Calphad modeling - introduction

Daniel Lindberg

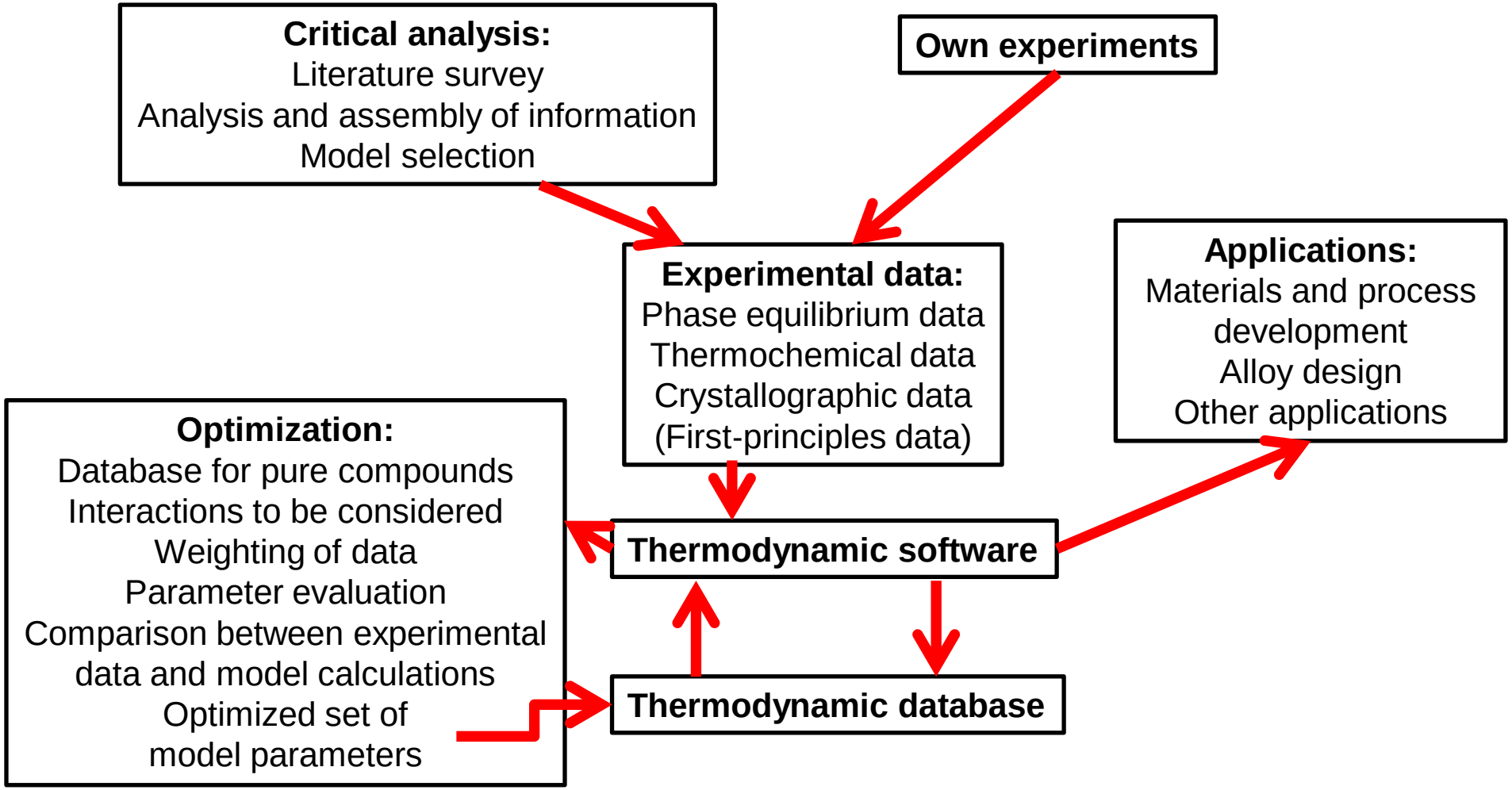
Learning outcomes

- Familiarize yourself with Calphad method
- Understand the common tangent method
- Recognize phase diagrams of different order

Introduction

- Calphad method (**Cal**culations of **Pha**se **D**iagrams)
  - “The “Calphad method” means the use of all available experimental and theoretical data to assess the parameters of the Gibbs energy models selected for each phase” (Lukas, Fries, Sundman:Computational Thermodynamics: The Calphad Method)
  - A technique to evaluate and optimize thermodynamic data and phase equilibrium data and develop consistent thermodynamic databases for multicomponent, multiphase equilibrium calculations including non-ideal solution phases
  - Unary→Binary→Ternary→Higher order systems

Procedure for the Calphad method



Adopted from lic. thesis of I. Vaajamo

Experimental input

Thermodynamic data

Enthalpy data for pure compounds

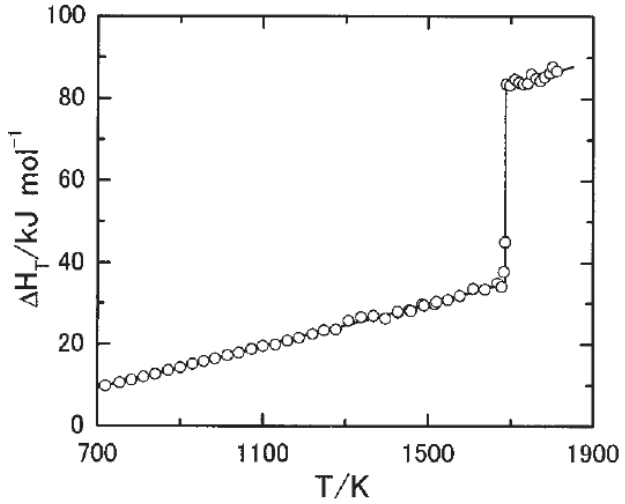
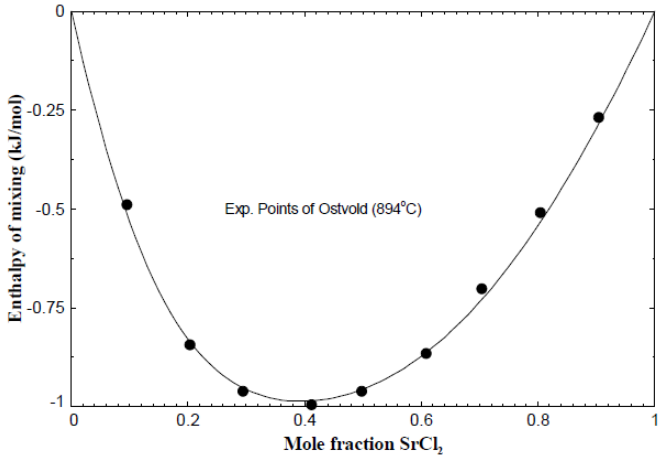
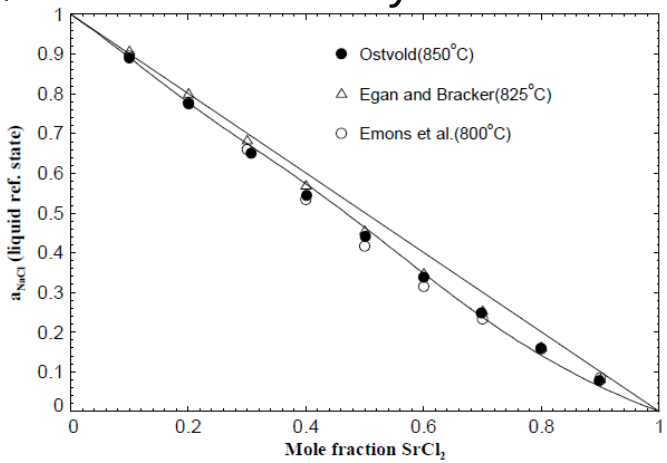


Fig. 4 Heat content of silicon

Enthalpy of mixing in the liquid state

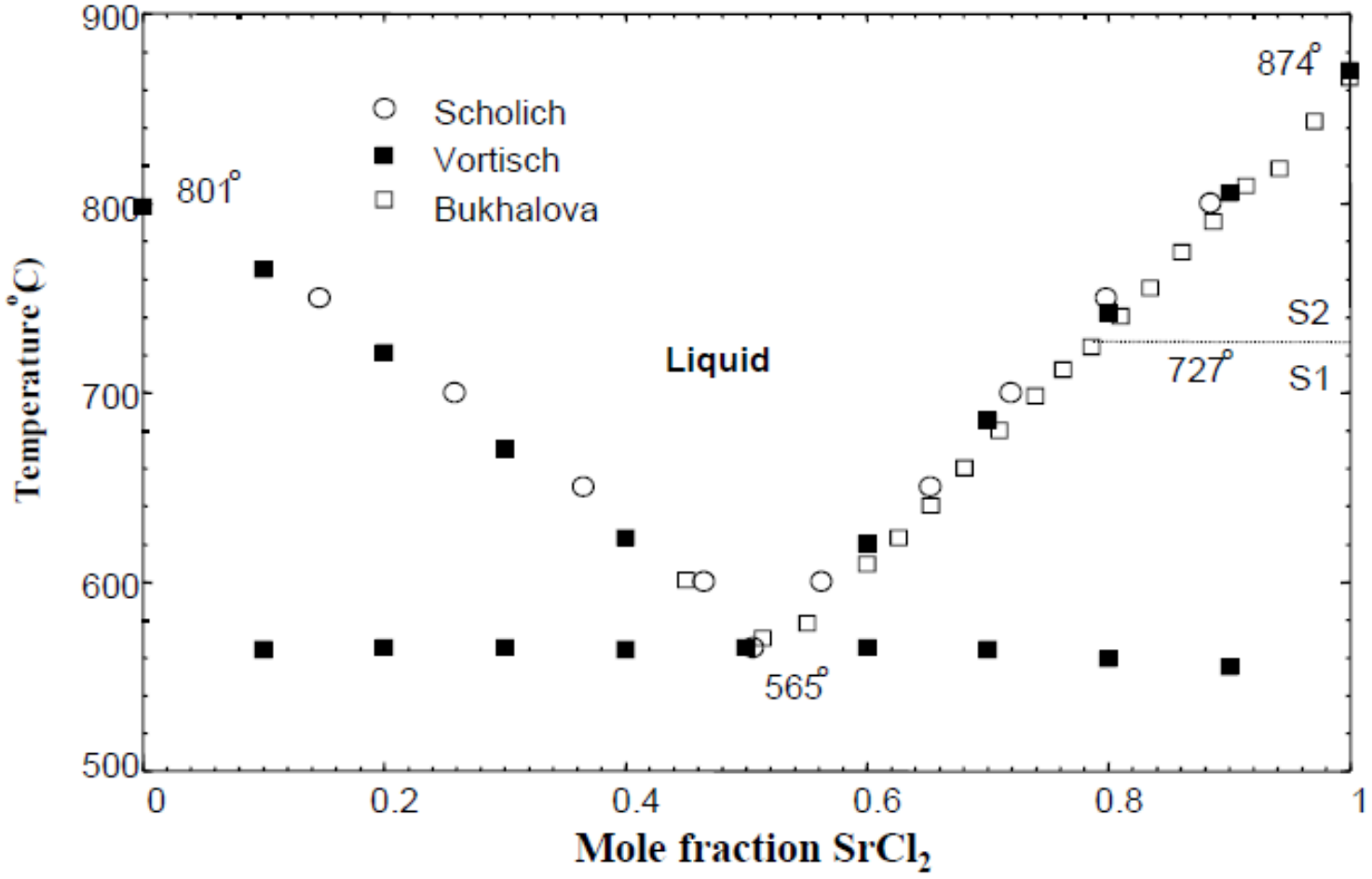


Activity data



Experimental input

Phase equilibrium data

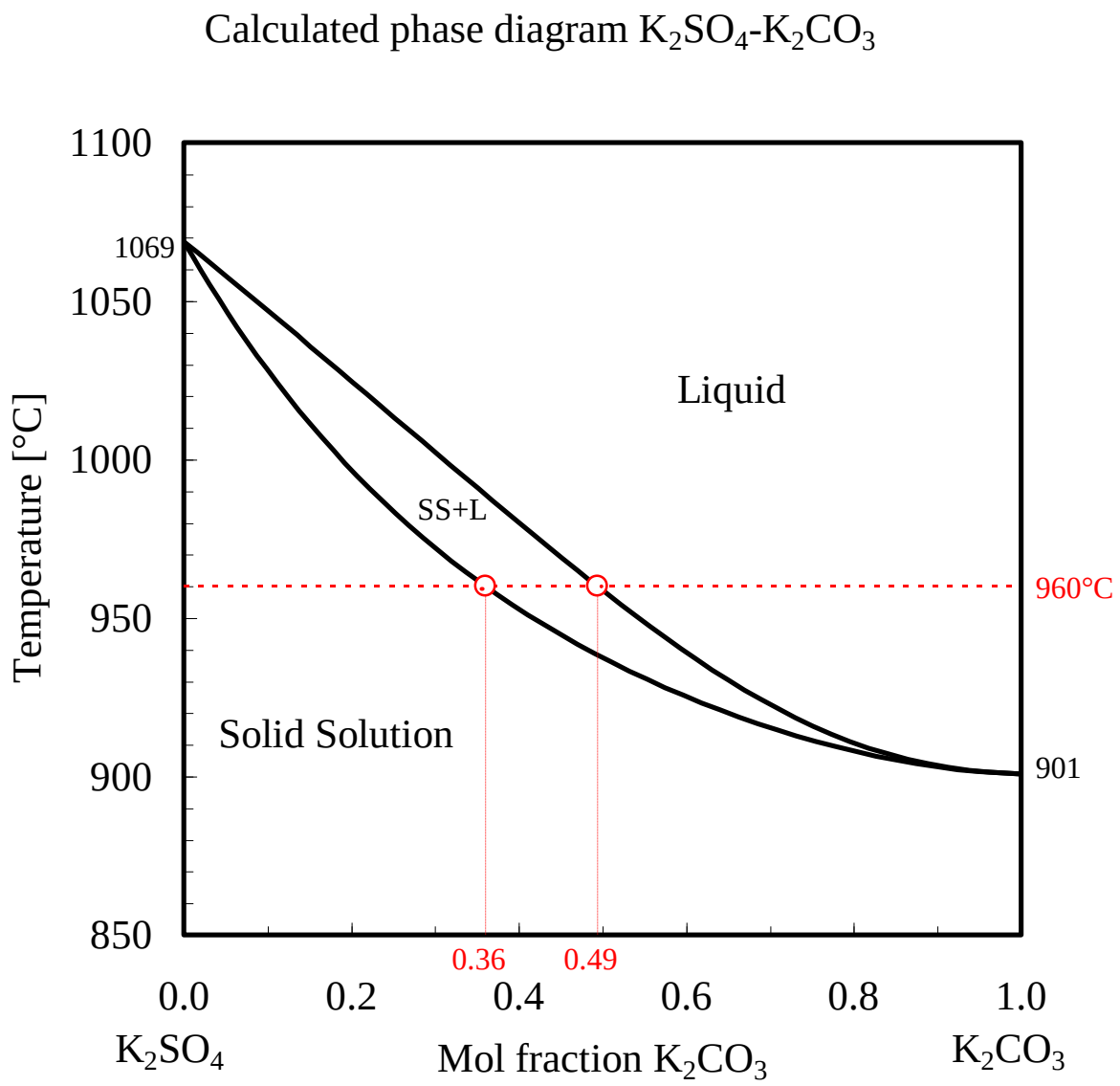


Phase diagrams and thermodynamic properties

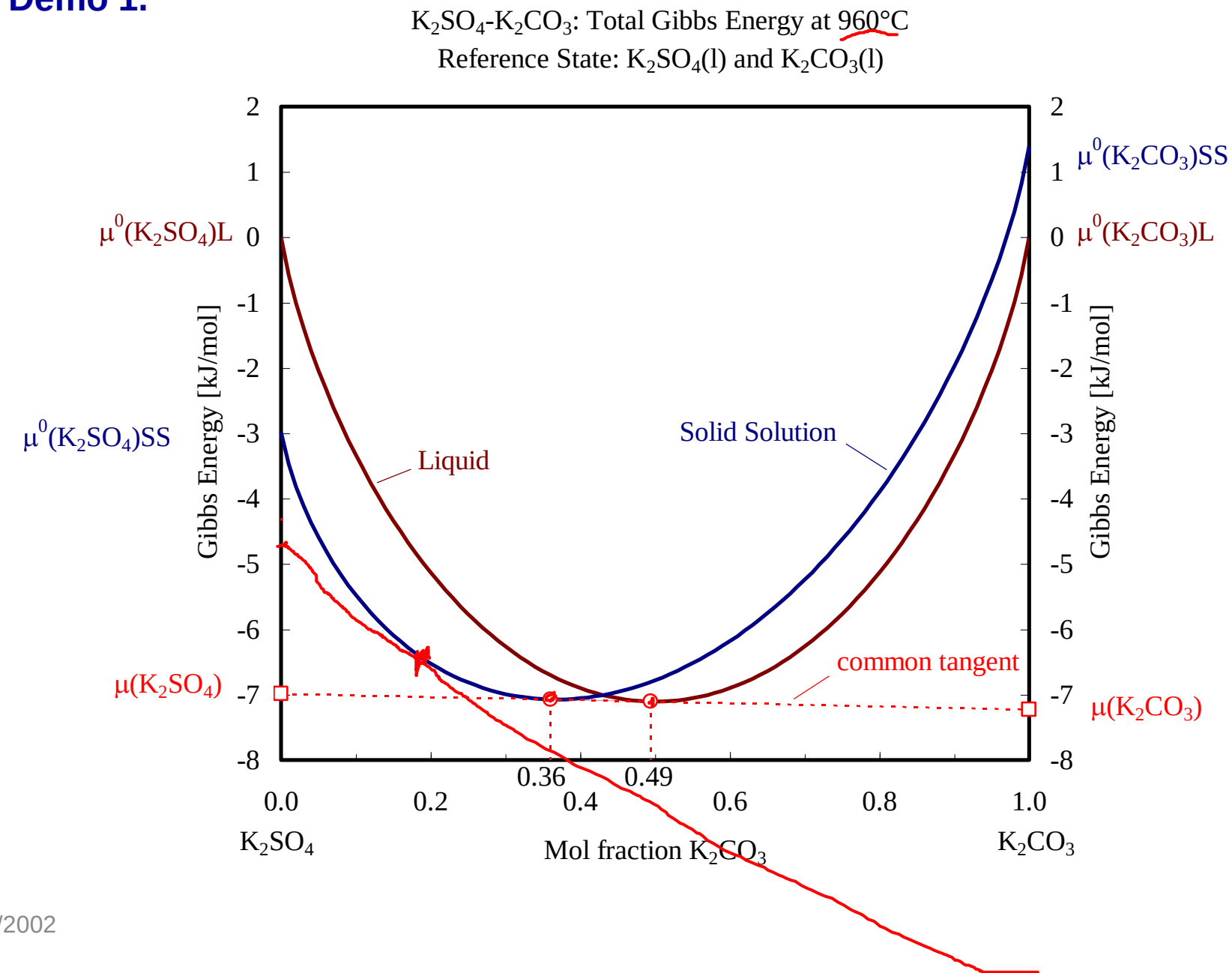
The common tangent method is demonstrated for the following binary cases:

