PCM Screening: current state of experimental work on high temperature PCMs

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PCM Screening

Mitglied der Helmholtz-Gemeinschaft

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PCM-Screening:

Evaluation of Eutectic Mixtures for Use as PCM: Thermodynamic Modelling and Experimental Methods

High Temperature PCMs
(anhydrous salts)

JÜLICH Forschungszentrum

Low Temperature PCMs
(salt hydrates)

TECHNISCHE UNIVERSITÄT DRESDEN

b-tu Brandenburgische Technische Universität Cottbus - Senftenberg

Modelling

GTT - TECHNOLOGIES

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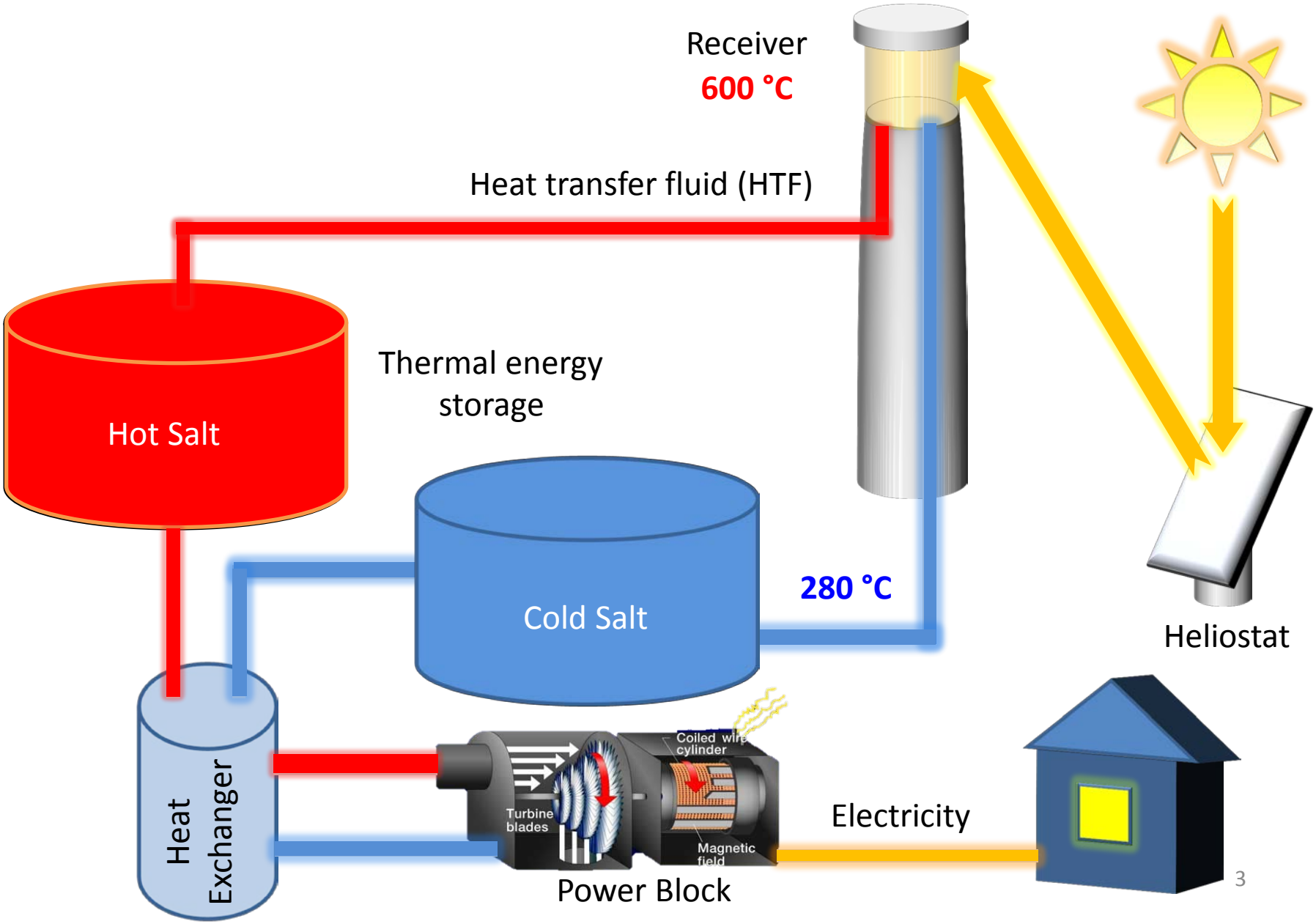
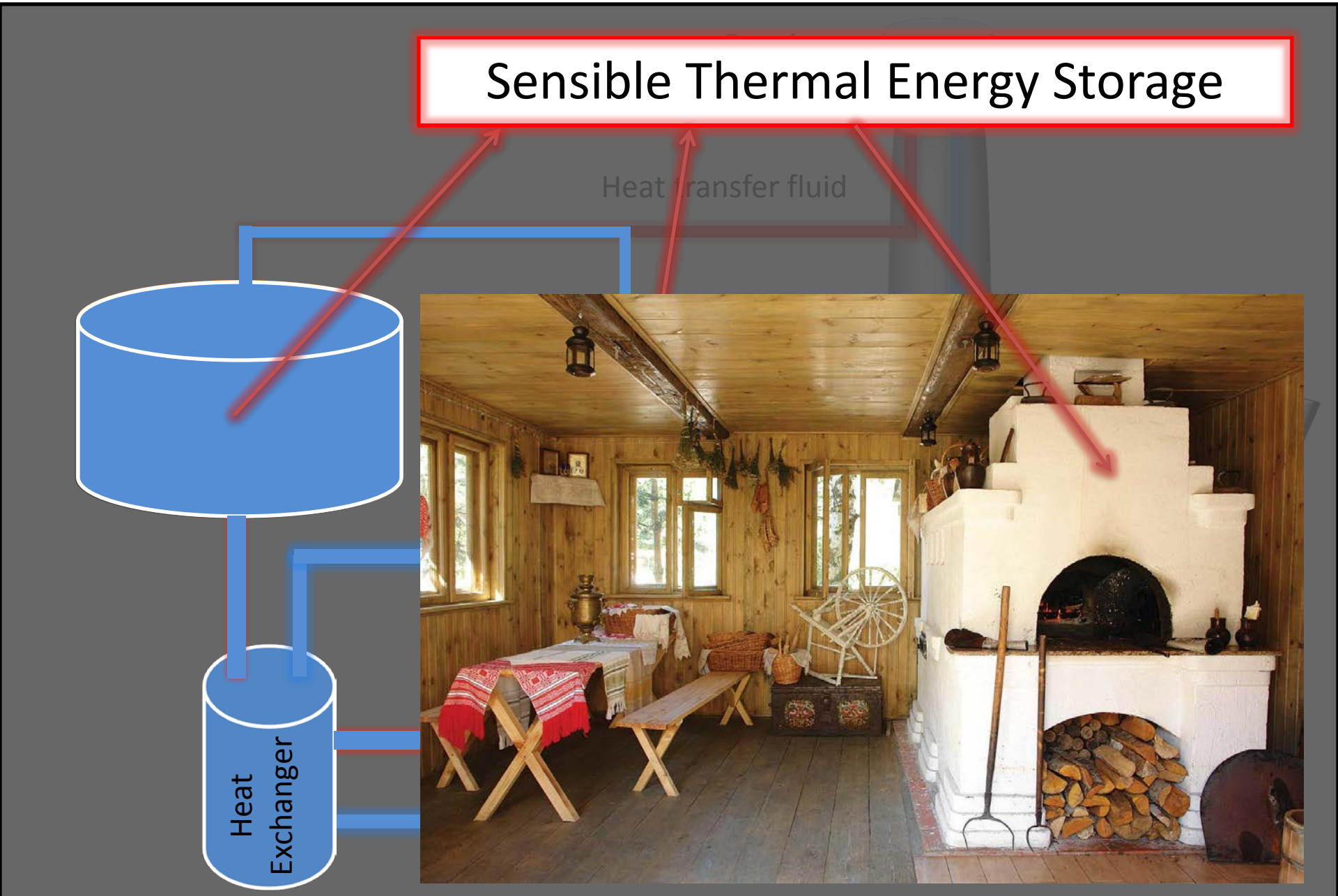
Scheme of Solar Power Plant

