JÜLICH
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Including SO_3 into the HotVeGas oxide database

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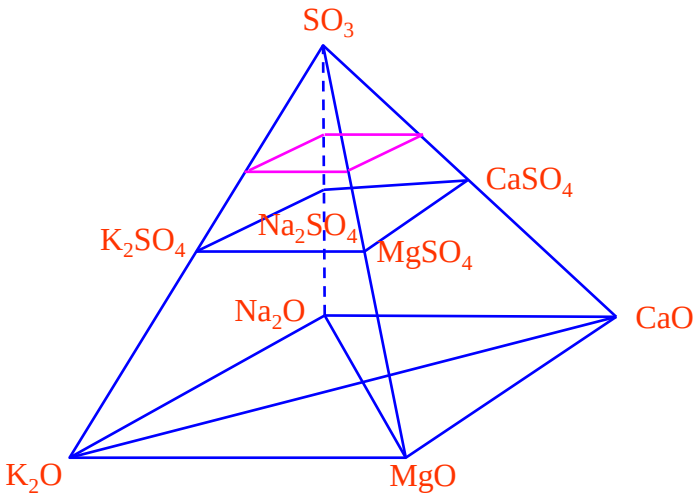
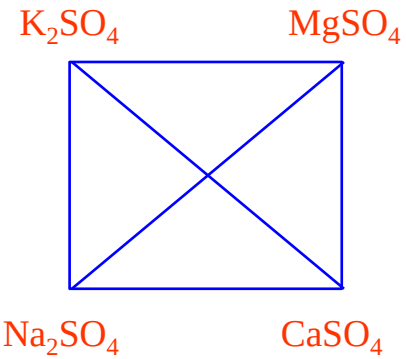


HOTVEGAS



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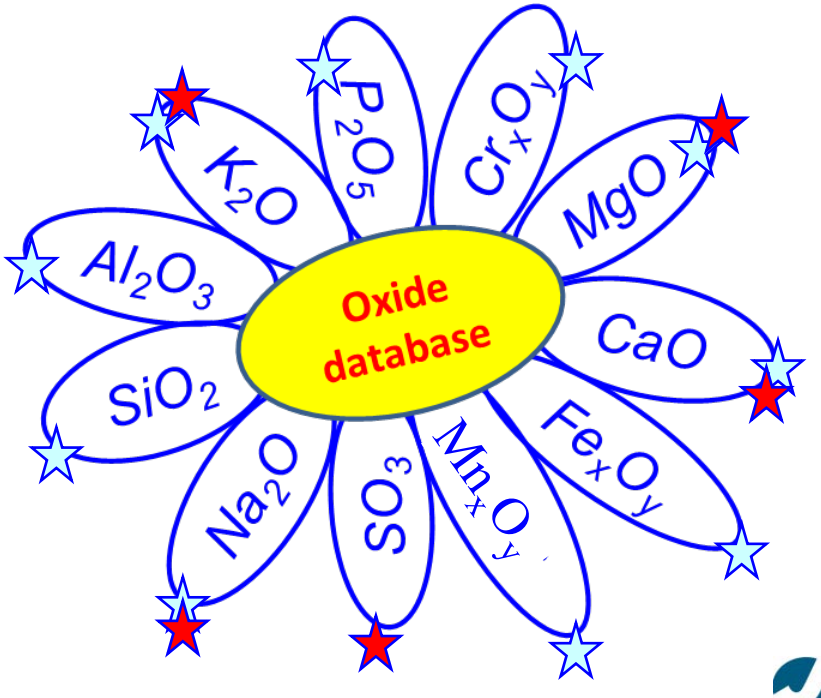
Motivation and aim of work



State of the art:

- ✓ 2-, 3- and multicomponent systems have been thermodynamically assessed using all available experimental data
- ✓ phase diagrams and other thermodynamic properties can be calculated with the obtained self-consistent datasets

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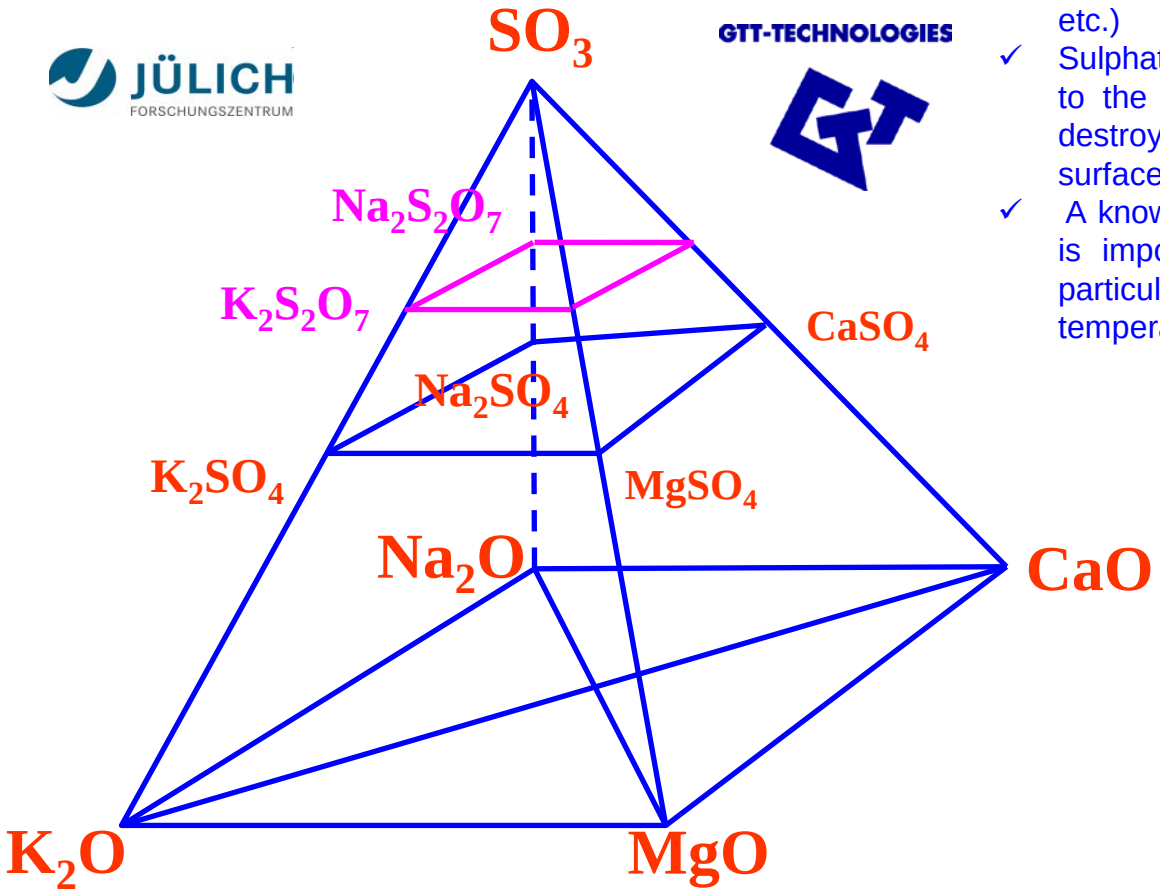
Aim of our work:
development of a new data base, which is applicable for the slag relevant system containing oxides of Si, Al, Na, K, Ca, Mg, Fe, P, S, Cr etc. and suitable for the calculations and/or predictions of the phase equilibria and other thermodynamic properties by variation of T and composition

*E. Yazhenskikh, T. Jantzen, K. Hack, M. Müller, Critical thermodynamic evaluation of oxide systems relevant to fuel ashes and slags: Potassiumoxide–magnesium oxide–silica, Calphad, **47 (2014)** 35–49.*

Including SO_3

HOTVEGAS



- ✓ SO_3 is a next important slag component to be added into the database
- ✓ Sulphates are essentially components for biomass ashes and metallurgical slags, they are widely used in industry (cement, paper, manufactory of glass etc.)
- ✓ Sulphates and pyrosulphates deposits arising due to the presence of S in coals and biomass can destroy the normally protective oxide on the metal surface in the heat exchange
- ✓ A knowledge of the phase equilibria in the system is important for process control and simulation, particularly a knowledge of the liquidus temperatures and the solubility limits of sulphate.

Aim:
Extending our slag relevant database by the addition the SO_3 and corresponding sulphates to the liquid and solid phases

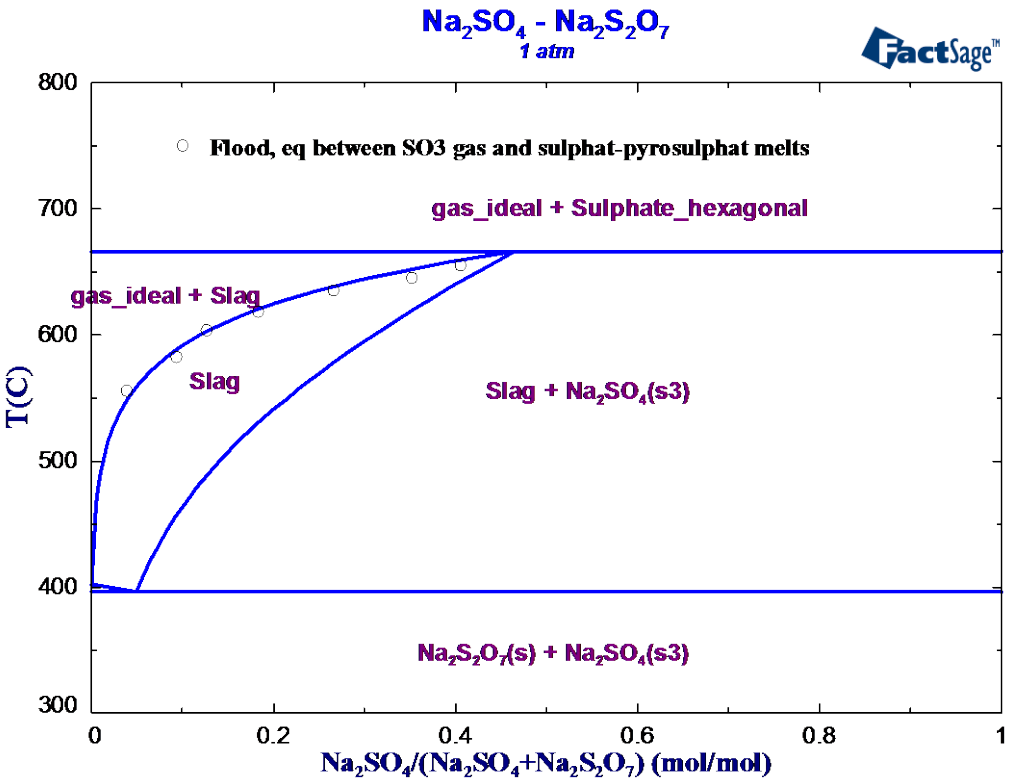
Modelling of binary SO_3-containing phases

The species in the non-ideal associate solution containing SO_3 were added in order to describe the liquid phase. Binary solid phases were considered as stoichiometric compounds

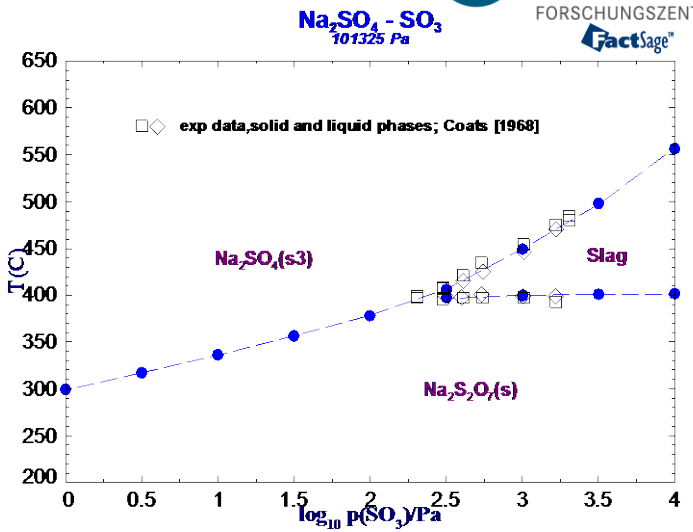
System	***Associate species in the liquid***	***Solid phase***	***Description of solid phase***	***Data***
Na_2O-SO_3	Na_2O, Na_2SO_4, $Na_2S_2O_7$, SO_3, (Na_2S)	SO_3 Na_2SO_4 (s1,s2,s3) $Na_2S_2O_7$ (s1)	stoichiometric stoichiometric stoichiometric	SGPS SGPS Pulp*
K_2O-SO_3	K_2O, K_2SO_4, $K_2S_2O_7$, SO_3, (K_2S)	K_2SO_4 (s1,s2) $K_2S_2O_7$ (s1,s2)	stoichiometric stoichiometric	SGPS Pulp*
Na_2O-K_2O	Na_2O, K_2O (ideal solution)	Na_2O(s3,s2,s1) K_2O(s3,s2,s1)	stoichiometric stoichiometric	SGPS SGPS

D. Lindberg, R. Backman, P. Chartrand, J. Chem. Thermodyn., **38, 1568-1583 (2006).*

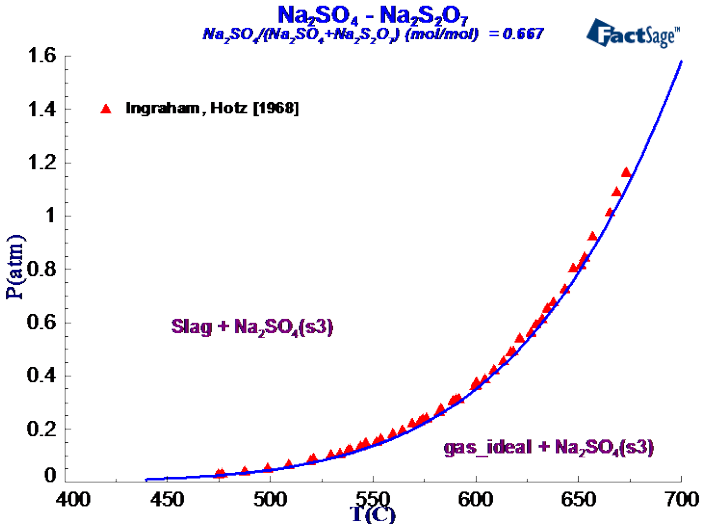
System Na_2SO_4-$Na_2S_2O_7$



The database obtained allows the description of the equilibria liquid-gas-solids and gives the good agreement with the experimental data.