1. **Solid solution in whole composition range**
   K_2SO_4-K_2CO_3
2. **Solid solution – azeotropic system**
   KCl-NaCl
3. **Solid solution – miscibility gap**
   KCl-NaCl

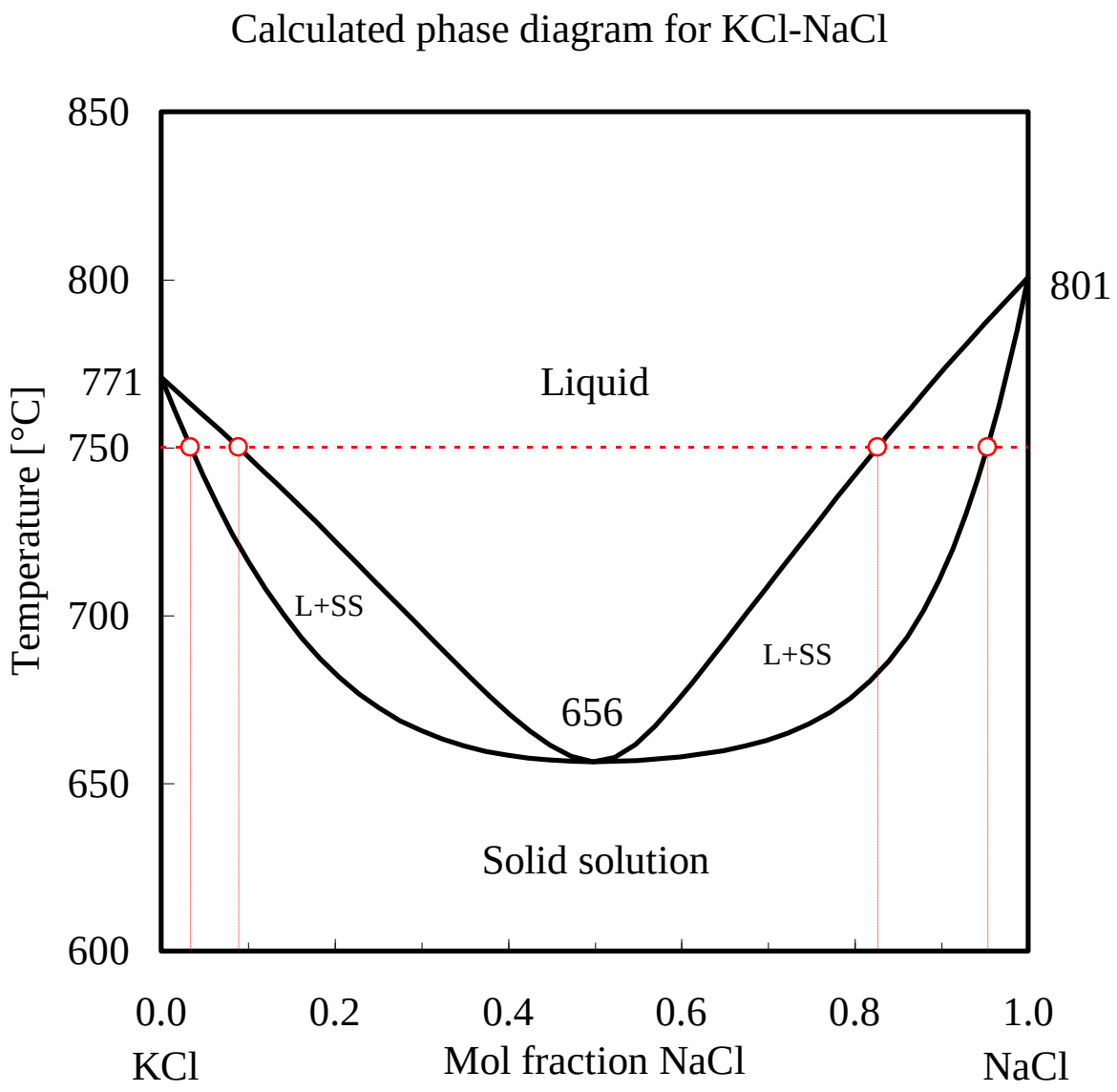
Demo 1.


Calculated phase diagram K_2SO_4-K_2CO_3
1100
1069
1050
1000
950
900
850
Temperature [°C]
Liquid
SS+L
Solid Solution
960°C
901
0.36
0.49
0.0
0.2
0.4
0.6
0.8
1.0
K_2SO_4
Mol fraction K_2CO_3
K_2CO_3

Demo 1.

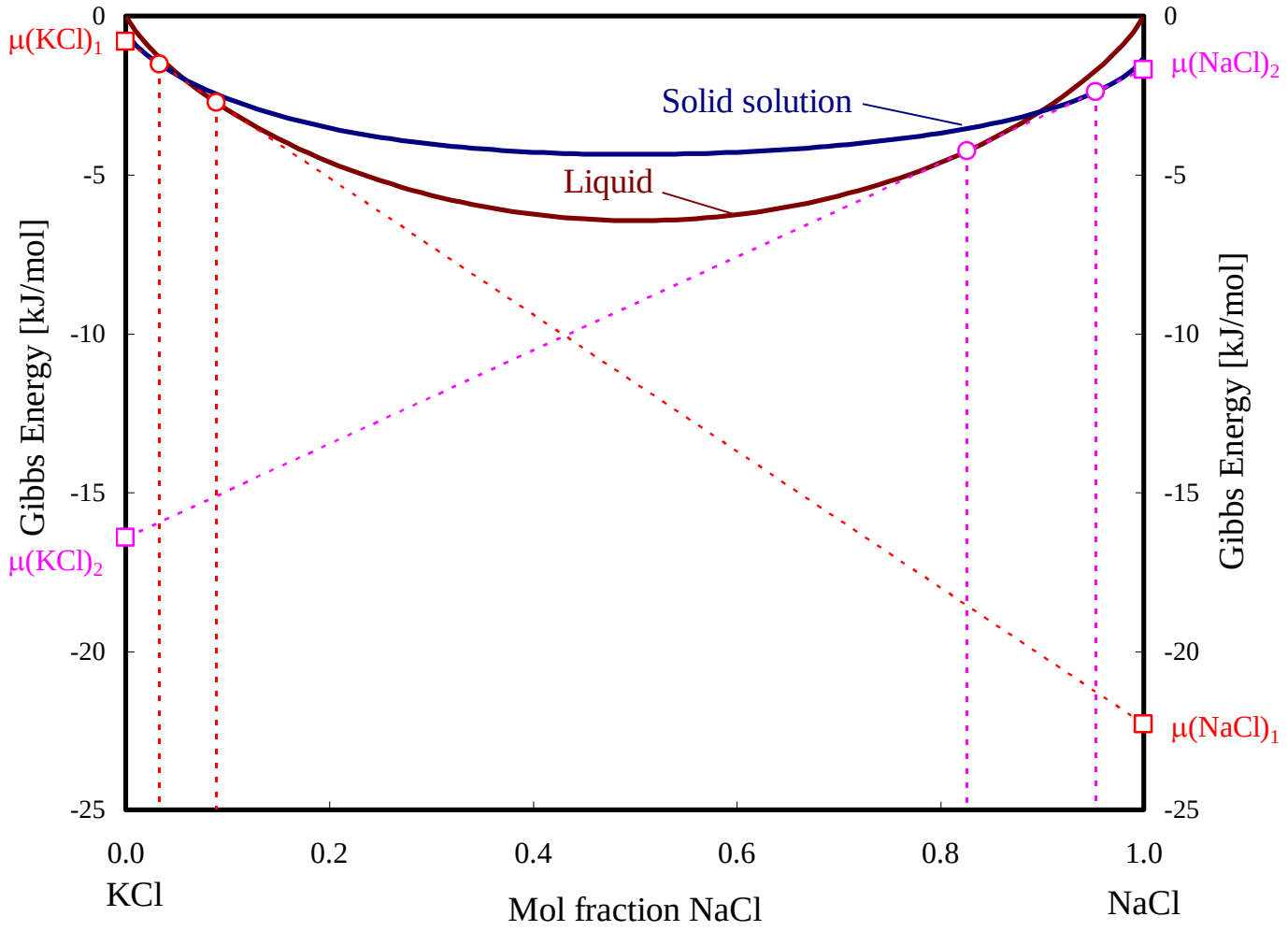

K2SO4-K2CO3: Total Gibbs Energy at 960°C
Reference State: K2SO4(l) and K2CO3(l)
μ0(K2SO4)L
μ0(K2SO4)SS
μ0(K2CO3)SS
μ0(K2CO3)L
Liquid
Solid Solution
common tangent
μ(K2SO4)
μ(K2CO3)
Gibbs Energy [kJ/mol]
Gibbs Energy [kJ/mol]
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
0.0
0.2
0.36
0.4
0.49
0.6
0.8
1.0
K2SO4
K2CO3
Mol fraction K2CO3

Demo 2.

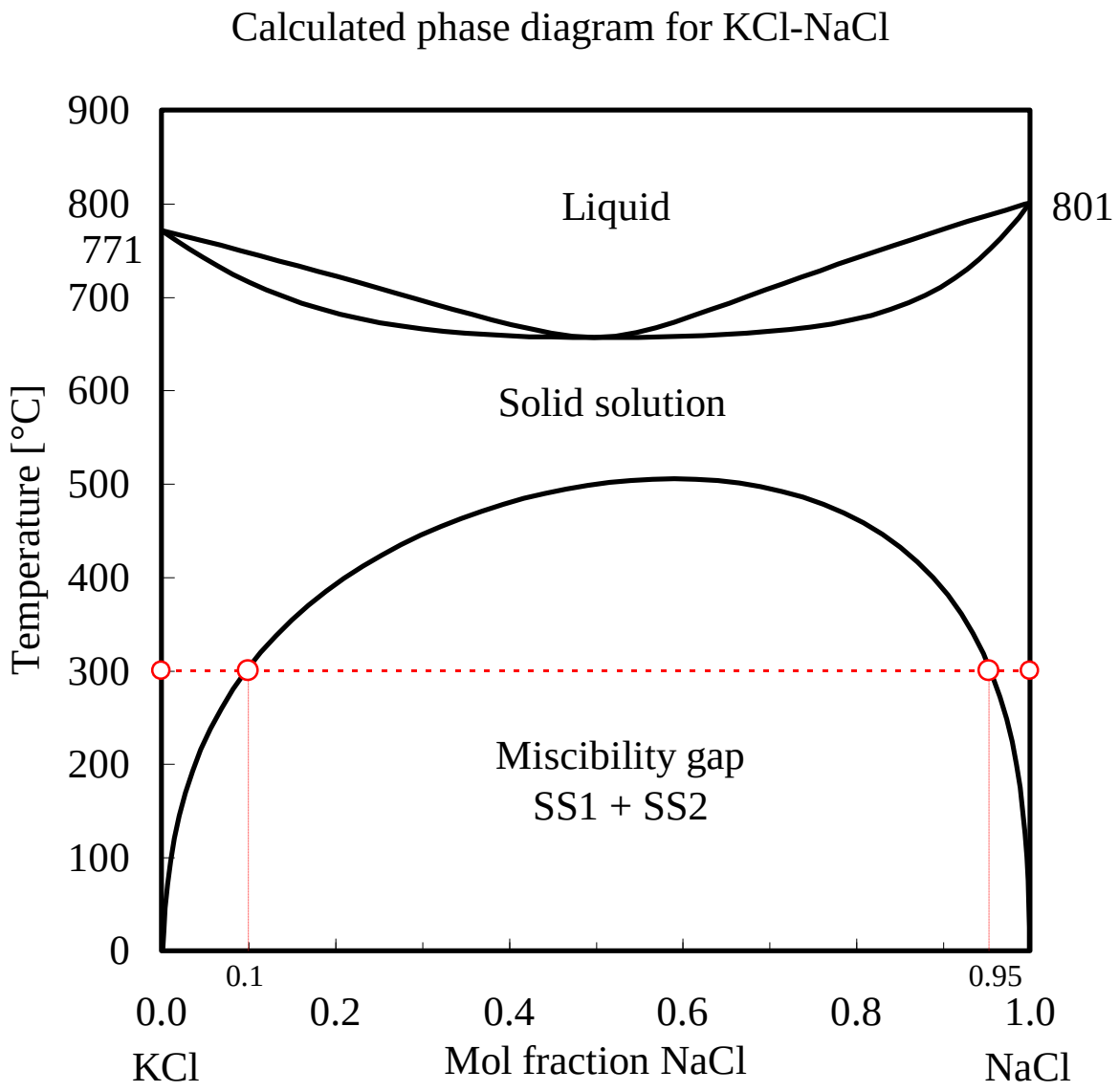

Calculated phase diagram for KCl-NaCl
850
800
771
750
700
650
600
Temperature [°C]
801
Liquid
L+SS
L+SS
656
Solid solution
0.0
0.2
0.4
0.6
0.8
1.0
KCl
Mol fraction NaCl
NaCl

Demo 2.

