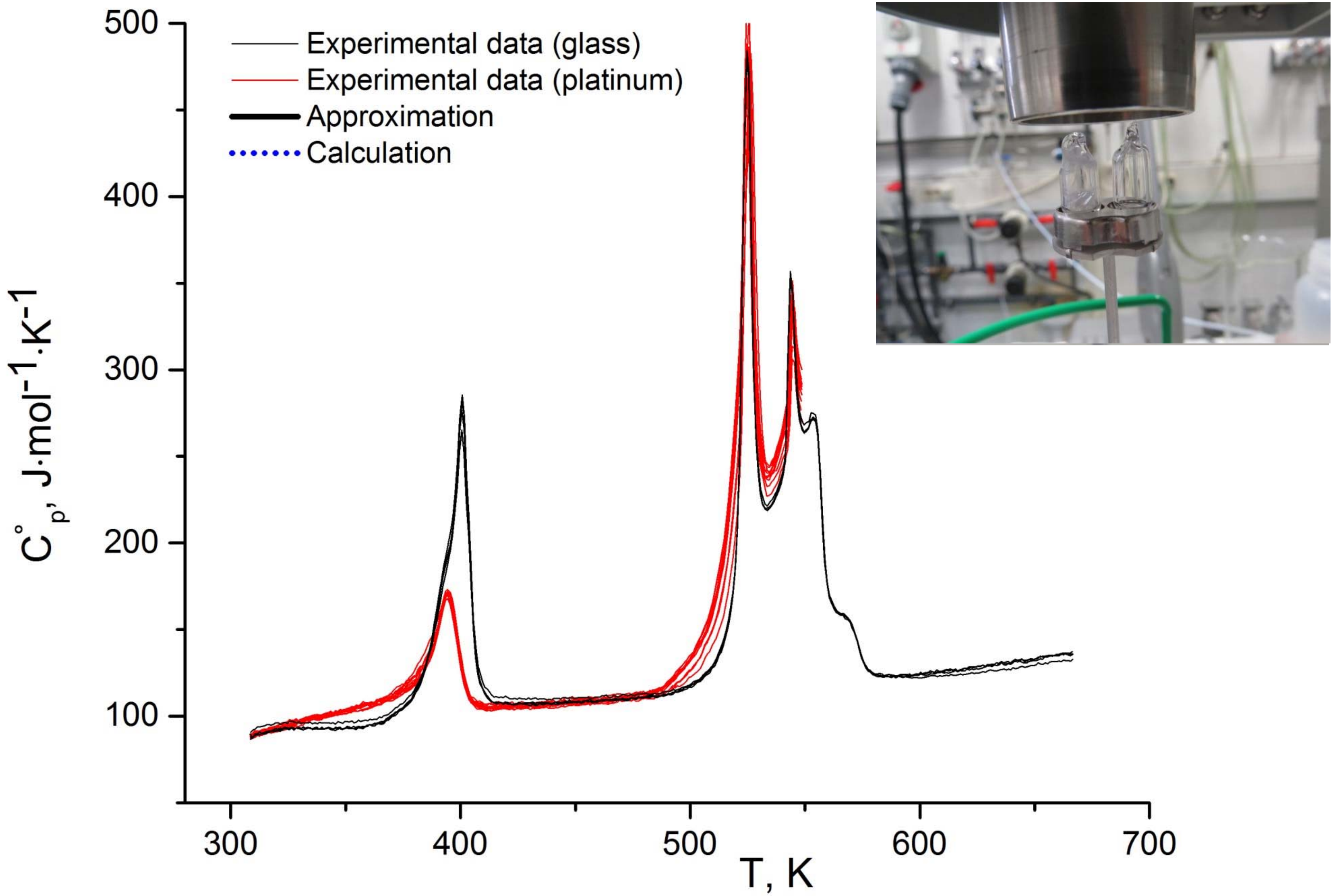
$$C^{\circ}_{p(s)} = \frac{m_r}{m_s} \cdot \frac{\Delta DSC_s}{\Delta DSC_r} \cdot C^{\circ}_{p(r)}$$

where m – mass of the substance (g), ΔDSC – difference signal (μV), $C^{\circ}_{p(r)}$ – heat capacity of a reference.

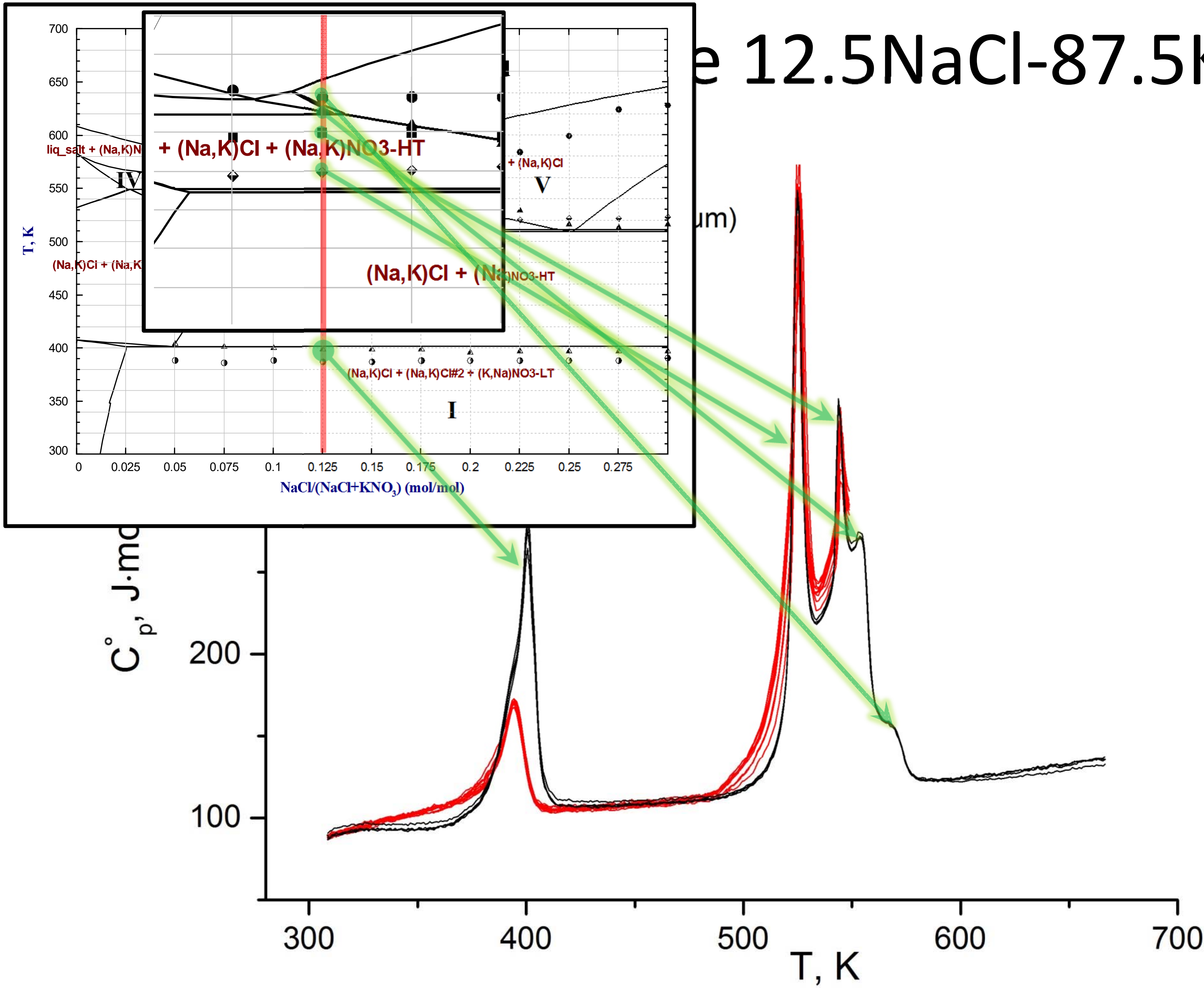
DSC curves


DSC /µV
Reference: Sapphire, heat rate 10 K/min, Gas: nitrogen
↓ exo
10
8
6
4
2
0
Reference: Sapphire, heat rate 10 K/min, Gas: helium
[4.2]
[10]
50
100
150
200
250
300
Temperature /°C