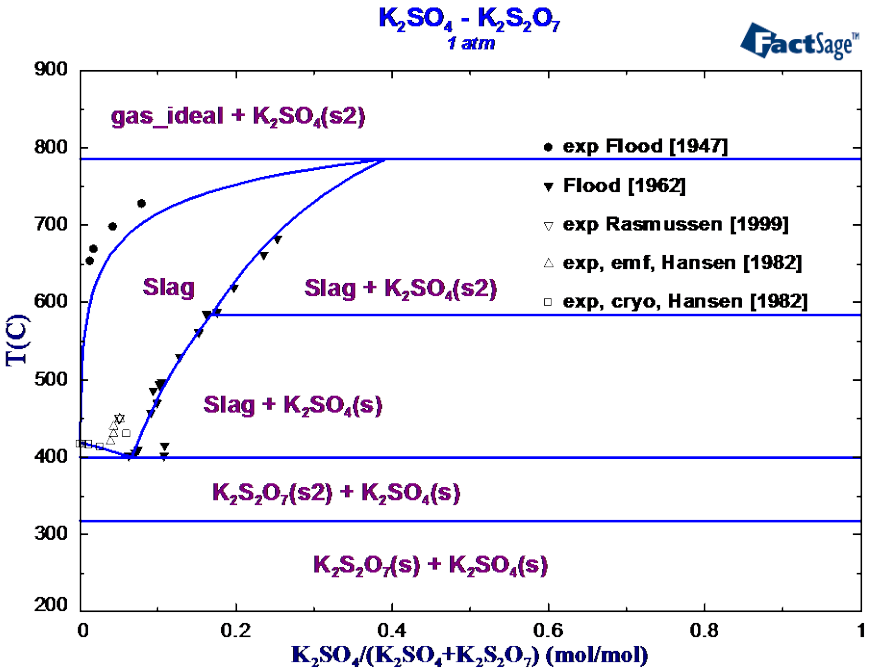


Calculated transition points of (Na_2SO_4+$Na_2S_2O_7$) as a function of p(SO_3) at a total pressure of1 atm.

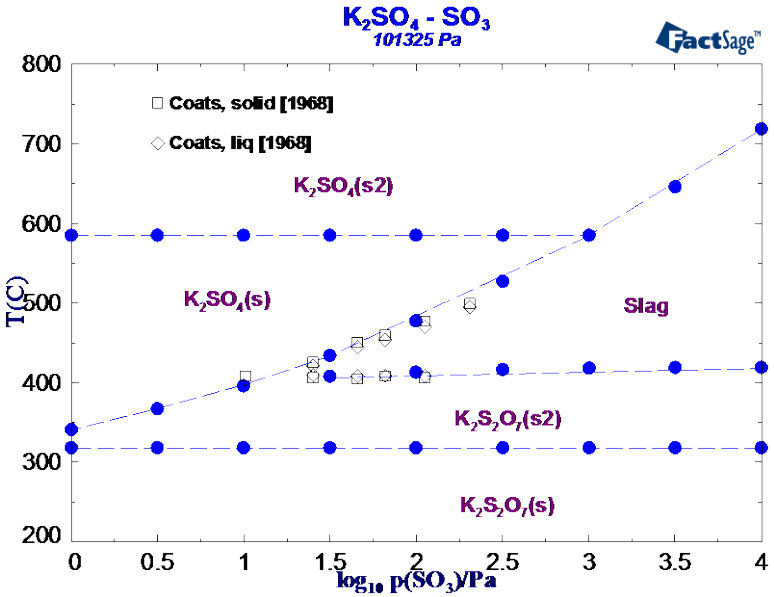


Calculated equilibrium between Na_2SO_4(s3), liquid and gas (SO_3, SO_2, O_2) as a function of temperature and total pressure

System K_2SO_4-$K_2S_2O_7$

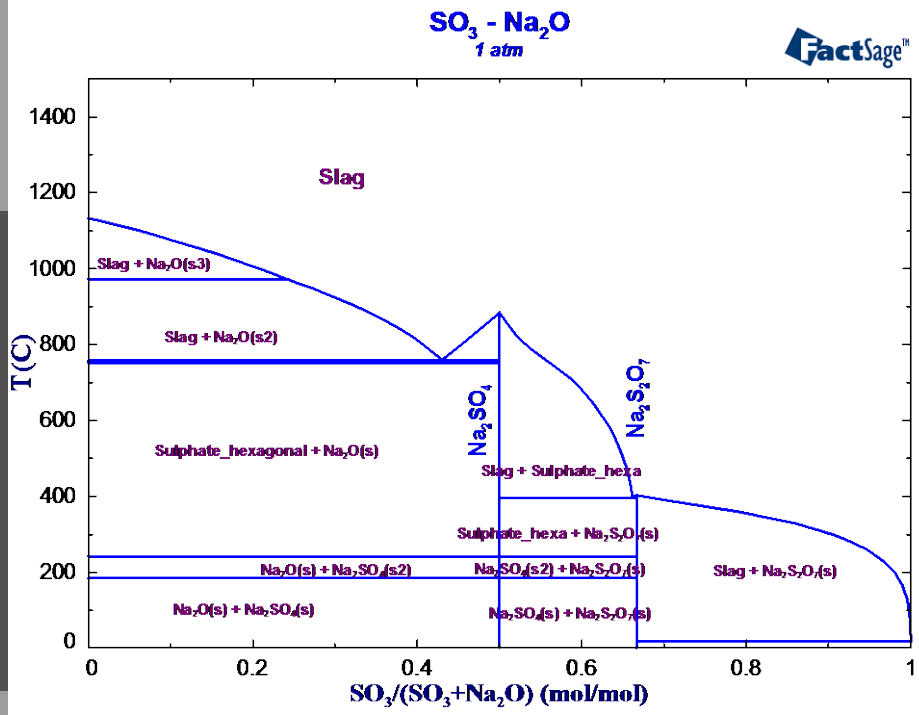


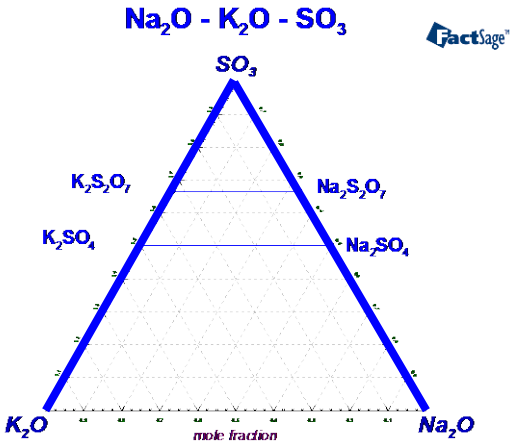
The database obtained allows the description of the equilibria liquid-gas-solids and gives the good agreement with the experimental data.

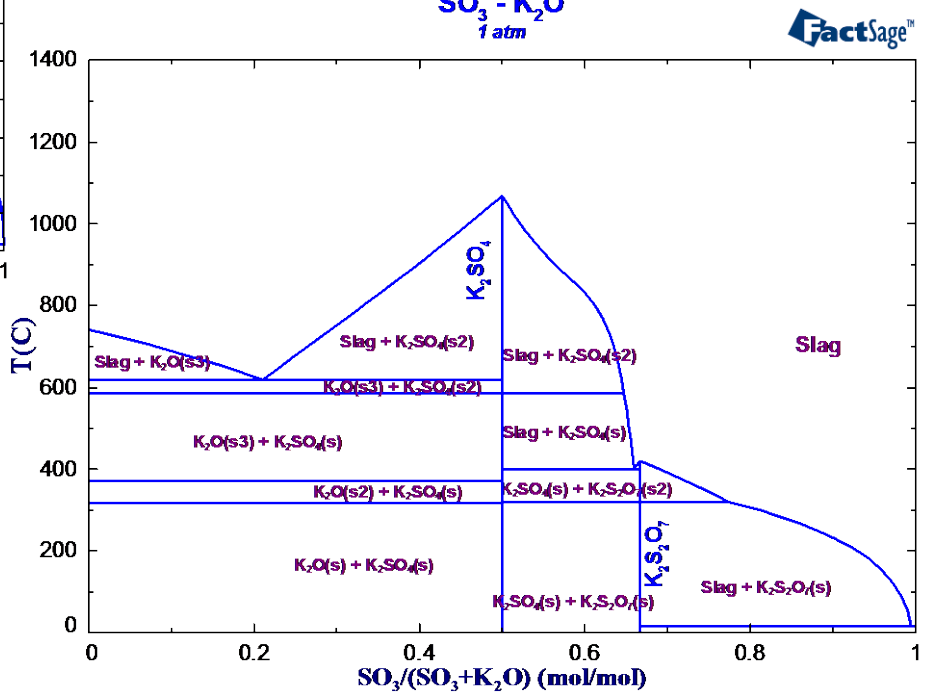


Calculated transition points of (K_2SO_4+$K_2S_2O_7$) as a function of p(SO_3) at a total pressure of 1 atm.

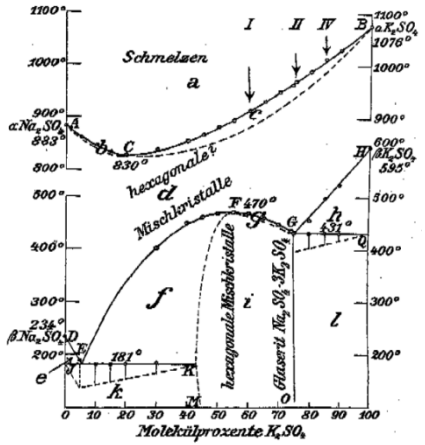
Systems Alk_2O-SO_3 (Alk=Na, K)



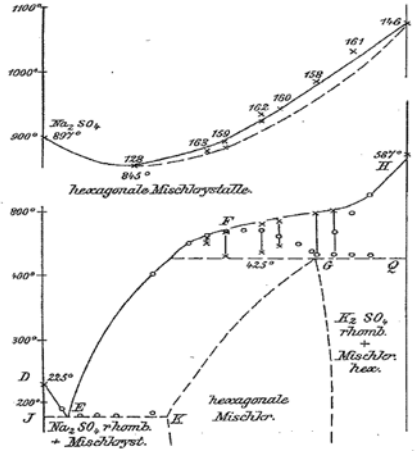




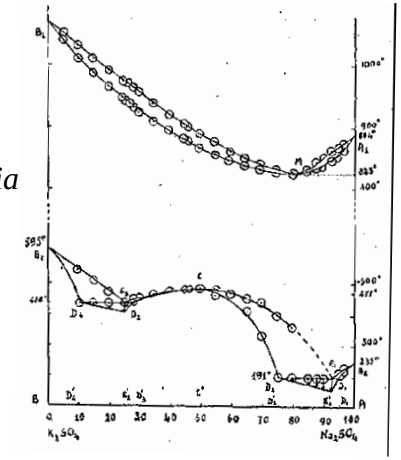
System Na_2SO_4-K_2SO_4: experimental data



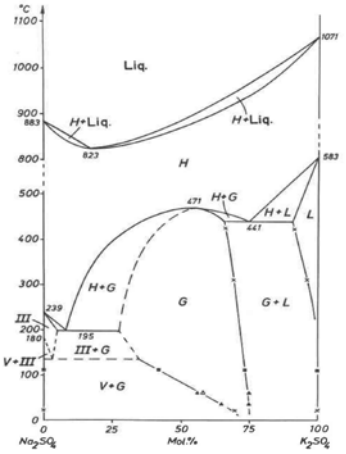
Nacken, R. *Neues Jahrb. Mineral., Geol. Palaeontol., Beilageband,* 1907, *24*, 1.