KCl-NaCl: Total Gibbs Energy at 750°C
Reference State: KCl(l) and NaCl(l)

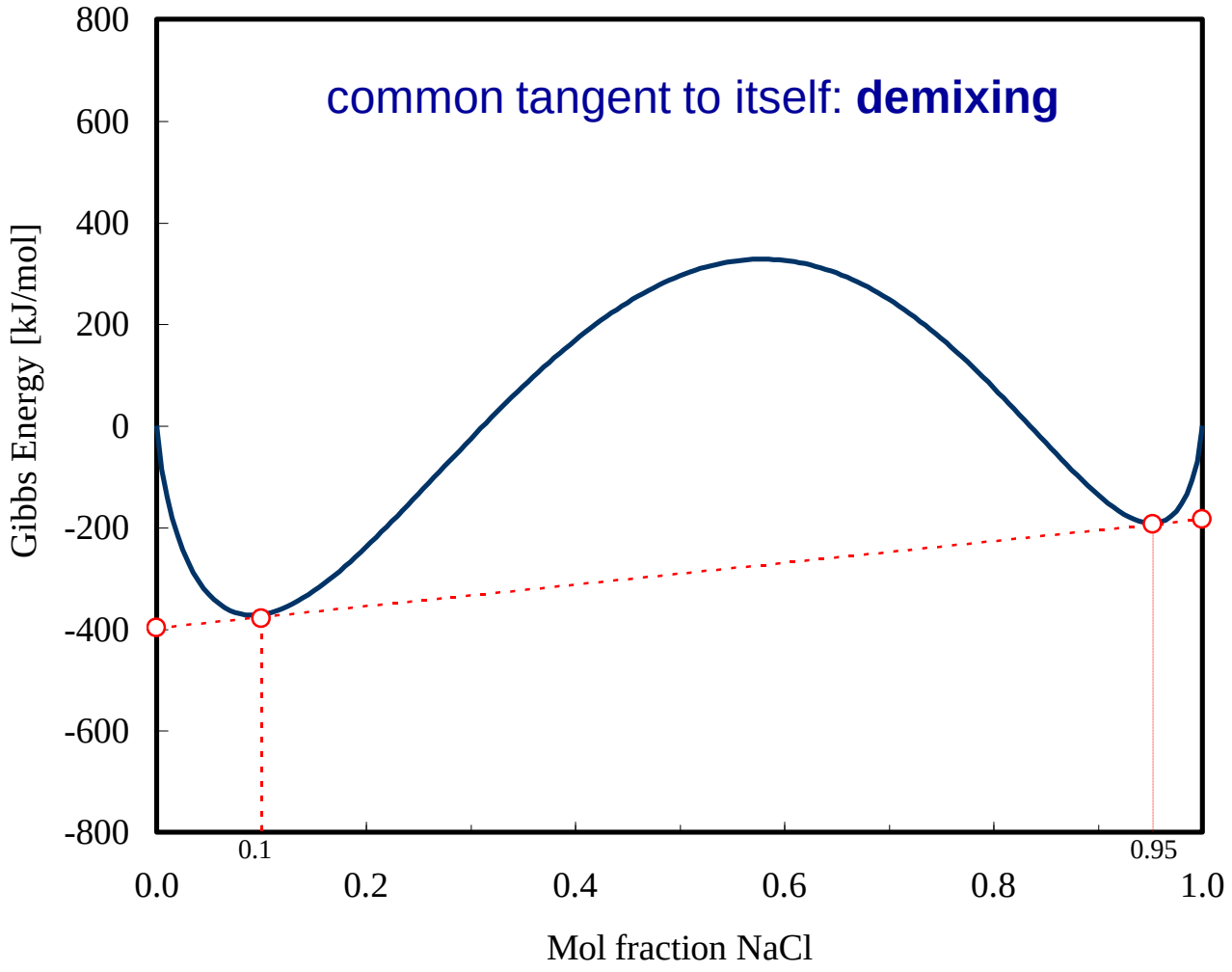


Demo 3.


Calculated phase diagram for KCl-NaCl
900
800
771
700
600
500
400
300
200
100
0
Temperature [°C]
Liquid
801
Solid solution
Miscibility gap
SS1 + SS2
0.1
0.95
0.0
0.2
0.4
0.6
0.8
1.0
KCl
Mol fraction NaCl
NaCl

Demo 3.

KCl-NaCl solid solution: Total Gibbs Energy at 300°C
Reference State: KCl(ss) and NaCl(ss)



Other input

- Crystallographic data for sublattice configurations and site distribution in solid solutions
- Ab-initio (first-principles) data for phase stabilities
- Other estimations for thermodynamic data of phases

Choice of solution models

- Ideal solution

$$G_m = \sum_i x_i G_i^o + RT \sum_i x_i \ln x_i$$

- Regular solution model

$$G_m = \sum_i x_i G_i^o + RT \sum_i x_i \ln x_i + \sum_i \sum_{j>i} x_i x_j \Omega_{ij}$$

Choice of solution models

- Models that consider the physical properties of the solution phase are often more suitable than purely mathematical models
  - Easier to fit realistic model parameters
  - Easier to expand when new components are added to the database
- Ionic models for ionic phases
- Sublattice models for phases with clearly defined sublattices
- Associate or quasichemical models for solutions with shortrange ordering

Calphad method

- An evaluated thermodynamic database takes into account all experimental data:
  - Phase equilibrium
  - Calorimetric data
  - Activity data (EMF)
  - Crystal structure, crystallographic data

- A good thermodynamic model/database for solids and liquid should:

  - predict the phase equilibrium of binary and higher order systems within the uncertainties of experimental investigations of these systems

  - give good predictions of the phase equilibrium for conditions where no experimental data exist

Uncertainties when comparing experiments and calculations

Experimental melting/solidification data are not always related to equilibrium melting

- Supercooling of liquids ($T_{experiment} < T_{equilibrium}$)
- Equilibration of solid solutions
  - Melting related to local heterogenities
- Volatilization and chemical reactions

Estimating thermodynamic properties

Daniel Lindberg

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Thermochimica Acta 314 (1998) 1–21

thermochimica acta

Estimation of thermodynamic data for metallurgical applications

P.J. Spencer*

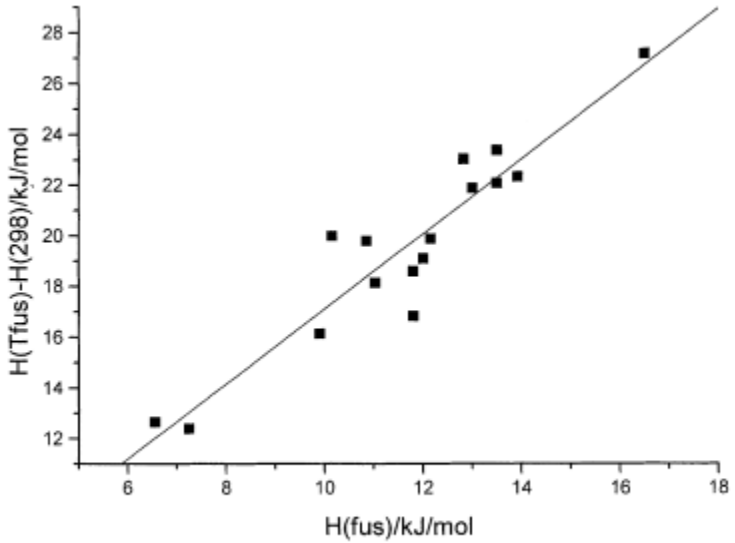


Fig. 3. Enthalpy of fusion vs. enthalpy at the melting point for alkali metal halides.

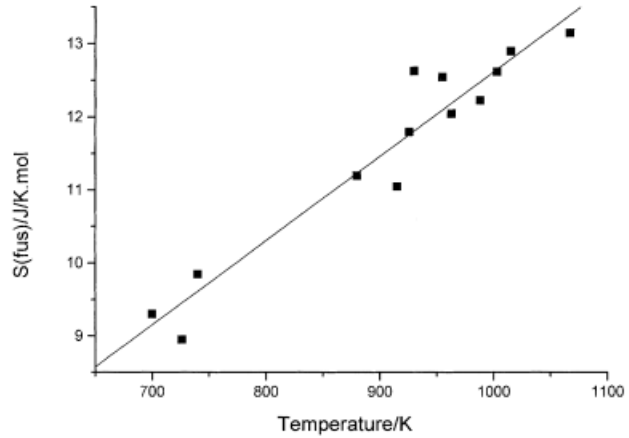


Fig. 1. Entropy of fusion vs. temperature of fusion for alkali metal halides.

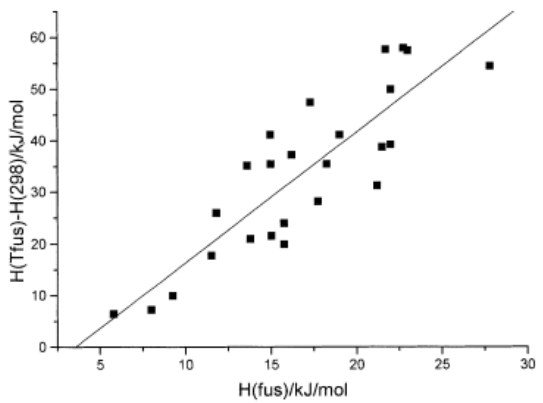
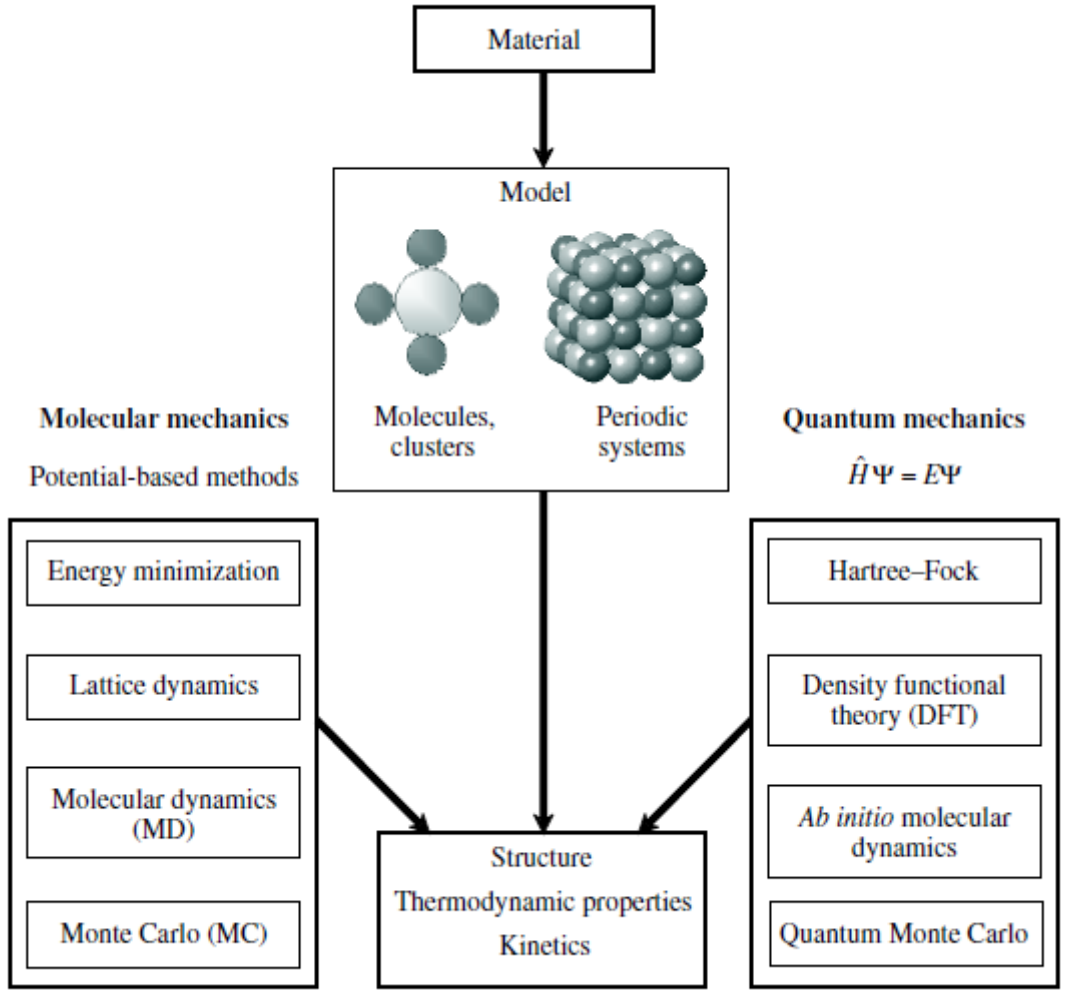


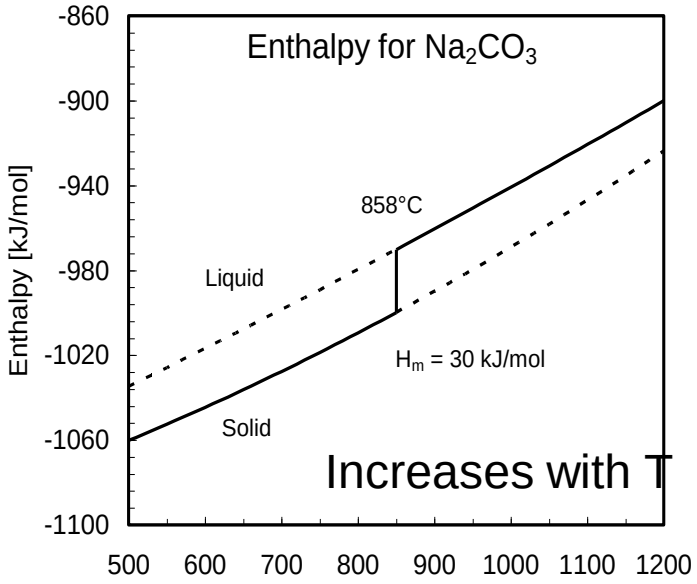
Fig. 4. Enthalpy of fusion vs. enthalpy at the melting point for a selection of inorganic compounds with different structures.

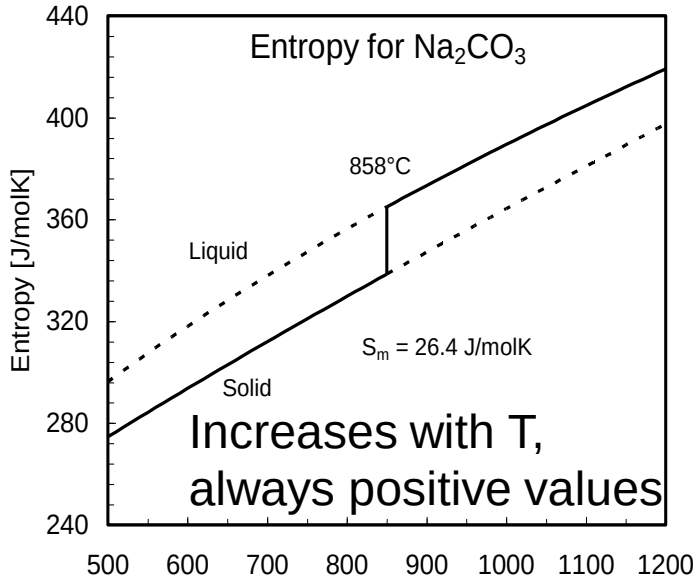
$$\Delta S_{\mathrm{fus}} = S(298\ \mathrm{K}) + A[0.023a(\log T_{\mathrm{m}} - 2.4742) + 10^{-3}b(T_{\mathrm{m}} - 298) + 0.005c(1.1261 - 10^{5}/T_{\mathrm{m}}^{2})] \qquad (9)$$

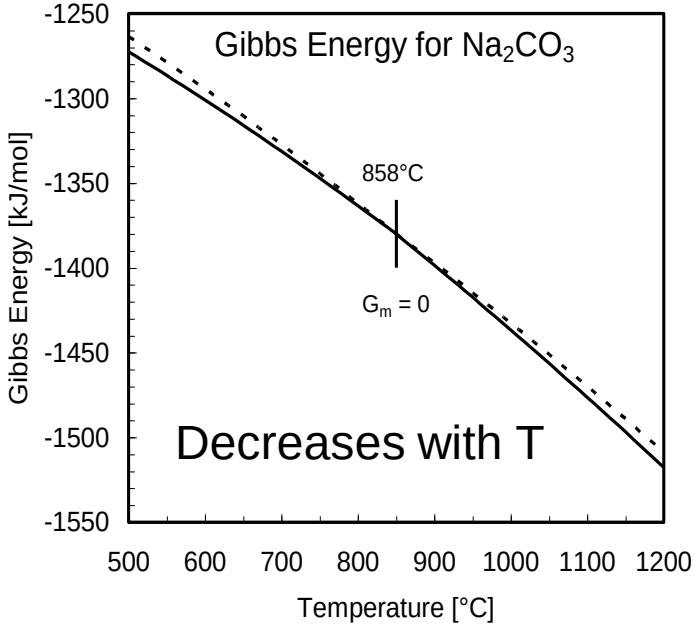

Material
Model
Molecules, clusters
Periodic systems
Molecular mechanics
Potential-based methods
Quantum mechanics
$\hat{H}\Psi = E\Psi$
Energy minimization
Lattice dynamics
Molecular dynamics (MD)
Monte Carlo (MC)
Structure
Thermodynamic properties
Kinetics
Hartree–Fock
Density functional theory (DFT)
Ab initio molecular dynamics
Quantum Monte Carlo