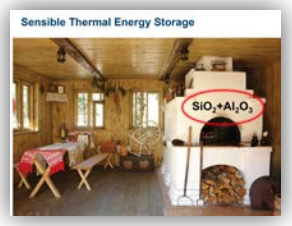


Scheme of Solar Power Plant

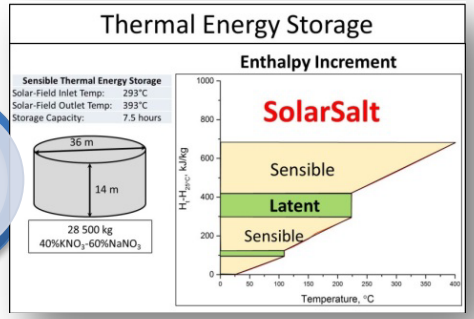


Thermal Energy Storage

Sensible



TES

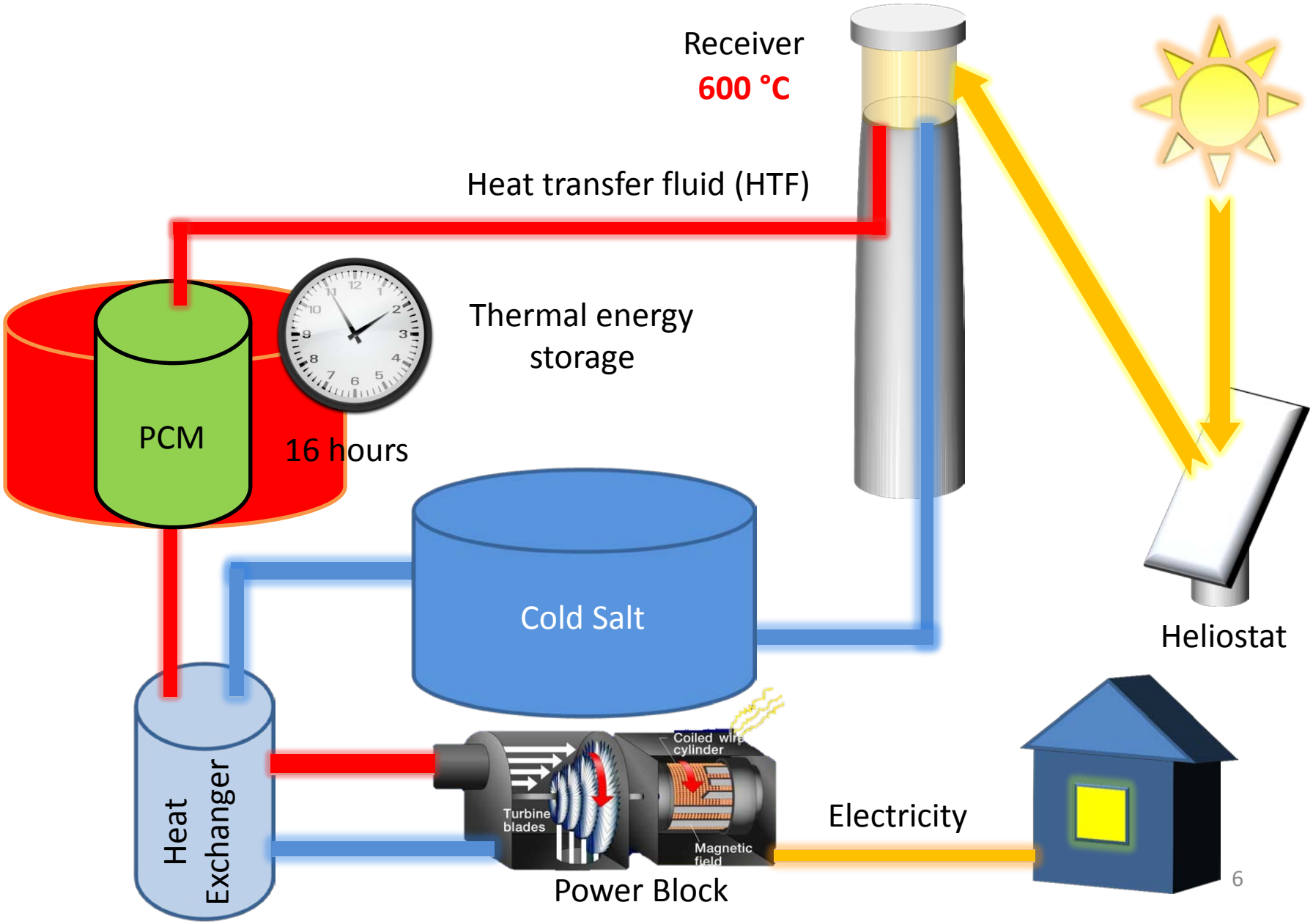


Thermal Reactions

Latent

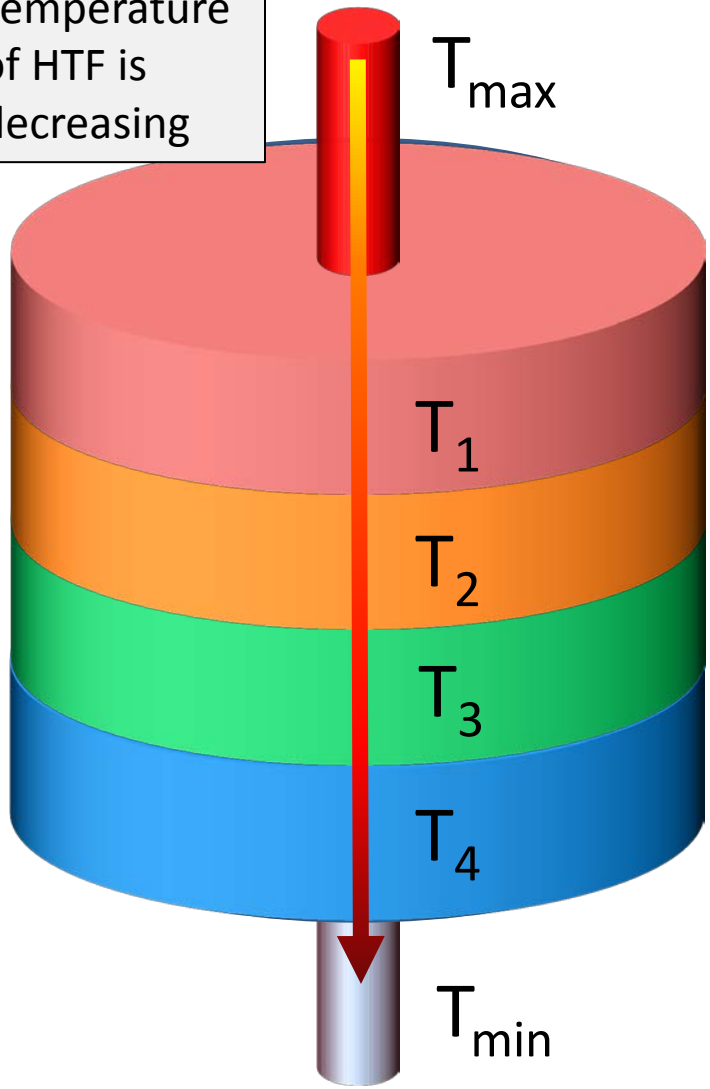
PCM Screening

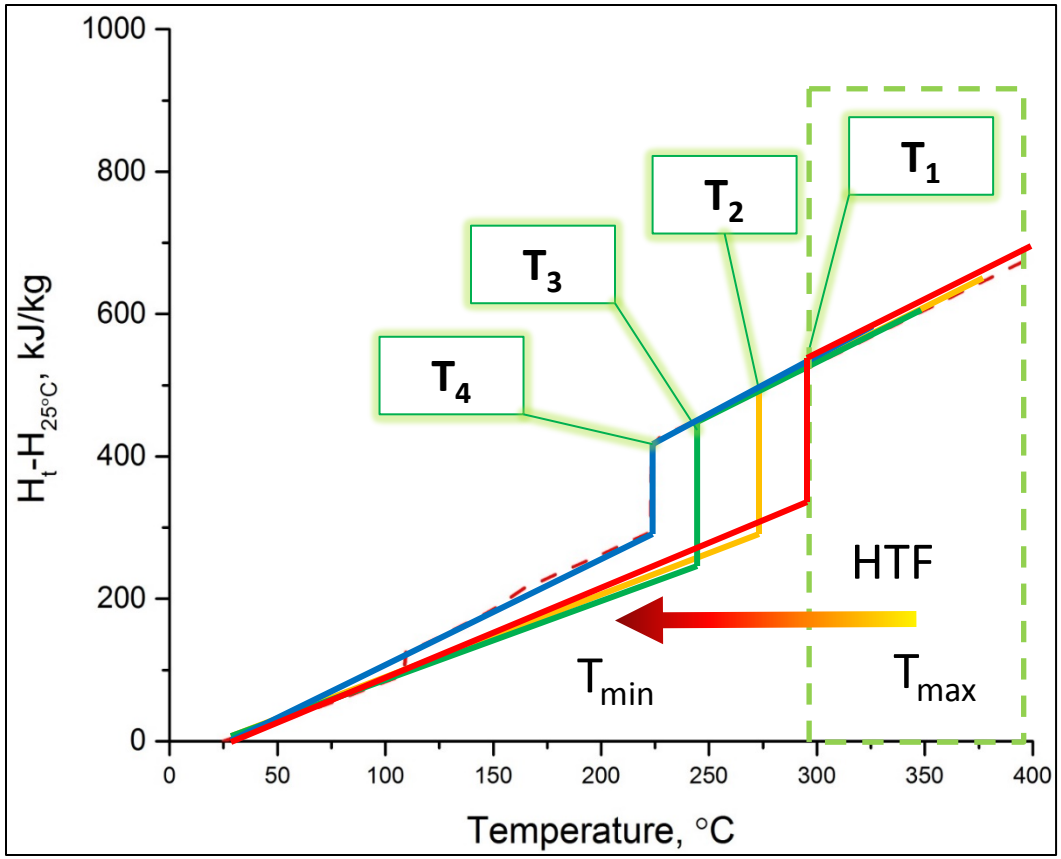
Scheme of Solar Power Plant



Cascaded Latent Heat Storage

Temperature of HTF is decreasing





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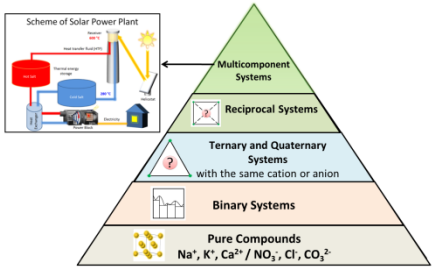

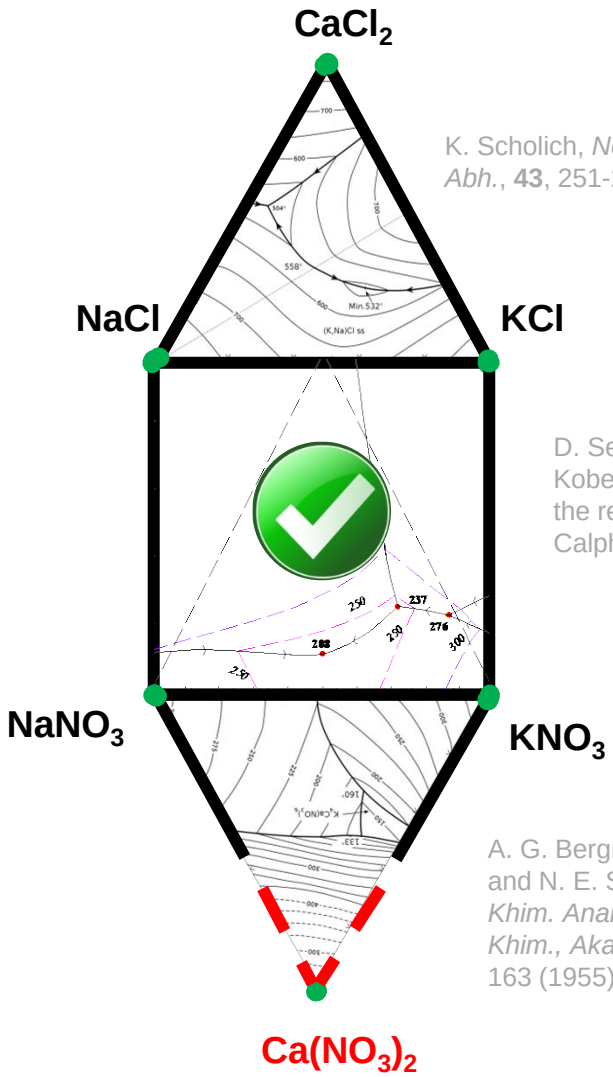

K. Scholich, *Neues Jahrb. Mineral., Abh.*, **43**, 251-294 (1920)

D. Sergeev, E. Yazhenskikh, N. Talukder, D. Kobertz, K. Hack, M. Müller, Thermodynamics of the reciprocal NaCl–KCl–NaNO3–KNO3 system, Calphad, 53 (2016) 97-104.

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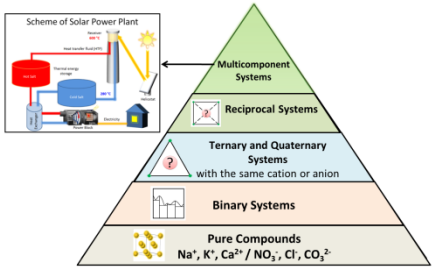

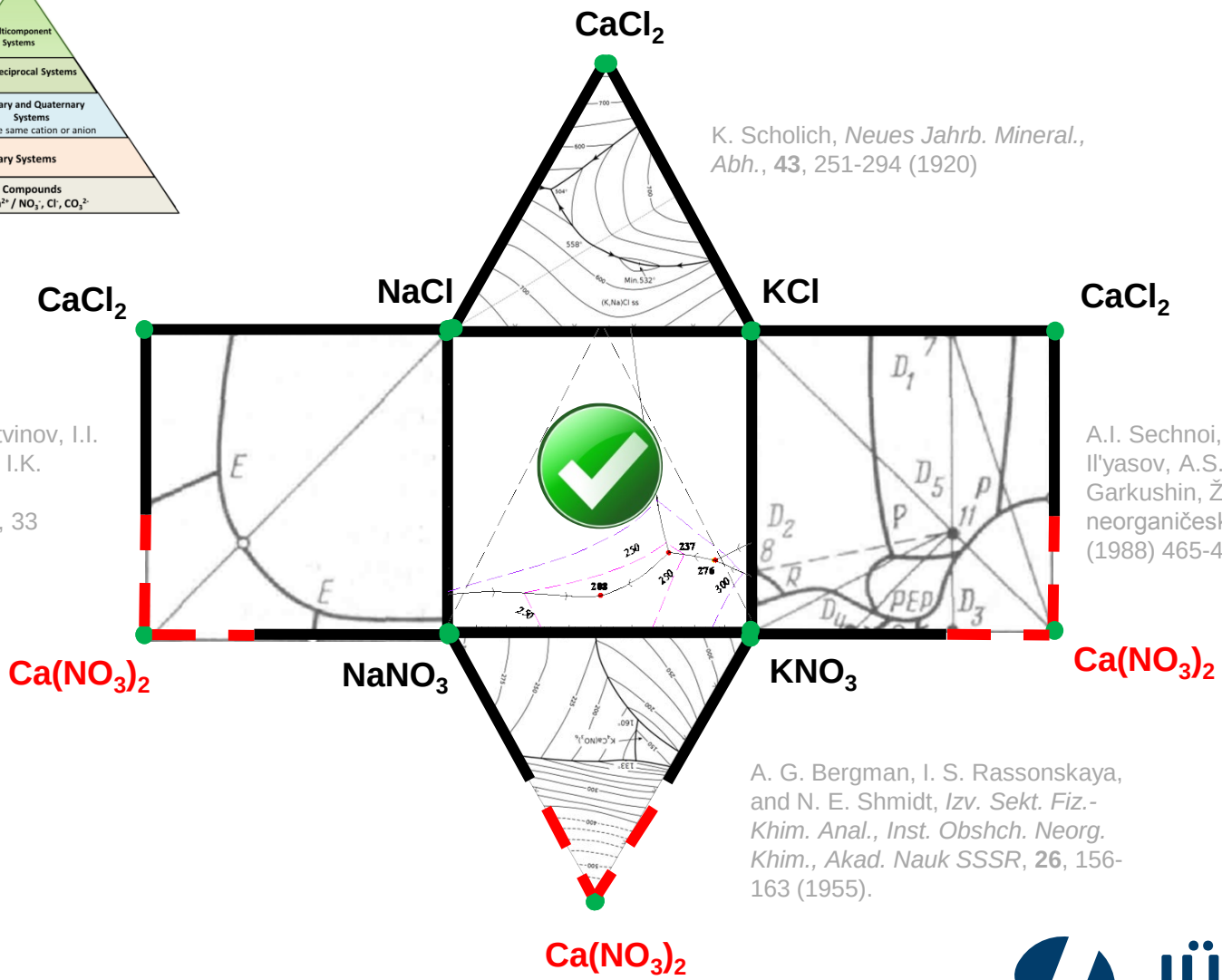

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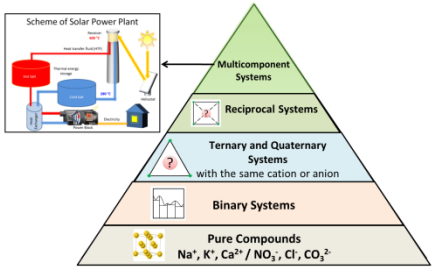