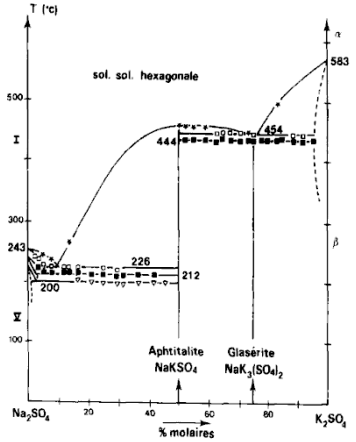
Jänecke, E. *Z. Phys. Chem.Stoechiom.Verwandschaftsl.* 1908, *64*, 343



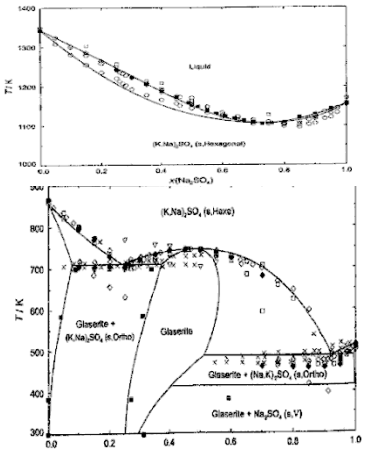
Bellanca, A. *Period. Mineral.* 1942, *13*, 21



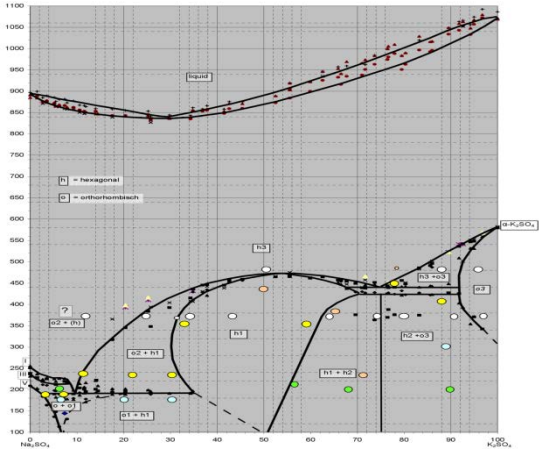
Eysel, W. *American Mineralogist* 1973, *58*, 736.



Mofaddel, N.; Bouaziz, R.; Mayer, M. *Thermochimica Acta* 1991, *185*, 141



Lindberg, D.; Backman, R.; Chartrand, P. *J. Chem. Thermodynamics* 2006, *38*, 1568



D. Kobertz (IEK-2, FZJ), CALPHAD Meeting, 2011
Phase diagram was obtained by DTA/TG studies

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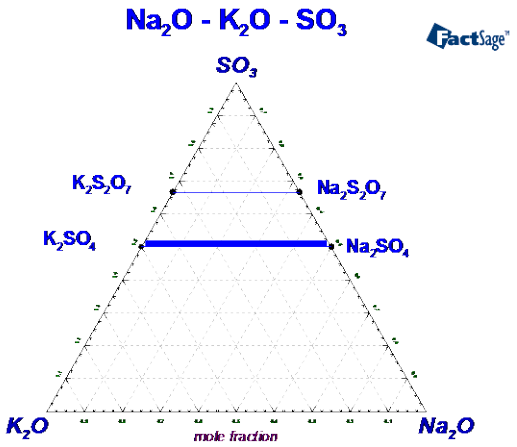
Modelling of phases in system Na_2SO_4-K_2SO_4

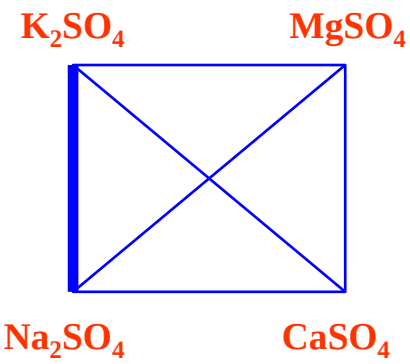
The species in the non-ideal associate solution containing SO_3 have already added in order to describe the liquid phase. Solid solutions were considered using multi-sublattice model

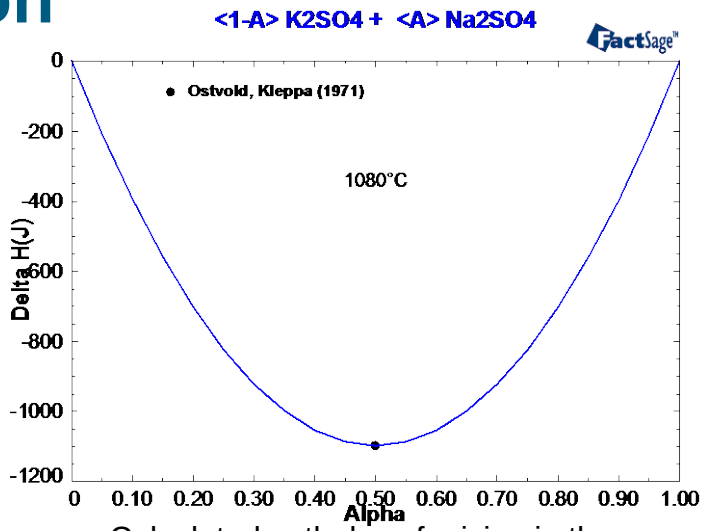
Phase	*Description of solid phase*	*Solubility*	*Data*
HEXA	Hexagonal solution: **$(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-})$**	Cation sublattice: **$(Na, K)_2SO_4$** $(Na, Mg)_2SO_4$ $(K, Mg)_2SO_4$ $(K, Ca)_2SO_4$ Anion sublattice: $K_2(SO_4, S)$ $Na_2(SO_4, S)$	Model from H. Du*, data on solution species from SGPS, parameter optimised by FZJ and GTT
GLAS	Glaserite: **$(K^{1+}, Na^{1+})_3(Na^{1+})(SO_4^{2-})_2$**	$K_3Na(SO_4)_2$ $Na_4(SO_4)_2$	Model from H. Du*, data on solution species from SGPS, parameter optimised by FZJ
Alpha	Solutions based on Na_2SO_4 (s2) and K_2SO_4 (s1) **$(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-})$**	2 solubilities: Na_2SO_4(s2) + K_2SO_4(s1) K_2SO_4(s1) + Na_2SO_4(s2)	Model from H. Du*, data on solution species from SGPS, parameter optimised by FZJ and GTT

H. Du, J. Phase Equilibria, **21 [1] 6-18 (2000).*

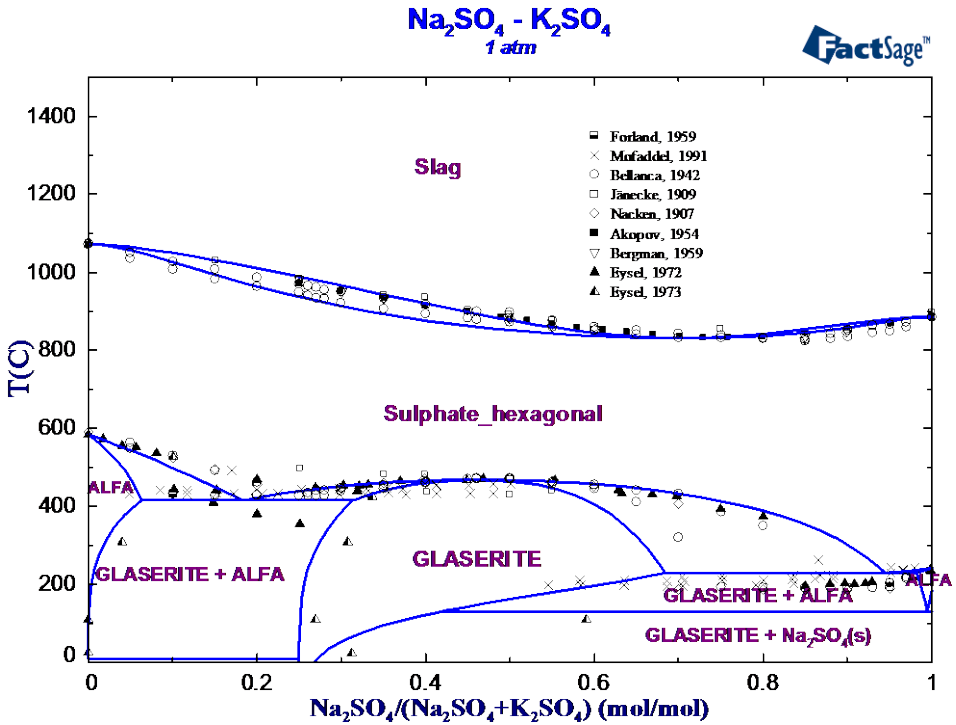
System Na_2SO_4-K_2SO_4: calculation

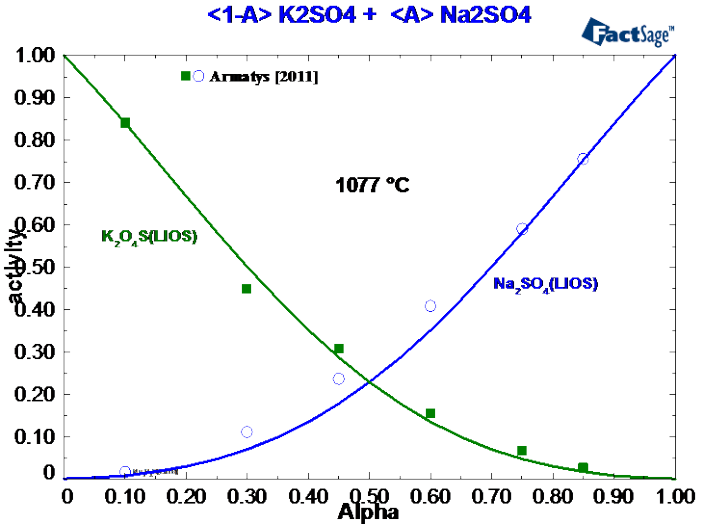






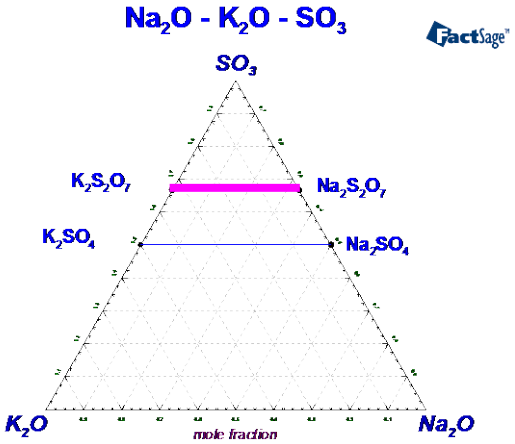
Calculated enthalpy of mixing in the liquid phase K_2SO_4-Na_2SO_4 at 1080°C.





Calculated activities in the liquid K_2SO_4-Na_2SO_4 at 1077°C

Modelling of phases in system $Na_2S_2O_7$-$K_2S_2O_7$

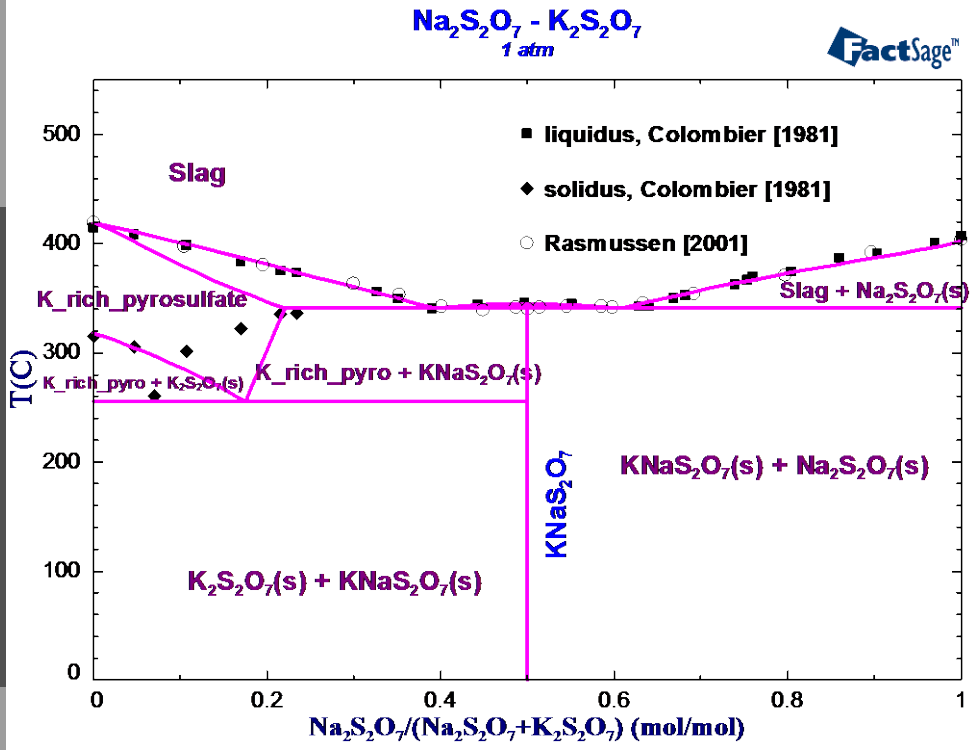


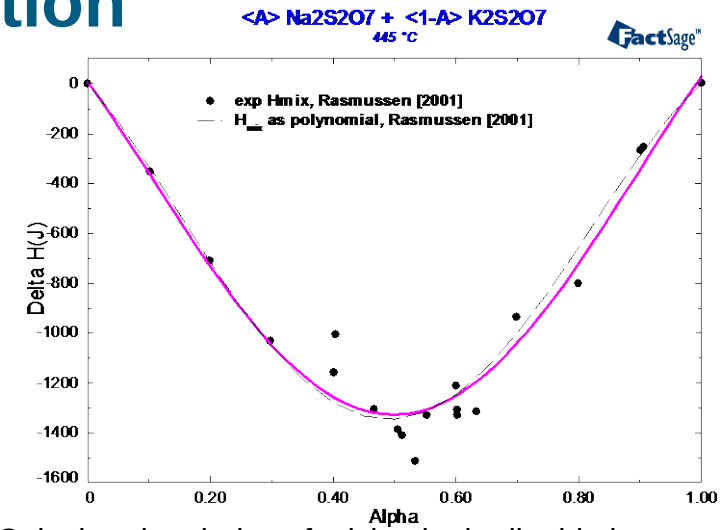
The compound $KNaS_2O_7$ was taken from Pulp*