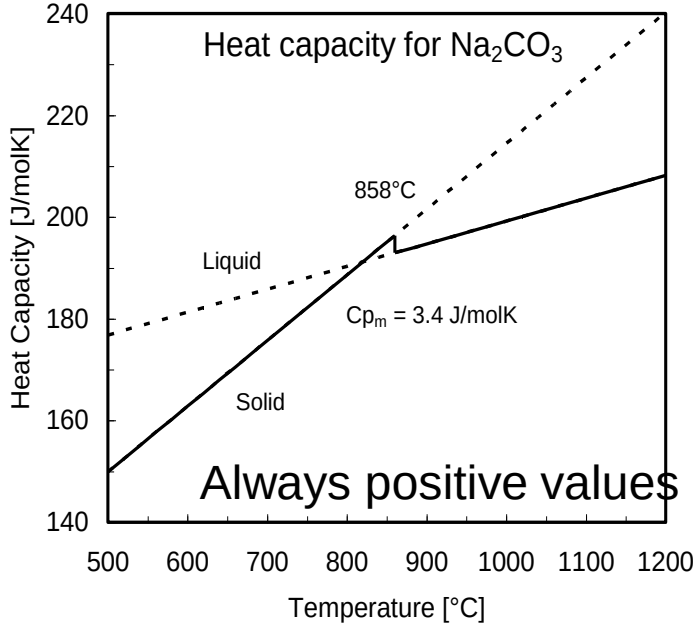
Unary data

Thermodynamic quantities of compounds



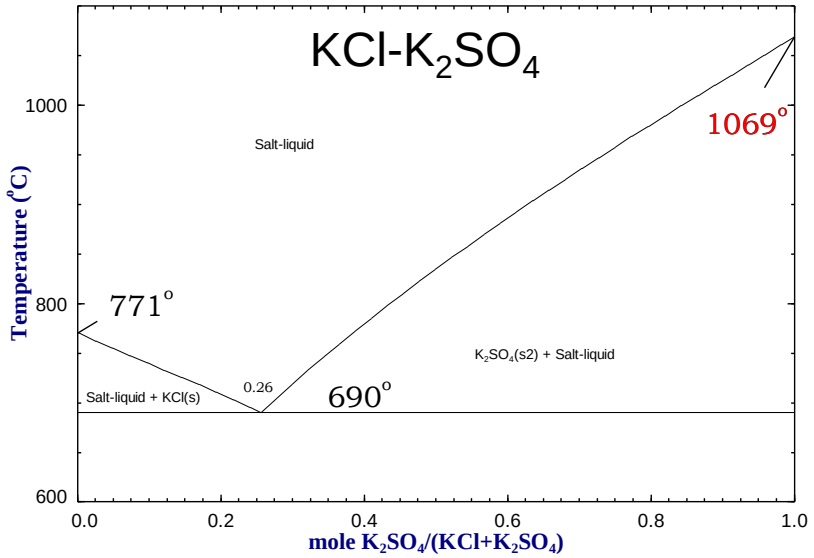


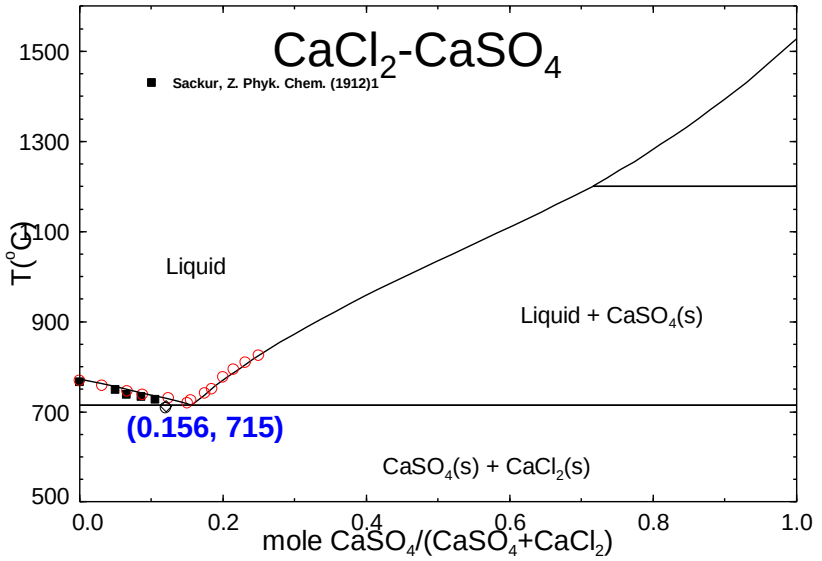


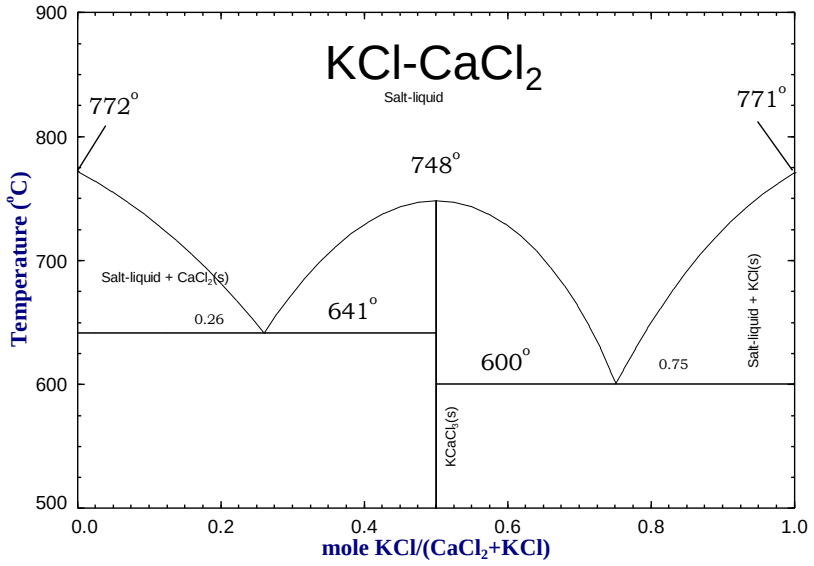


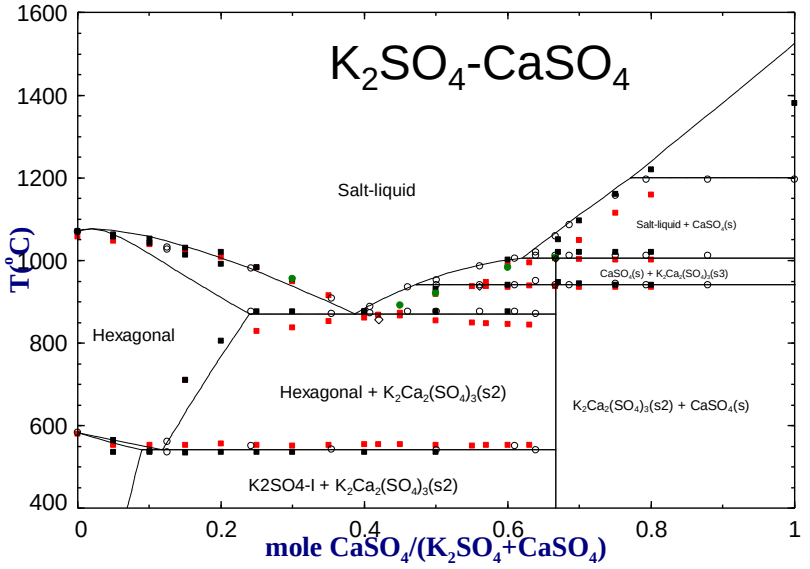
Binary data

$CaCl_2$-$CaSO_4$-KCl-K_2SO_4



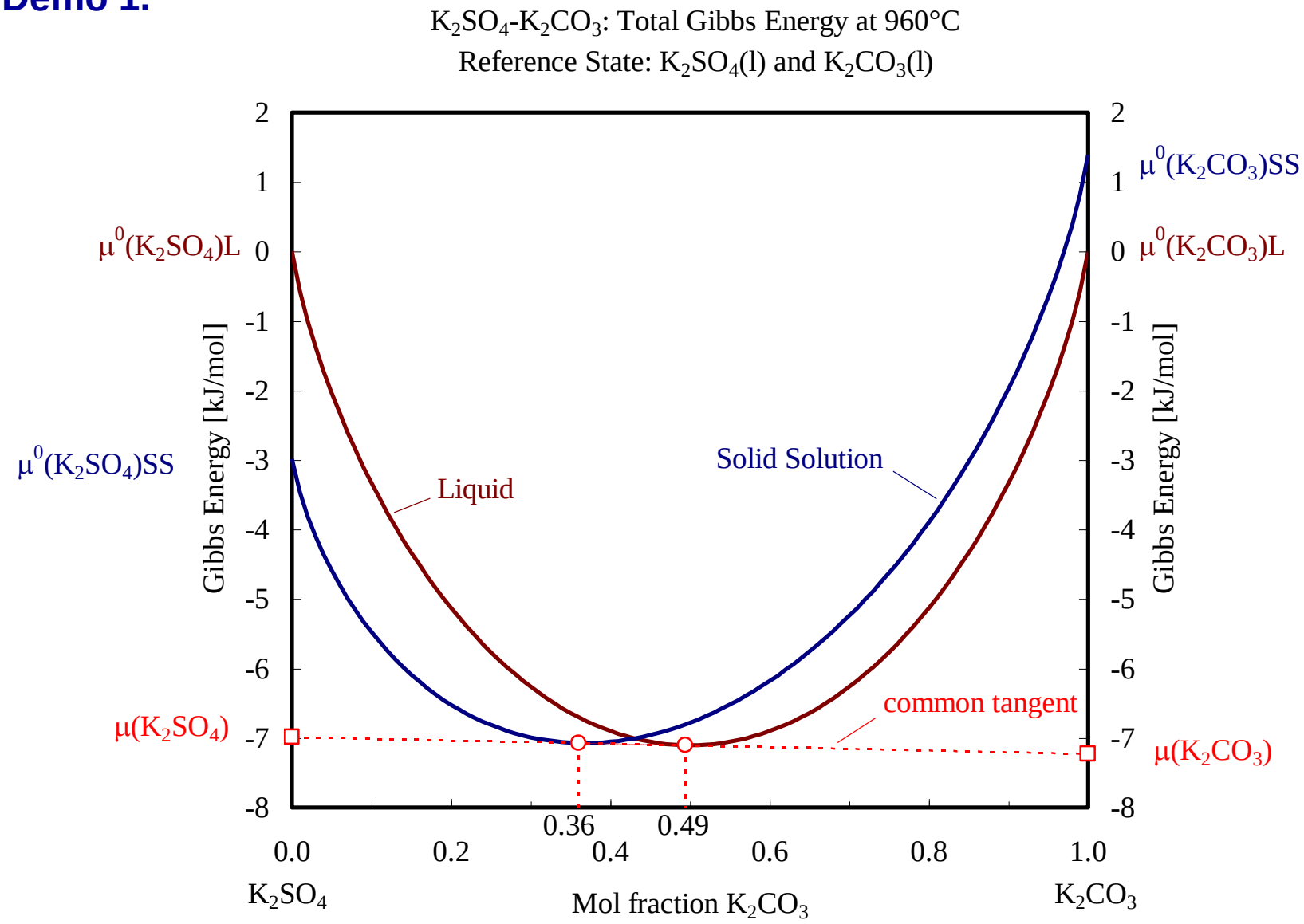






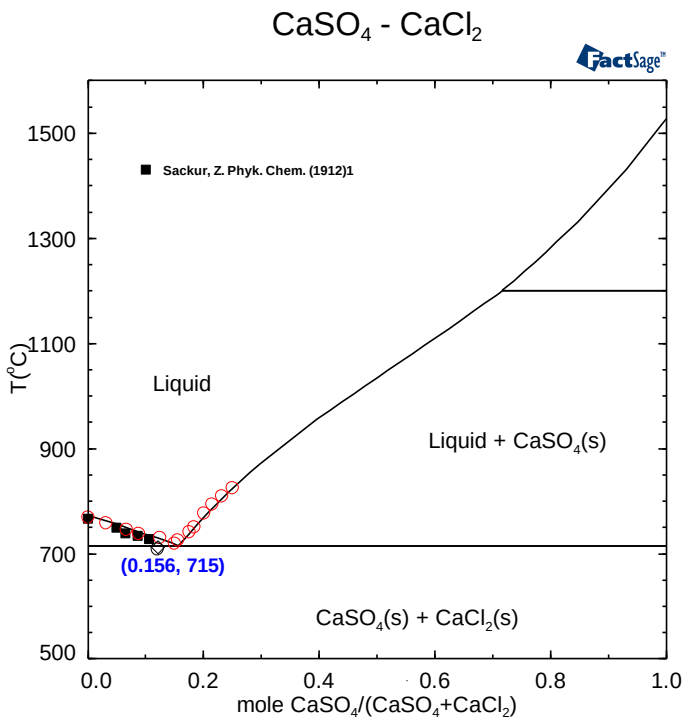
Gibbs energies of solutions

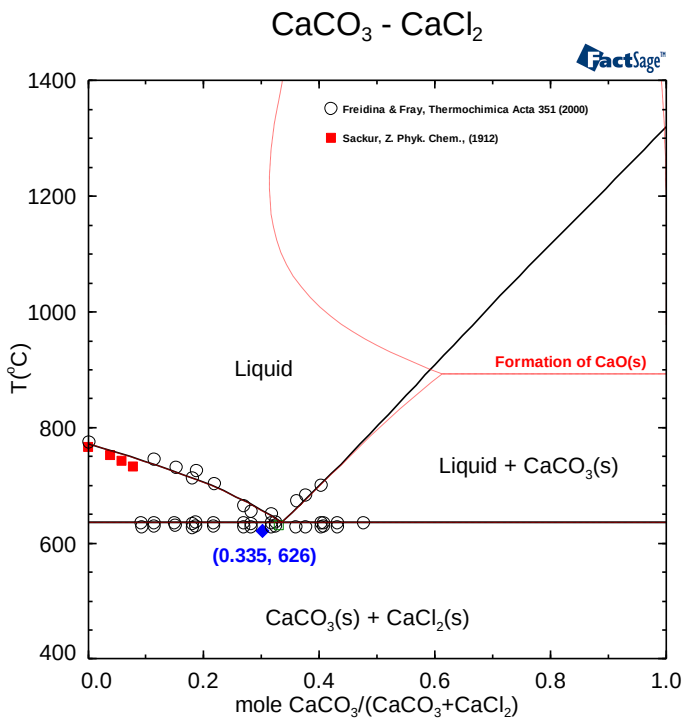
Demo 1.