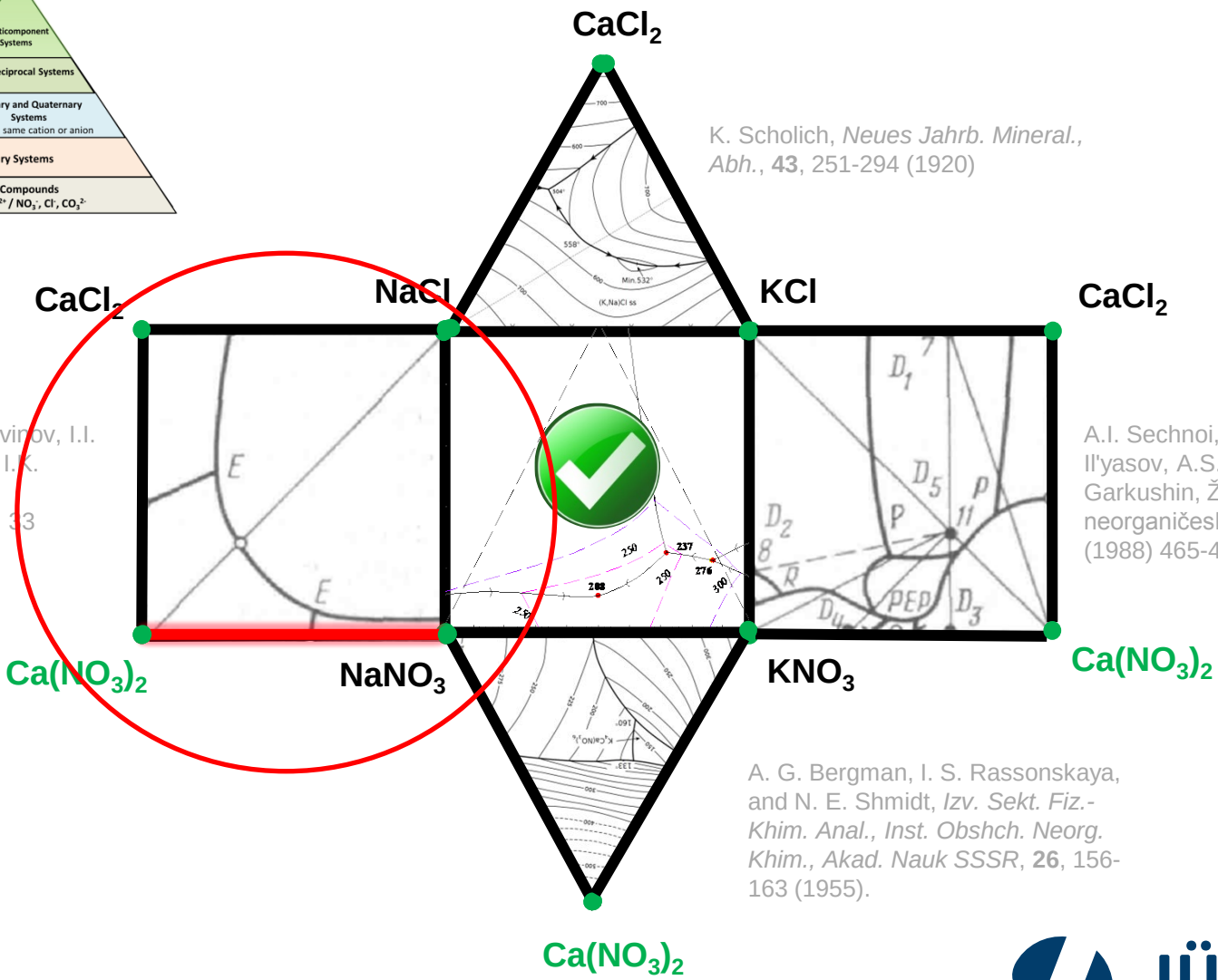

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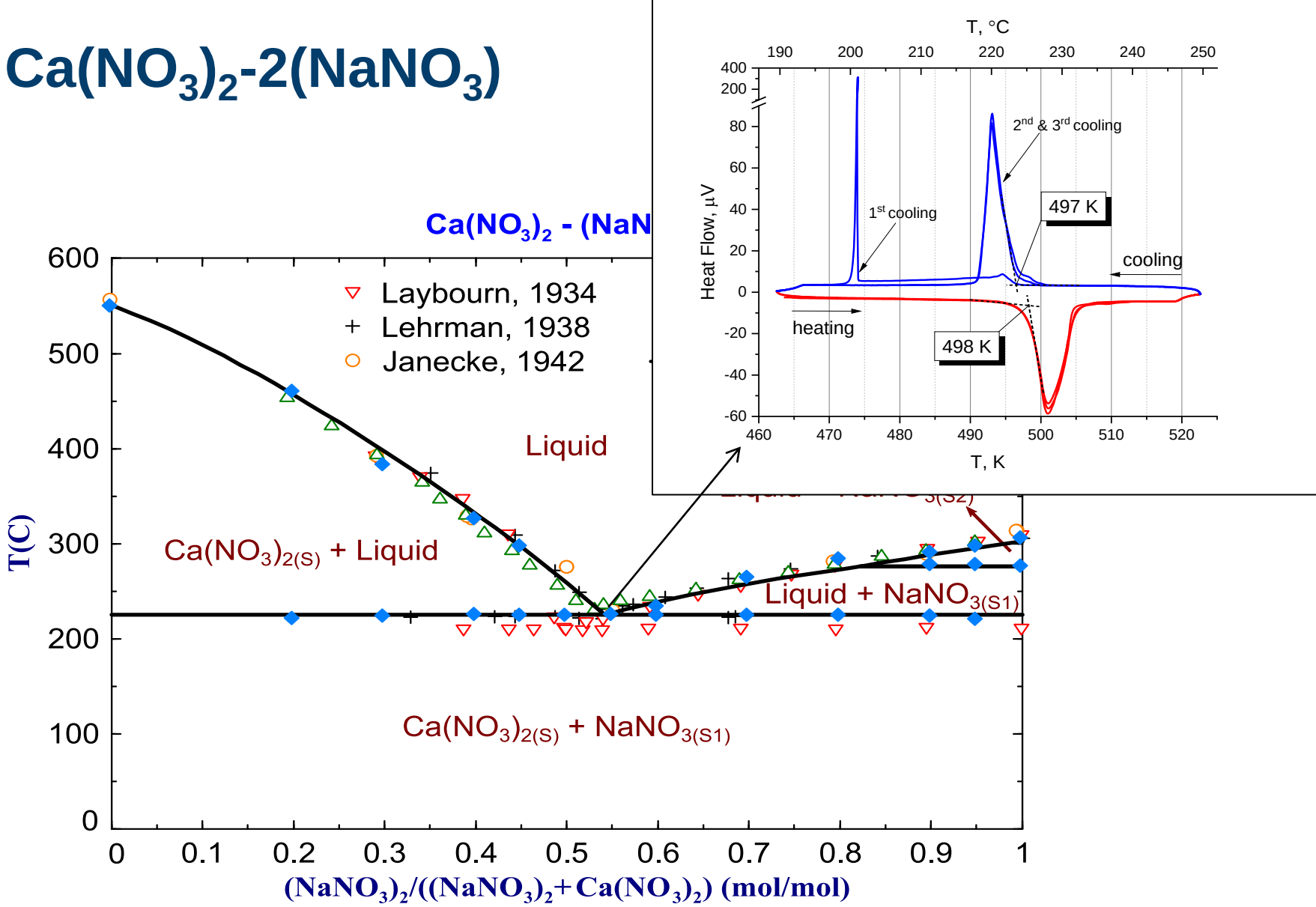
$Ca(NO_3)_2$-2($NaNO_3$)



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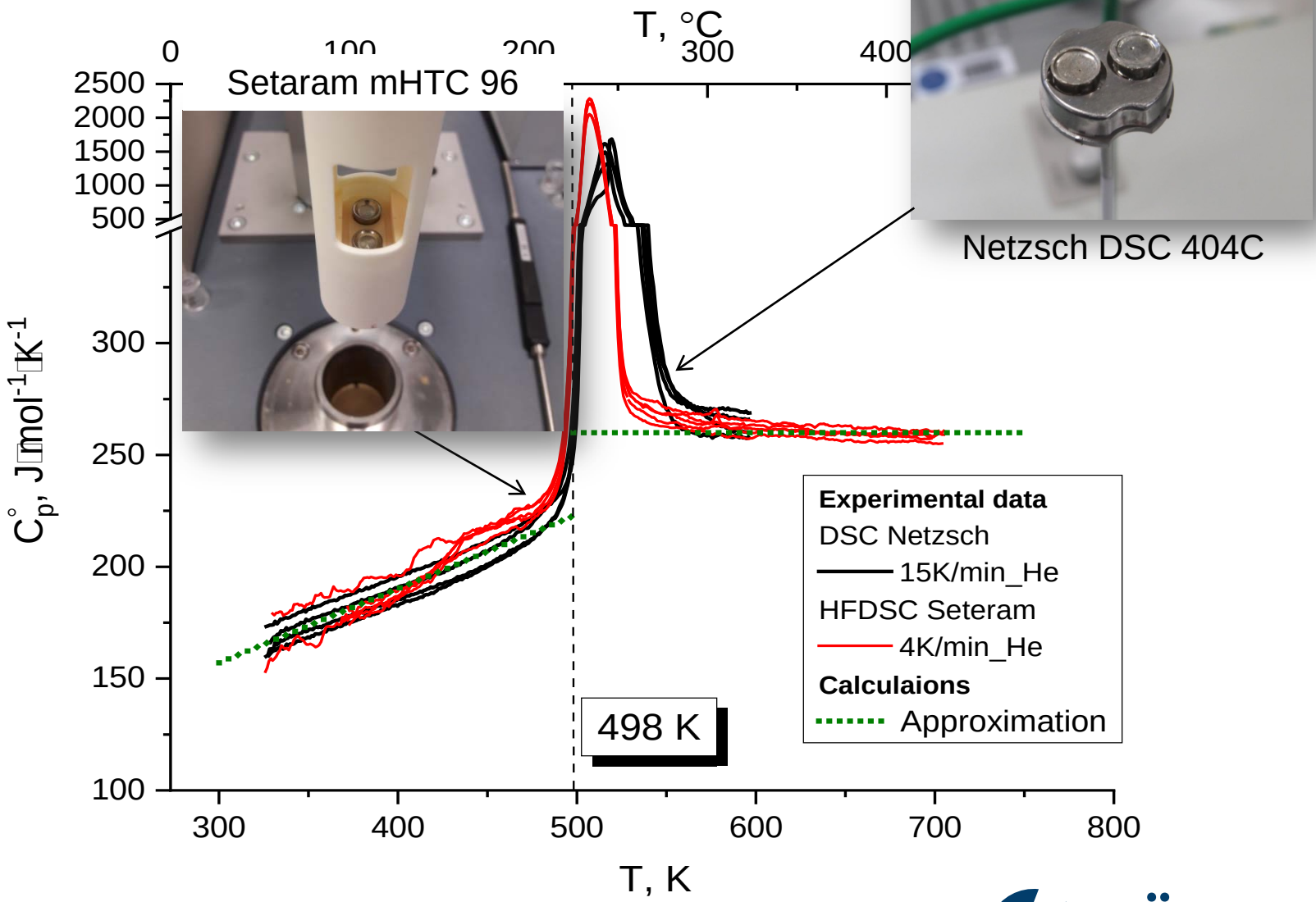
Heat capacity of $45Ca(NO_3)_2$-$55(NaNO_3)_2$



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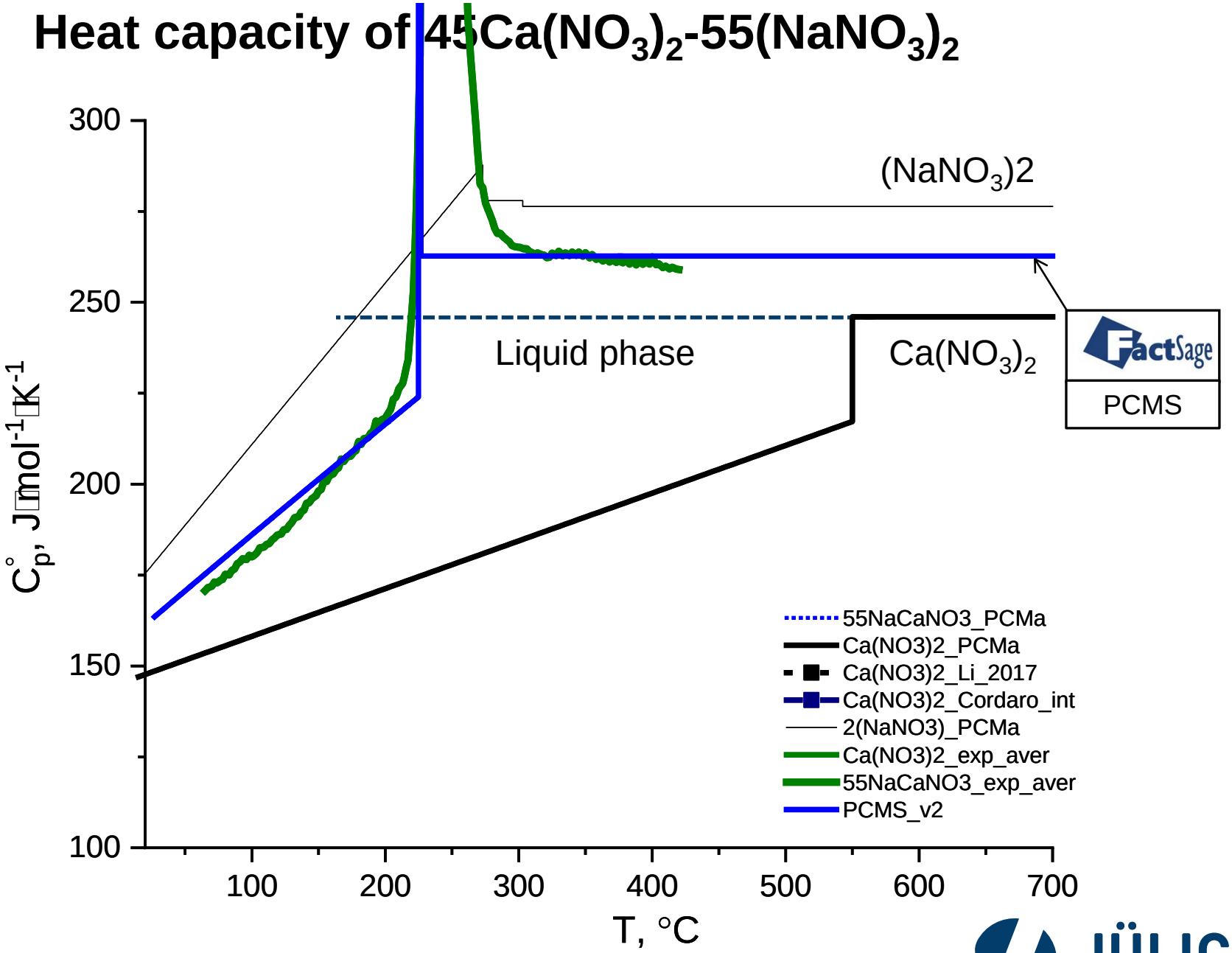
Heat capacity of $45Ca(NO_3)_2$-$55(NaNO_3)_2$