Phase	*Description of phase*	*Solubility*	*Data*
Slag	Na_2O, Na_2SO_4, $Na_2S_2O_7$, SO_3, (Na_2S), K_2O, K_2SO_4, $K_2S_2O_7$, (K_2S)		parameter optimised by FZJ
PYRO	K-rich pyrosulphate: **$(K^{1+}, Na^{1+})_2(S_2O_7^{2-})$**	$K_2S_2O_7$ (s2) $Na_2S_2O_7$ (s1)	data on solution species from Pulp*, parameter optimised by FZJ

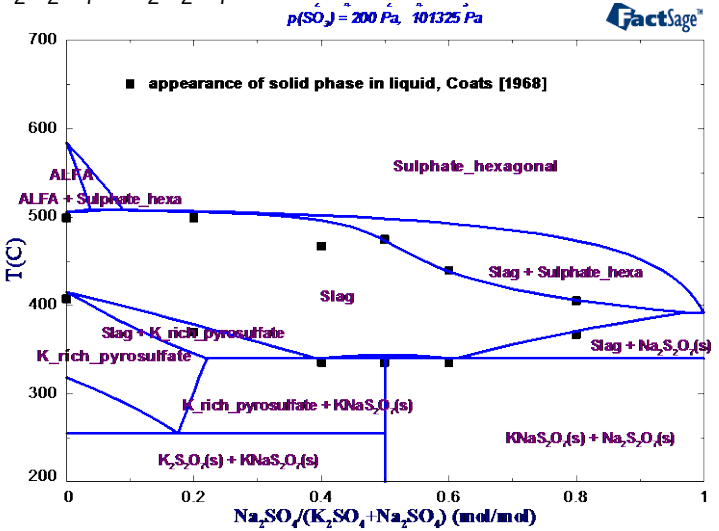
D. Lindberg, R. Backman, P. Chartrand, J. Chem. Thermodyn., **38, 1568-1583 (2006).*

System $Na_2S_2O_7$-$K_2S_2O_7$: calculation



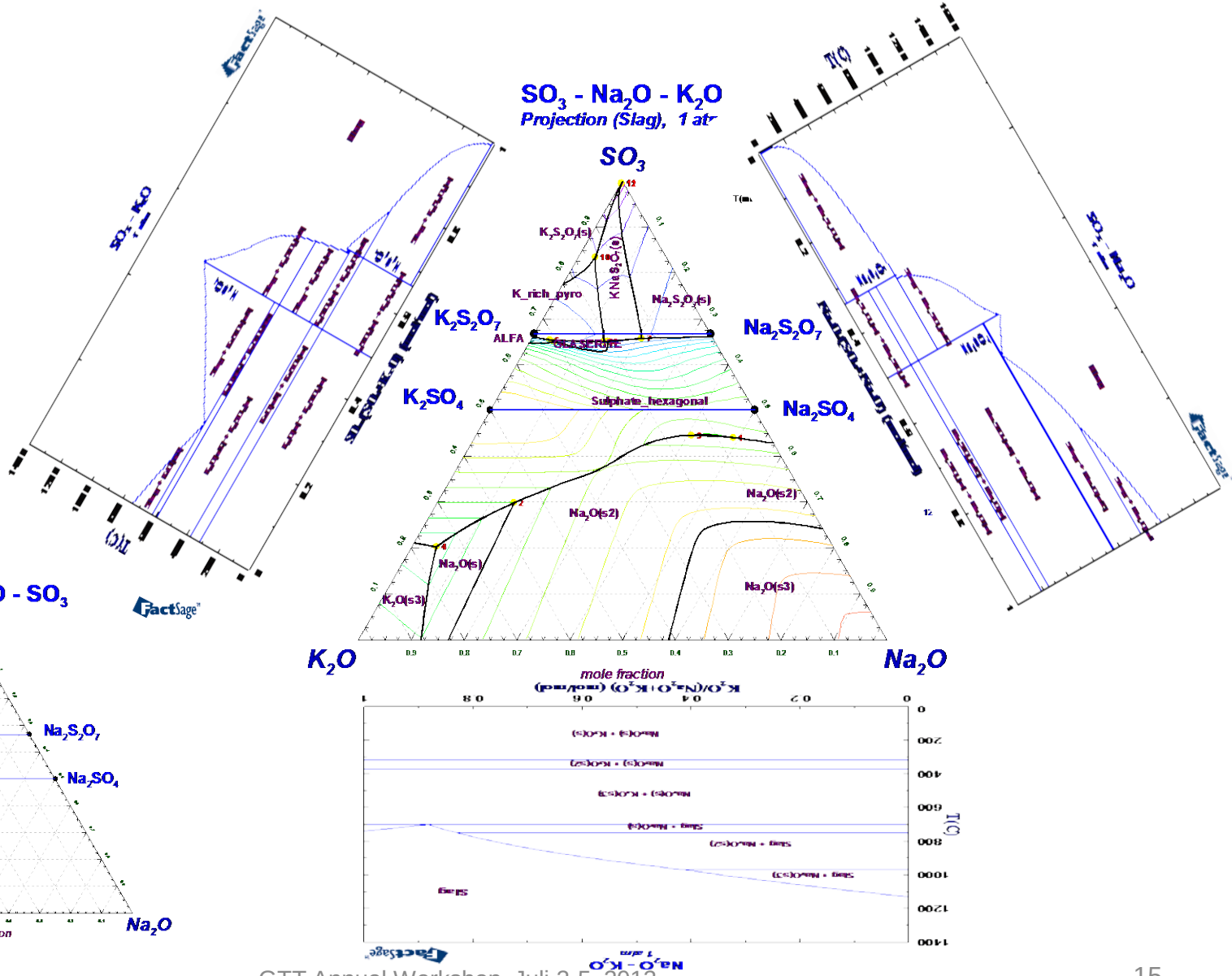


Calculated enthalpy of mixing in the liquid phase $K_2S_2O_7$-$Na_2S_2O_7$ at 445°C.



Alk_2SO_4-Alk_2S2O_7 system: calculated phase equilibrium of the condensed phases at $p(SO_3)$=200 Pa and a total pressure of 1 atm

System Na_2O-K_2O-SO_3



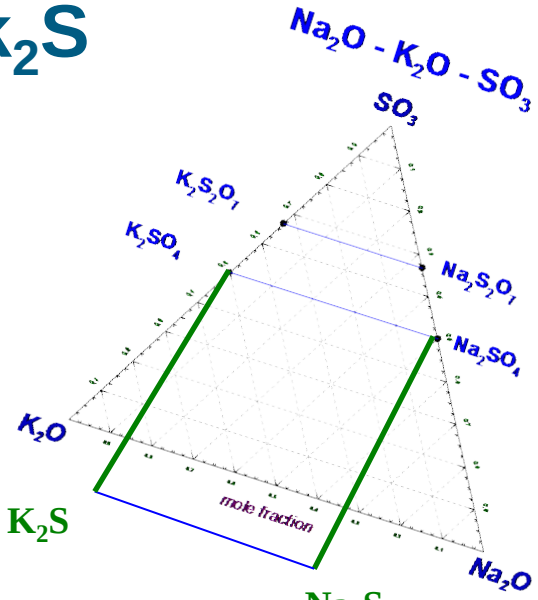
Systems Alk_2SO_4-Alk_2S (Alk=Na, K

The species in the non-ideal associate solution containing SO_3 and S^{2-} have already added in order to describe the liquid phase. Solid solutions were considered using multi-sublattice model

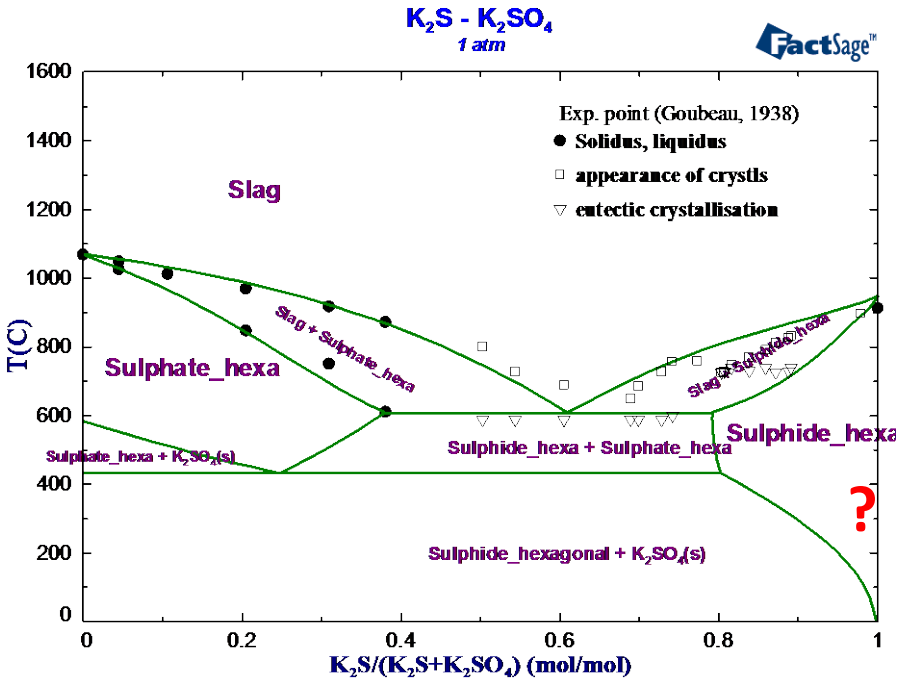
Phase	*Description of solid phase*	*Solid solutions*	*Data*
HEXA	Hexagonal solution: **$(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-})$**	Cation sublattice: **$(Na, K)_2SO_4$** $(Na, Mg)_2SO_4$ $(K, Mg)_2SO_4$ $(K, Ca)_2SO_4$ Anion sublattice: **$K_2(SO_4, S)$** **$Na_2(SO_4, S)$**	Model from H. Du*, data on solution species from SGPS, parameter optimised by FZJ and GTT
HEXB	Hexagonal solution based on Alk_2S **$(K^{1+}, Na^{1+})_2(S^{2-}, SO_4^{2-})$**	Cation sublattice: **$(Na, K)_2S$** Anion sublattice: **$K_2(S, SO_4)$** **$Na_2(S, SO_4)$**	Data on solution species from SGPS, parameter optimised by FZJ

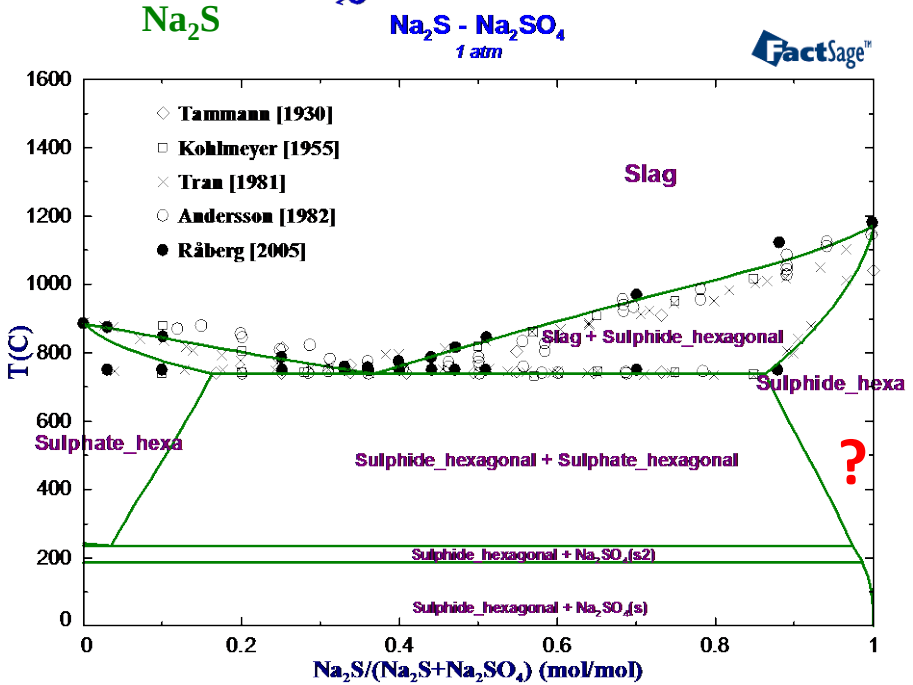
H. Du, J. Phase Equilibria, **21 [1] 6-18 (2000).*