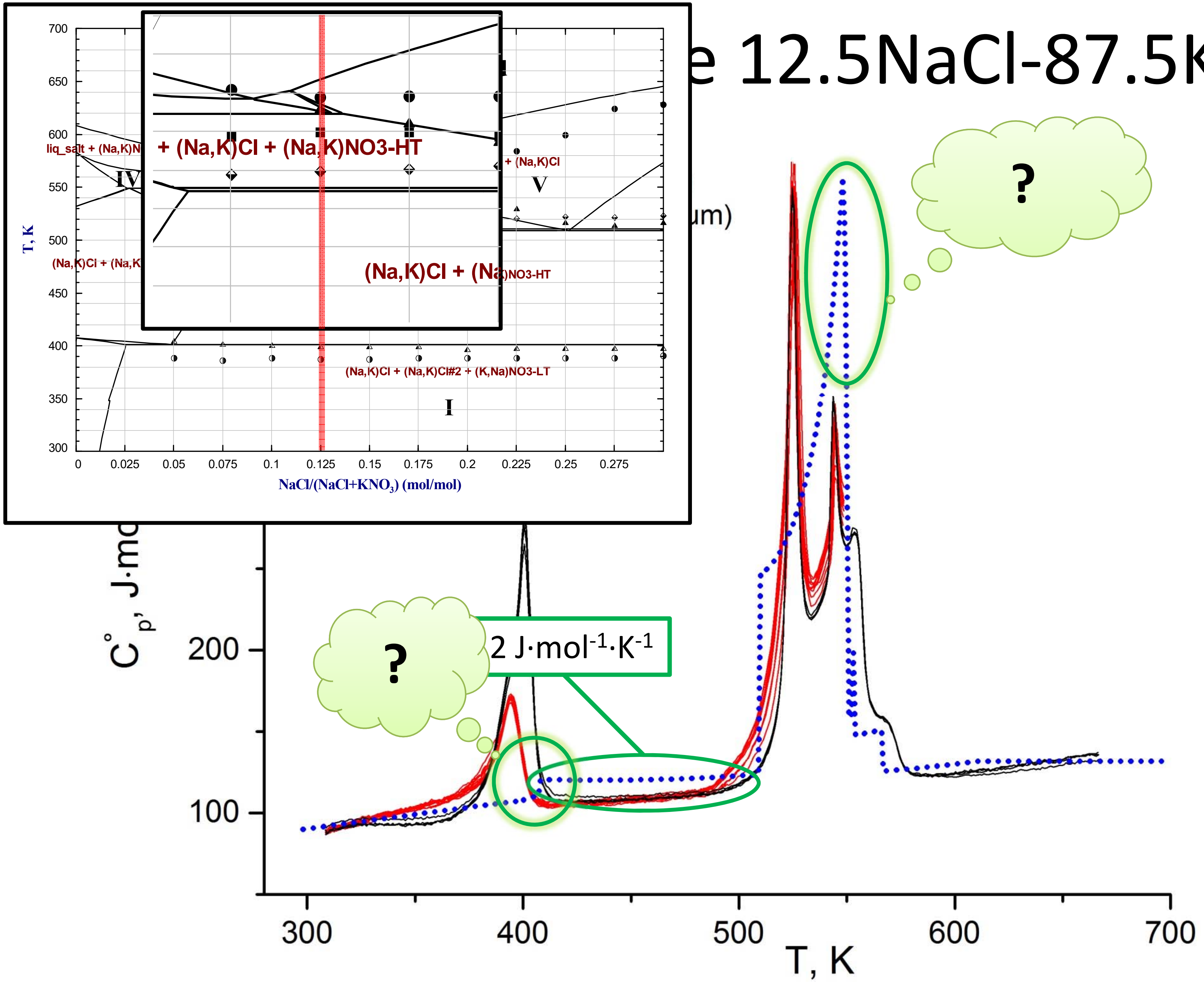
Heat capacity of the 12.5NaCl-87.5KNO_3



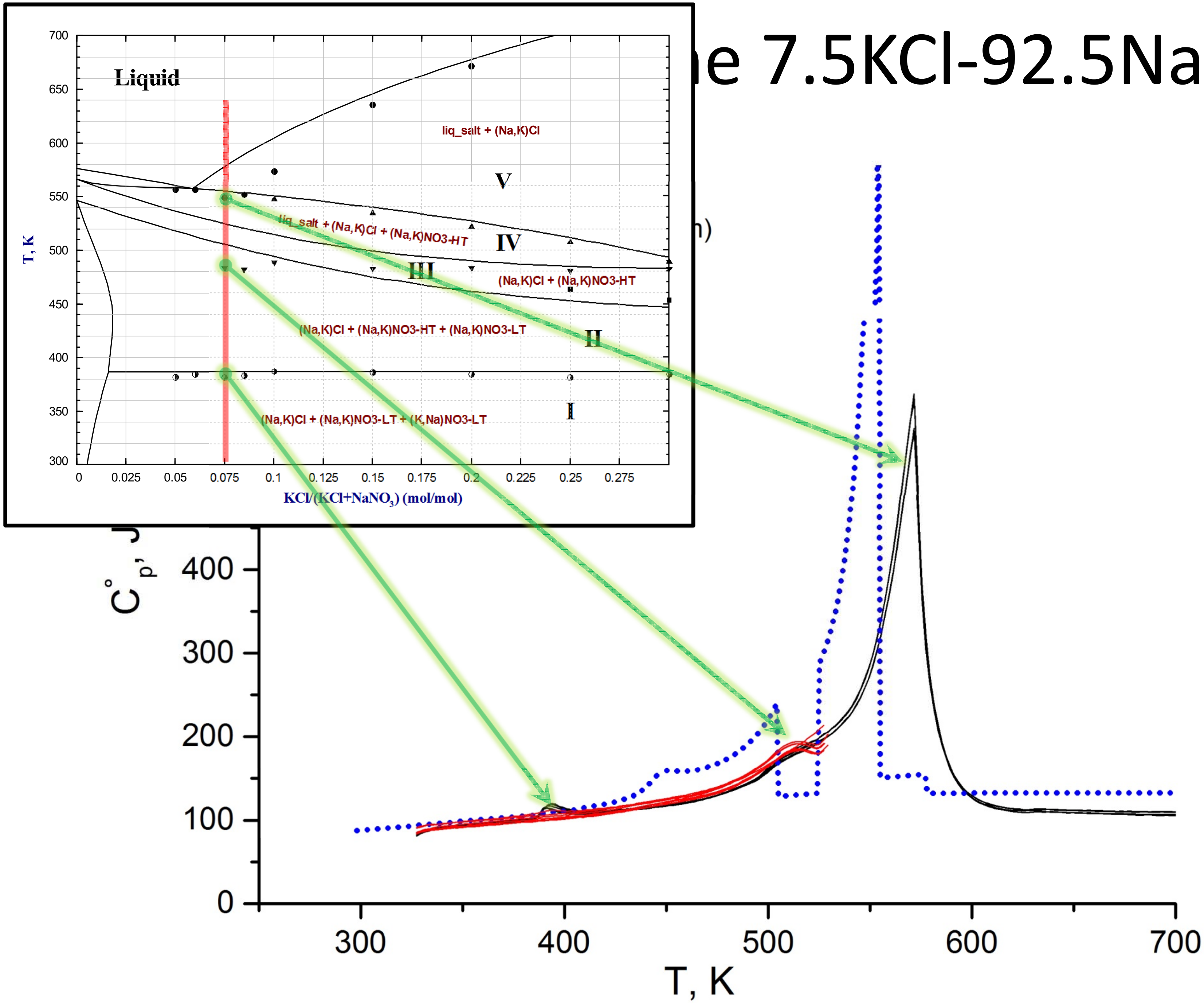
...e 12.5NaCl-87.5KNO_3



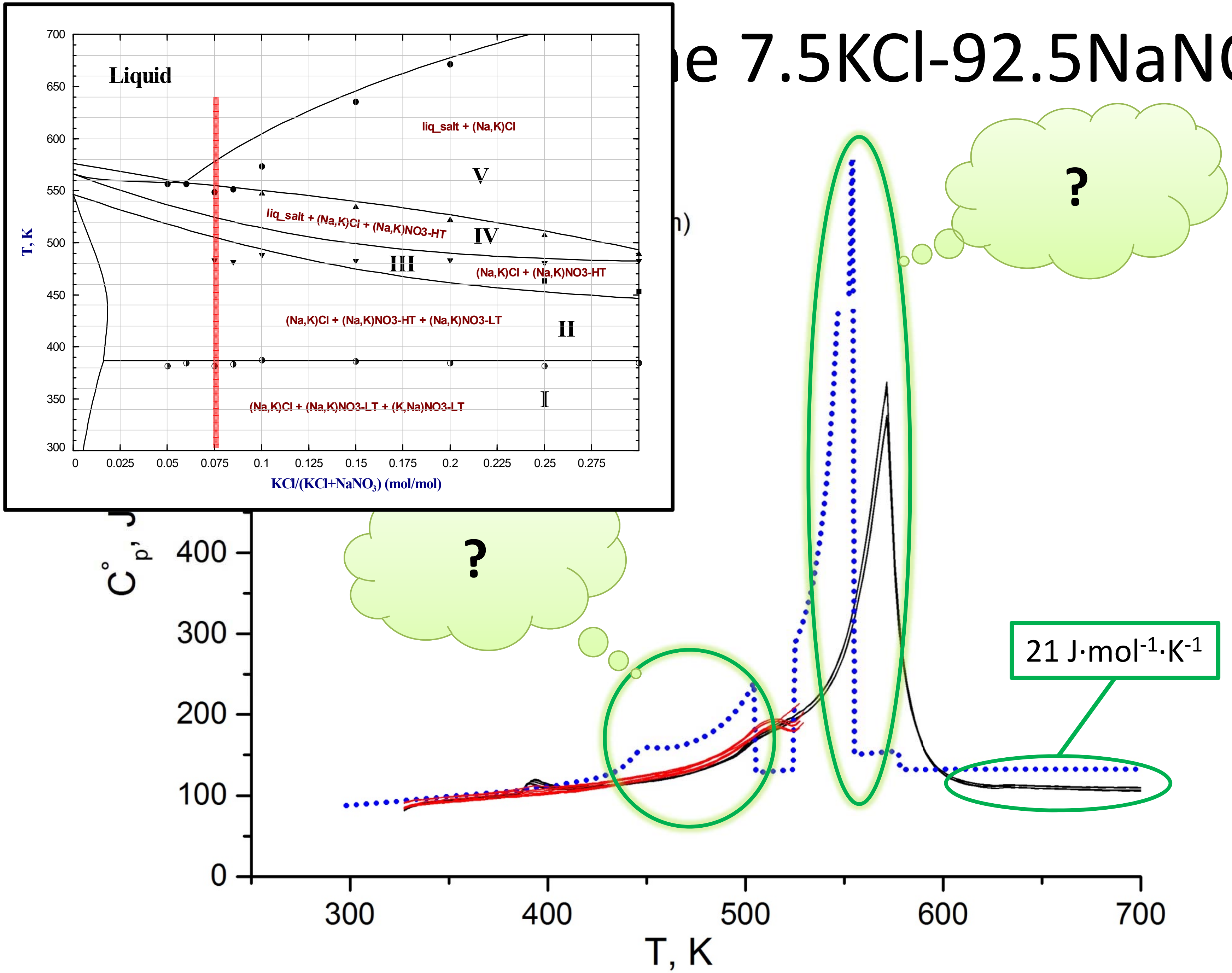
…e 12.5NaCl-87.5KNO$_3$



...e 7.5KCl-92.5NaNO$_3$



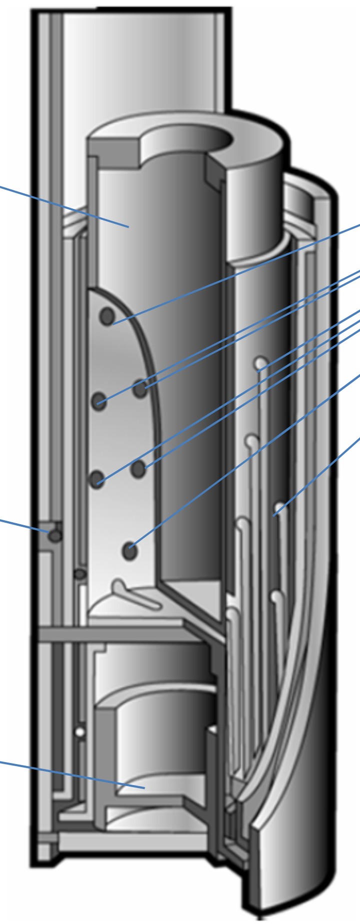
…e 7.5KCl-92.5NaNO$_3$



Drop Calorimeter

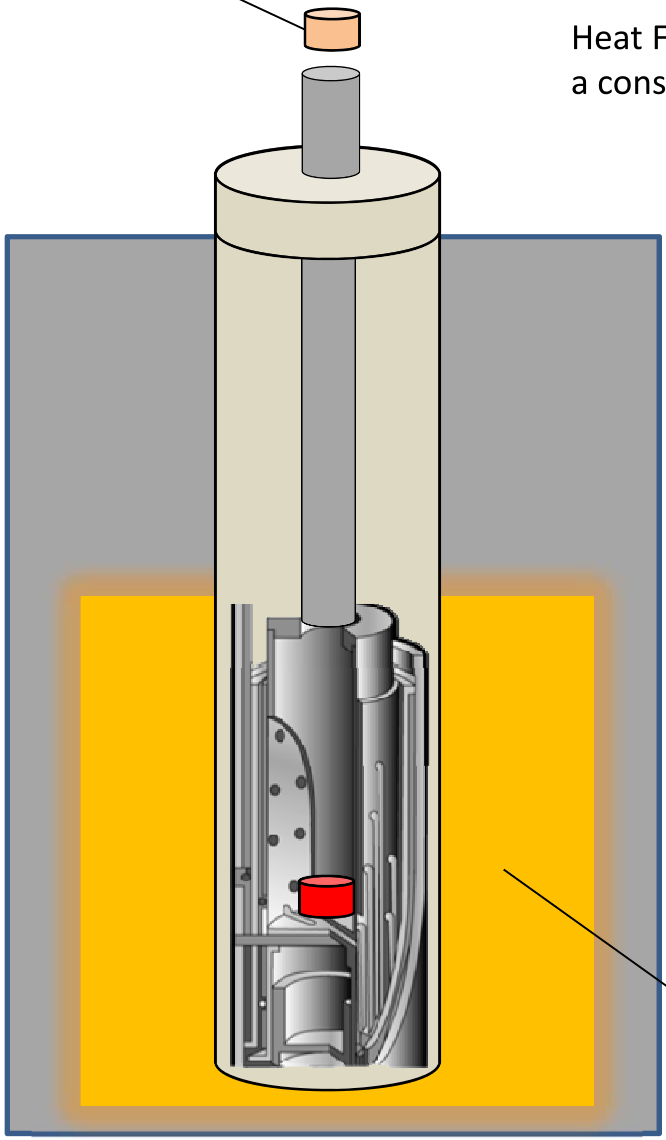