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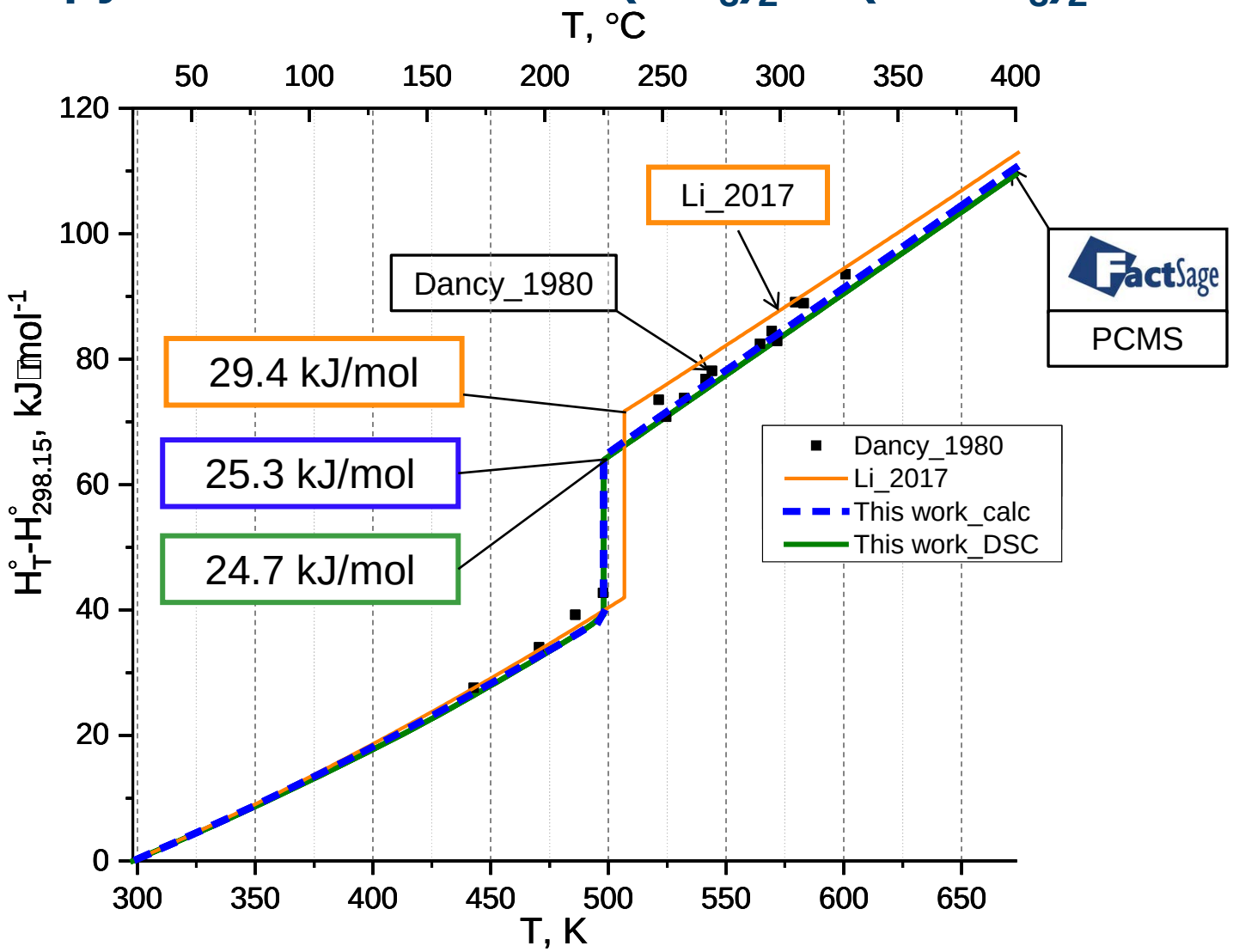
Enthalpy Increment of $45Ca(NO_3)_2$-$55(NaNO_3)_2$



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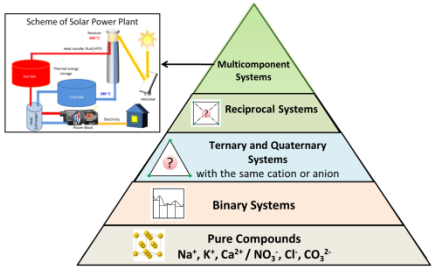
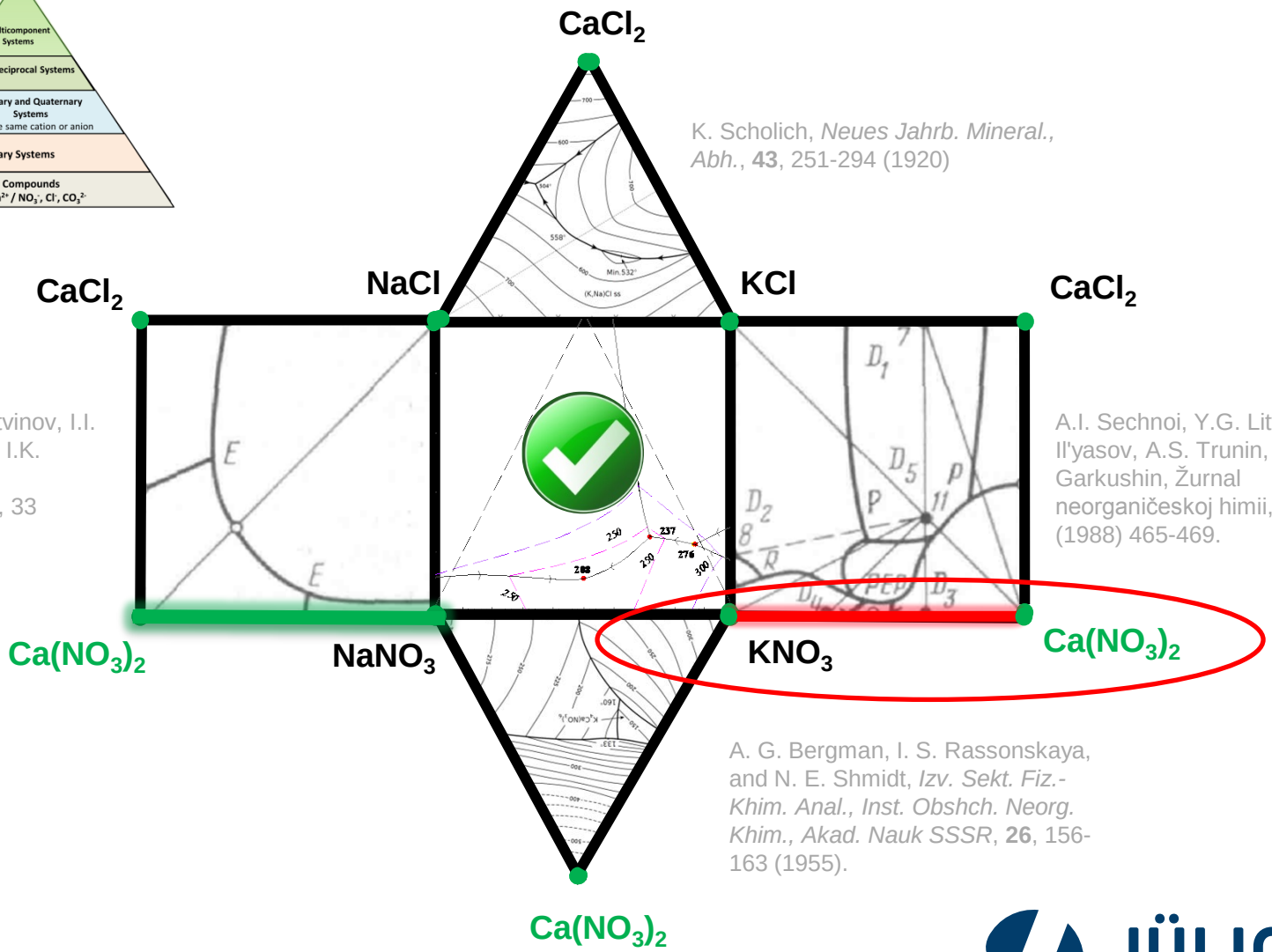
PCM Screening





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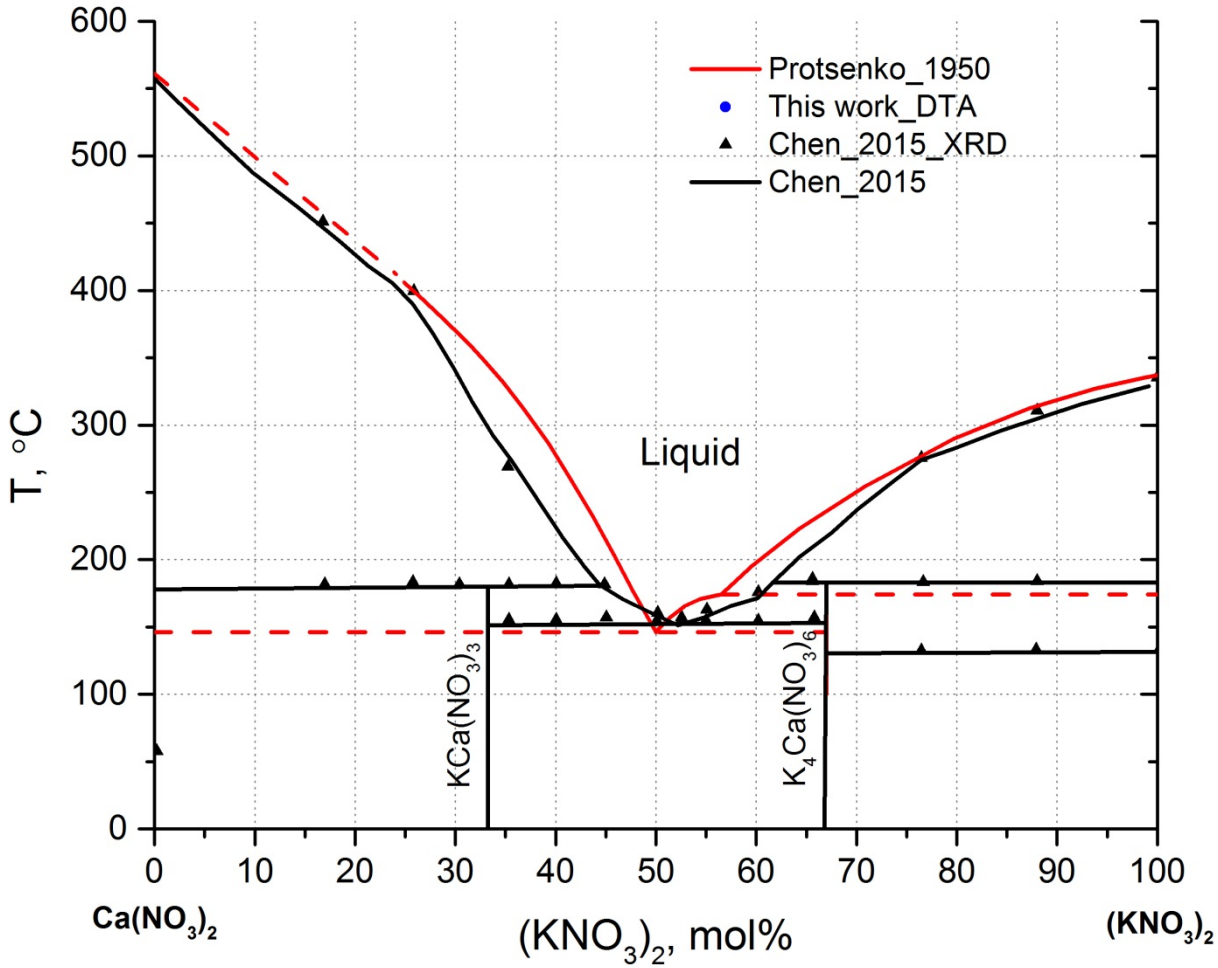
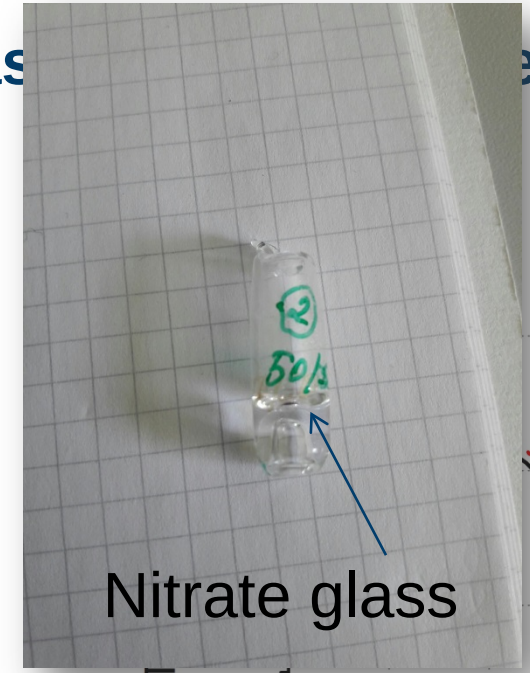
Phase Diagram of the $Ca(NO_3)_2$-$(KNO_3)_2$ System

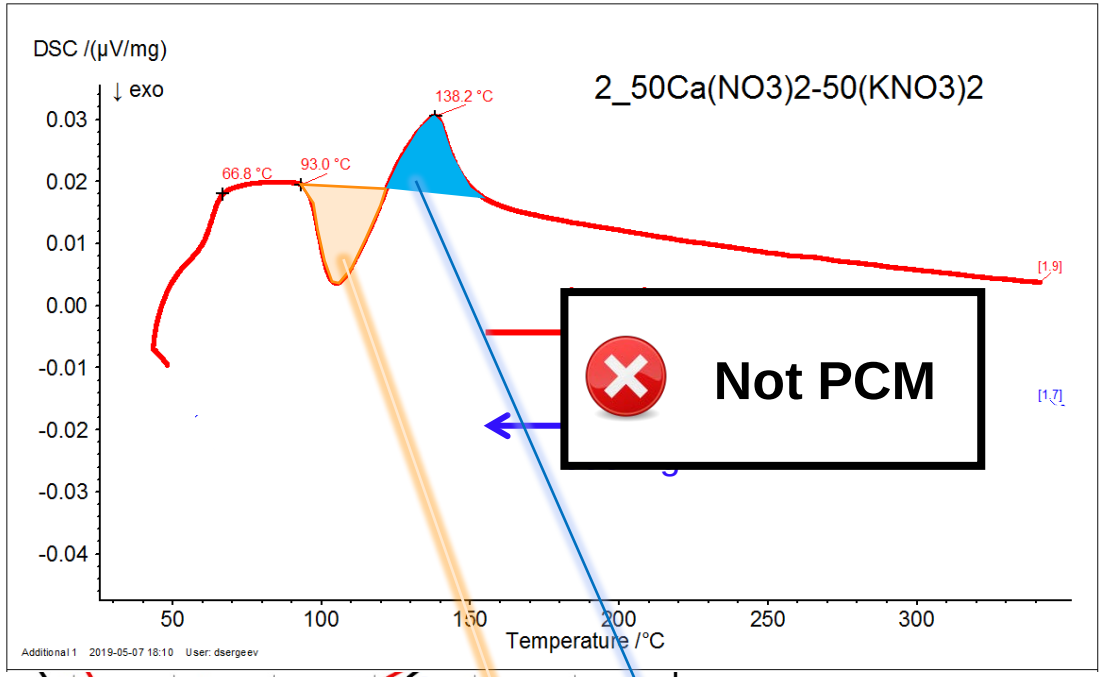


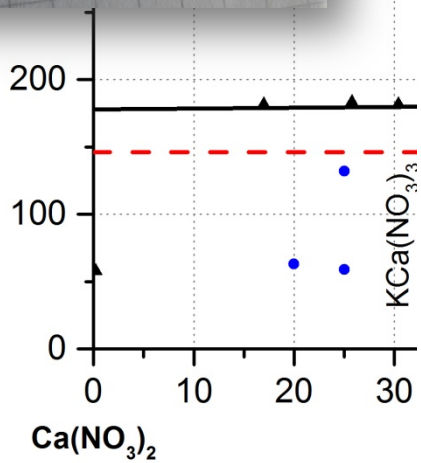
J. Chen, D.W. Zeng, D.D. Li, J.T. Wang, H.J. Han, L.J. Guo, Phase diagram and thermal stability of KNO3-Ca(NO3)2 binary system, Inorg. Chem. Ind. 47 (11),(2015) 38–41.