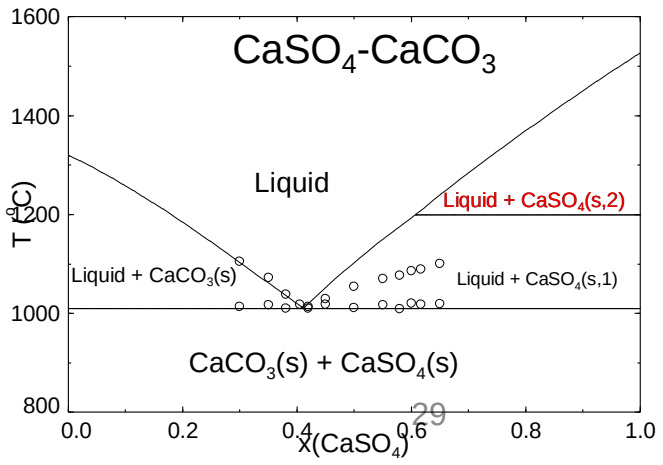


Ternary data

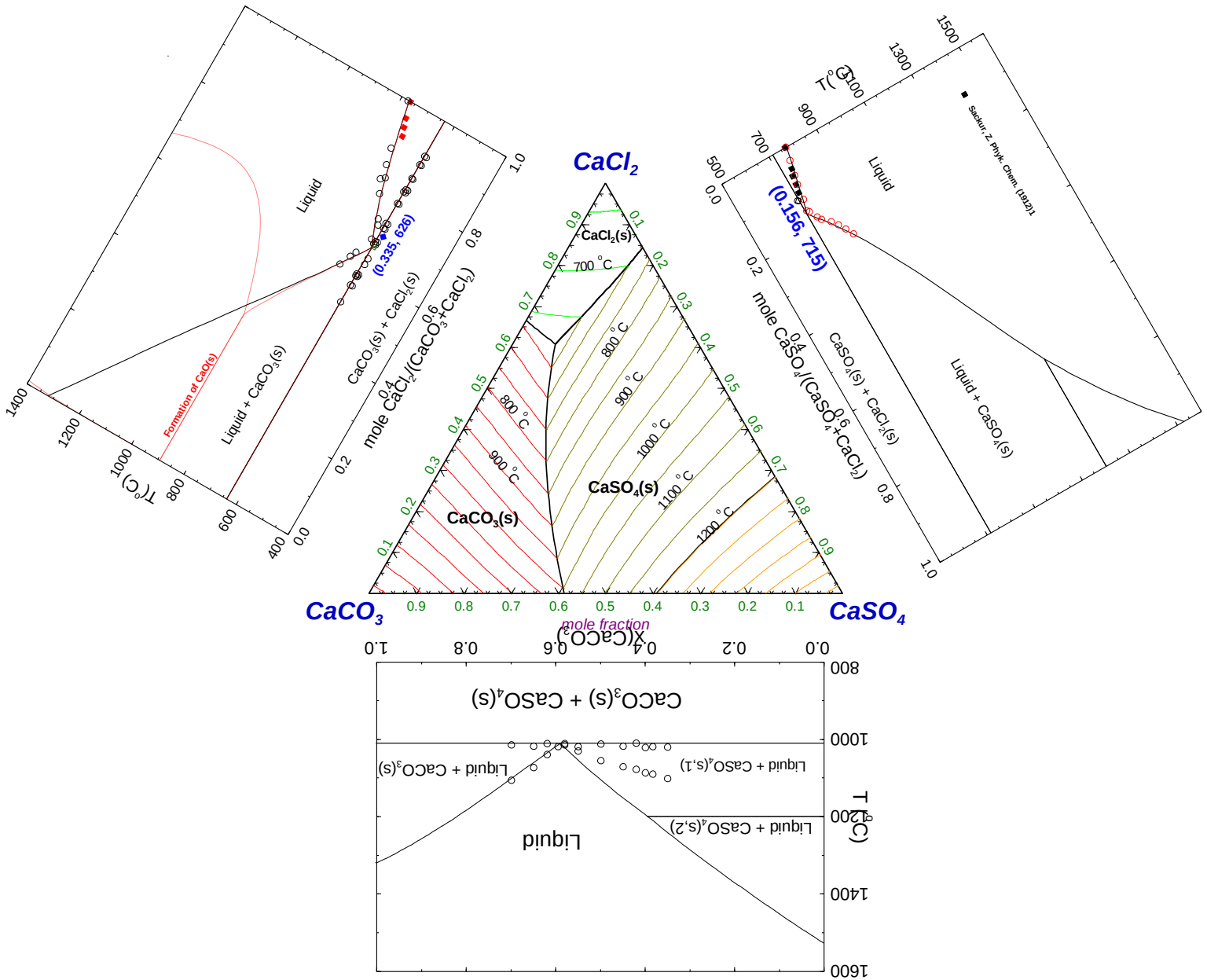
$CaCl_2$-$CaCO_3$-$CaSO_4$



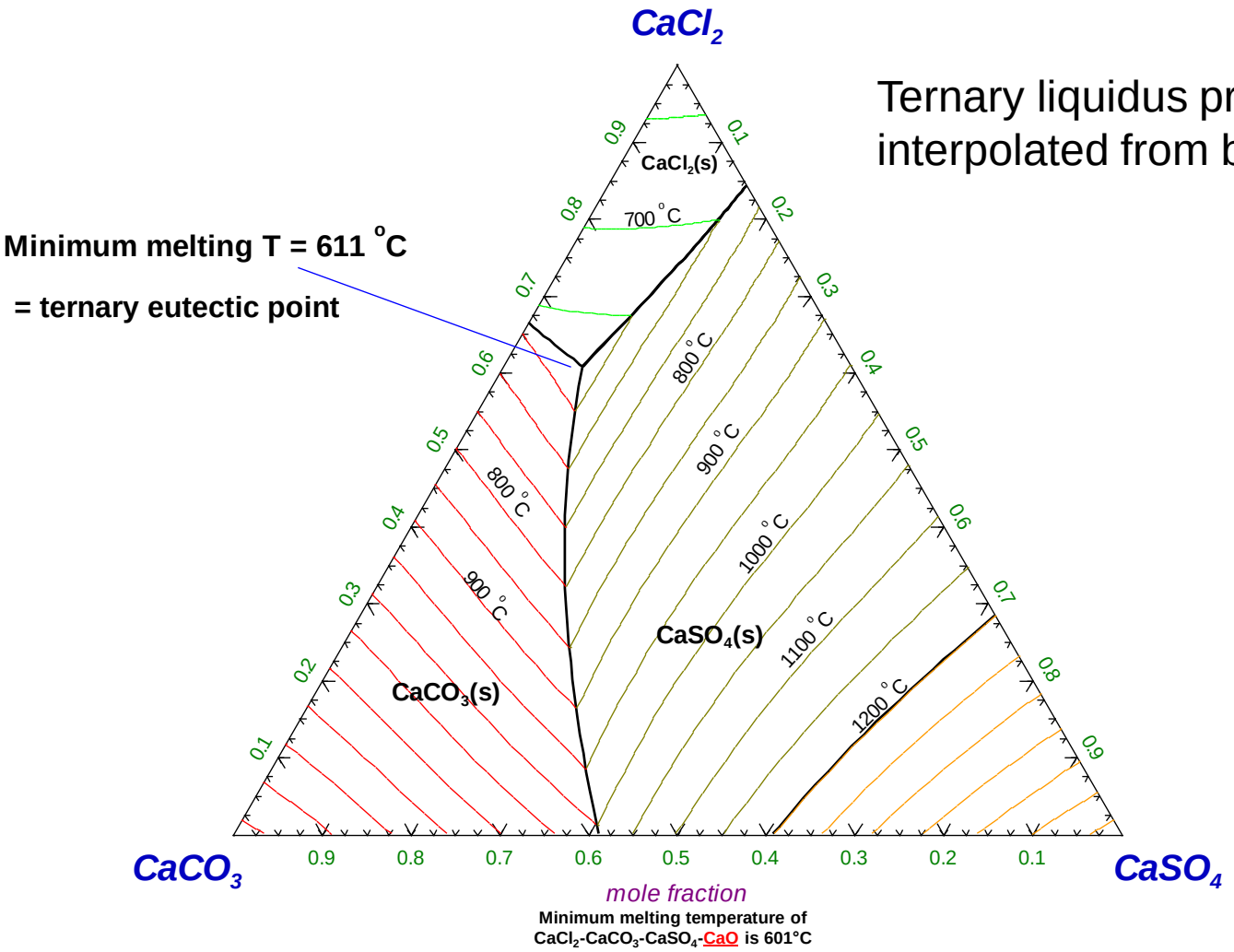




$CaCl_2$-$CaCO_3$-$CaSO_4$



$CaSO_4$ - $CaCl_2$ - $CaCO_3$

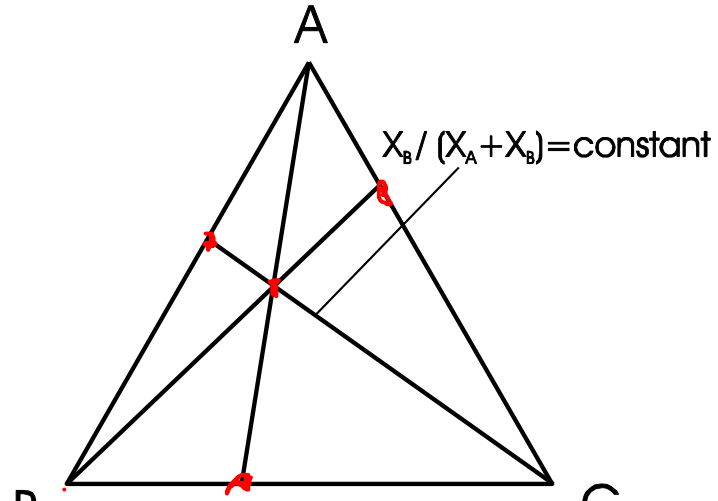


Minimum melting T = 611 °C

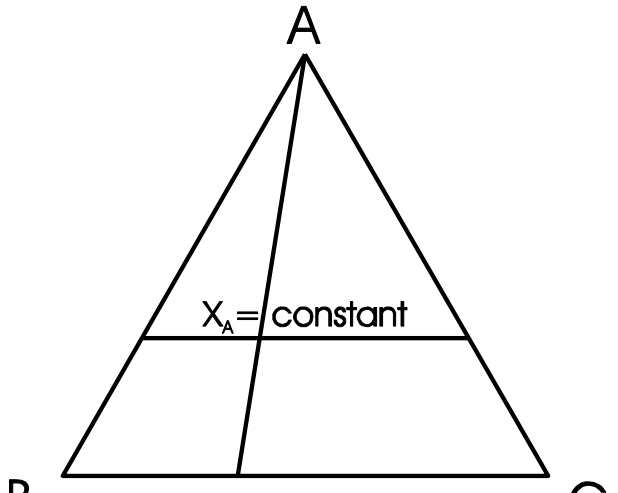
= ternary eutectic point

Ternary liquidus projection
interpolated from binary systems

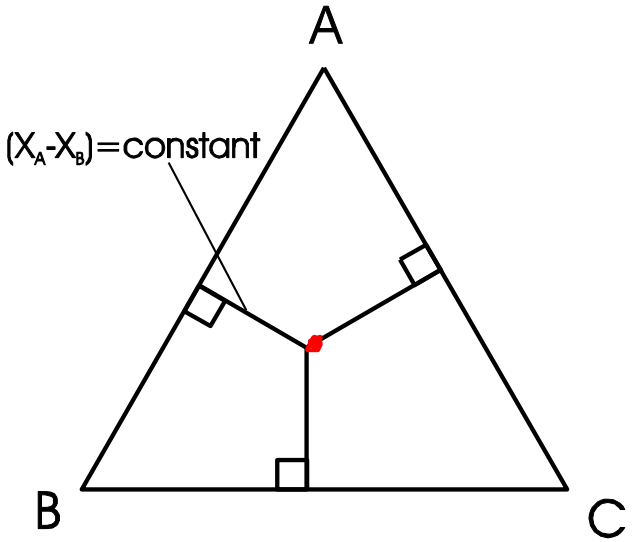
Extrapolation methods of binary parameters



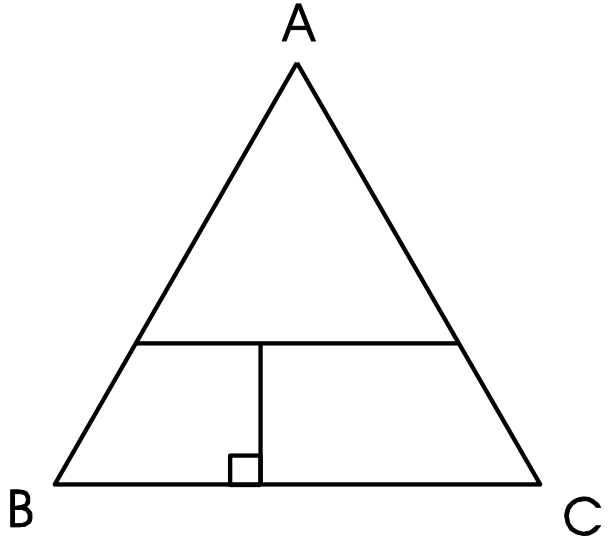
Kohler model



Kohler/Toop model



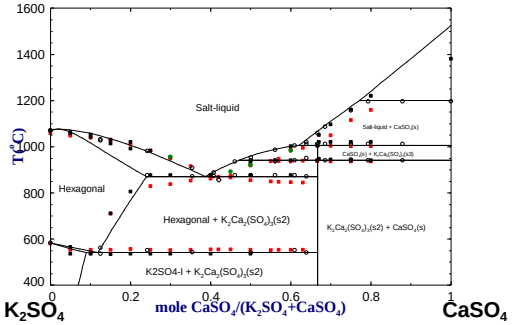
Muggianu model

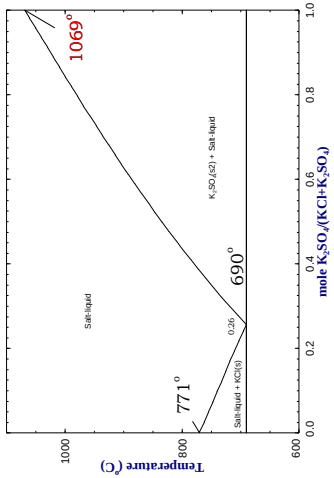


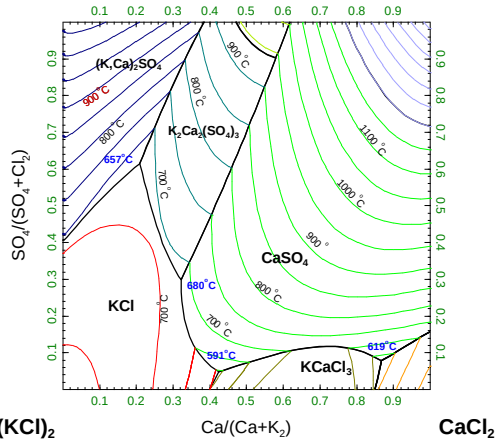
Muggianu/Toop model

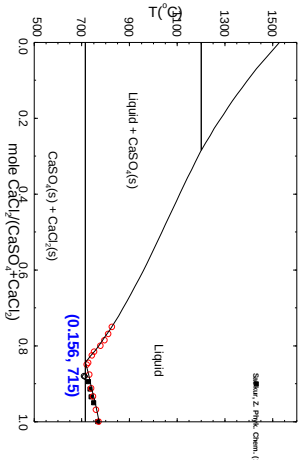
Reciprocal data

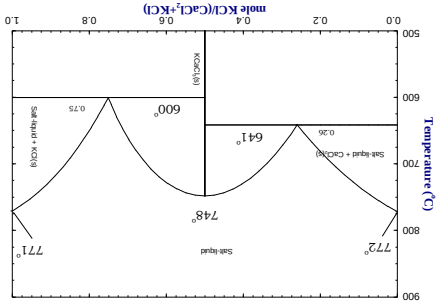
$K^+, Ca^{2+}//Cl^-, SO_4^{2-}$


T(°C)
Salt-liquid
Hexagonal
Hexagonal + K2Ca2(SO4)3(s2)
K2Ca2(SO4)3(s2) + CaSO4(s)
K2SO4-l + K2Ca2(SO4)3(s2)
K2SO4
mole CaSO4/(K2SO4+CaSO4)
CaSO4

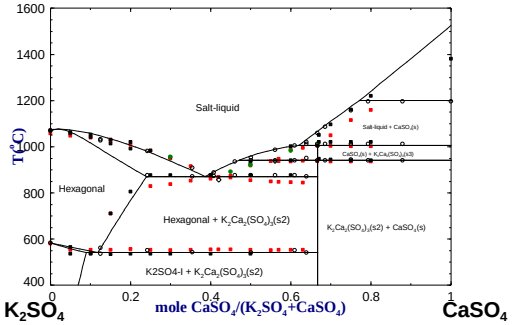

1069°
690°
771°
Salt-liquid
K2SO4(s2) + Salt-liquid
Salt-liquid + KCl(s)
Temperature (°C)
mole K2SO4/(KCl+K2SO4)

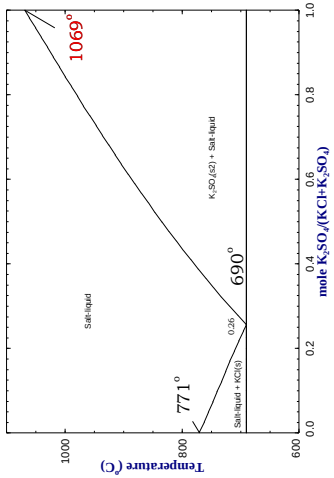

(K,Ca)2SO4
K2Ca2(SO4)3
CaSO4
KCl
KCaCl3
657°C
680°C
591°C
619°C
(KCl)2
CaCl2
Ca/(Ca+K2)
SO4/(SO4+Cl2)

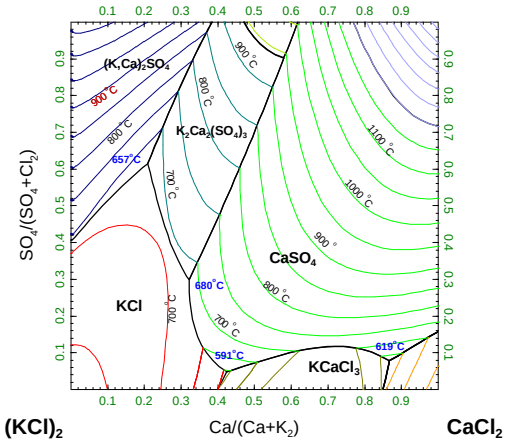

T(°C)
Liquid + CaSO4(s)
CaSO4(s) + CaCl2(s)
Liquid
(0.156, 715)
mole CaCl2/(CaSO4+CaCl2)

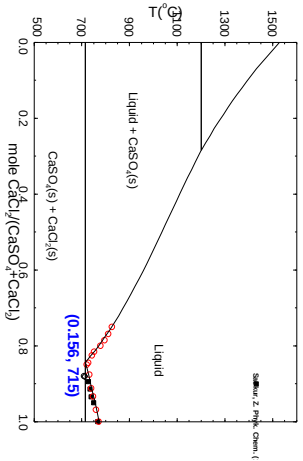

mole KCl/(CaCl2+KCl)
Salt-liquid
Salt-liquid + KCl(s)
Salt-liquid + CaCl2(s)
KCaCl3(s)
771°
748°
772°
641°
600°
Temperature (°C)

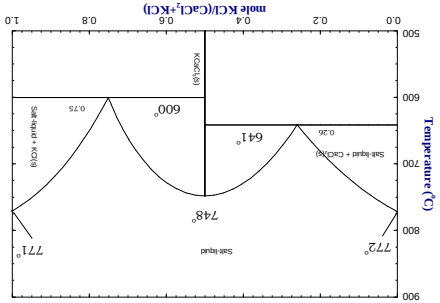
$K^+, Ca^{2+}//Cl^-, SO_4^{2-}$


T(°C)
Salt-liquid
Hexagonal
Hexagonal + K2Ca2(SO4)3(s2)
K2Ca2(SO4)3(s2) + CaSO4(s)
K2SO4-l + K2Ca2(SO4)3(s2)
K2SO4
mole CaSO4/(K2SO4+CaSO4)
CaSO4


1069°
690°
771°
Salt-liquid
K2SO4(s2) + Salt-liquid
Salt-liquid + KCl(s)
0.26
Temperature (°C)
mole K2SO4/(KCl+K2SO4)