mHTC 96 Seteram

Drop Calorimetric Detector



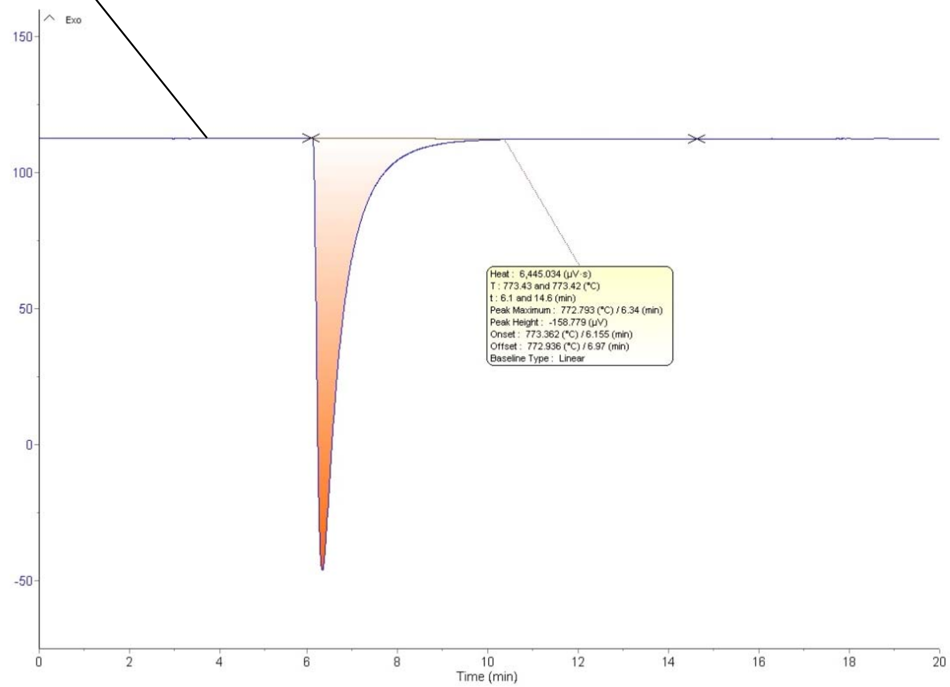
Drop Calorimetry

Sample (10-100mg)
at room temperature



Heat Flow (μV) at
a constant *T*

Experimental data



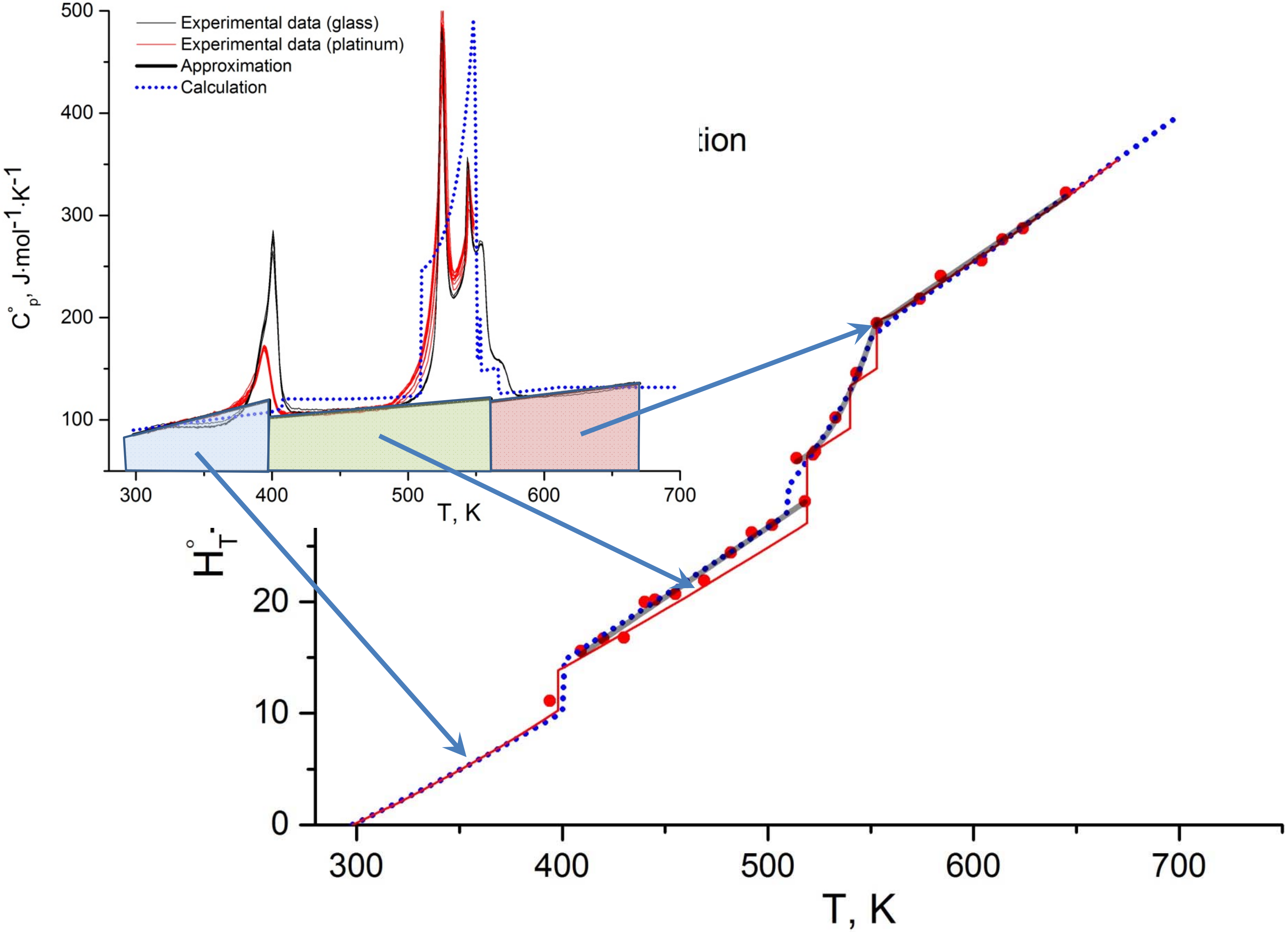
Hot zone,
constant temperature T

Enthalpy Increment

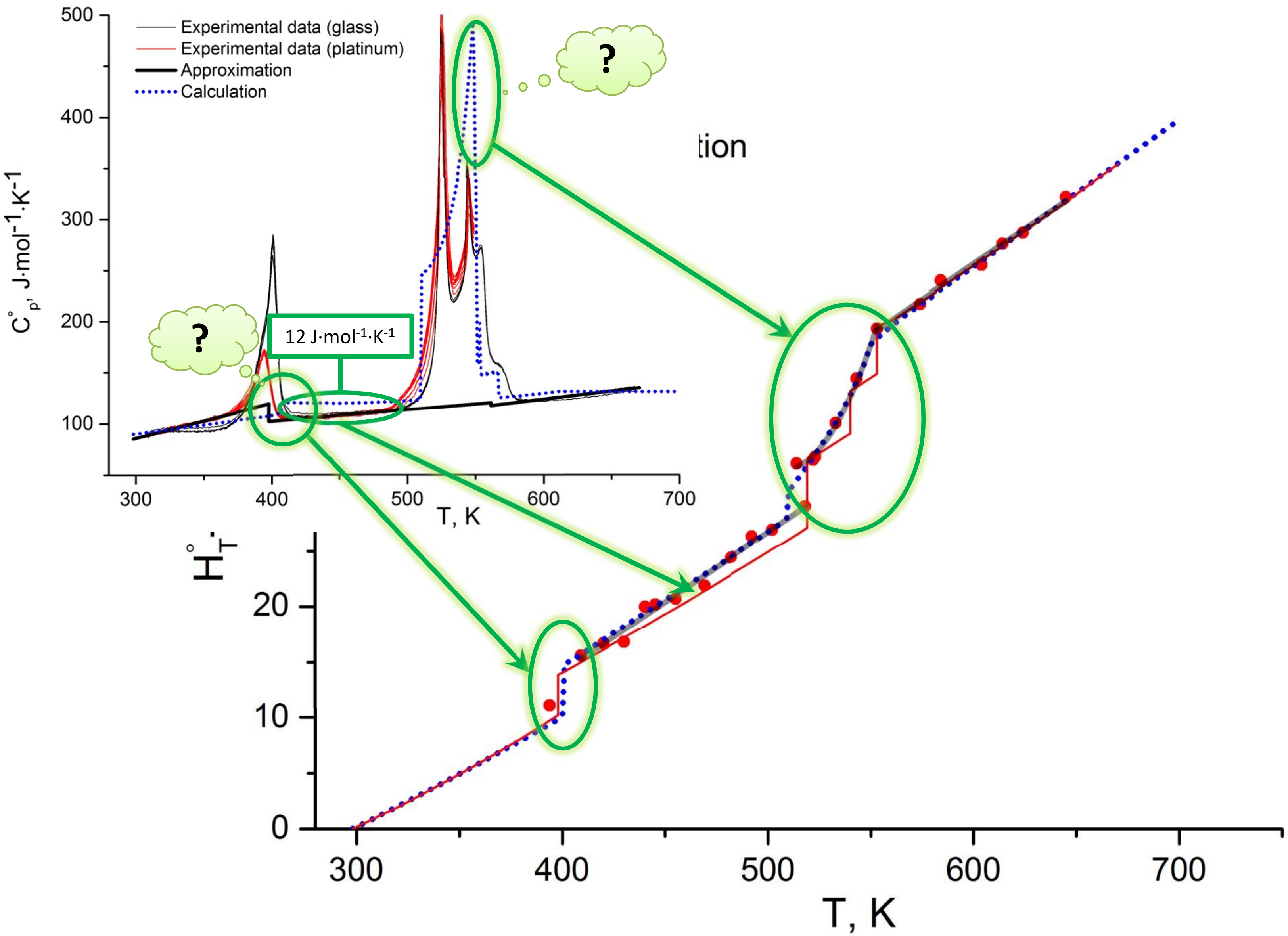