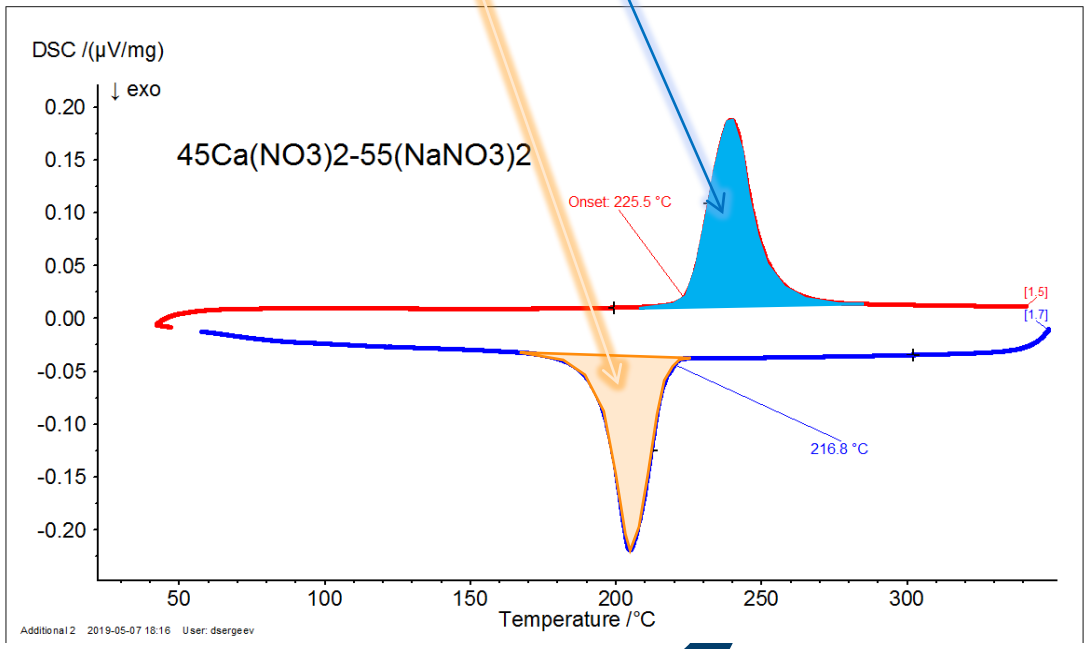
P.I. Protsenko, A.G. Bergman, Ternary system of fused nitrates of calcium, potassium, and sodium, Zhurnal Obshchei Khimii, 20 (1950) 1365-1375.

Phas e Ca









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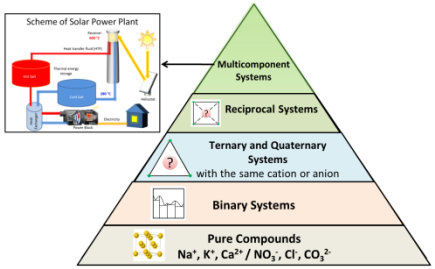
PCM Screening



K+Ca

K. Sch… …eral., *Abh.*, **43**

$CaCl_2$

$CaCl_2$ NaCl KCl $CaCl_2$

?

A.I. Sechnoi, Y.G. Litvinov, I.I. Il'yasov, A.S. Trunin, I.K. Garkushin, Žurnal neorganičeskoj himii, 33 (1988) 465-469.

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$Ca(NO_3)_2$ $NaNO_3$ KNO_3 $Ca(NO_3)_2$

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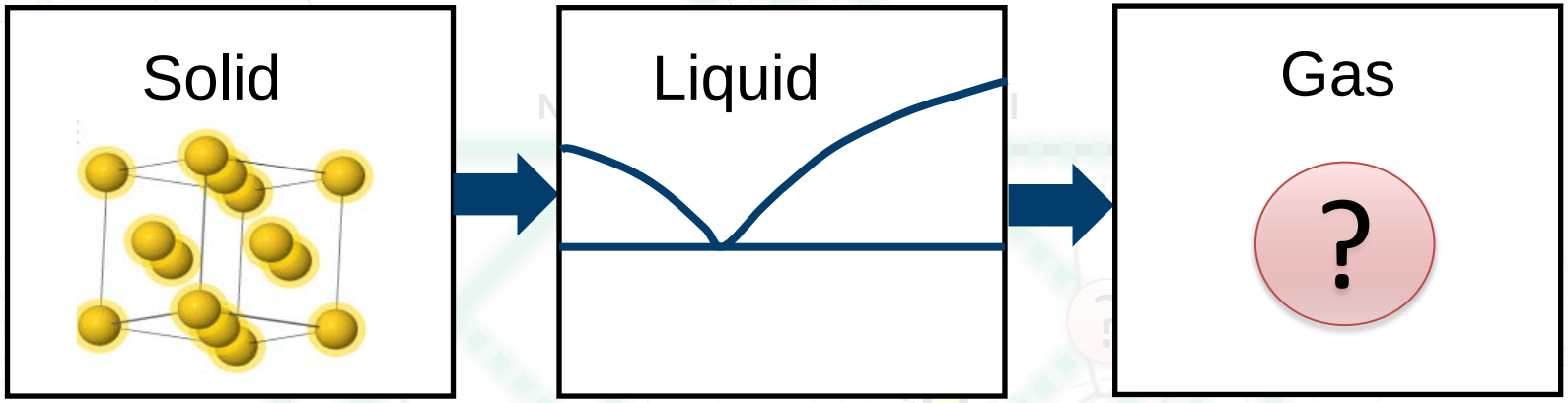
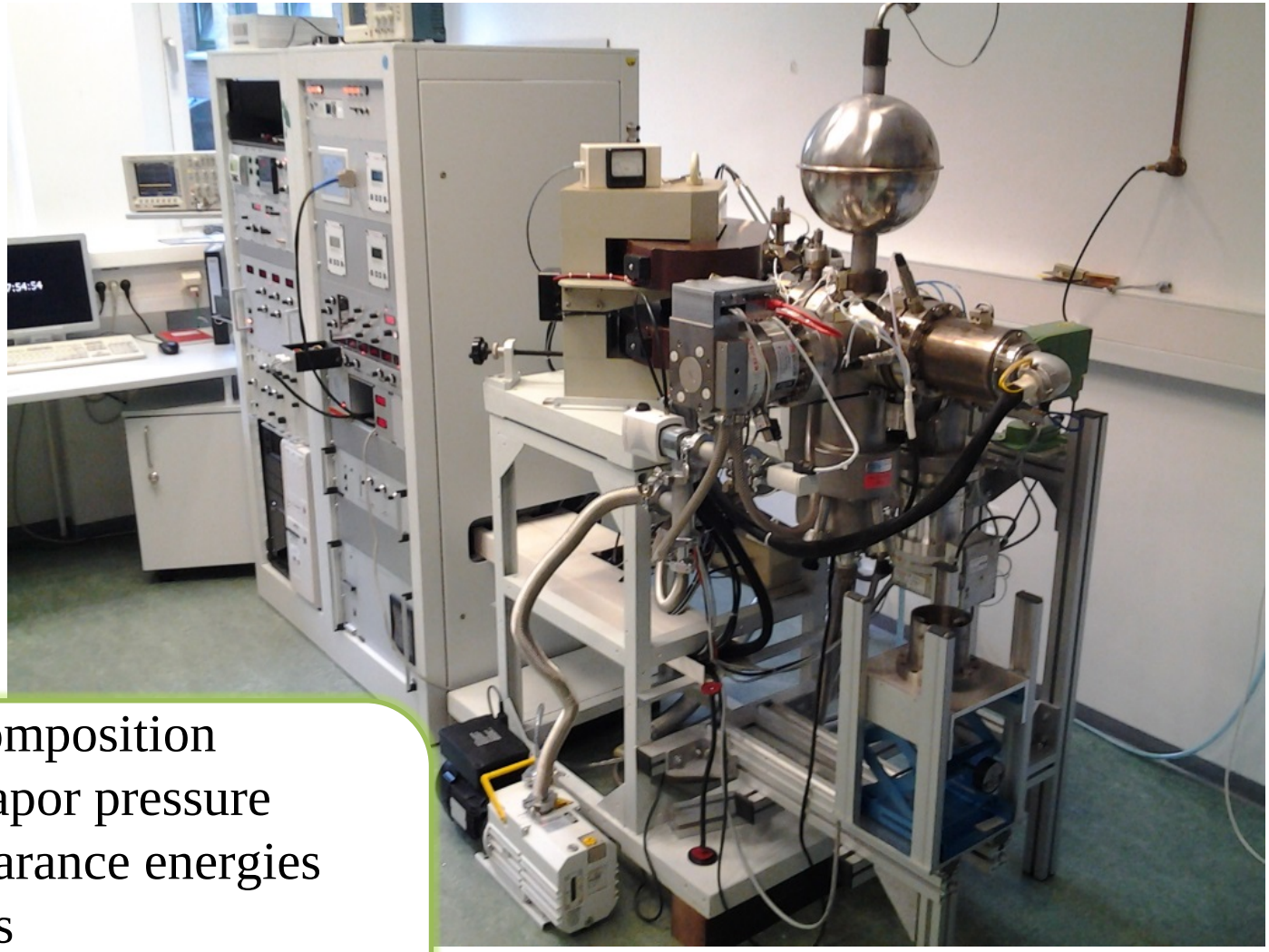
$Ca(NO_3)_2$


Solid
Liquid
Gas
?

Knudsen Effusion Mass Spectrometry



- Vapor composition
- Partial vapor pressure
- Ion appearance energies
- Activities
- Equilibrium constants
- Reaction enthalpies

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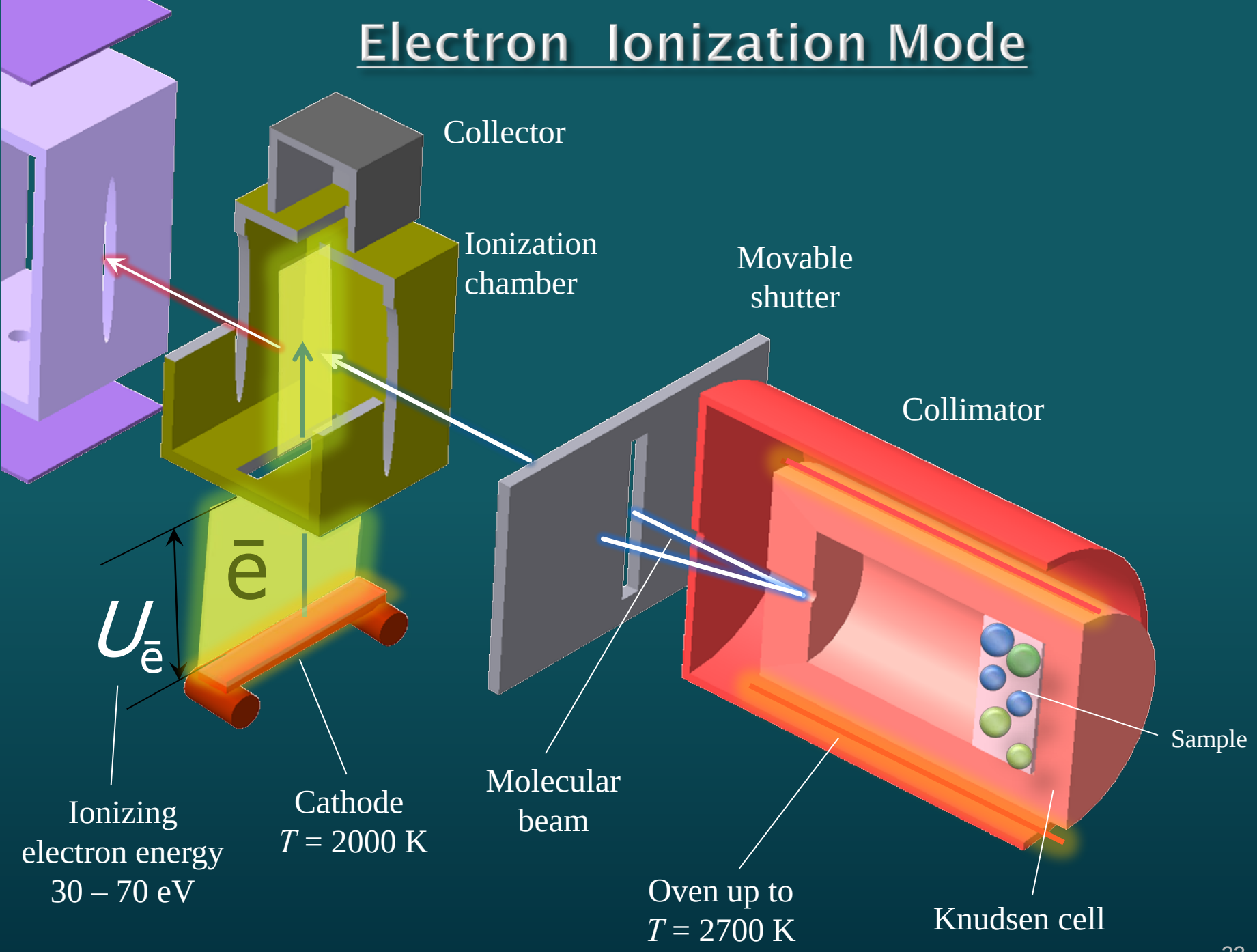
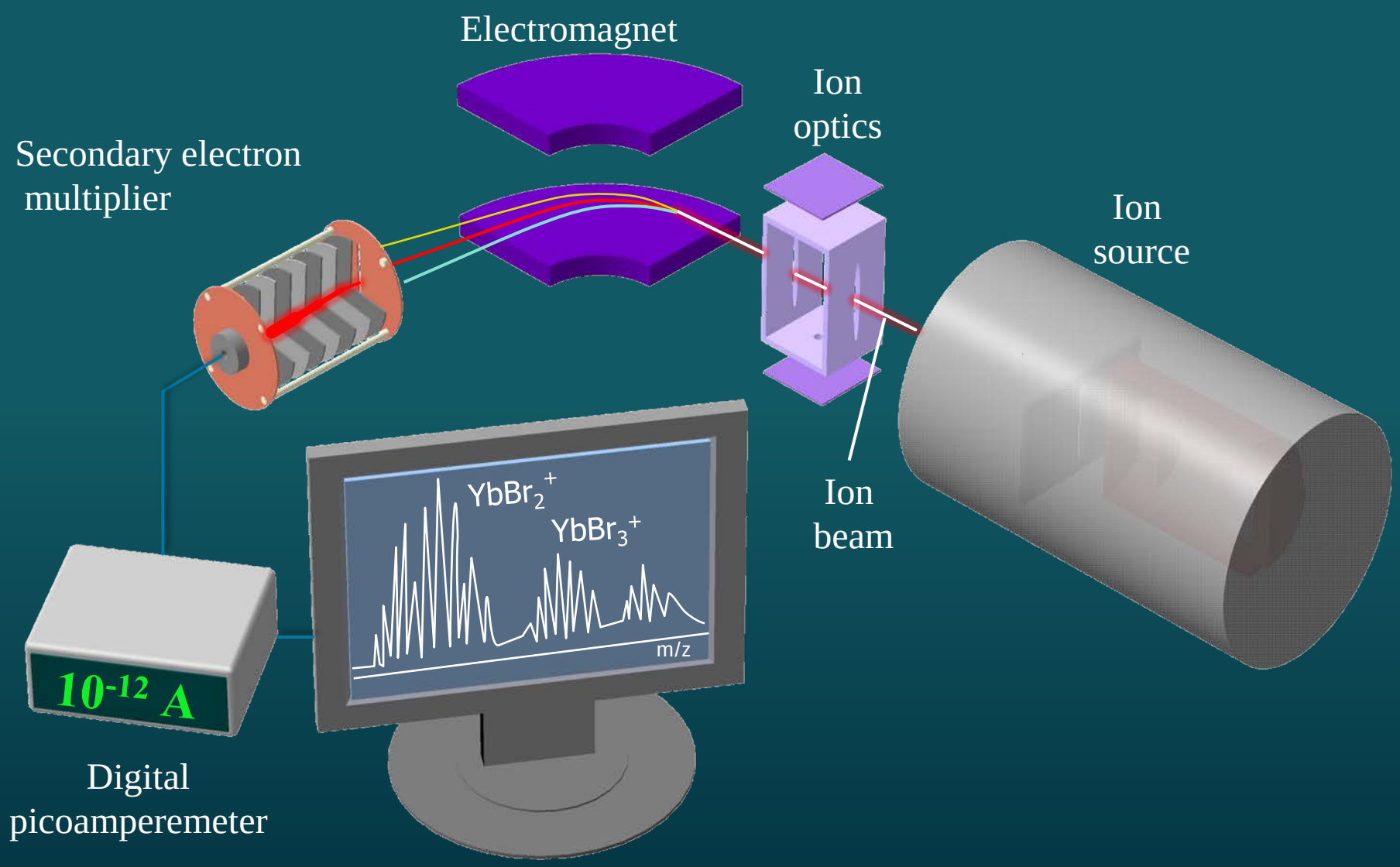
Electron Ionization Mode