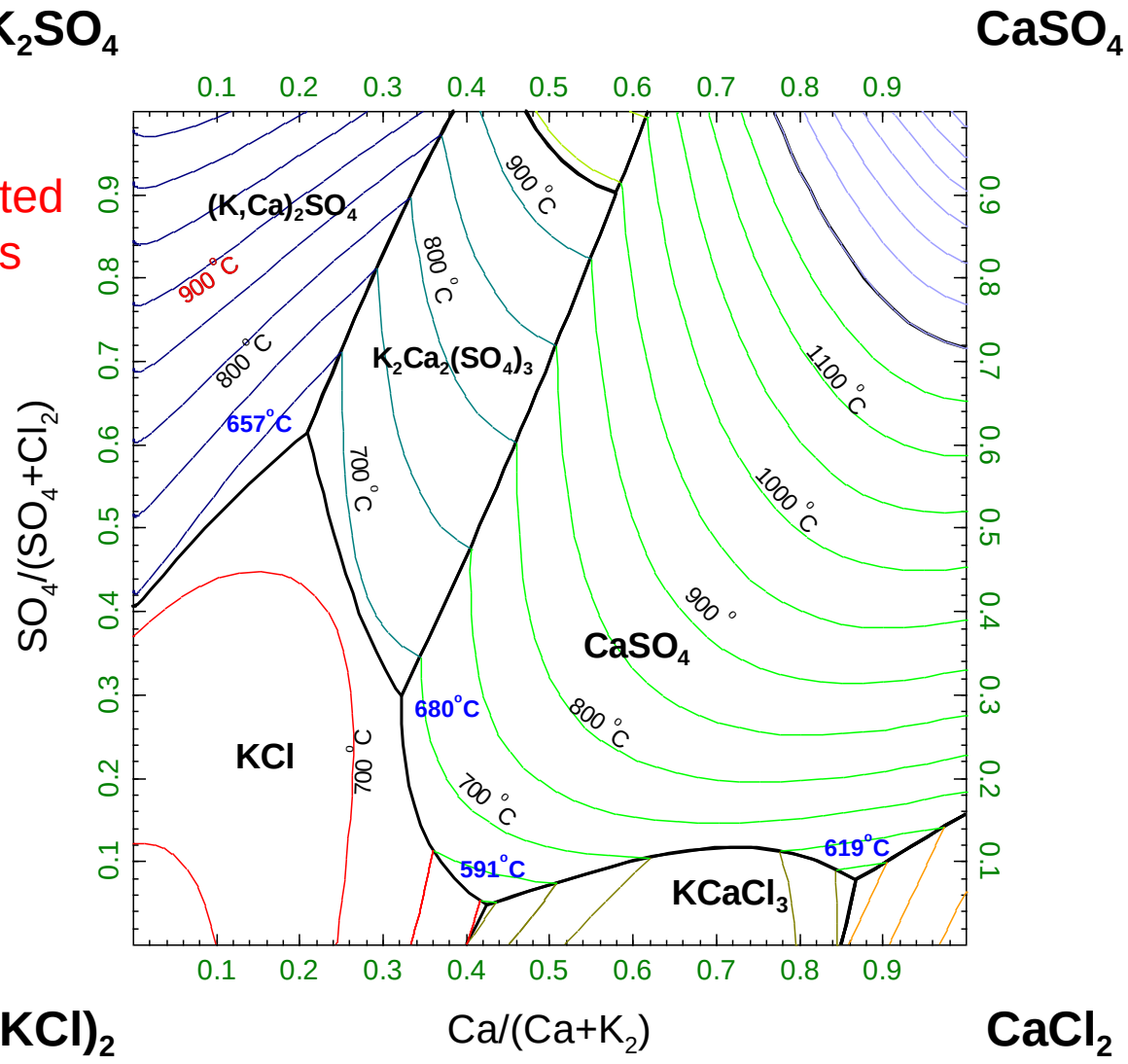

(K,Ca)2SO4
K2Ca2(SO4)3
CaSO4
KCl
KCaCl3
680°C
657°C
591°C
619°C
SO4/(SO4+Cl2)
Ca/(Ca+K2)
(KCl)2
CaCl2


T(°C)
Liquid + CaSO4(s)
CaSO4(s) + CaCl2(s)
Liquid
(0.156, 715)
mole CaCl2/(CaSO4+CaCl2)

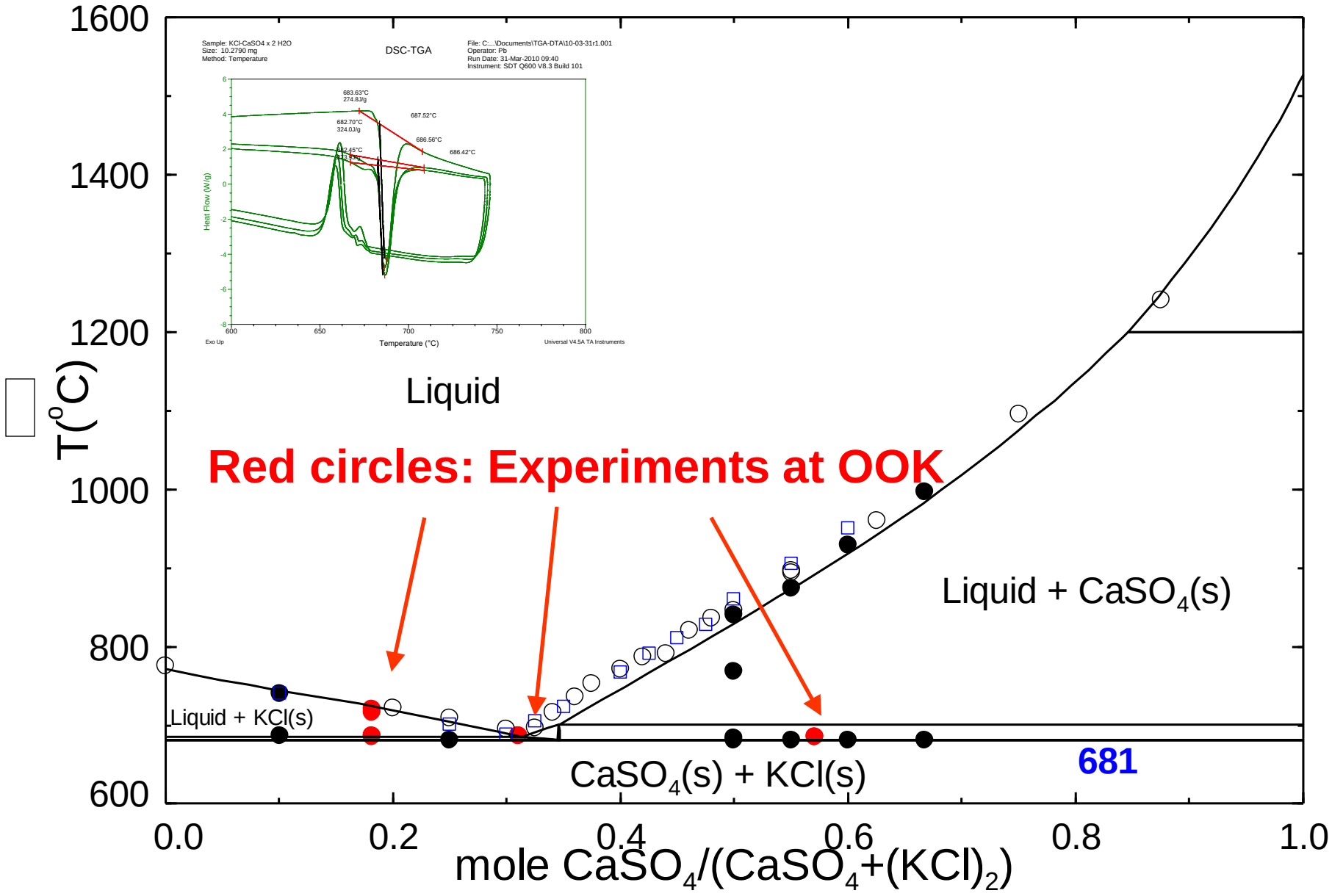

mole KCl/(CaCl2+KCl)
KCaCl3(s)
Salt-liquid + KCl(s)
Salt-liquid
Salt-liquid + CaCl2(s)
600°
641°
748°
771°
772°
Temperature (°C)

$K^+, Ca^{2+}//Cl^-, SO_4^{2-}$

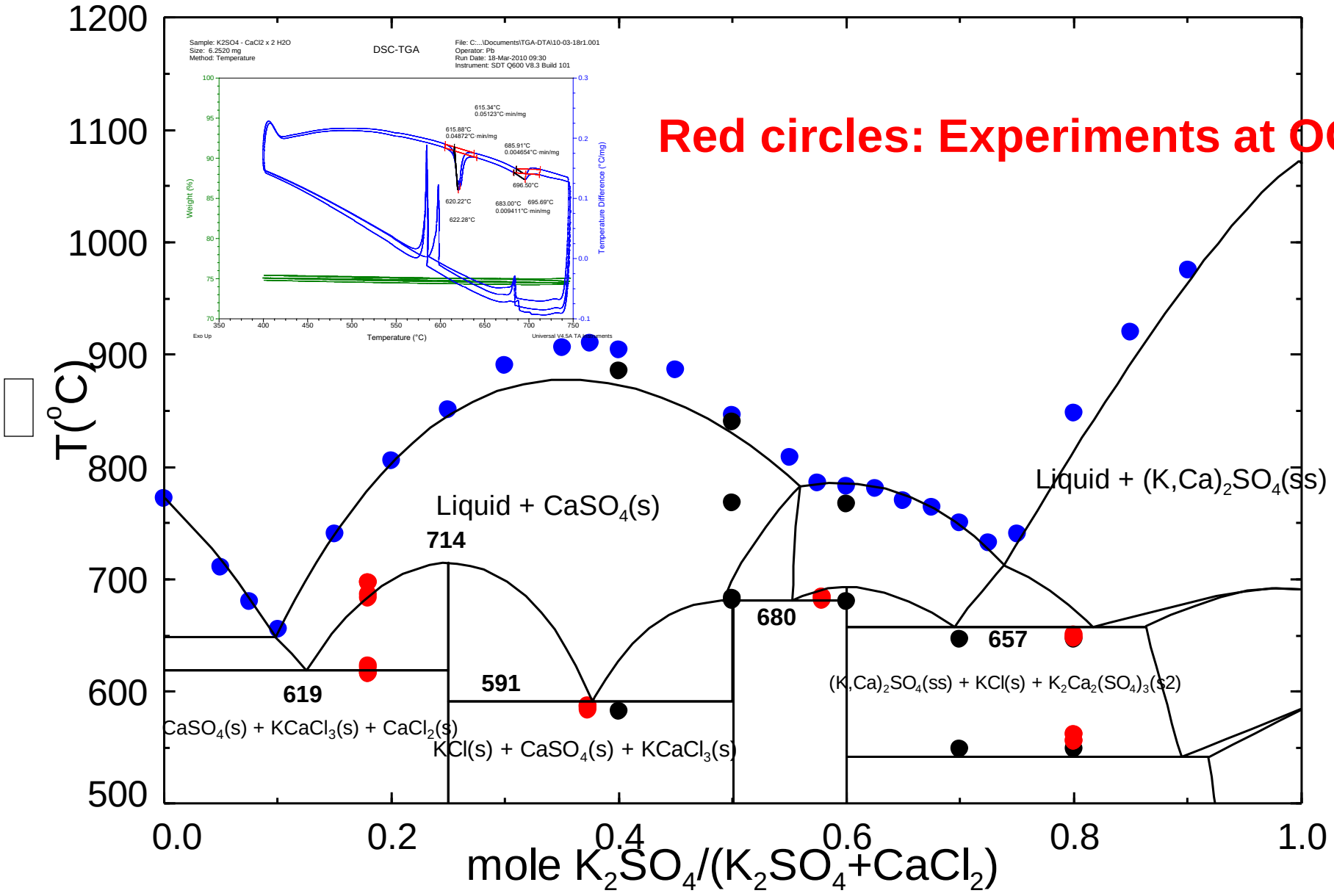
Liquidus (T100) projection interpolated from binary systems



$CaSO_4$ - $(KCl)_2$


1600
1400
1200
1000
800
600
T(°C)
0.0
0.2
0.4
0.6
0.8
1.0
mole CaSO4/(CaSO4+(KCl)2)
Sample: KCl-CaSO4 x 2 H2O
Size: 10.2790 mg
Method: Temperature
DSC-TGA
File: C:...\Documents\TGA-DTA\10-03-31r1.001
Operator: Pb
Run Date: 31-Mar-2010 09:40
Instrument: SDT Q600 V8.3 Build 101
683.63°C
274.8J/g
687.52°C
682.70°C
324.0J/g
686.56°C
686.42°C
Heat Flow (W/g)
Exo Up
Temperature (°C)
Universal V4.5A TA Instruments
Liquid
Red circles: Experiments at OOK
Liquid + CaSO4(s)
Liquid + KCl(s)
CaSO4(s) + KCl(s)
681

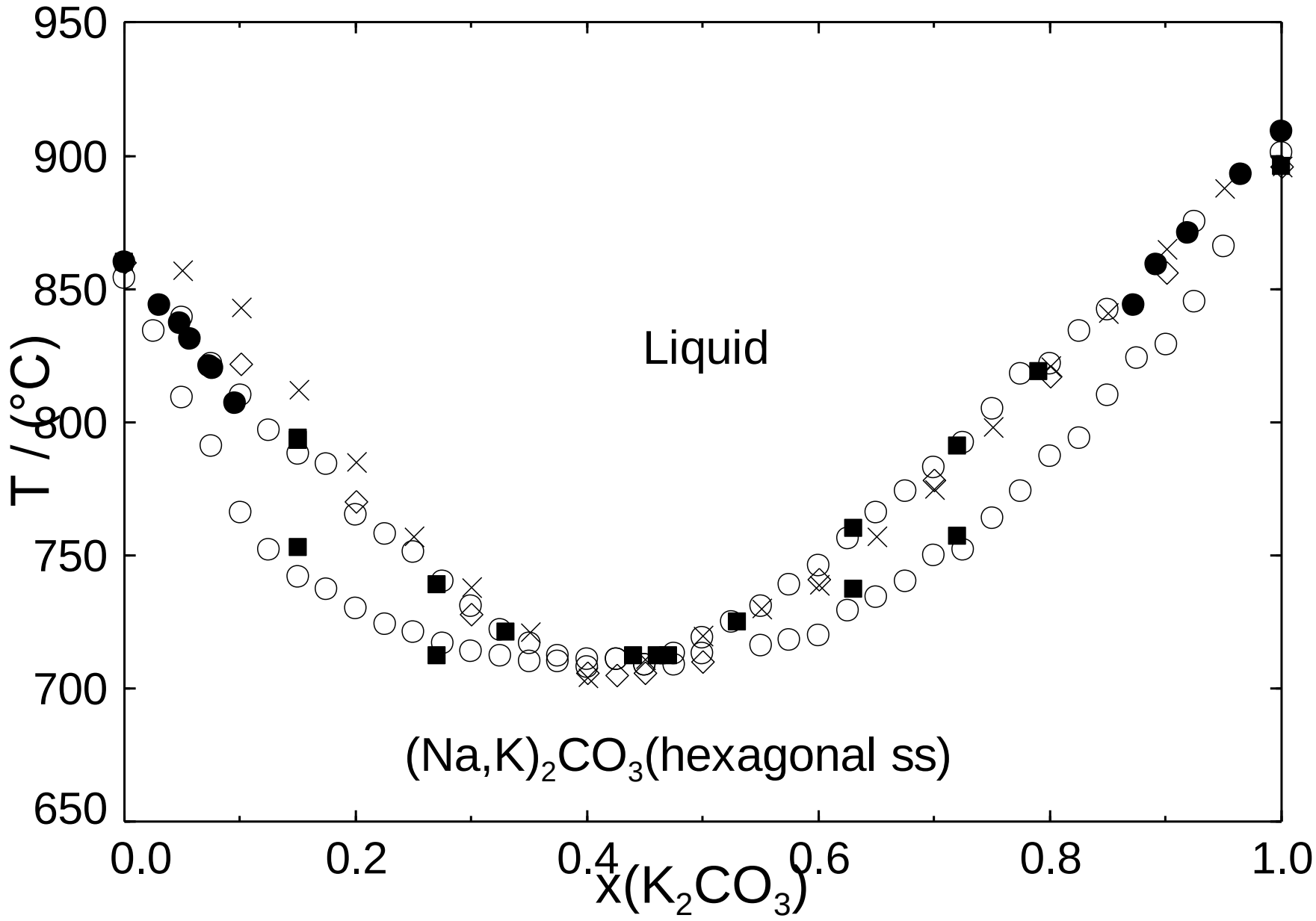
K_2SO_4 - $CaCl_2$


Red circles: Experiments at OOK
T(°C)
mole $K_2SO_4/(K_2SO_4+CaCl_2)$
Liquid + $CaSO_4$(s)
Liquid + $(K,Ca)_2SO_4$(ss)
714
680
657
591
619
$(K,Ca)_2SO_4$(ss) + KCl(s) + $K_2Ca_2(SO_4)_3$(s2)
$CaSO_4$(s) + $KCaCl_3$(s) + $CaCl_2$(s)
KCl(s) + $CaSO_4$(s) + $KCaCl_3$(s)
DSC-TGA
Temperature (°C)
Weight (%)
Temperature Difference (°C/mg)