Systems Alk_2SO_4-Alk_2S

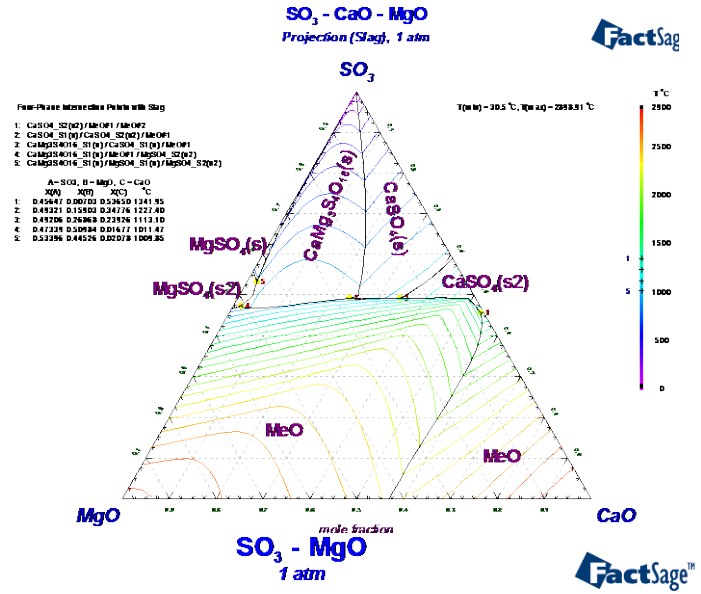


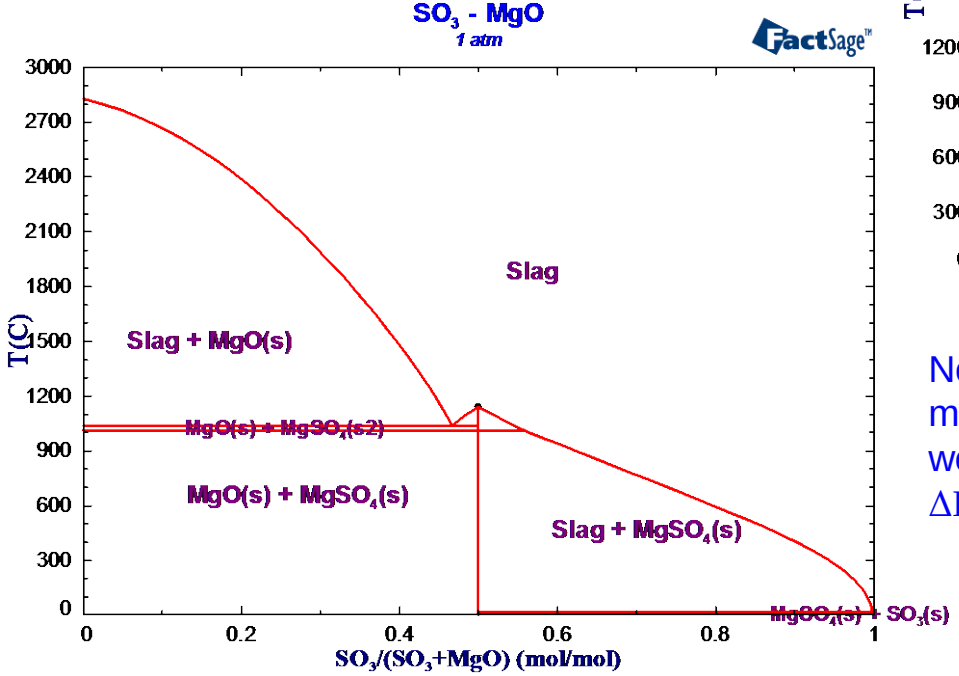
The system K_2S-Na_2S has been optimised

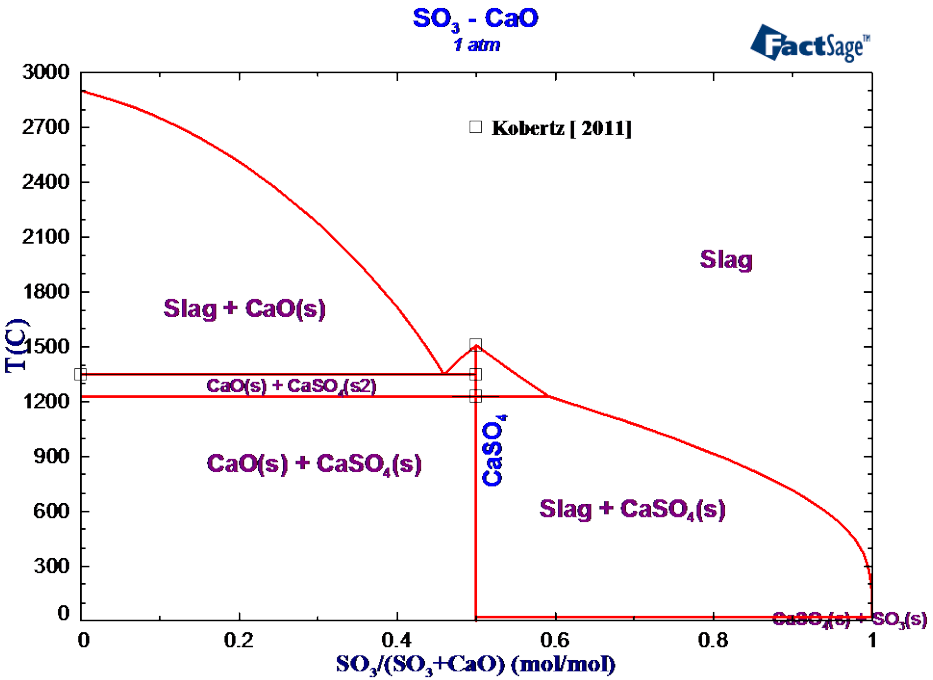




System $CaO-SO_3$ and $MgO-SO_3$





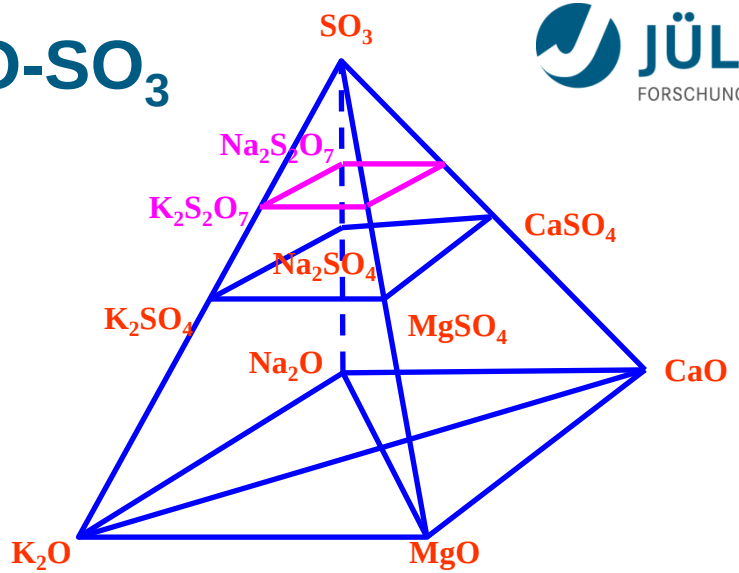


New experimental data on $CaSO_4$ (DTA measurements, closed cruicible D.Kobertz [2011]) were used for the optimisation: T_{tr} and ΔH_{tr}, T_m and ΔH_m.

System Na_2O-K_2O-CaO-MgO-SO_3

All phases in the system are considered, the solid solubilities between alkali and earth-alkali cations in HEXA phase are included, the quasi-binary compounds are created from the sulphates.

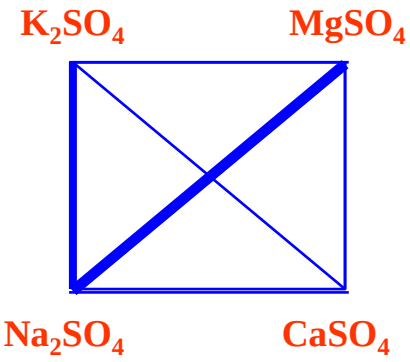
- $CaSO_4$*$3MgSO_4$
- K_2SO_4*$2MgSO_4$
- $3Na_2SO_4$*$CaSO_4$
- Na_2SO_4*$CaSO_4$
- $3Na_2SO_4$*$MgSO_4$
- Na_2SO_4*$MgSO_4$
- Na_2SO_4*$3MgSO_4$
- K_2SO_4*$2CaSO_4$

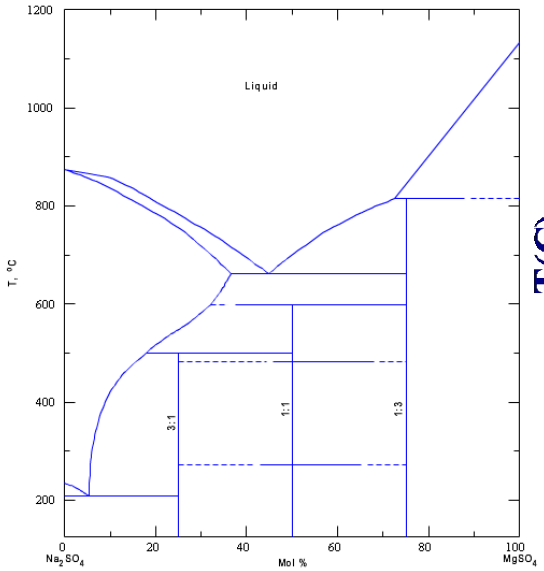


Phase	*Description of solid phase*	*Solubility*	*Data*
HEXA	Hexagonal solution: **$(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-})$**	Cation sublattice: **$(Na, K)_2SO_4$** **$(Na, Mg)_2SO_4$** **$(K, Mg)_2SO_4$** **$(K, Ca)_2SO_4$** Anion sublattice: $K_2(SO_4, S)$ $Na_2(SO_4, S)$	Model from H. Du*, data on solution species from SGPS, parameter optimised by FZJ and GTT
Alpha	Solutions based on Na_2SO_4 (s2) and K_2SO_4 (s1) **$(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-})$**	2 solubilities: Na_2SO_4(s2) + K_2SO_4(s1) K_2SO_4(s1) + Na_2SO_4(s2)	Model from H. Du*, data on solution species from SGPS, parameter optimised by GTT and FZJ

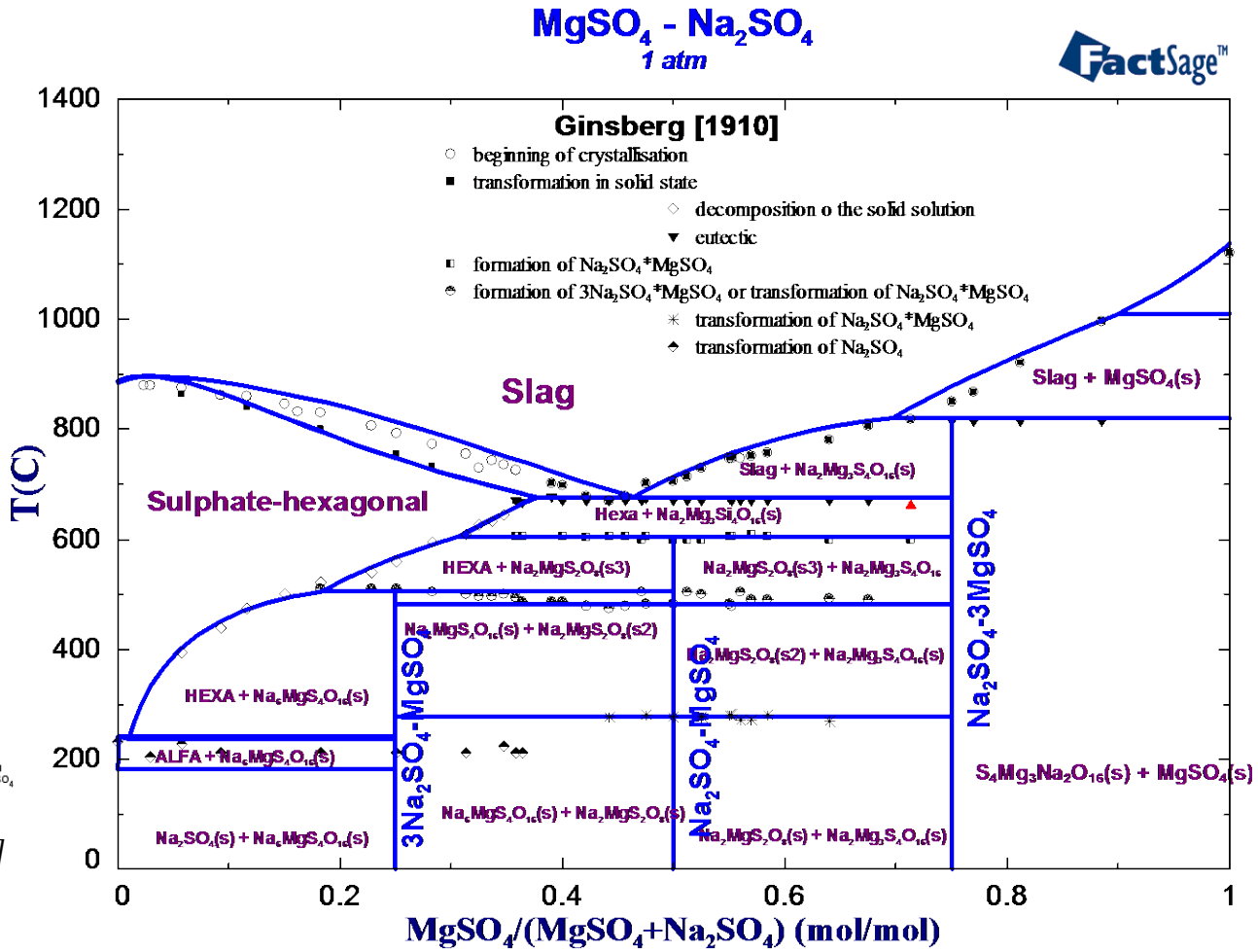
H. Du, J. Phase Equilibria, **21 [1] 6-18 (2000).*