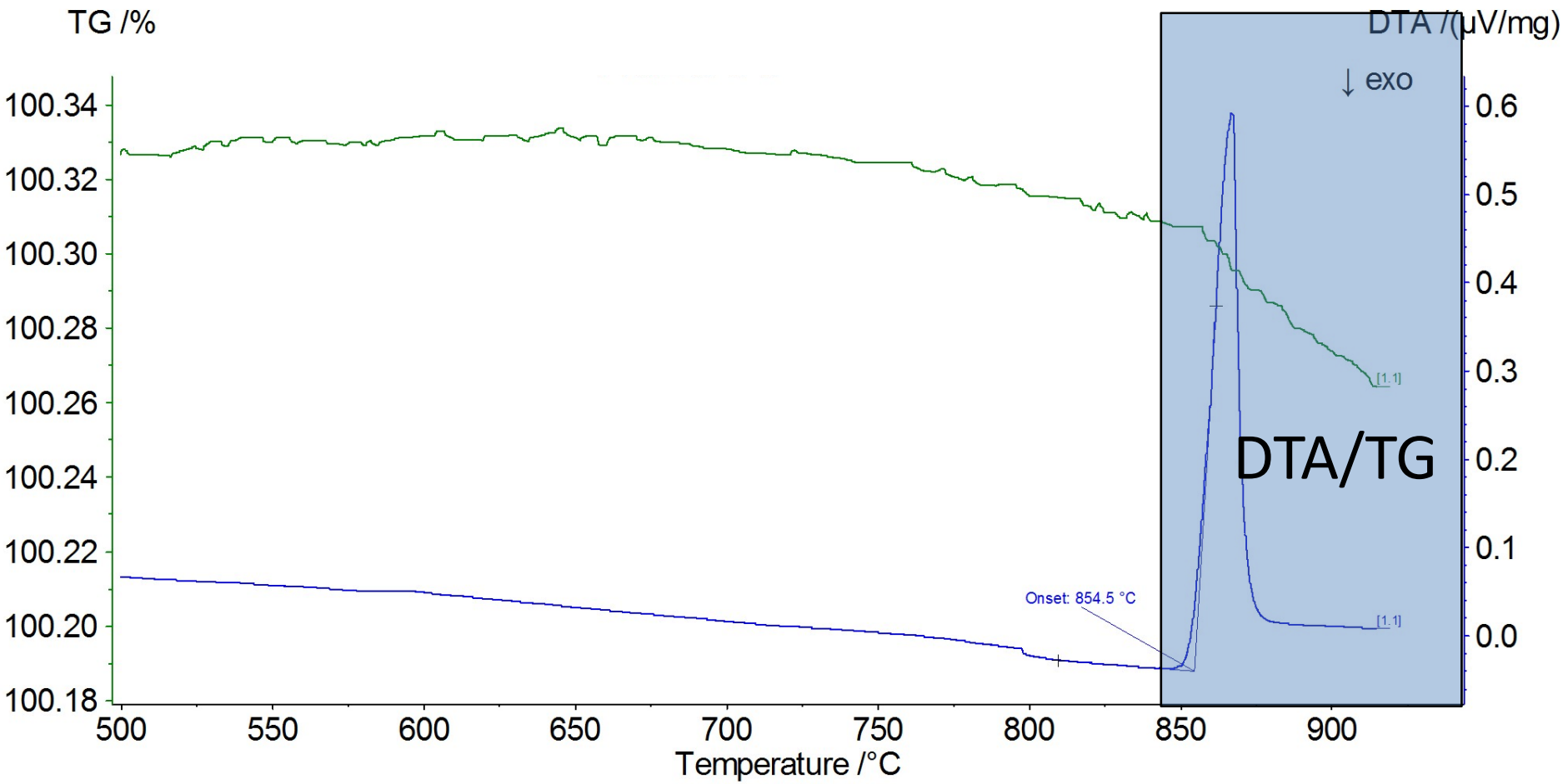


Mass Spectrometry

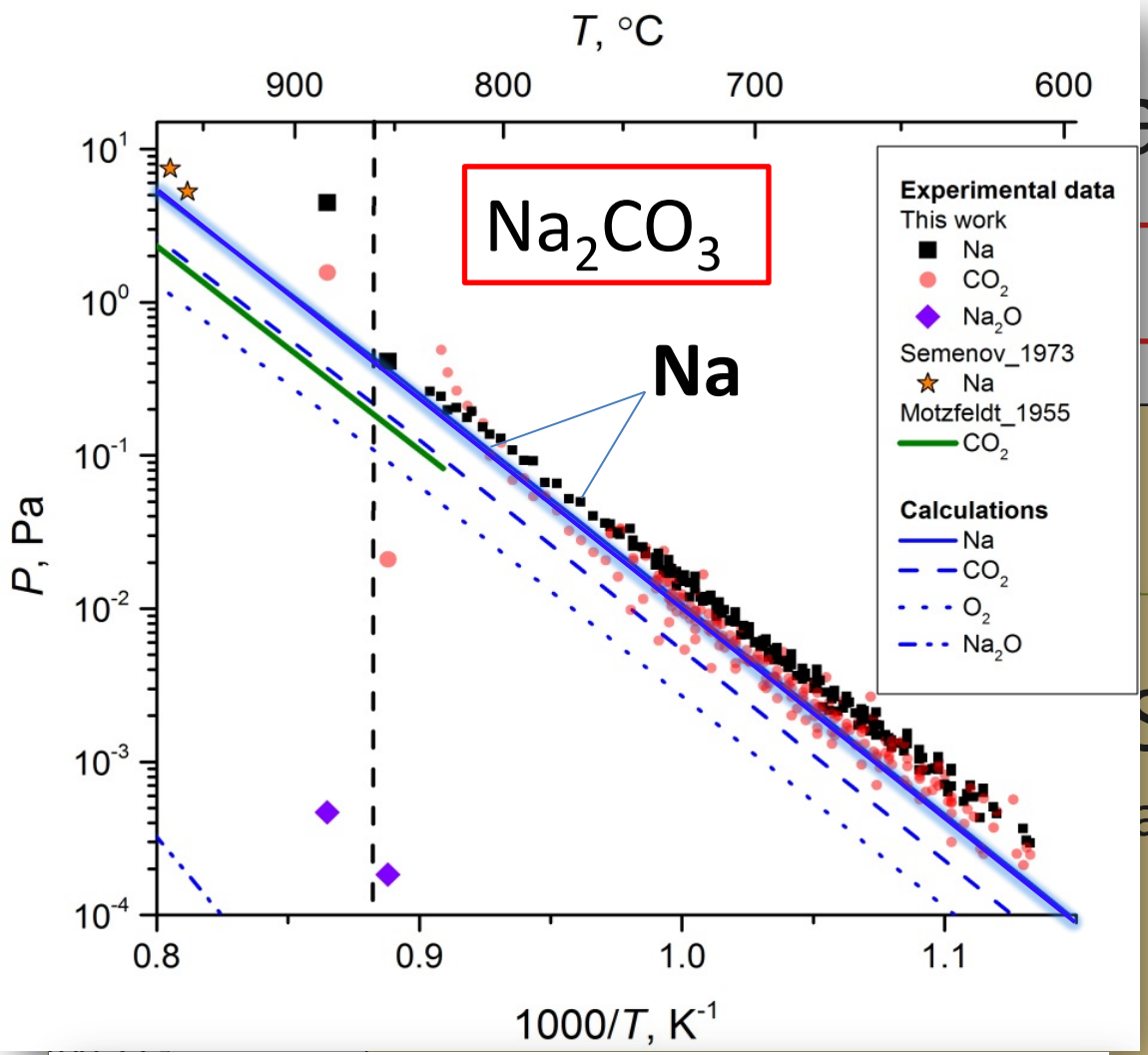


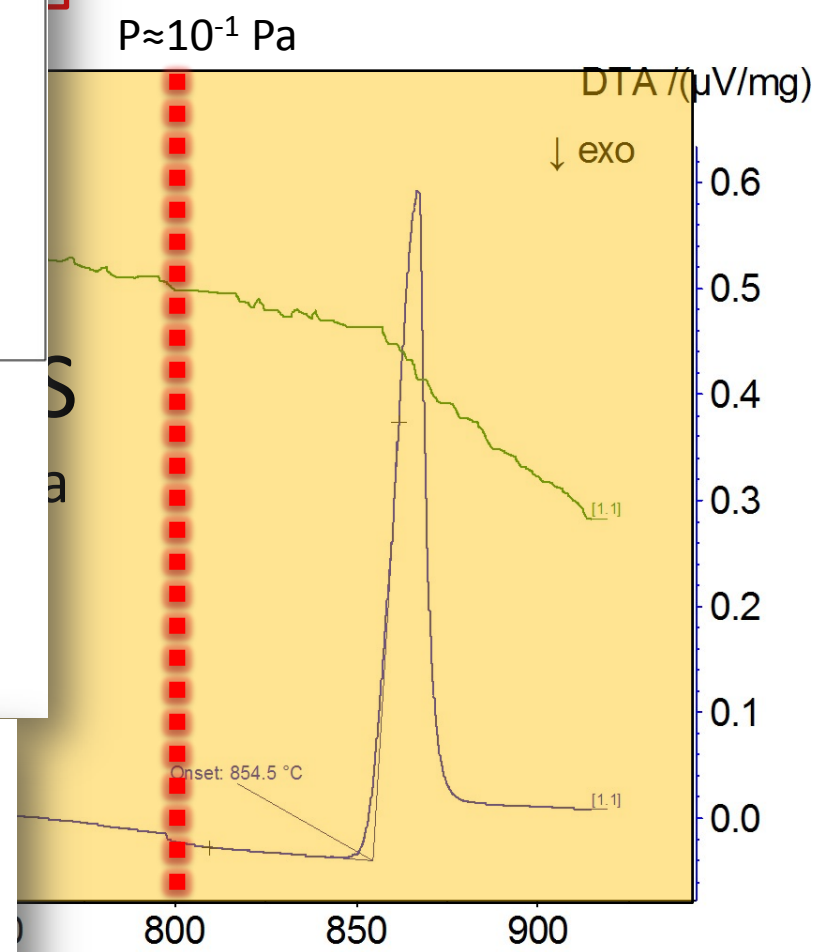
Sensibility of TG and KEMS

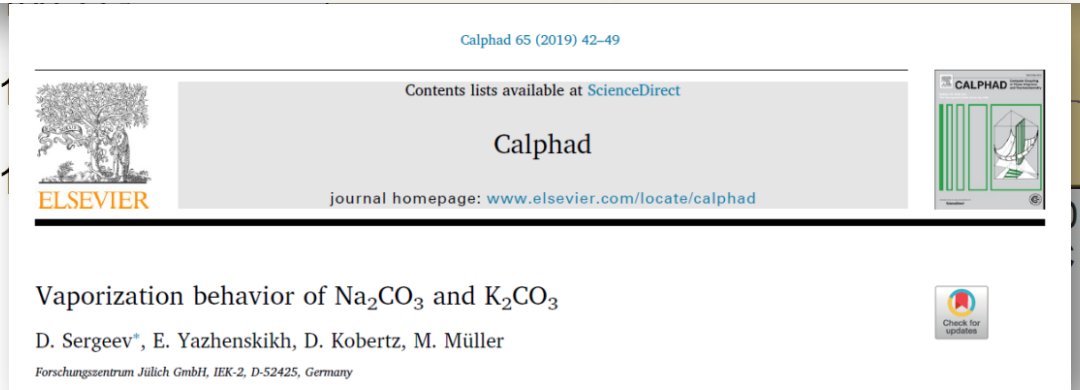
Na_2CO_3



and KEMS







Calphad 65 (2019) 42–49

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Vaporization behavior of Na_2CO_3 and K_2CO_3