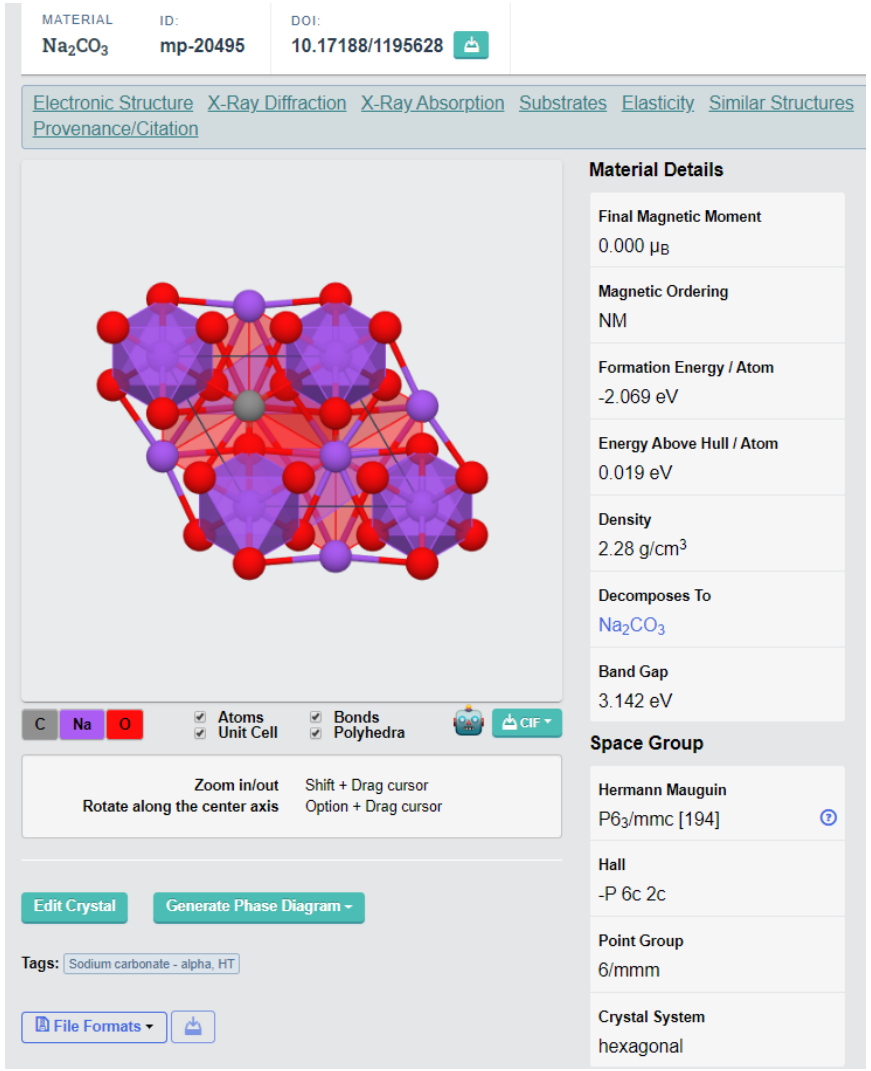
Demonstration

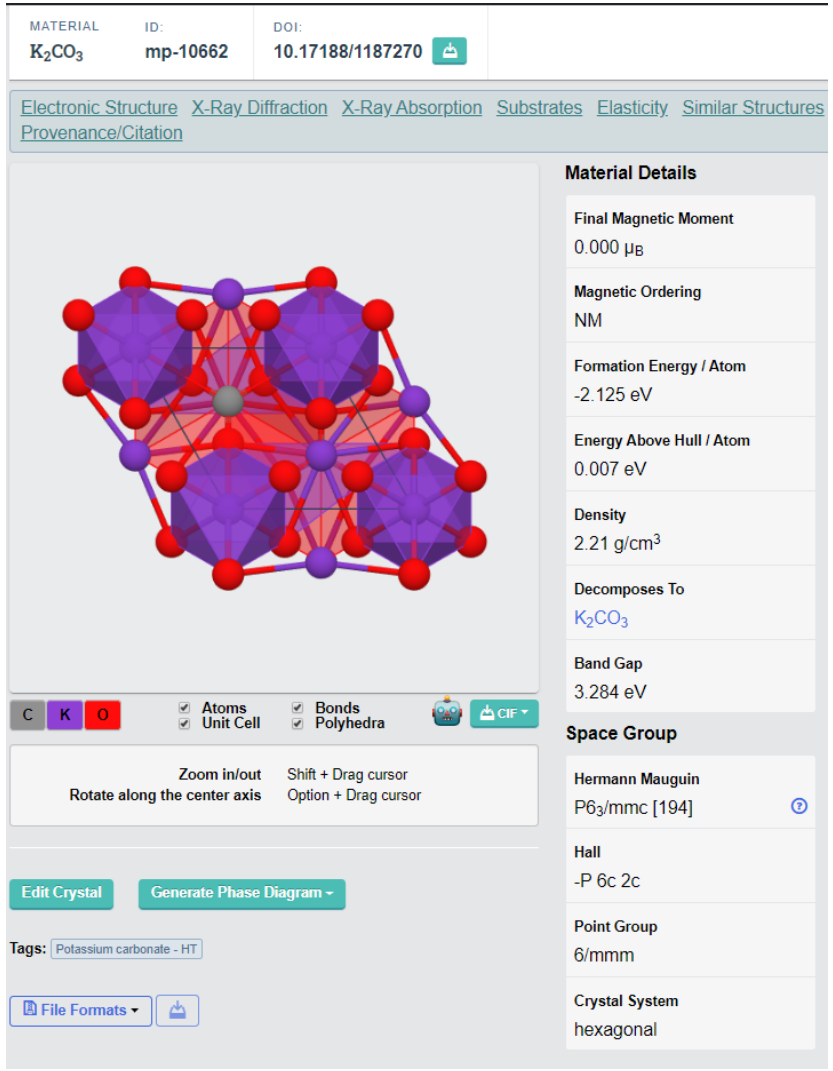
- Thermodynamic evaluation of the binary Na_2CO_3-K_2CO_3 system
- Based on
  - Phase diagram data (solidus & liquidus)
  - Enthalpy of mixing of Na_2CO_3(l) and K_2CO_3(l)