System Na_2SO_4-$MgSO_4$

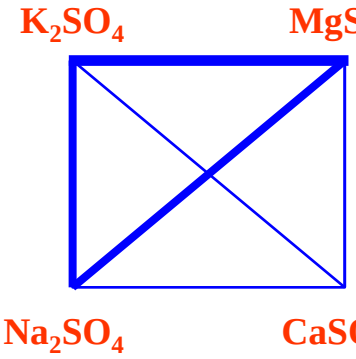


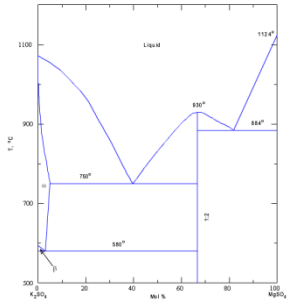


*A.S. Ginsberg, Z. Anorg. Chem., **61** [1] 122-136 (1910).*

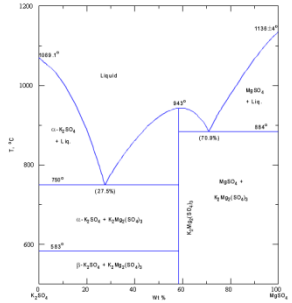


Preliminary phase diagram of the system K_2SO_4-$MgSO_4$

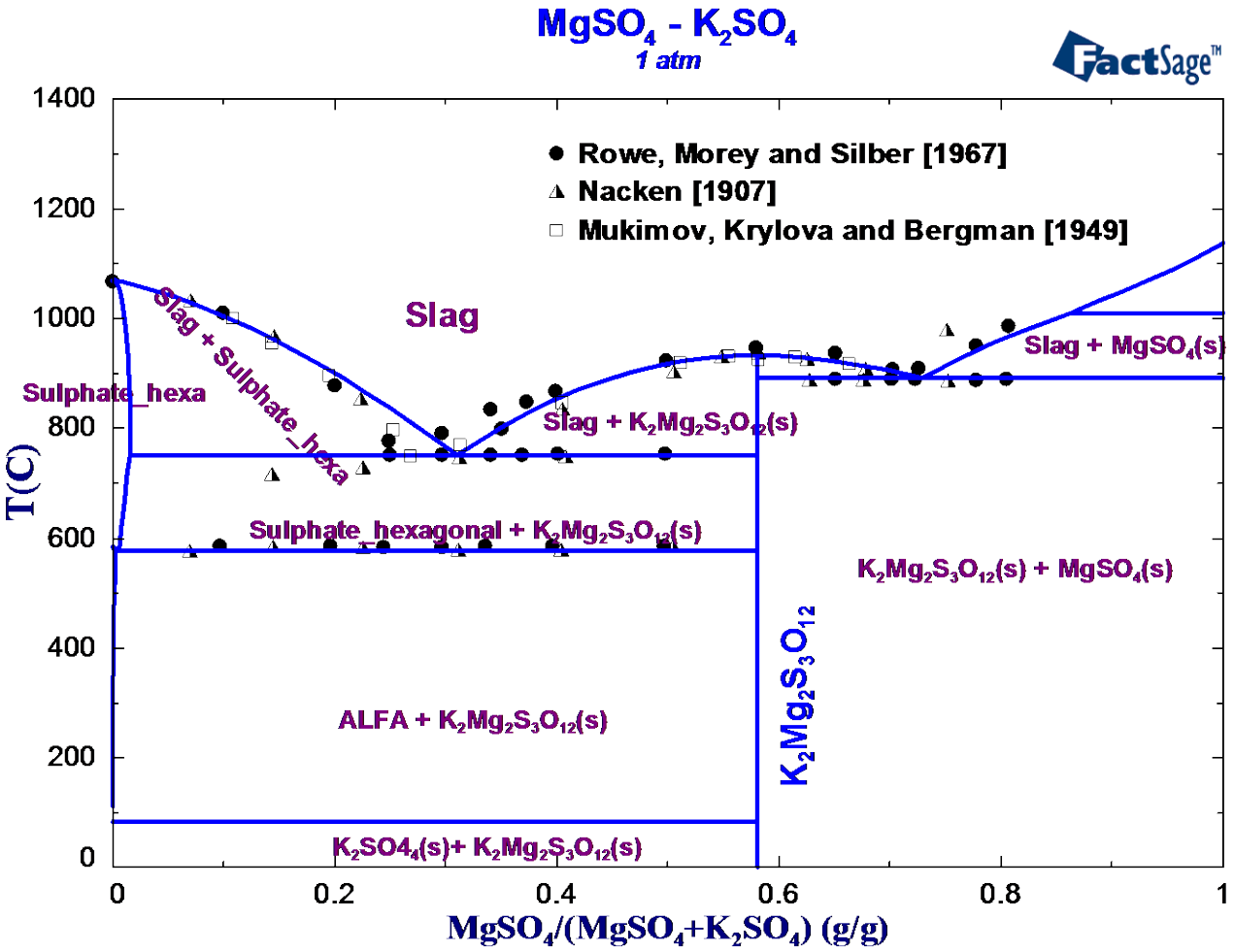




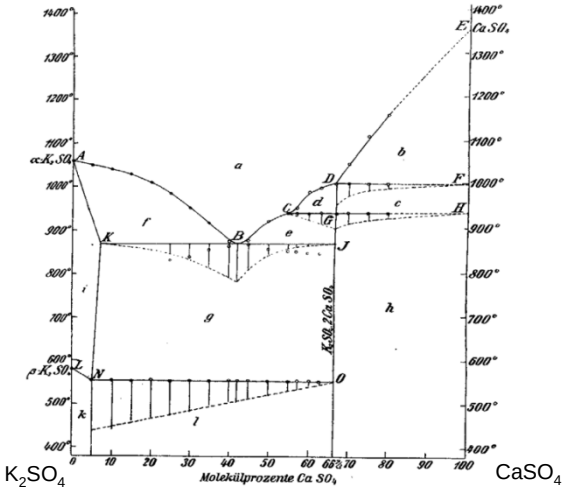
W. Grahmann, *Z. Anorg. Chem.*, **81** [3] 257-314 (1913).



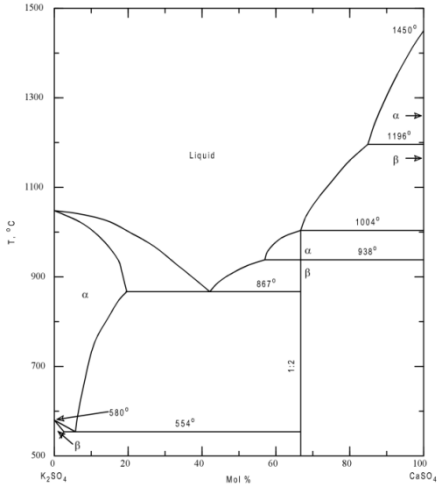
J. J. Rowe, G. W. Morey, and C. C. Silber, *J. Inorg. Nucl. Chem.*, **29** [4] 925-942 (1967).



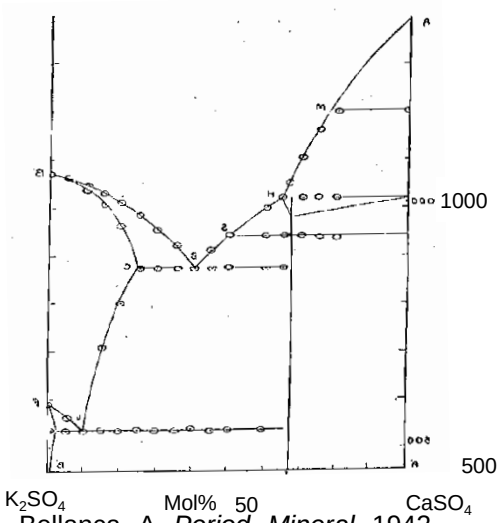
Different existing diagrams of the system K_2SO_4 - $CaSO_4$



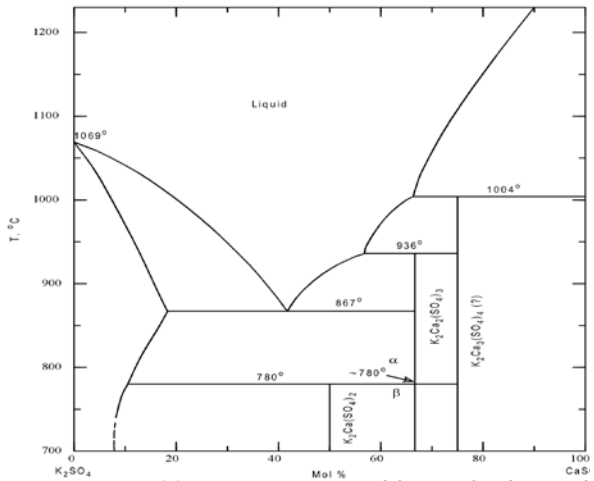
Müller, H. *Neues Jahrb. Mineral., Geol. Palaeontol., Beilageband* 1910, *30*, 1-54.



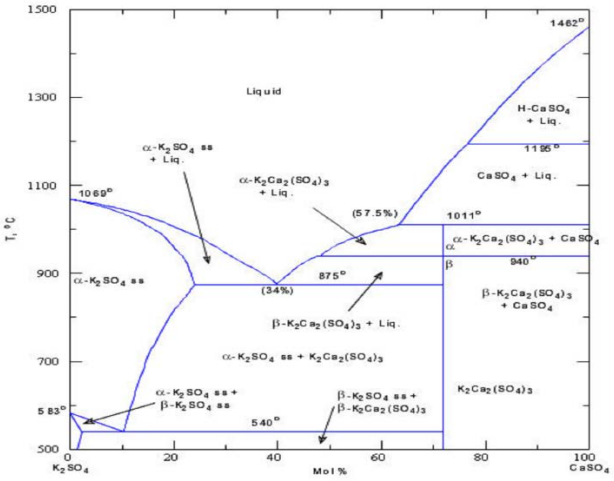
W. Grahmann, *Z. Anorg. Chem.*, 81 [3] 257-314 (1913).



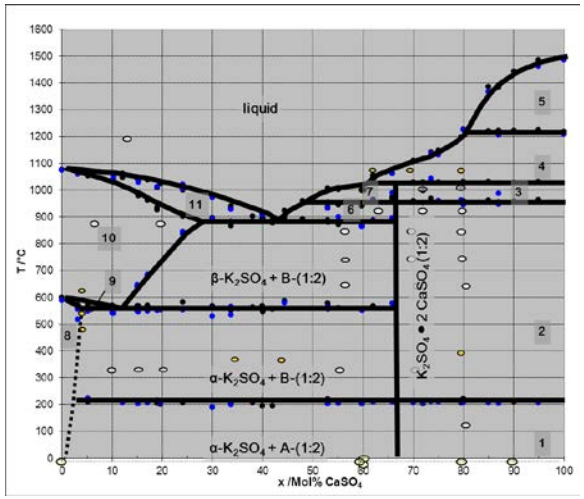
Bellanca, A. *Period. Mineral.* 1942, *13*, 21-85.