D. Sergeev*, E. Yazhenskikh, D. Kobertz, M. Müller

Forschungszentrum Jülich GmbH, IEK-2, D-52425, Germany

$Ca(NO_3)_2$: Vapour Pressure

Equilib - Results 400 C (page 18/38)

Output Edit Show Pages

T(C) P(Pa) Energy(J) Mass(mol) Vol(litre)

250 C | 258.01 C | 258.01 C | 260 C | 270 C | 280 C | 290 C | 300 C | 310 C | 320 C | 330 C | 450 C | 460 C | 470 C | 340 C | 350 C | 360 C | 370 C | 380 C | 390 C | 400 C | 410 C | 420 C | 430 C | 440 C |

```
                                                                    FactSage 7.2
T = 400 C
P = 1.0132E+05 Pa
V = 193.33 dm3

STREAM CONSTITUENTS            AMOUNT/mol
Ca(NO3)2                       1.0000E+00
N2                             0.0000E+00
O2                             0.0000E+00

                              EQUIL AMOUNT  MOLE FRACTION     FUGACITY
PHASE: gas_ideal                  mol                          Pa
O2                             2.5000E+00     7.1429E-01     7.2375E+04
N2                             1.0000E+00     2.8571E-01     2.8950E+04
NO2                            1.7523E-06     5.0065E-07     5.0729E-02
NO                             5.8417E-07     1.6691E-07     1.6912E-02
N2O                            5.0094E-11     1.4313E-11     1.4502E-06
O                              1.8787E-16     5.3677E-17     5.4388E-12
CaO                            4.3736E-43     1.2496E-43     1.2662E-38
TOTAL:                         3.5000E+00     1.0000E+00     1.0000E+00
   System component            Amount/mol    Amount/gram   Mole fraction  Mass fraction
   Ca                          4.3736E-43     1.7528E-41     6.2480E-44     1.6229E-43
   O                           5.0000         79.997         0.71429        0.74064
   N                           2.0000         28.013         0.28571        0.25936
                                  mol                          ACTIVITY
CaO_S1(s)                      1.0000E+00                     1.0000E+00
Ca(NO3)2_solid(s)              0.0000E+00                     6.5009E-07
Ca(NO3)2_liquid(liq)           0.0000E+00                     2.4525E-07
*******************************************************************
     Cp            H            S            G            V
   J.K-1           J          J.K-1          J           dm3
*******************************************************************
 1.62836E+02  -5.76728E+05   8.84998E+02  -1.17246E+06   1.93330E+02

                              Cp           H            S            G
                            J.K-1          J          J.K-1          J
```

Gas phase

Solid phase

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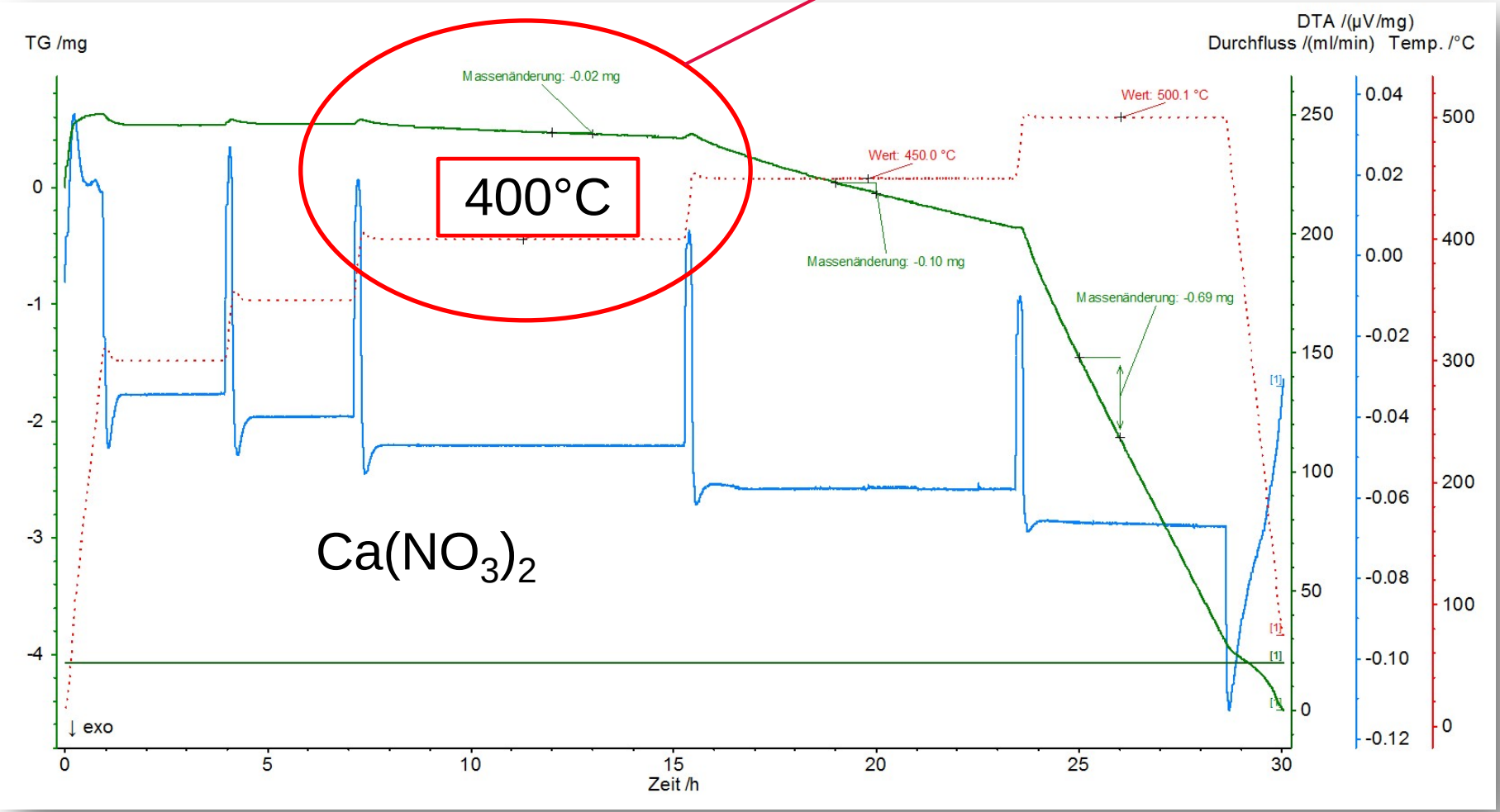
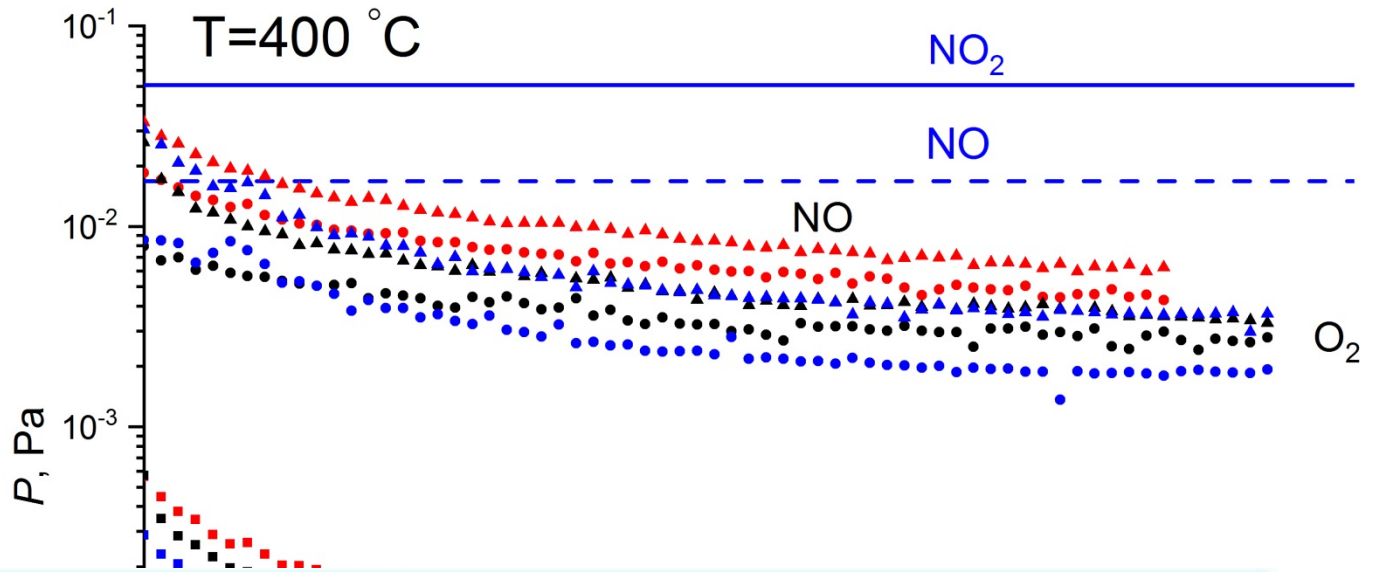
$Ca(NO_3)_2$: Step-wise TG

Vaporisation rate
0.02 mg/h



$Ca(NO_3)_2$: Vapour Pressure



PHASE: gas_ideal	EQUIL AMOUNT mol	MOLE FRACTION	FUGACITY Pa
O2	2.5000E+00	7.1429E-01	7.2375E+04
N2	1.0000E+00	2.8571E-01	2.8950E+04
NO2	1.7523E-06	5.0065E-07	5.0729E-02
NO	5.8417E-07	1.6691E-07	1.6912E-02
N2O	5.0094E-11	1.4313E-11	1.4502E-06
O	1.8787E-16	5.3677E-17	5.4388E-12
CaO	4.3736E-43	1.2496E-43	1.2662E-38
TOTAL:	3.5000E+00	1.0000E+00	1.0000E+00

KNO_3: Vapour Pressure

Equilib - Results 400 C (page 18/28)

Output Edit Show Pages

T(C) P(Pa) Energy(J) Mass(mol) Vol(litre)

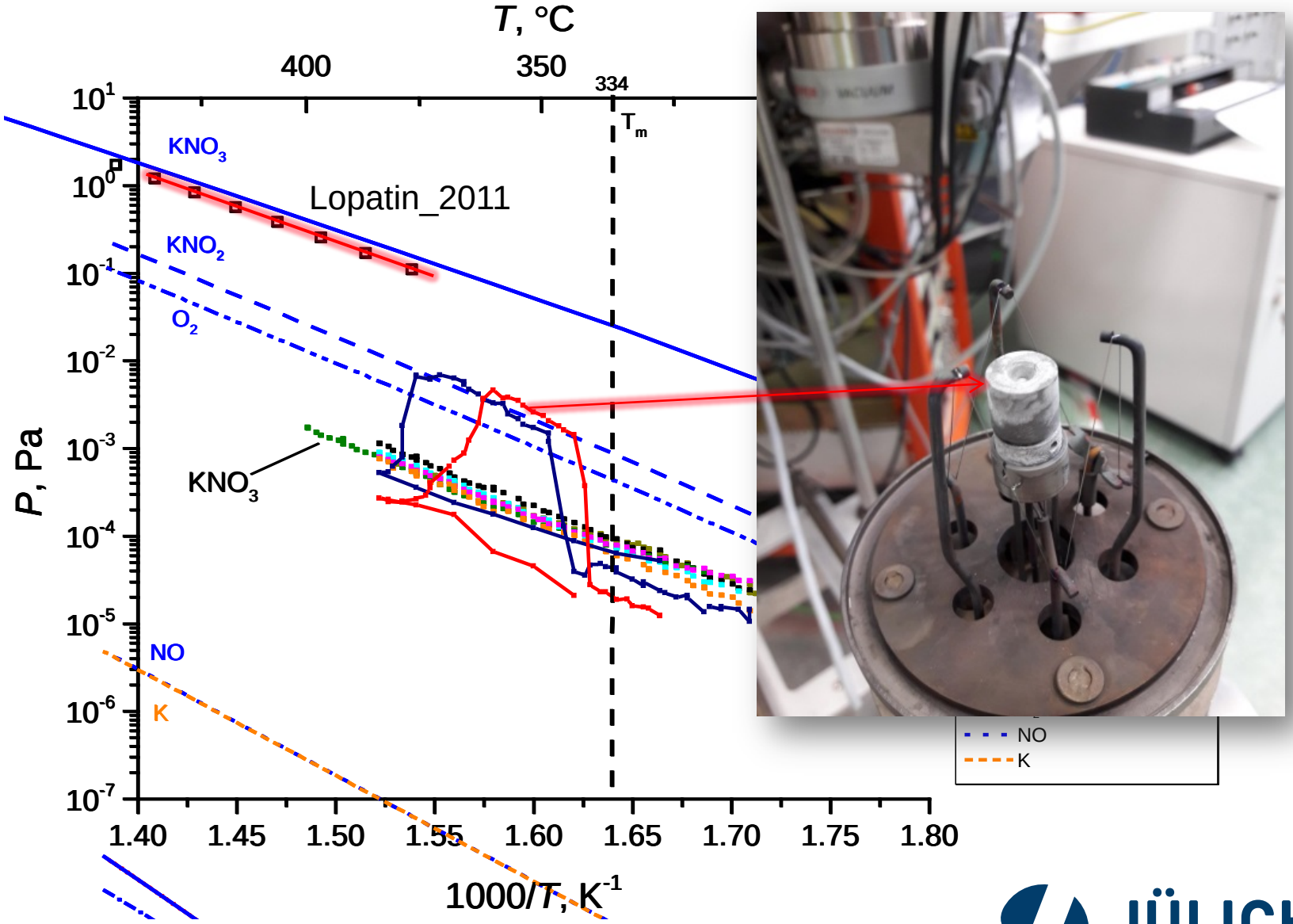
250 C | 260 C | 270 C | 280 C | 290 C | 300 C | 310 C | 320 C | 330 C | 335 C | 335 C | 340 C | 350 C | 360 C |
370 C | 380 C | 390 C | - 400 C - | 410 C | 420 C | 430 C | 440 C | 450 C | 460 C | 470 C |

```
                                                                    FactSage 7.2
T = 400 C
P = 1.0132E+05 Pa
V = 0 dm3

STREAM CONSTITUENTS            AMOUNT/mol
KNO3                           1.0000E+00

                              EQUIL AMOUNT  MOLE FRACTION     FUGACITY
PHASE: gas_ideal                  mol                          Pa
KNO3                           0.0000E+00     9.1266E-01     4.0141E-01
KNO2                           0.0000E+00     5.8228E-02     2.5610E-02
O2                             0.0000E+00     2.9115E-02     1.2805E-02
NO                             0.0000E+00     6.2954E-07     2.7689E-07
K                              0.0000E+00     6.2592E-07     2.7529E-07
K2O                            0.0000E+00     1.5720E-09     6.9142E-10
KO                             0.0000E+00     1.2728E-09     5.5981E-10
NO2                            0.0000E+00     7.9431E-10     3.4936E-10
N2O                            0.0000E+00     2.1013E-12     9.2419E-13
TOTAL:                         0.0000E+00     1.0000E+00     4.3407E-06
                                  mol
KNO3_liquid(liq)               1.0000E+00                    1.0000E+00
KNO3_solid(s2)                 0.0000E+00                    8.2592E-01
KNO3_solid(s)                  0.0000E+00                    4.5807E-01
KNO2_S2(s2)                    0.0000E+00                    2.7371E-01
KNO2_S1(s)                     0.0000E+00                    2.3496E-01
KNO2_L1(liq)                   0.0000E+00                    2.3351E-01
*******************************************************************
      Cp            H             S             G             V
    J.K-1           J           J.K-1           J            dm3
*******************************************************************
 1.42700E+02  -4.32604E+05   2.61184E+02  -6.08420E+05   0.00000E+00

                              Cp            H             S             G
                            J.K-1           J           J.K-1           J
KNO3_liquid(liq)         1.42700E+02 -4.32604E+05  2.61184E+02 -6.08420E+05
```