$$(H_T^\circ - H_{298.15}^\circ)_s = \frac{m_r}{m_s} \cdot \frac{\Delta H_s}{\Delta H_r} \cdot (H_T^\circ - H_{298.15}^\circ)_r$$

where m – mass of the substance (g), ΔH – measured peak area ($\mu\mathrm{V} \cdot s$), $(H^\circ_{\mathrm{T}} - H^\circ_{298.15})_r$ – enthalpy increment of a reference.

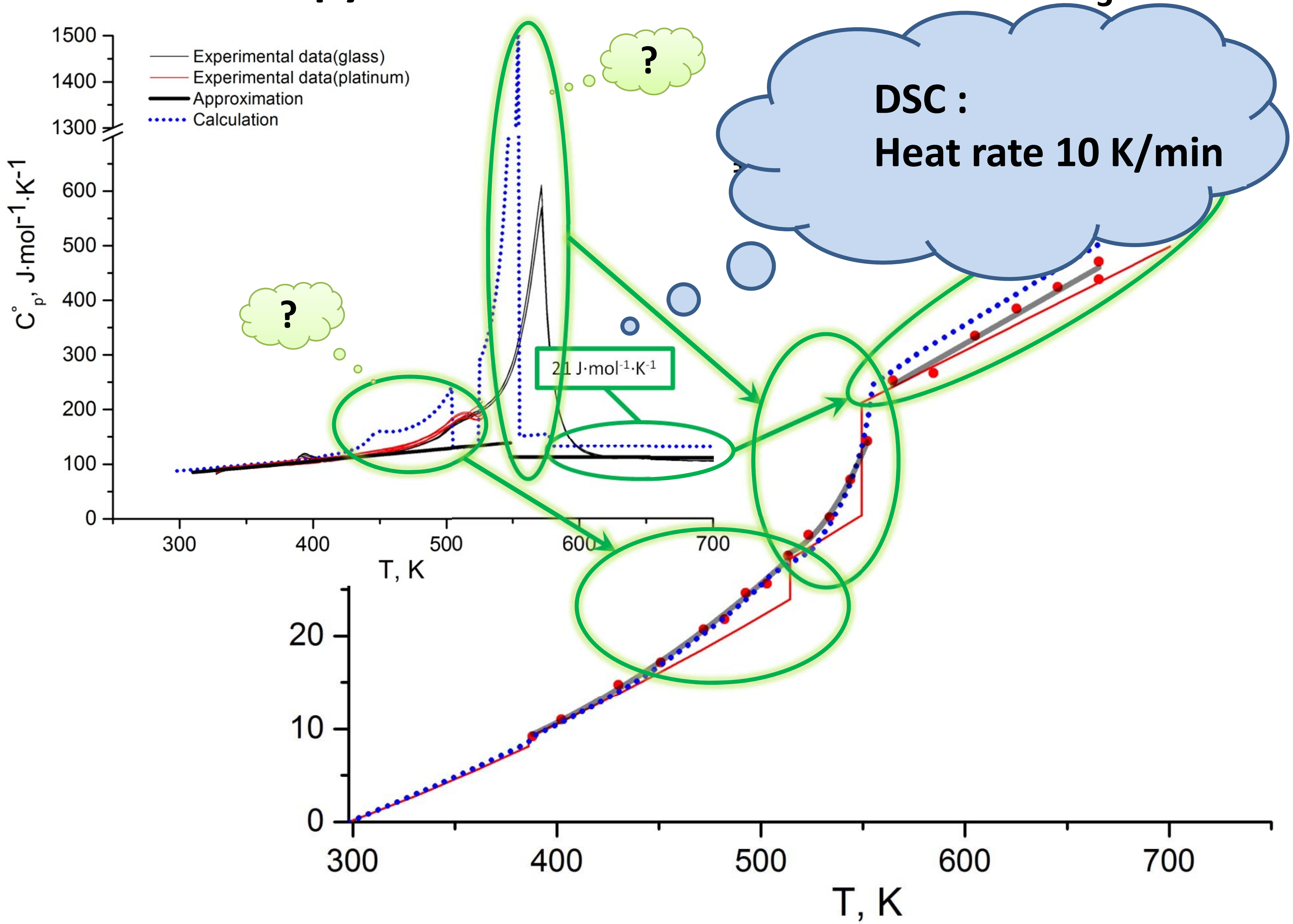
Enthalpy increment in the 12.5NaCl-87.5KNO_3