S. M. Mukimov, *Tr. Inst. Khim., Akad. Nauk Uzb. SSR*, No. 2, 94-112 (1949).

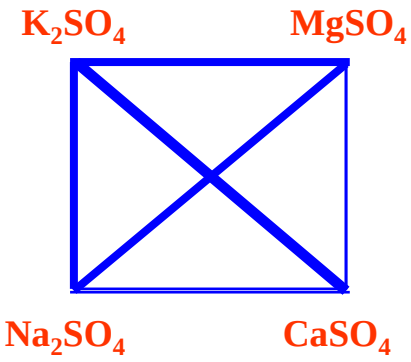


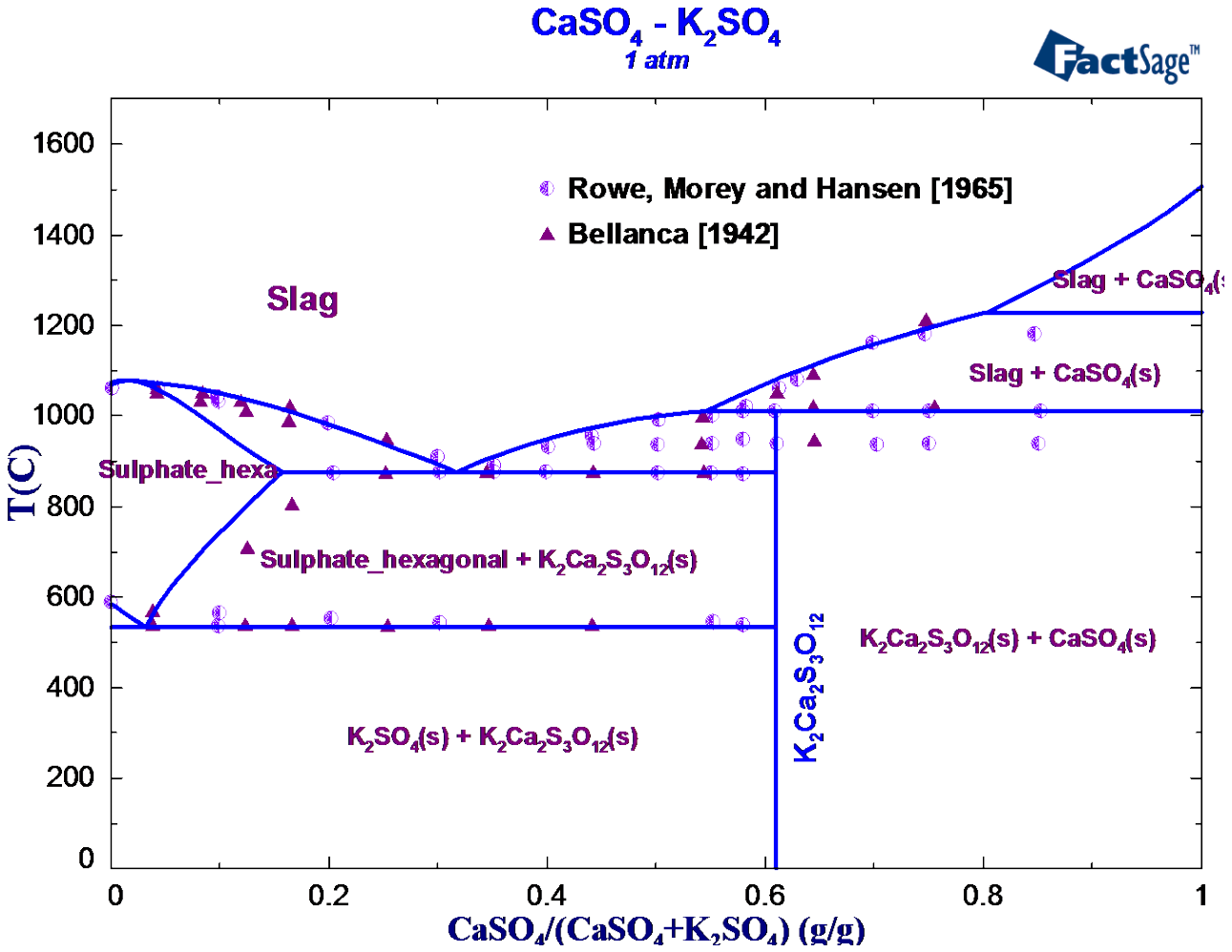
J. J. Rowe, G. W. Morey, and I. D. Hansen, *J. Inorg. Nucl. Chem.*, 27 [1] 53-58 (1965).



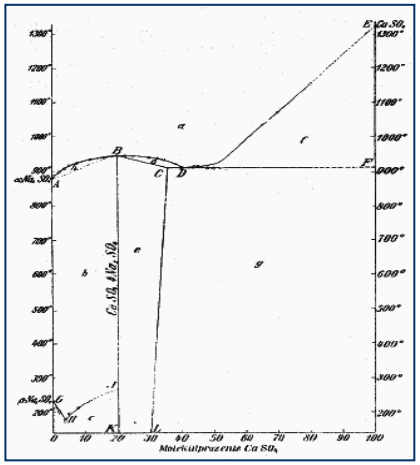
D. Kobertz (IEK-2, FZJ), Calphad Meeting (2011)

Preliminary phase diagram of the system K_2SO_4-$CaSO_4$

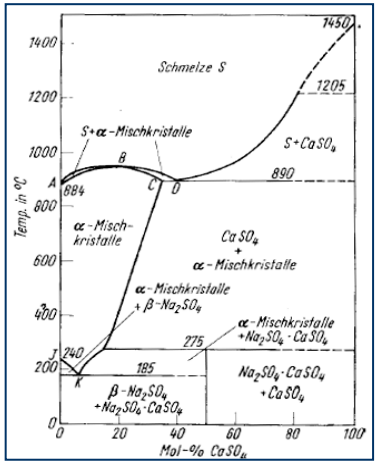




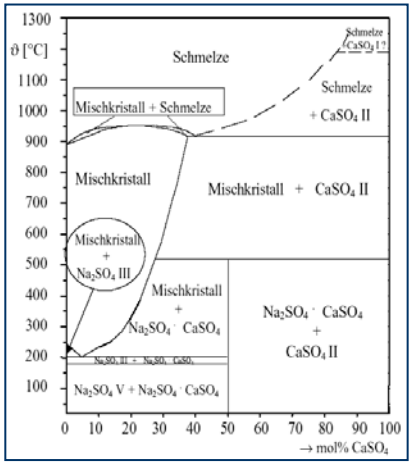
Different existing diagrams of the system Na_2SO_4 - $CaSO_4$



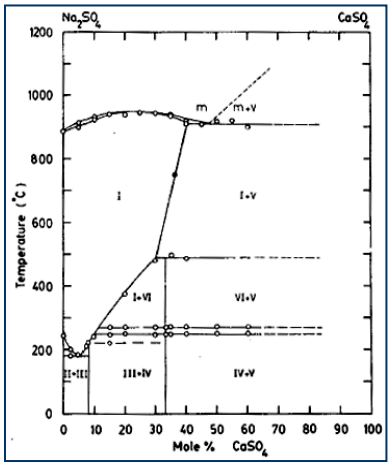
Hans Müller, Göttingen, 1910, Neues Jahrb. Mineral., Geol. Palaeontol., Beilageband, 30, 1-54 (1910)



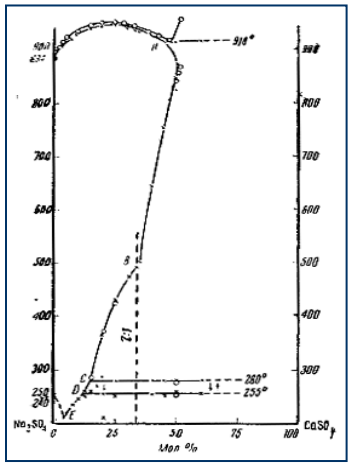
L.N. Komissarova et al. Trans. Mosk. Inst. Tonkoi Khim. Tekhnol., 5, 3, (1955)



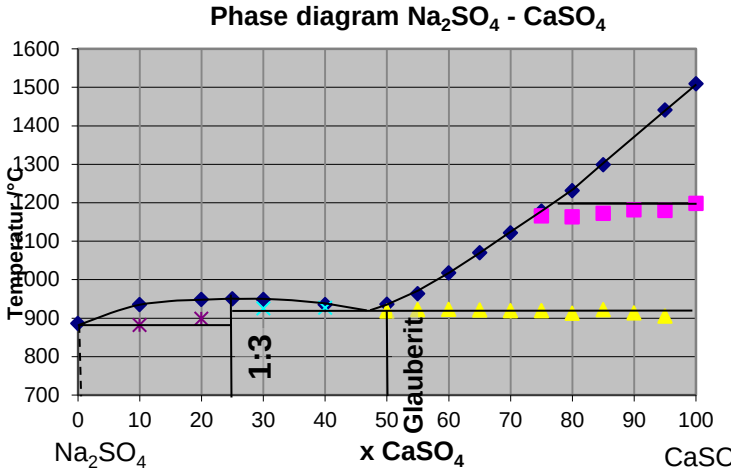
D. Freyer, Dissertation, TU Bergakademie Freiberg (2000)



P.W.S.K. Bandaranayake and B.E. Mellander, Solid State Ionics, 26, 33, (1988)

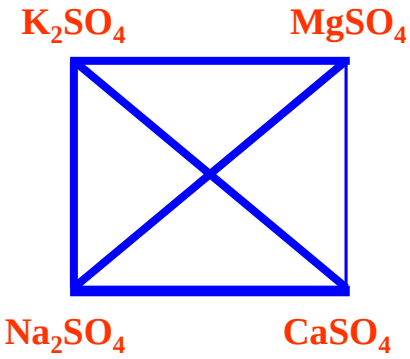


E.I. Speranskaja et al., Zh. Neorg. Khim., 6, 1392, (1961)

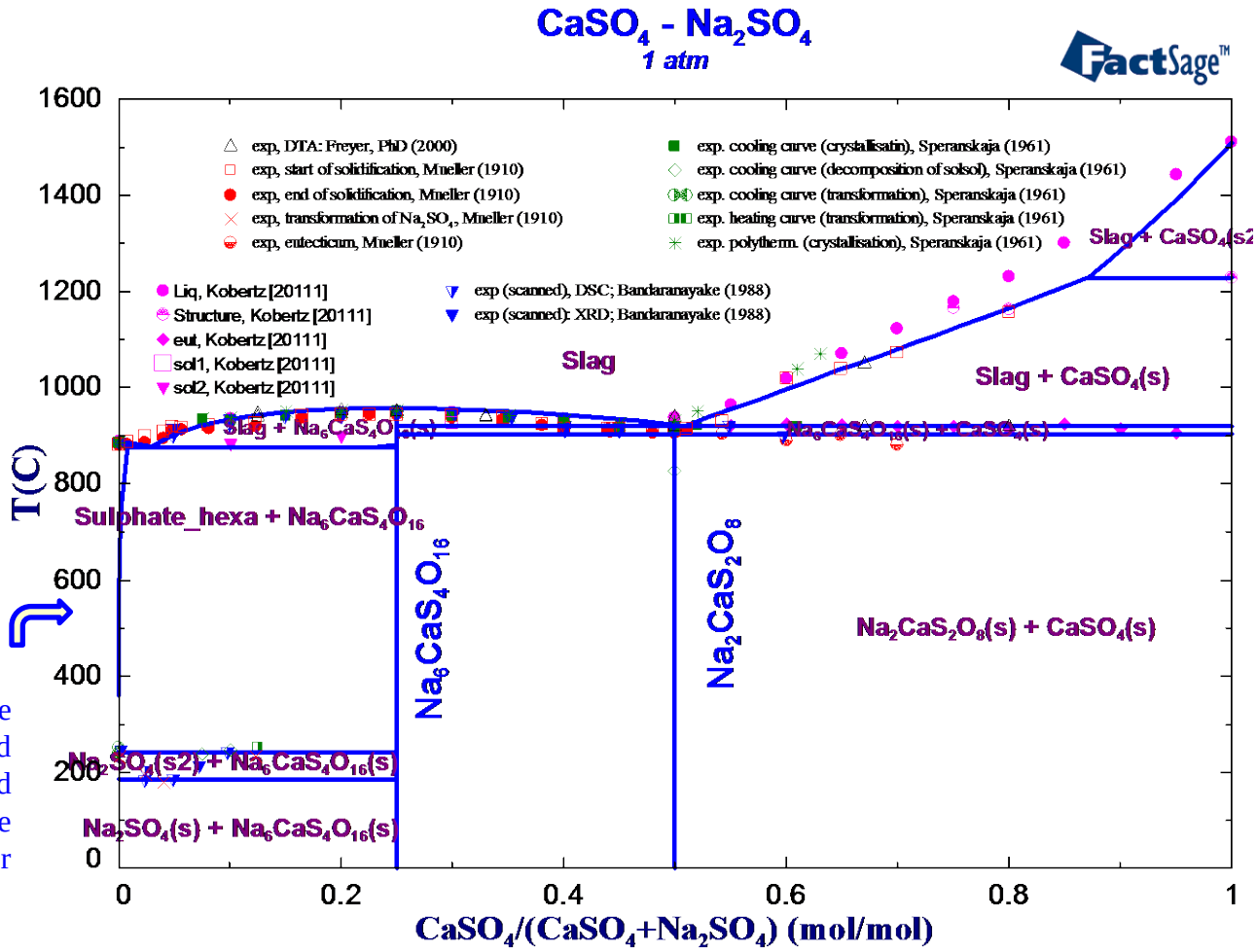


D. Kobertz (IEK-2, FZJ), Calphad Meeting (2011)

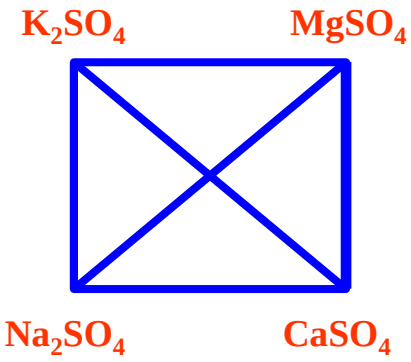
Preliminary phase diagram of the system Na_2SO_4-$CaSO_4$