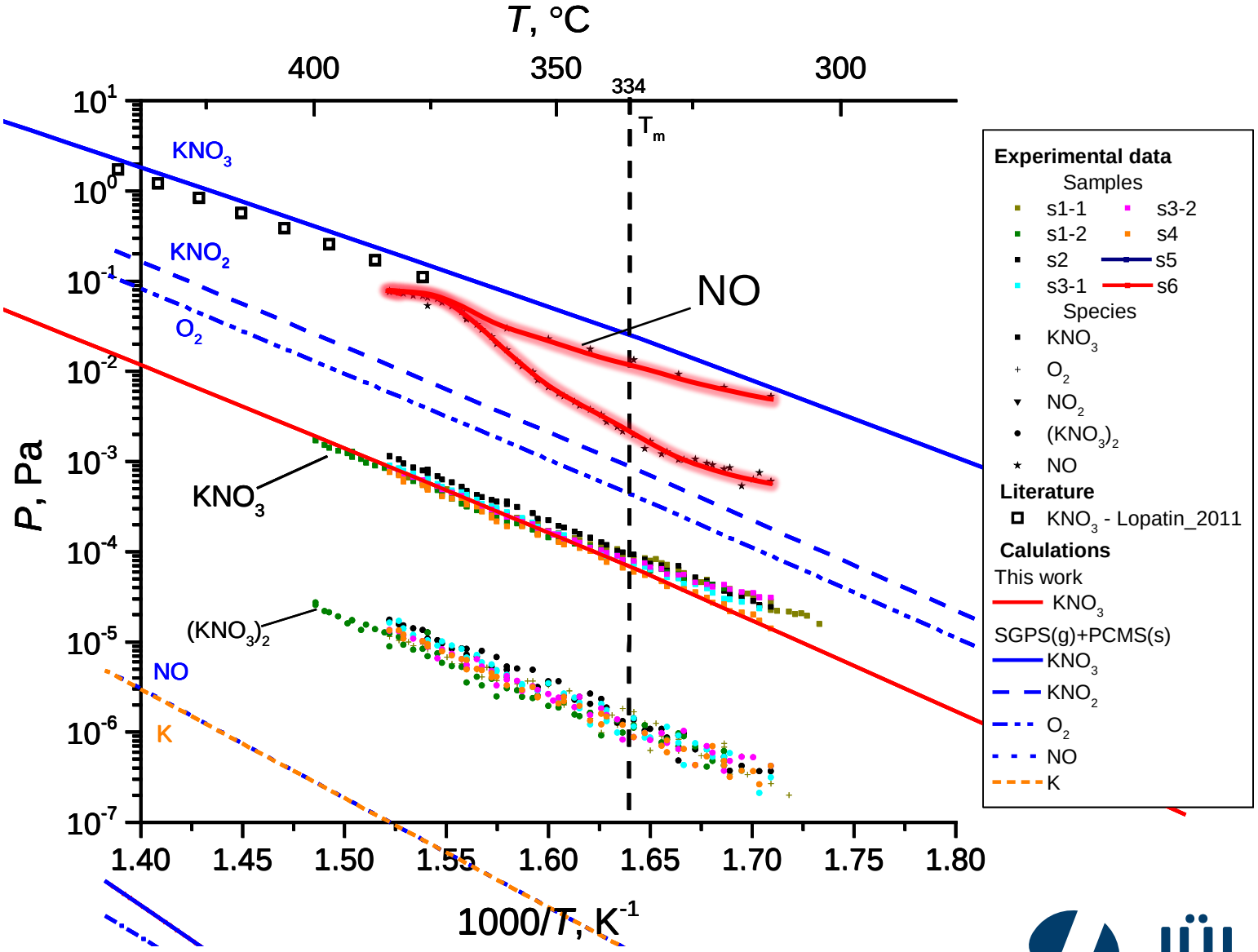
Gas phase

Solid phase

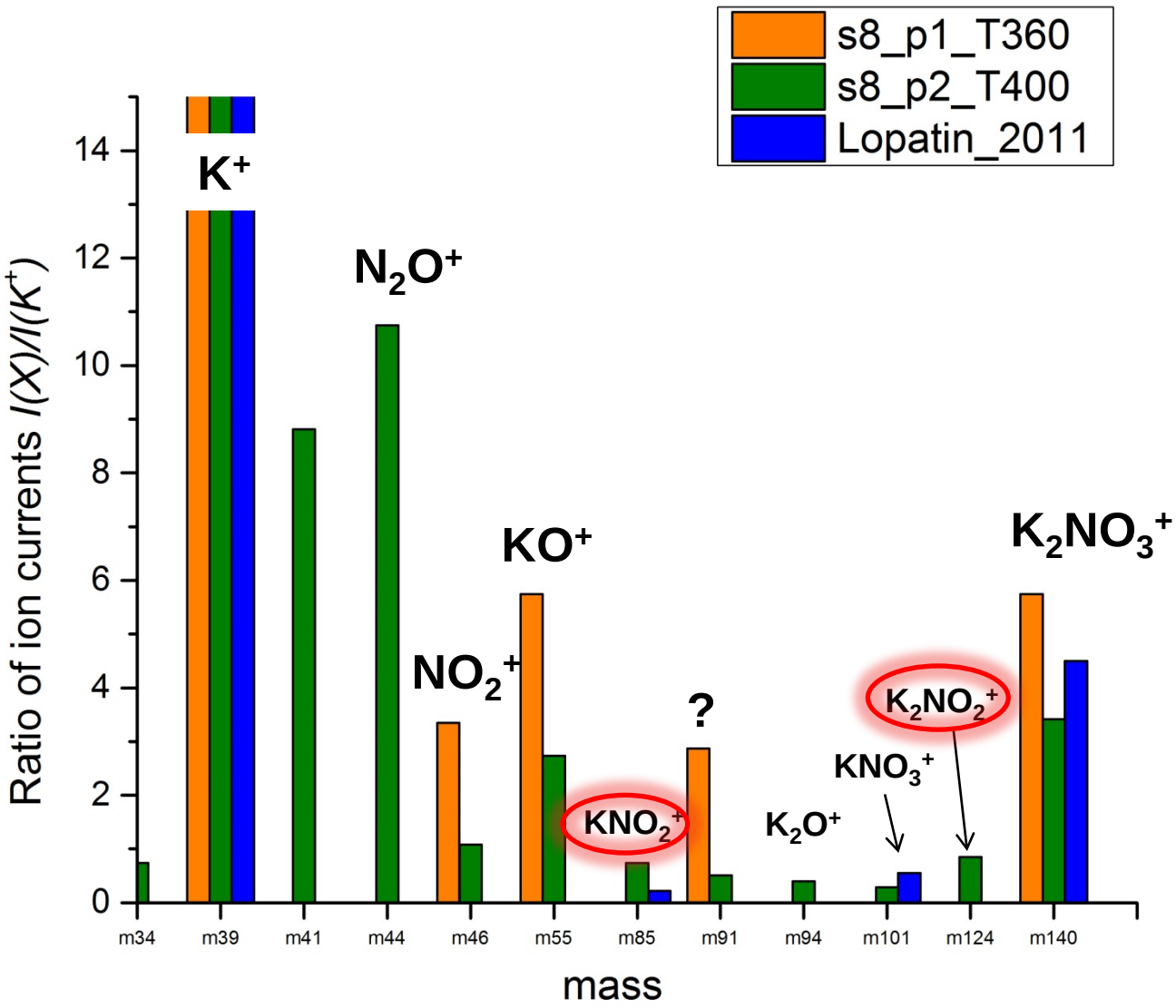
KNO_3: Vapour Pressure



KNO_3: Vapour Pressure

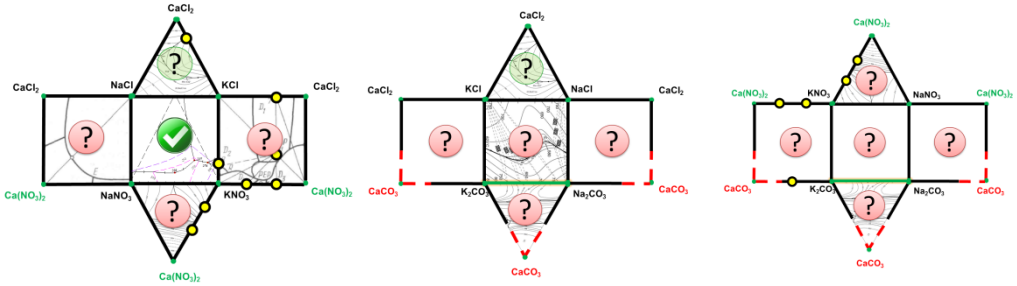


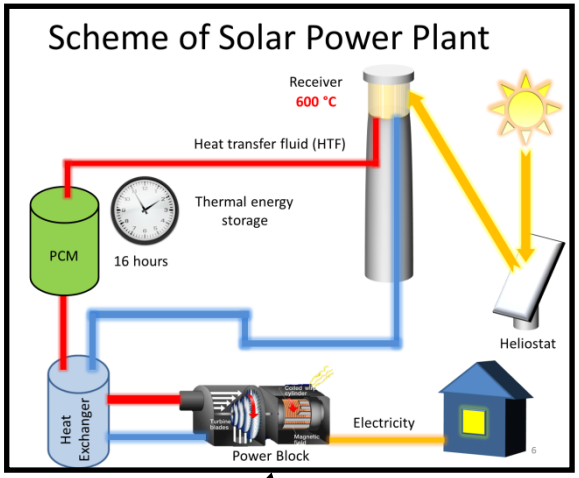
KNO_3: Mass Spectrum



Conclusions

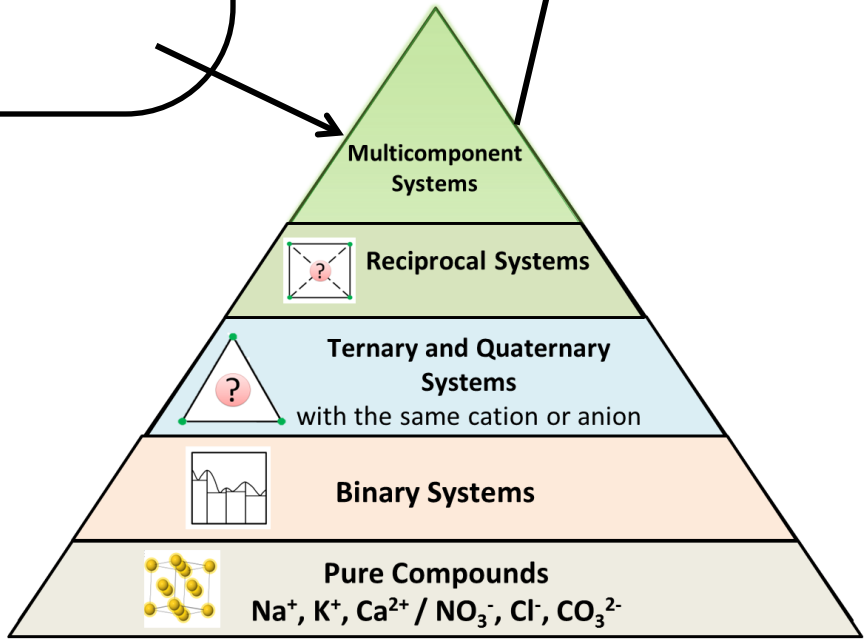
Thermodynamic Database





Main requirements

- Energy density
- Thermal conductivity
- Thermal stability
- Low Corrosion
- Low price



Jülich Solar Tower in NRW, Germany

Thank you for your kind attention!

JÜLICH Forschungszentrum