Enthalpy increment of the 12.5NaCl-87.5KNO_3 mixture



Enthalpy increment of the $7.5KCl\text{-}92.5NaNO_3$ mixture

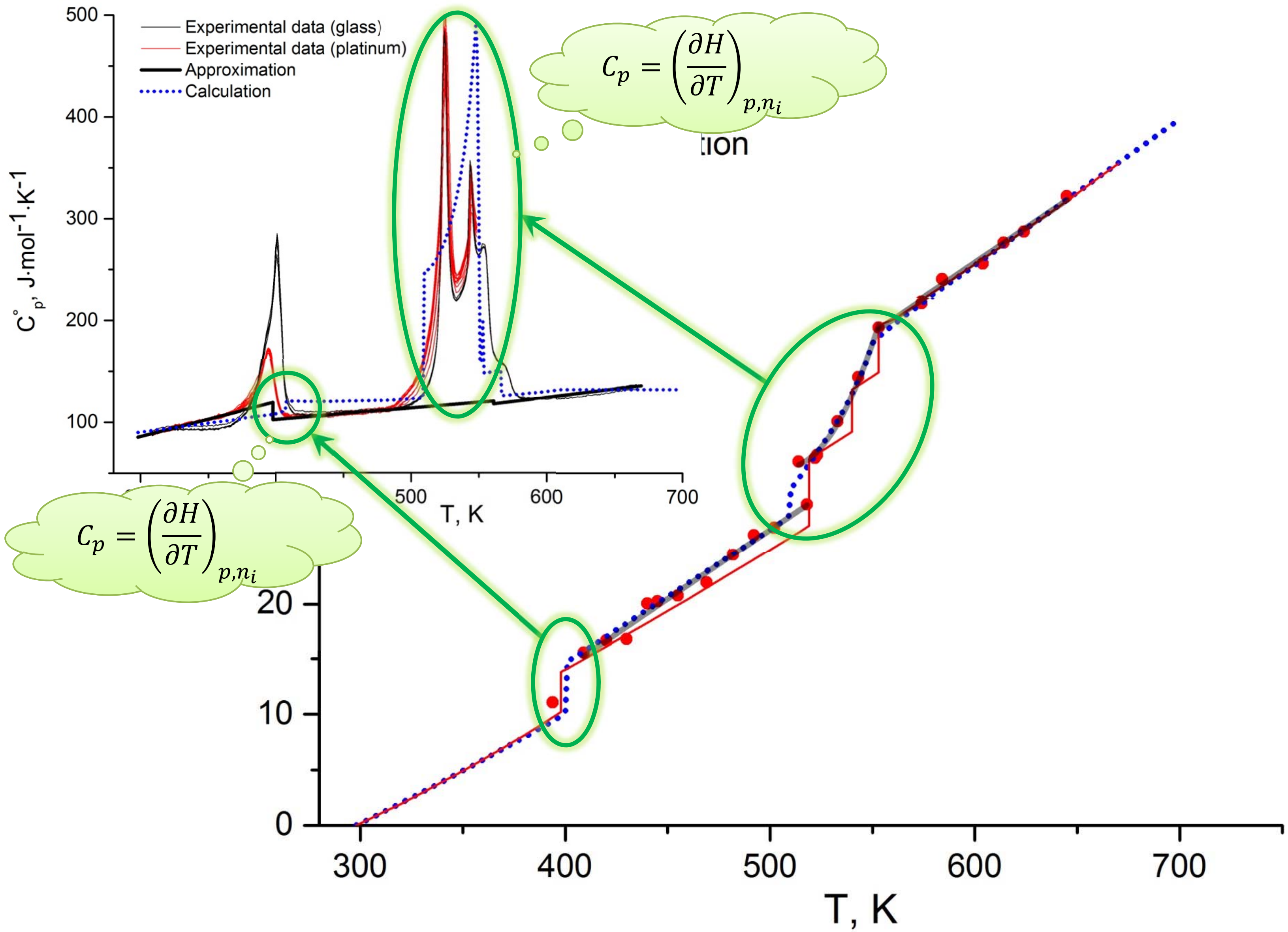


Calculation of C_p in the FactSage

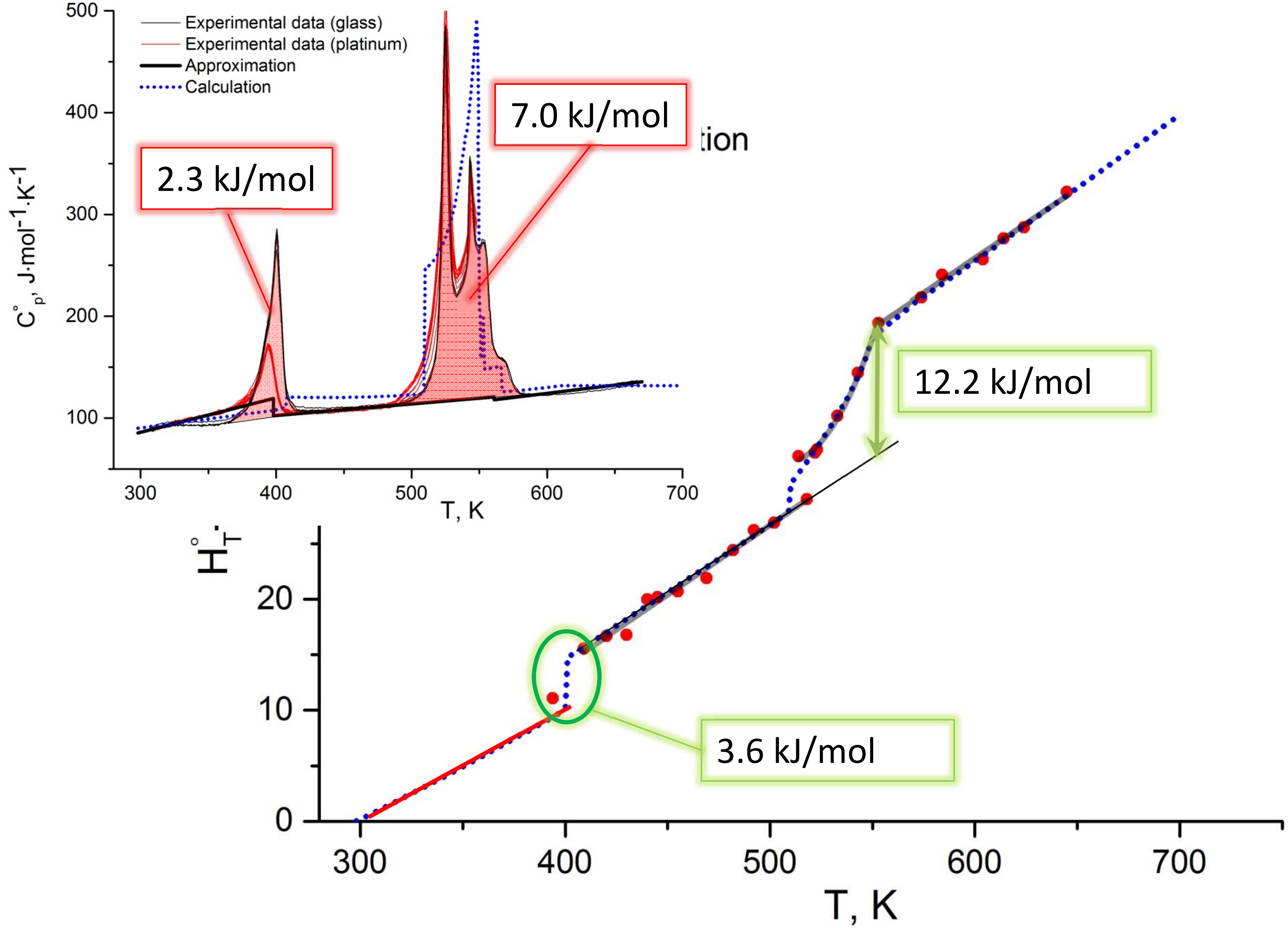
$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,n_i} = \sum_{\varphi} \frac{\partial n^{\varphi}}{\partial T} H_m^{\varphi} + \sum_{\varphi} \frac{\partial H_m^{\varphi}}{\partial T} n^{\varphi}$$

where φ is phase index, and n^{ϕ} is phase fraction of each phase.