Na_2CO_3 - K_2CO_3

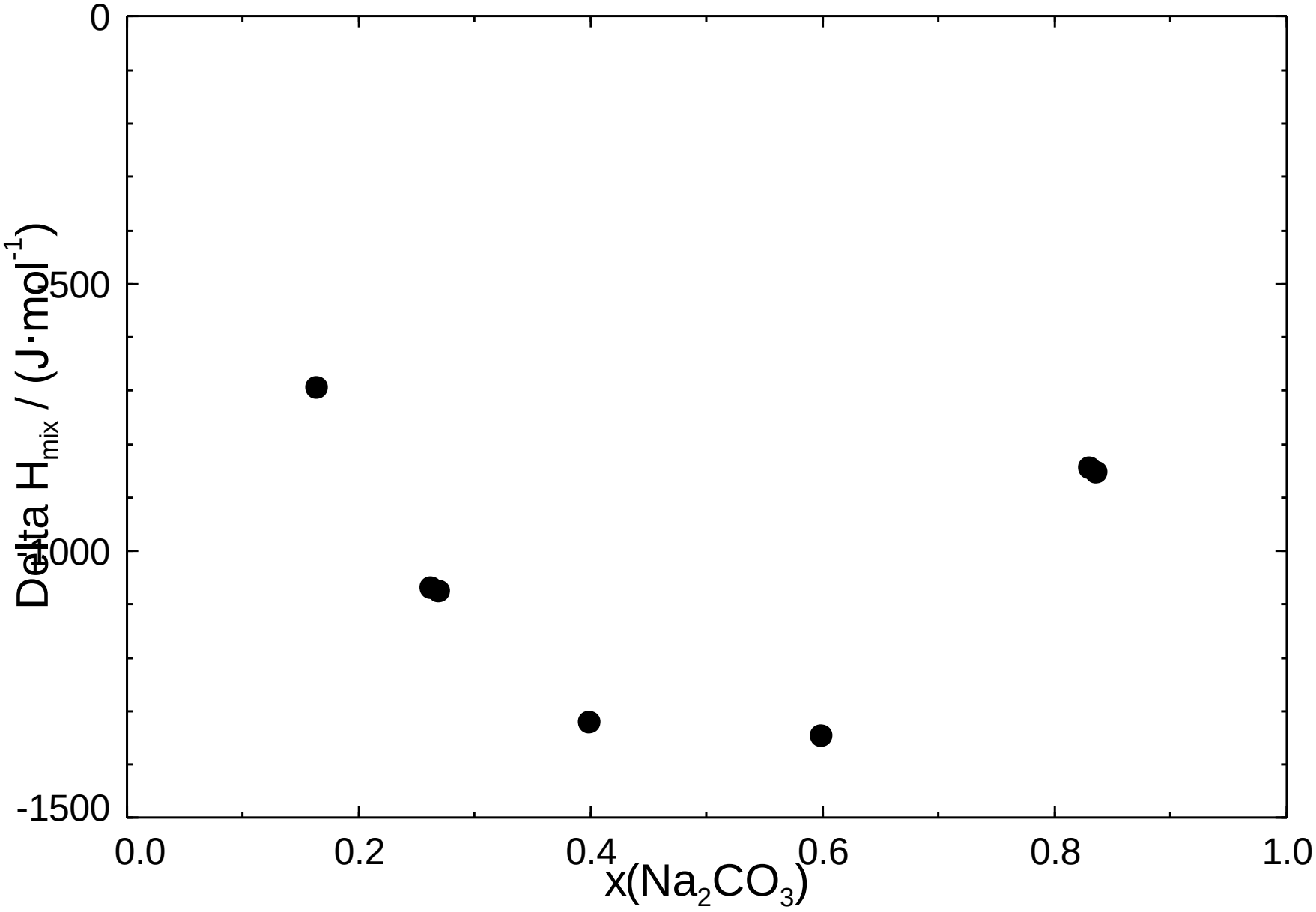


Crystal structure of Na_2CO_3 and K_2CO_3

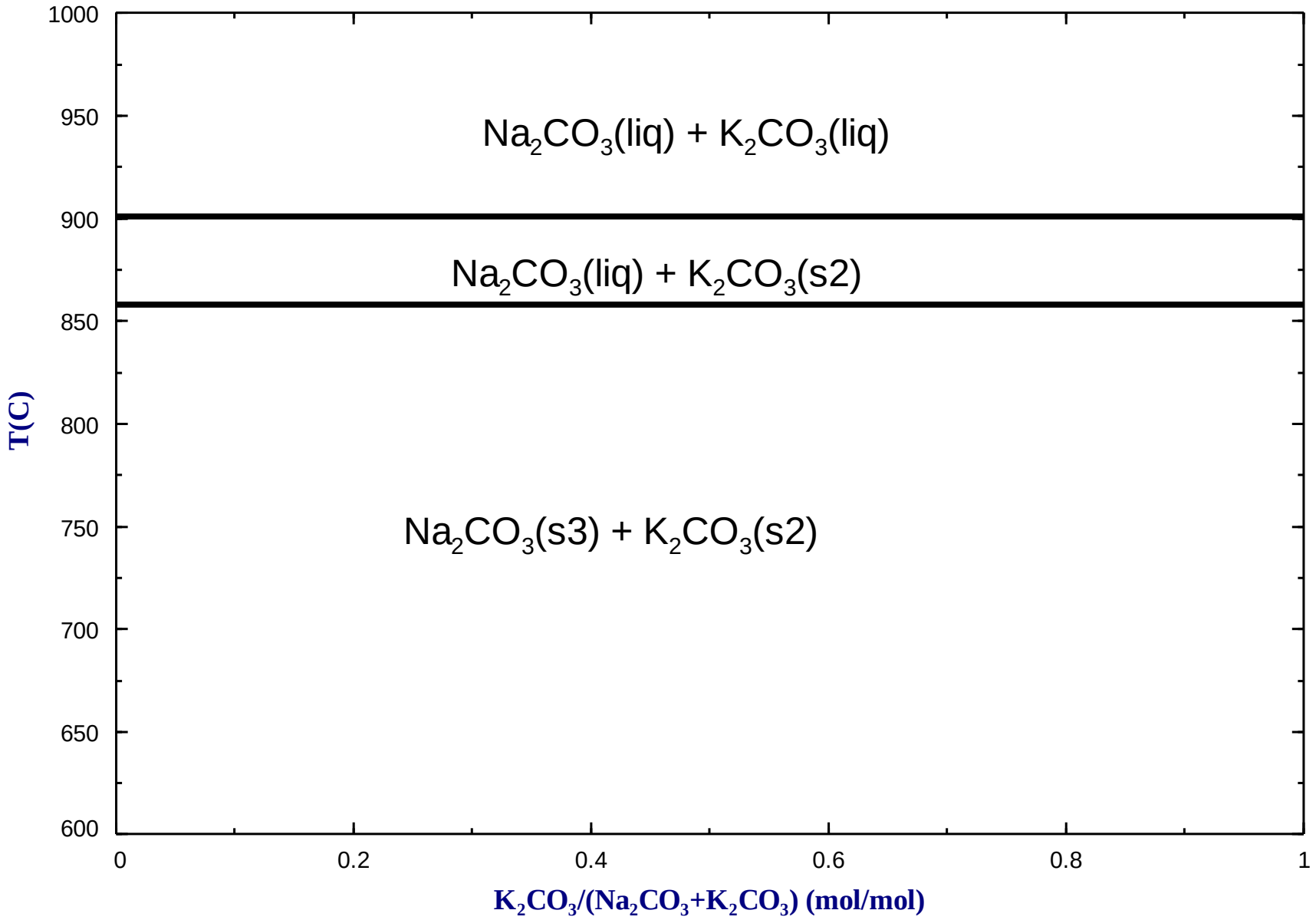




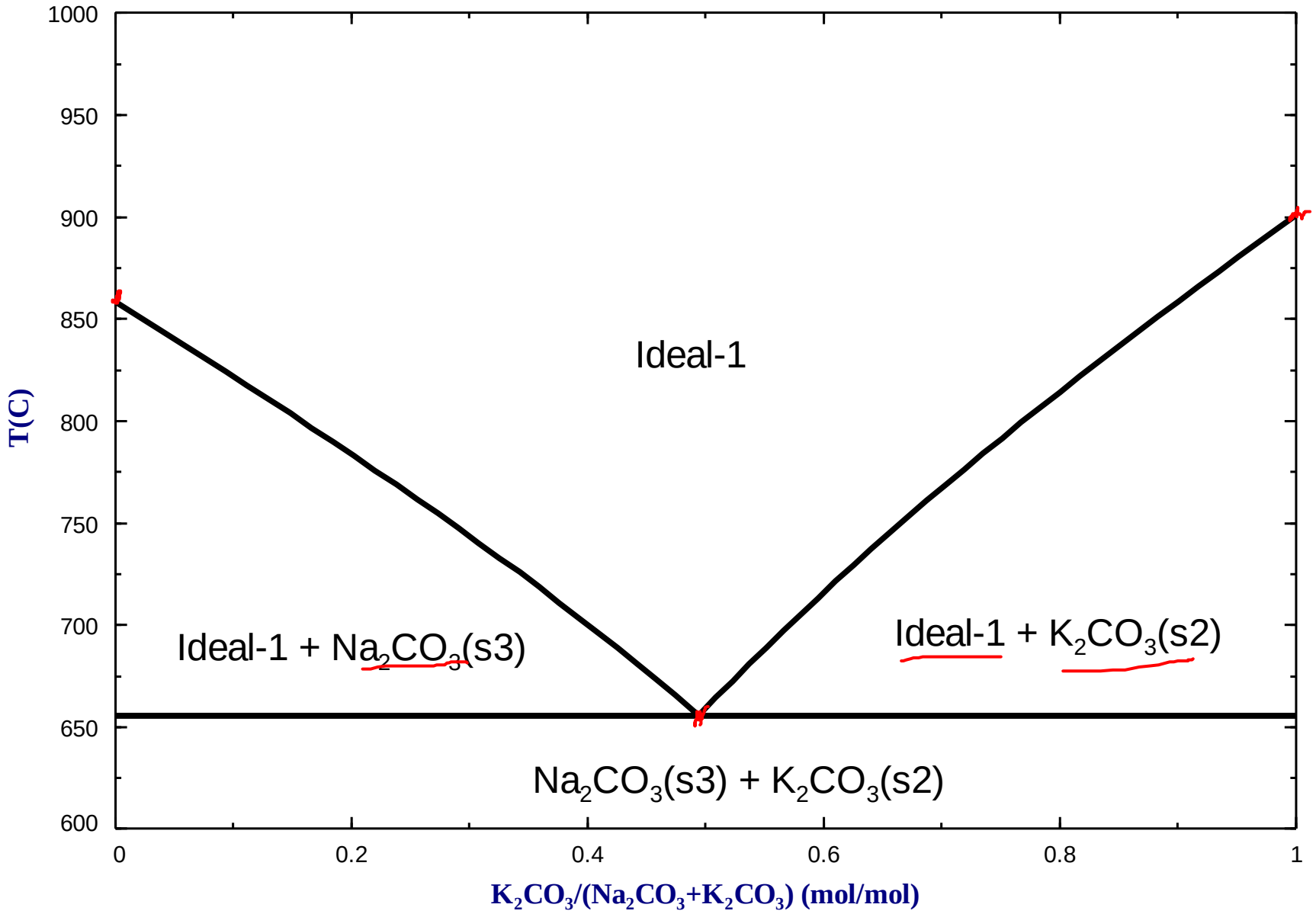
Enthalpy of mixing at 905°C



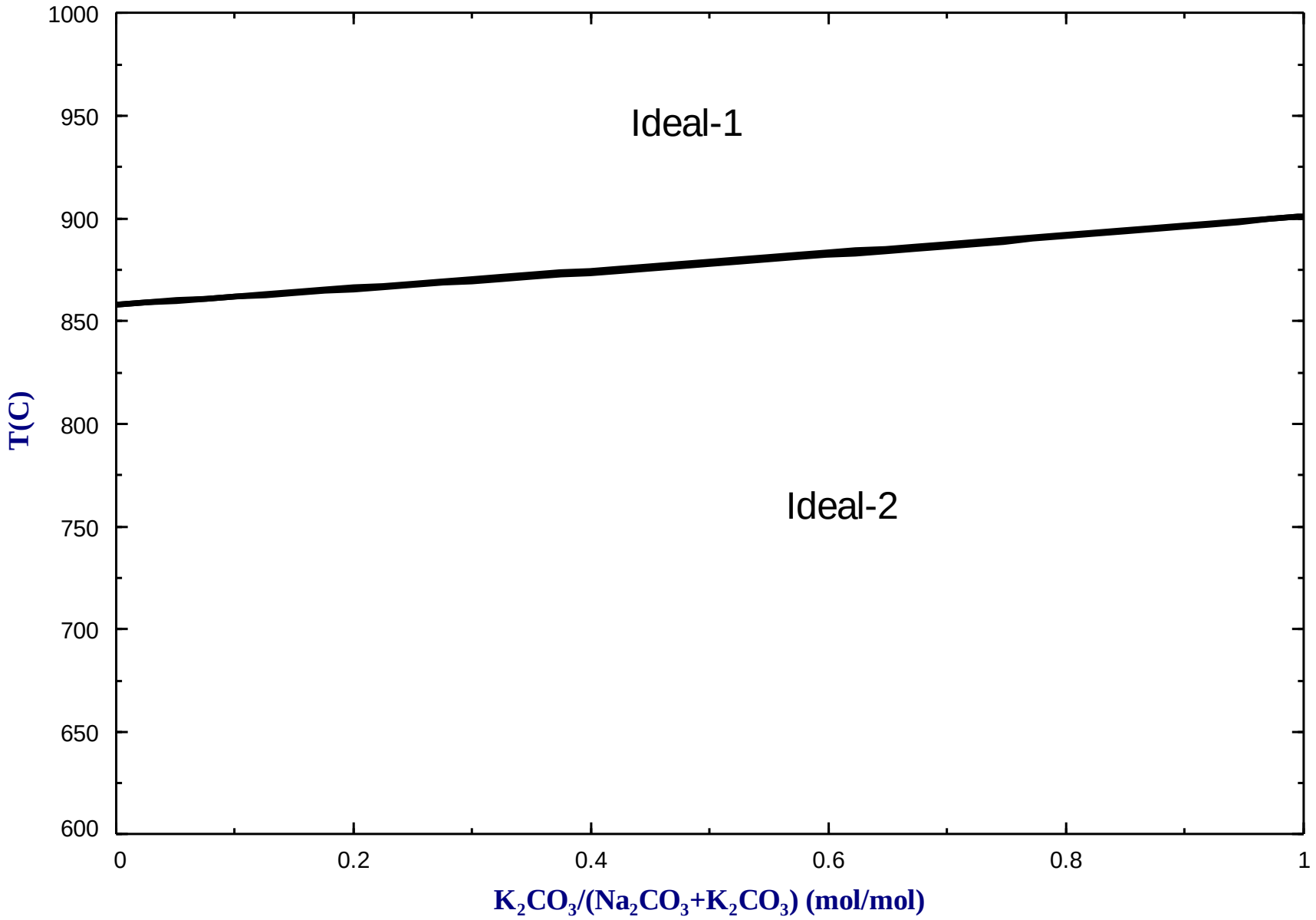
Na_2CO_3 - K_2CO_3

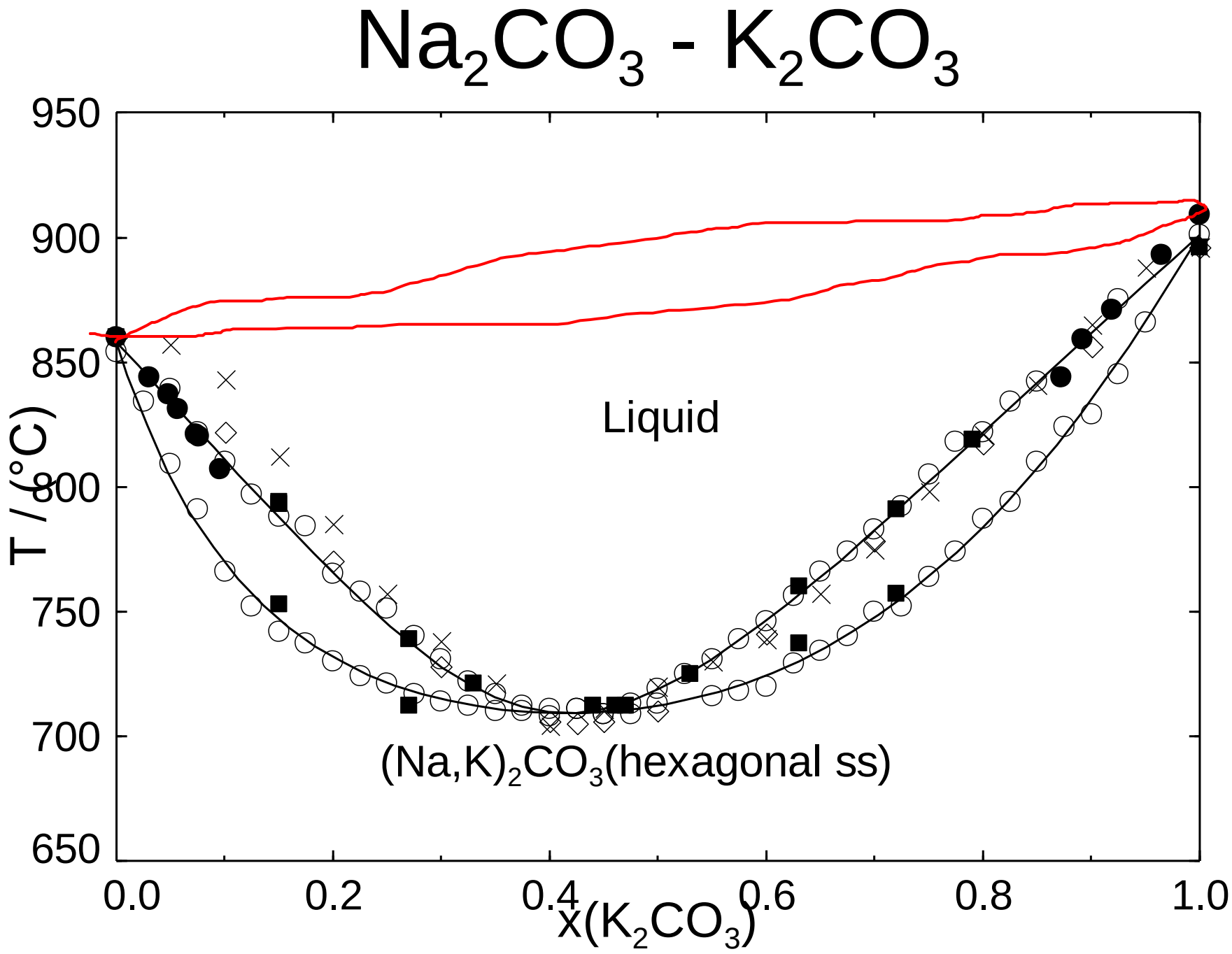


Na_2CO_3 - K_2CO_3

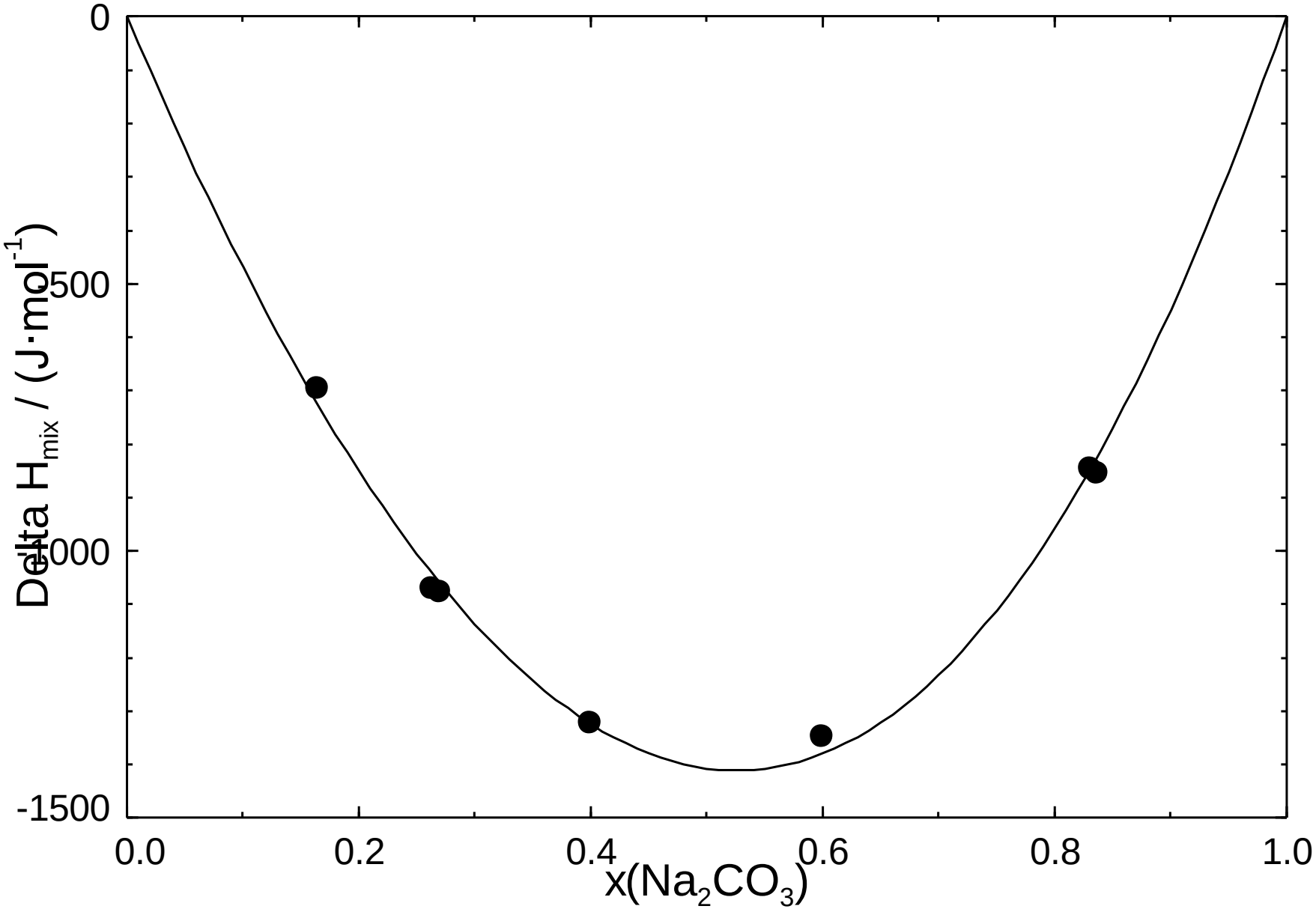


Na_2CO_3 - K_2CO_3

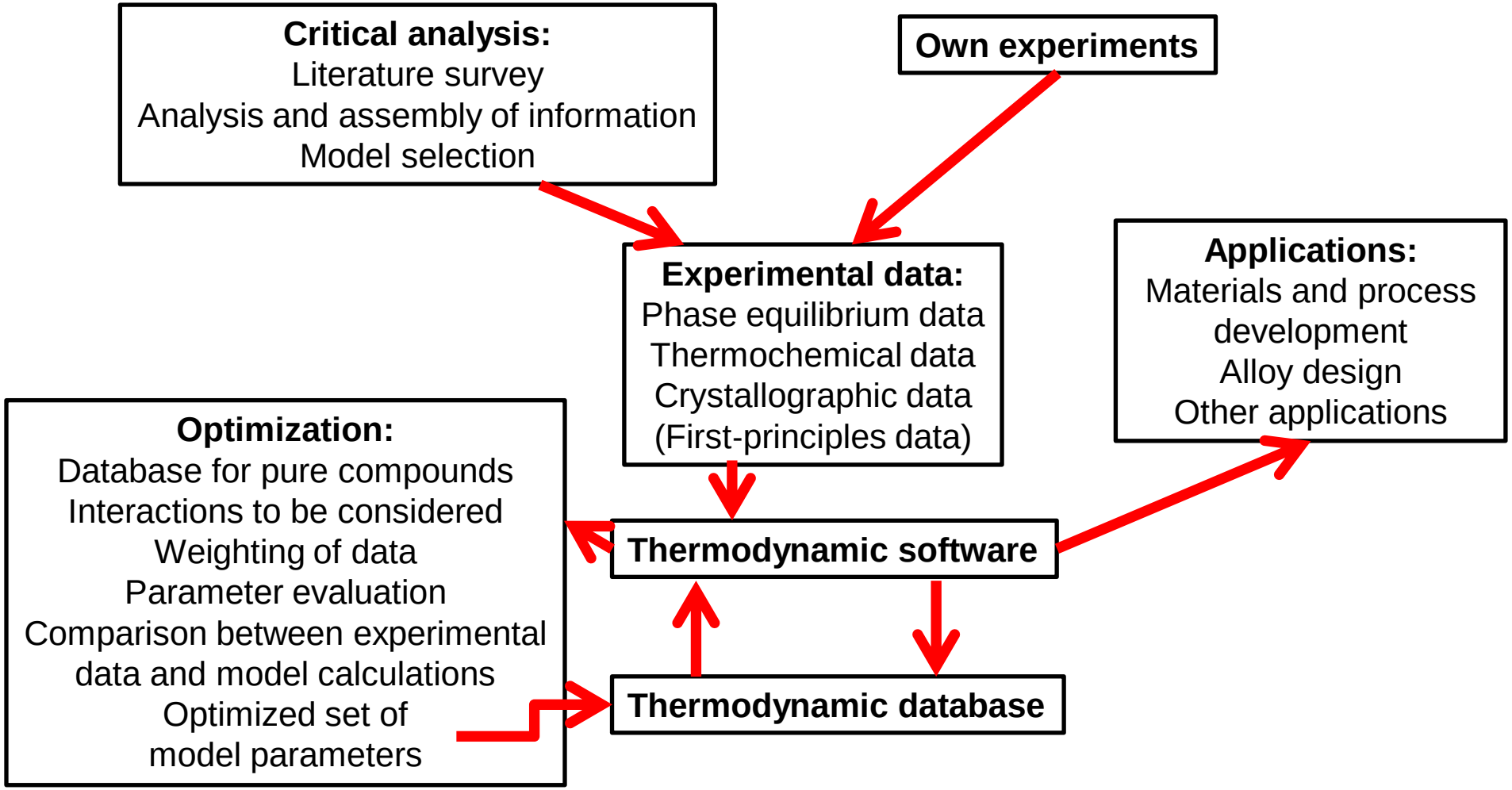



Na_2CO_3 - K_2CO_3
950
900
850
800
750
700
650
T /(°C)
Liquid
$(Na,K)_2CO_3$(hexagonal ss)
0.0
0.2
0.4
0.6
0.8
1.0
$x(K_2CO_3)$

Enthalpy of mixing at 905°C



Procedure for the Calphad method



Adopted from lic. thesis of I. Vaajamo

Summary

- Calphad method
- Procedure
- Experimental input
- Choice of solution phase
- Demonstration