Enthalpy increment of the 12.5NaCl-87.5KNO_3 mixture

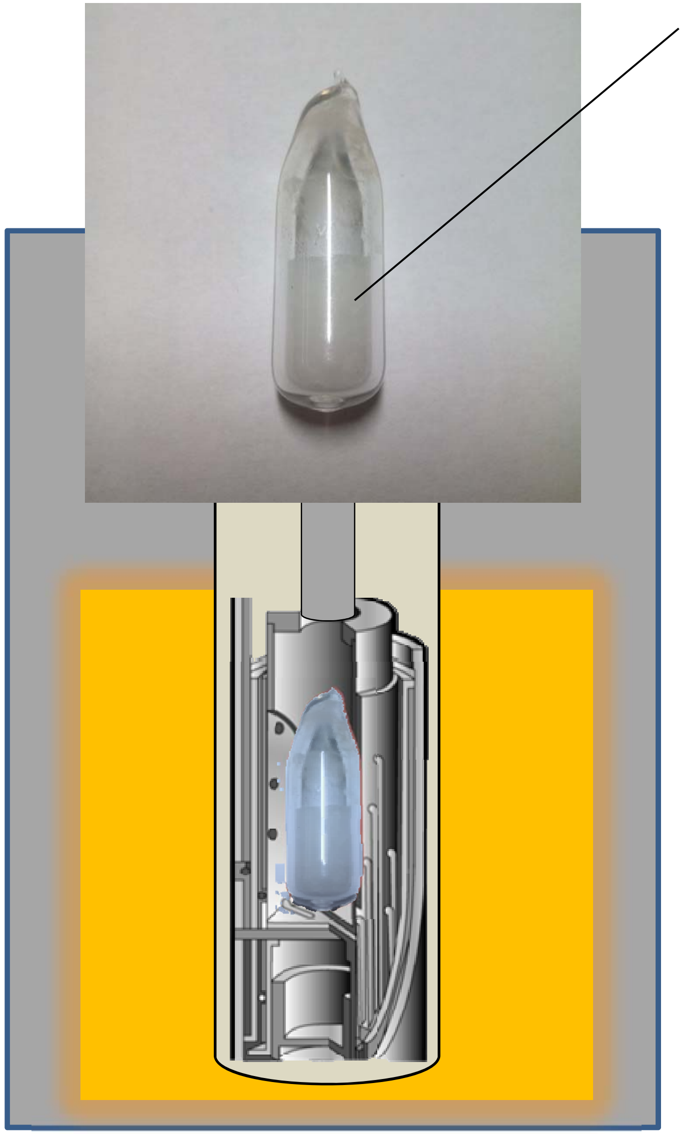


Enthalpy increment of the 12.5NaCl-87.5KNO_3 mixture

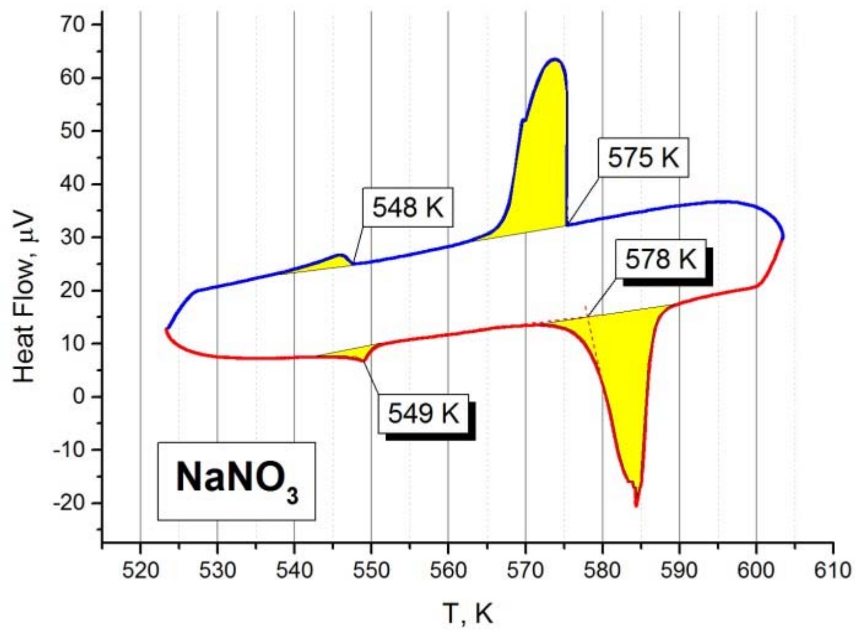


~~Drop~~ Calorimetry

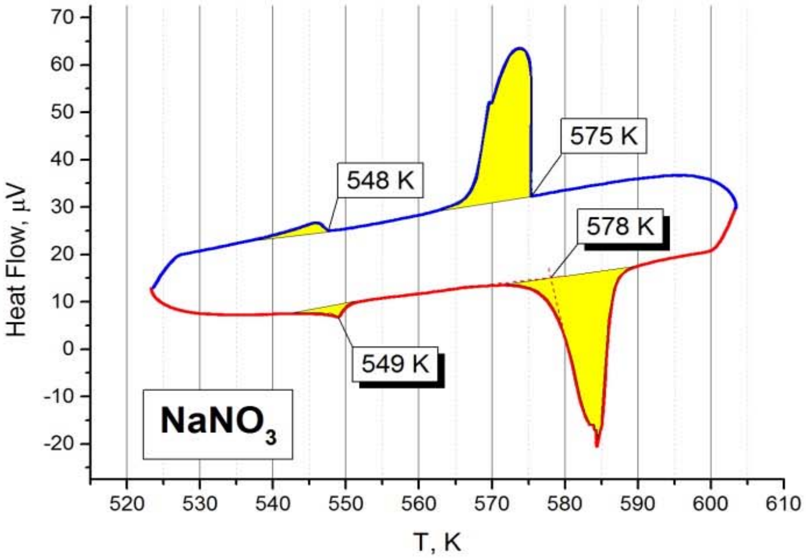
Sample (1500 mg) in closed glass container

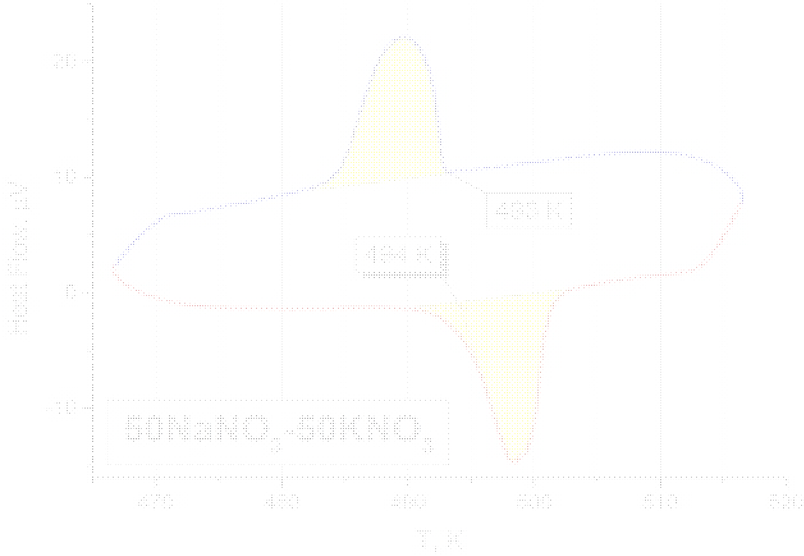


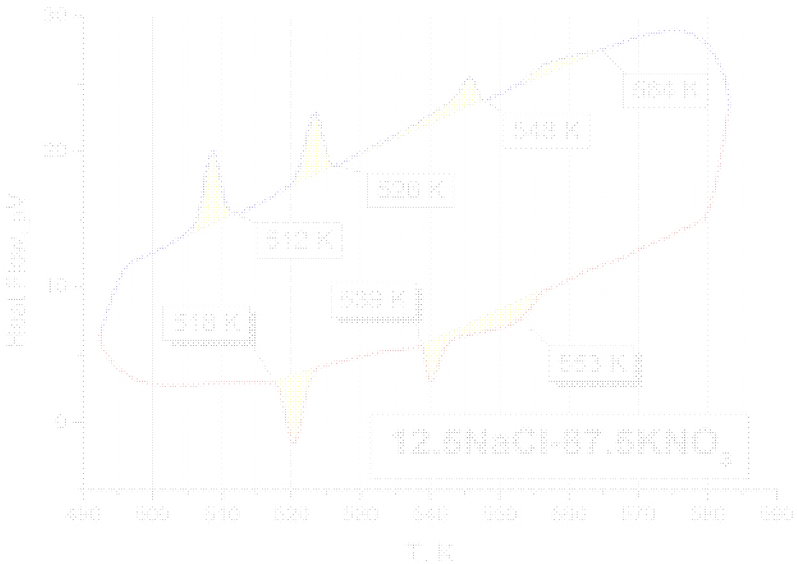
Heat rate 0.5 K/min

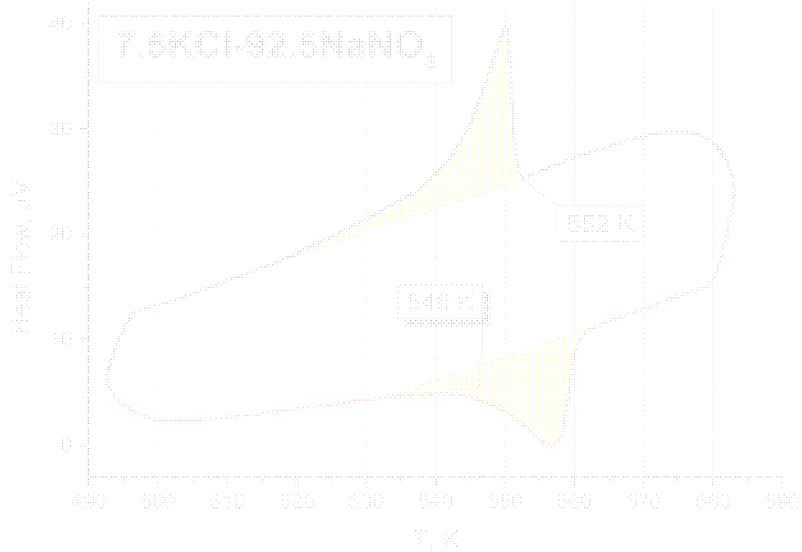


Slow Heating Rate Thermal Analysis









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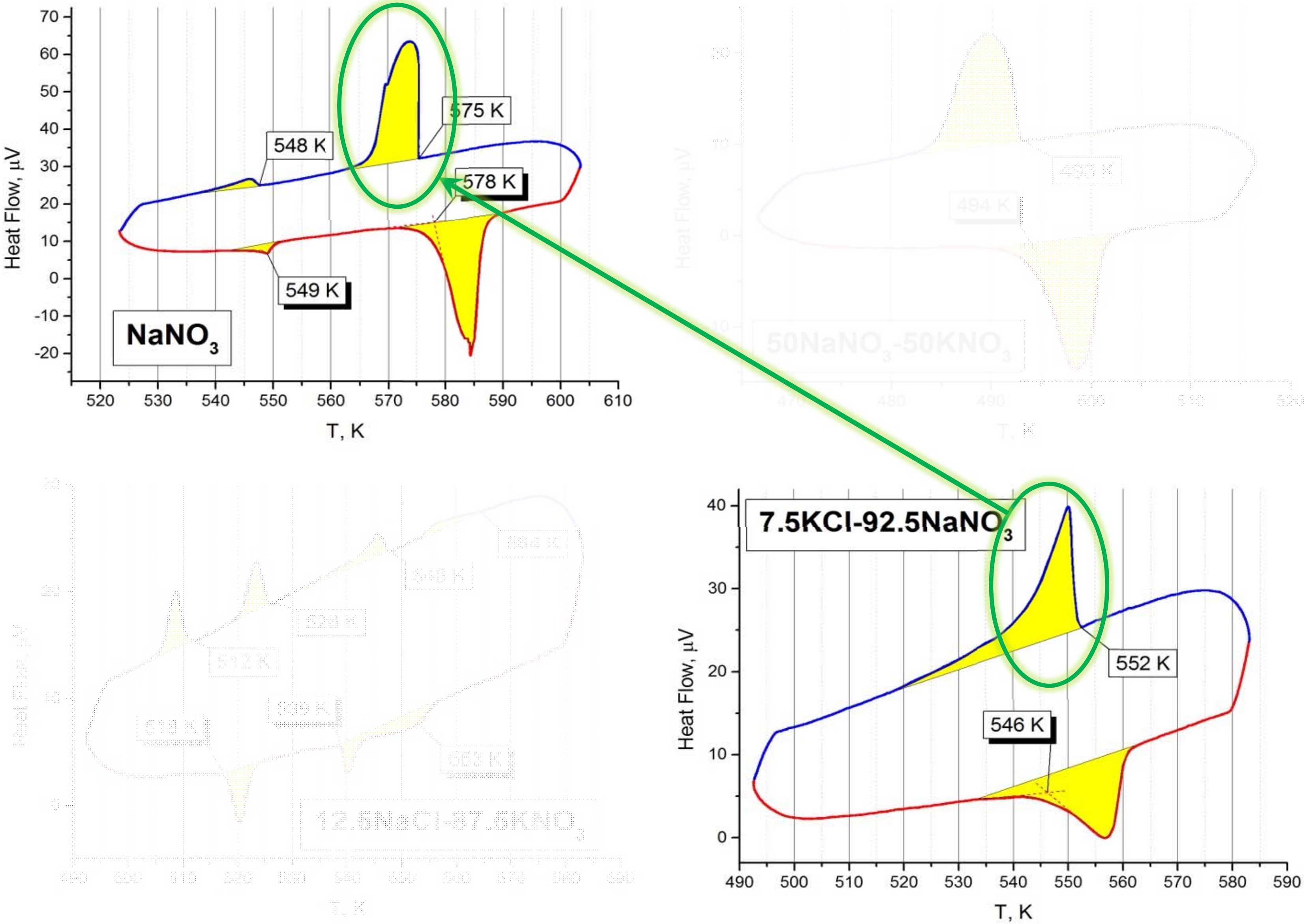
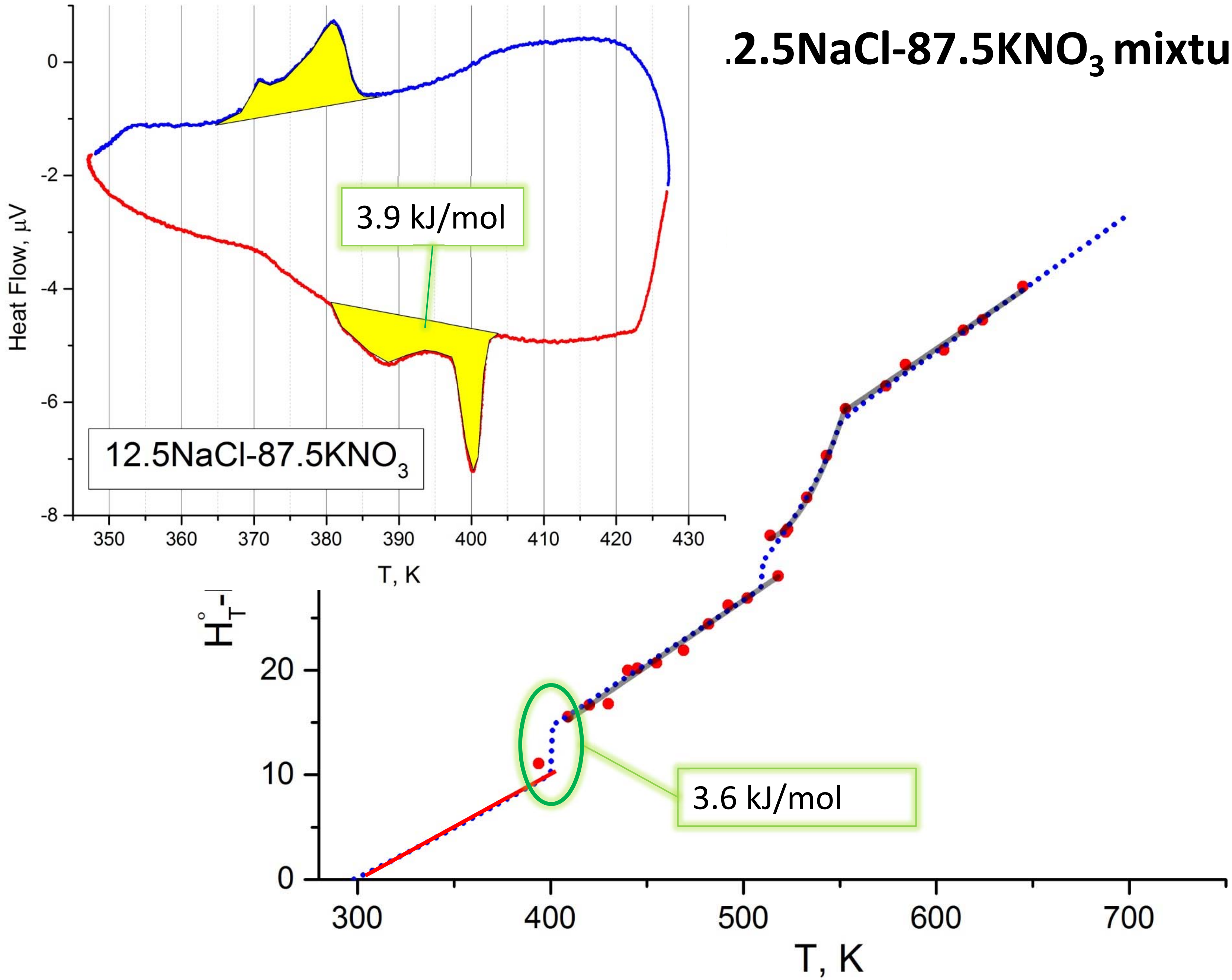
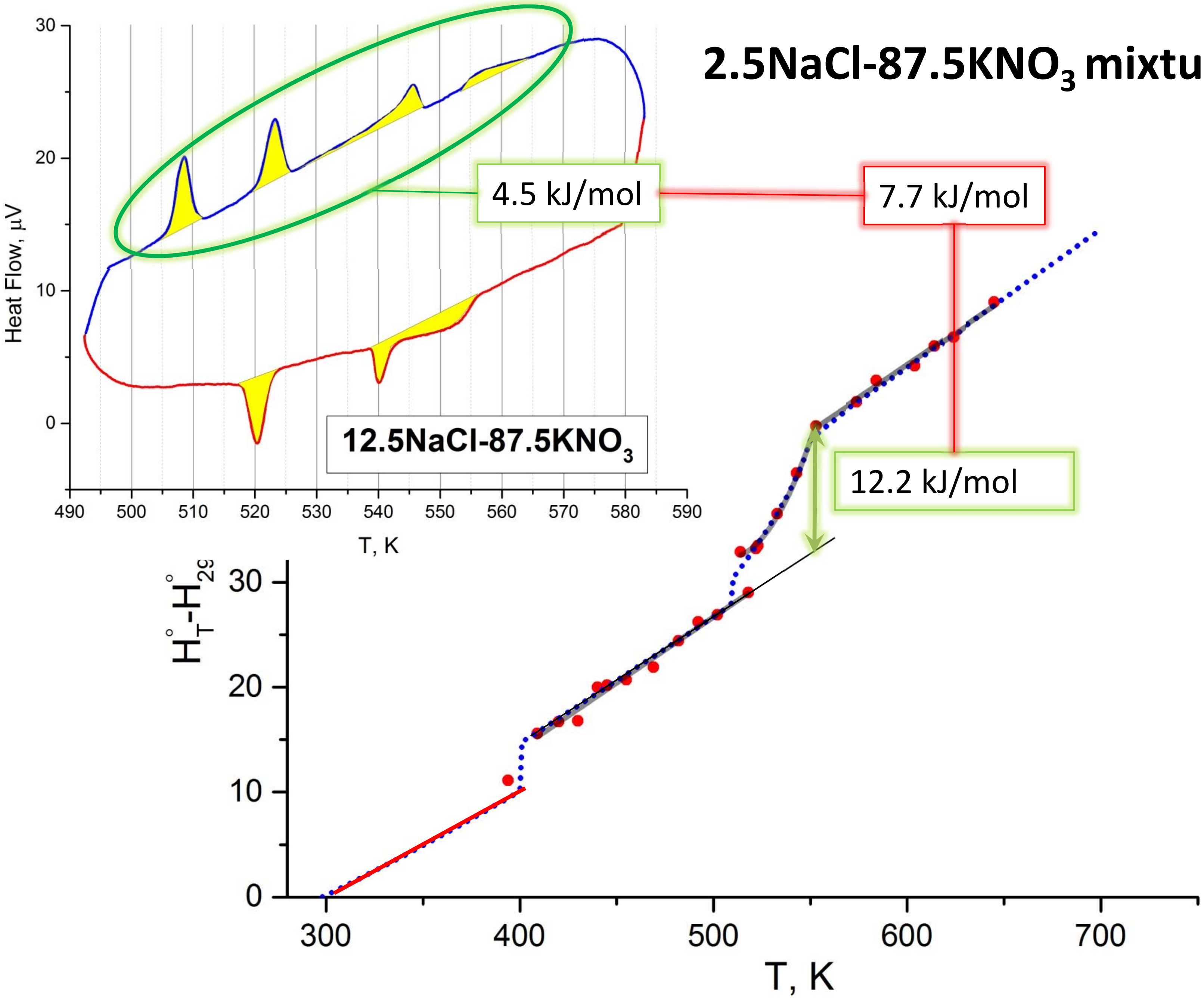


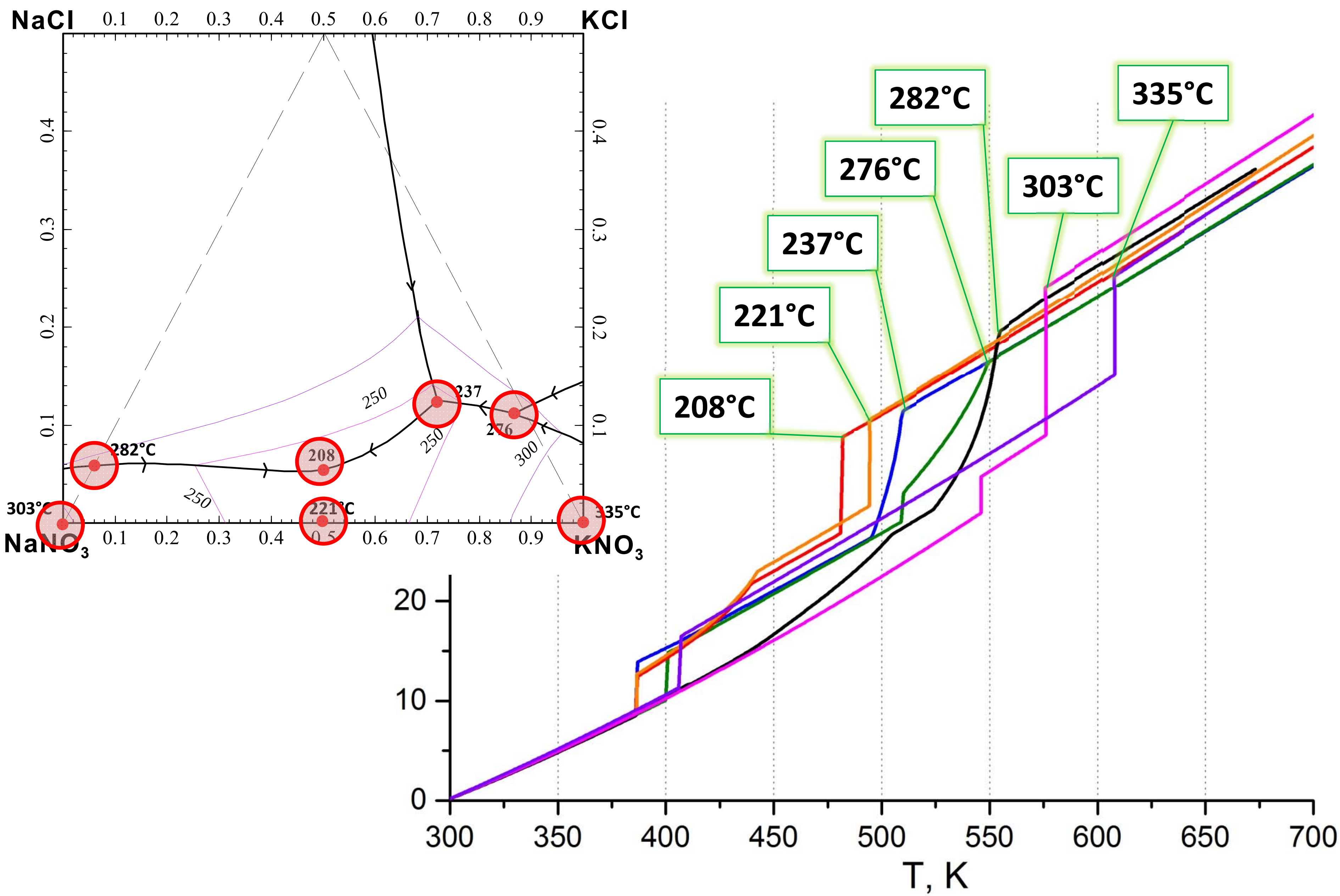
.2.5NaCl-87.5KNO$_3$ mixture



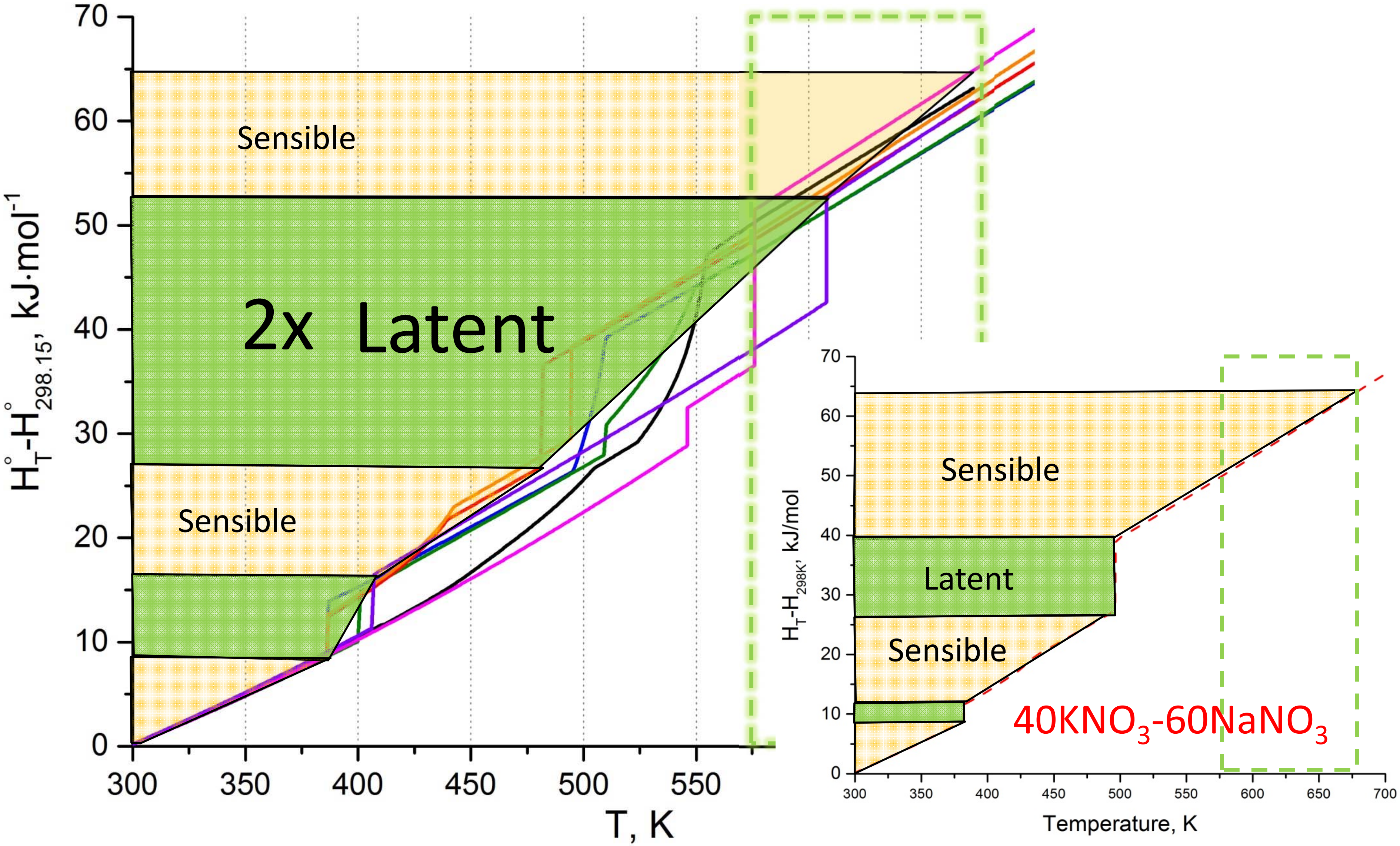
$2.5NaCl\text{-}87.5KNO_3$ mixture



Cascaded Latent Heat Storage



Cascaded Latent Heat Storage



Conclusions

- Three calorimetric methods were used for determination of thermodynamic characteristics:

  DSC, DROP and SHRTA

- The combination of these methods allows calculating the phase transition enthalpies of continuous reactions

- DSC (Netzsch) usually gives lower results of phase transition enthalpies

- Calculated heat capacity cannot reproduce experimental data of phase transition regions

- Experimental and calculated data of enthalpy increment show very good agreement

- Our database allows for calculating of thermodynamic properties of the reciprocal NaCl–KCl–$NaNO_3$–KNO_3 system with a low uncertainty

- Four compositions on the univariant line suggested as potential PCMs

Jülich Solar Tower in NRW, Germany

Thank you for your kind attention!