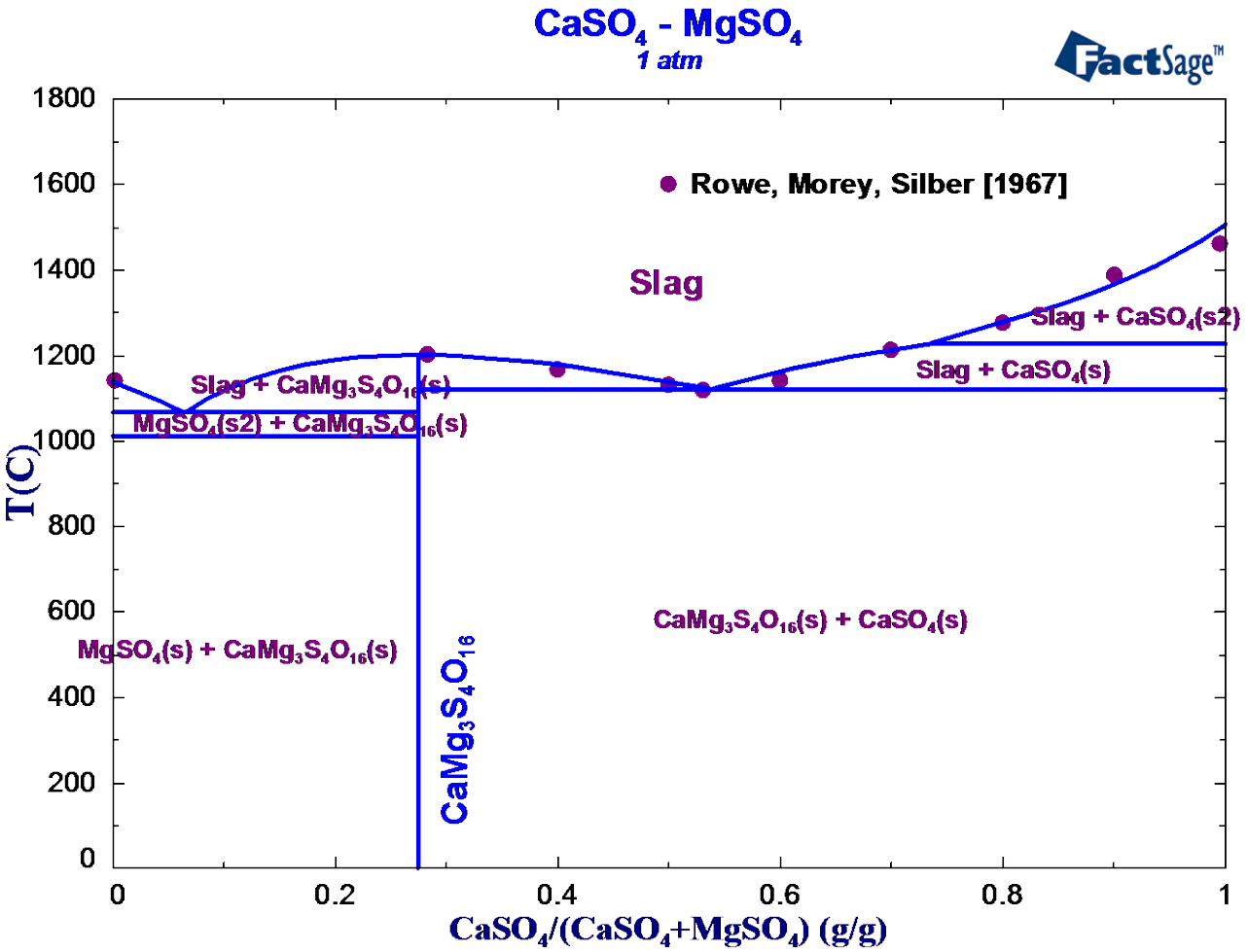


In the system Na_2SO_4-$CaSO_4$ the existence of the compound $3Na_2SO_4$*$CaSO_4$ instead of the solid solution was suggested from the experiments (DTA, XRD). The further measurements are carrying out.



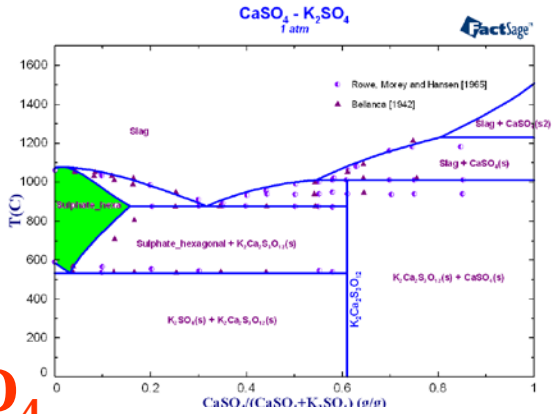
System $CaSO_4$-$MgSO_4$



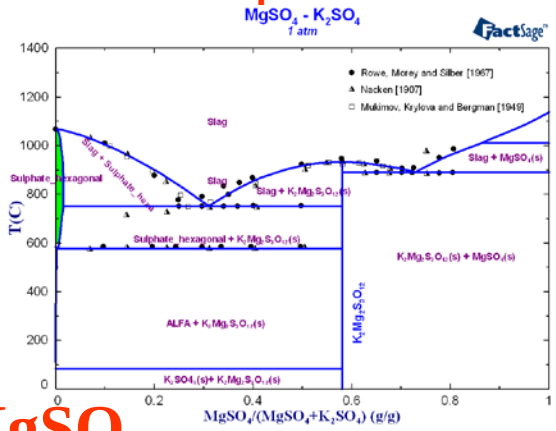


Hexagonal phase

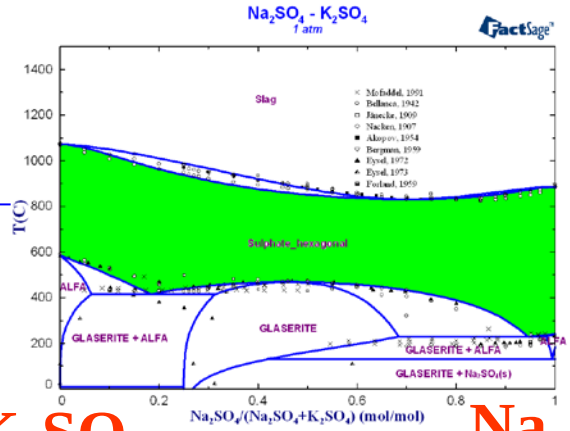
$(Ca^{2+}, K^{1+}, Mg^{2+}, Na^{1+})_2(SO_4^{2-}, S^{2-})$



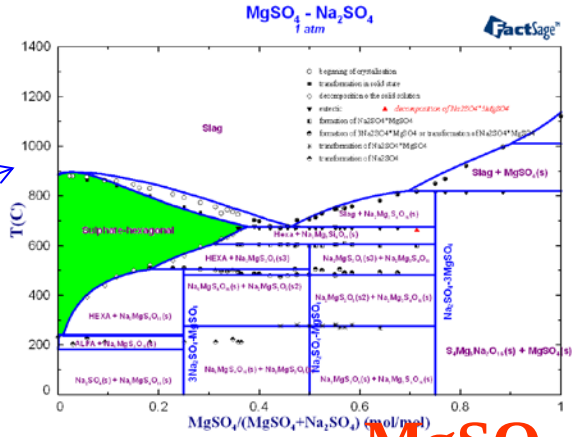
$CaSO_4$



$MgSO_4$

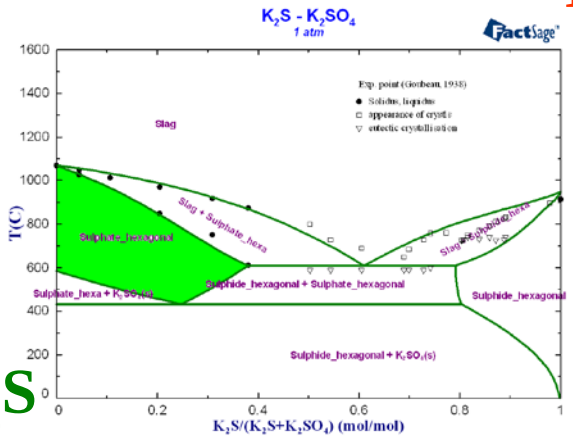


K_2SO_4



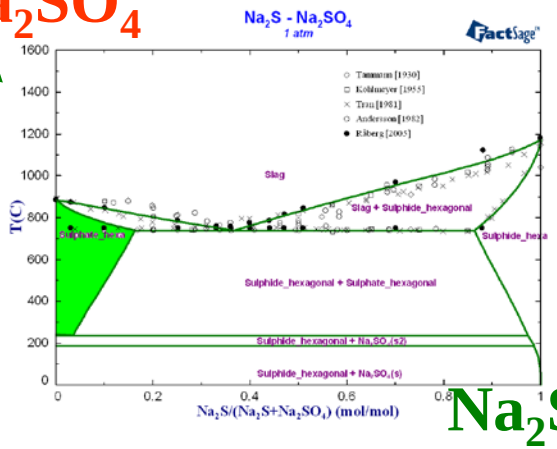
$MgSO_4$

Na_2SO_4



K_2S

In the system Na_2SO_4-$CaSO_4$ the new compound $3Na_2SO_4$*$CaSO_4$ instead of the solid solution was found. The experiments (DTA, XRD) are needed.



Na_2S

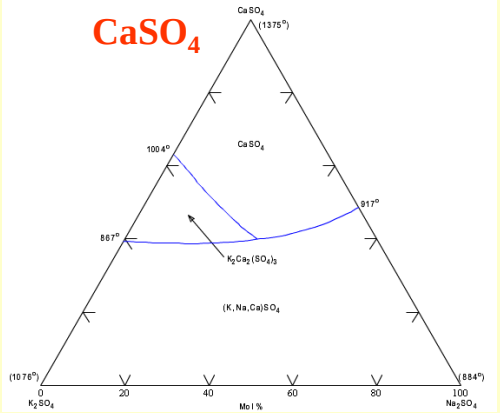
Conclusions

- ✓ SO_3 (liq) and solution species with S^{6+} have been included into the slag of the system Na_2O-K_2O-CaO-MgO-SO_3. The liquid phase in all subsystems was evaluated using non-ideal associate species model (two cations per species).
- ✓ The Sulphate hexagonal phase with the corresponding parameters can describe both solubilities in the cation (Na^{1+}, K^{1+}, Ca^{2+}, Mg^{2+}) and in the anion (SO_4^{2-}, S^{2-}) sublattices
- ✓ All systems were assessed using experimental phase diagram information.
- ✓ The quasi-binary sections between sulphates in the system Na_2O-K_2O-CaO-MgO-SO_3 have been calculated using the corresponding data

Outlook

- ✓ Thermodynamic assessment of ternary sulphate systems
- ✓ Addition of FeO_x to the system Na_2O-K_2O-CaO-MgO-SO_3

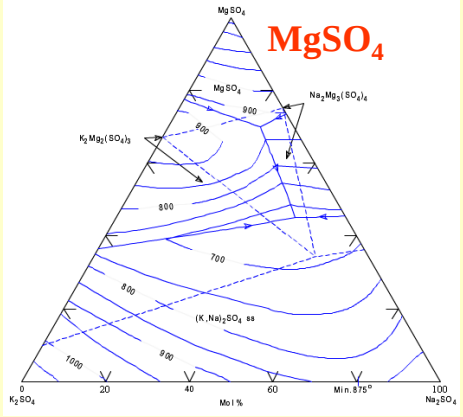
Ternary diagrams in the system Na_2O-K_2O-CaO-MgO-SO_3



$CaSO_4$

K_2SO_4 Na_2SO_4

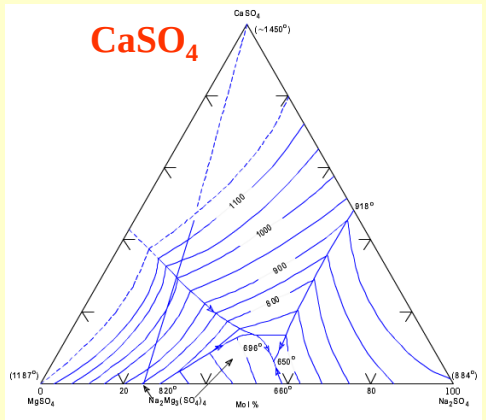
A. Bellanca, *Period. Mineral.*, **13** [1] 21-85 (1942).



$MgSO_4$

K_2SO_4 Na_2SO_4

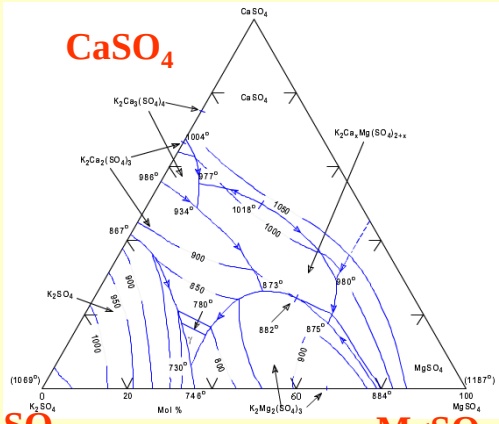
E. Jaenecke, *Z. Anorg. Chem.*, **261** [3-4] 213-225 (1950).



$CaSO_4$

$MgSO_4$ Na_2SO_4

S. M. Mukimov and Z. I. Filippova, *Tr. Inst. Khim., Akad. Nauk Uzb. SSR*, **No. 2**, 123-132 (1949).



$CaSO_4$

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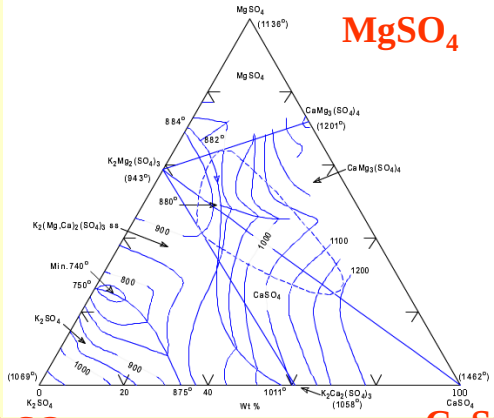
S. M. Mukimov et al., *Tr. Inst. Khim., Akad. Nauk Uzb. SSR*, **No. 2**, 94-112 (1949).



$MgSO_4$

K_2SO_4 $CaSO_4$

J. J. Rowe, G. W. Morey, and C. C. Silber, *J. Inorg. Nucl. Chem.*, **29** [4] 925-942 (1967)

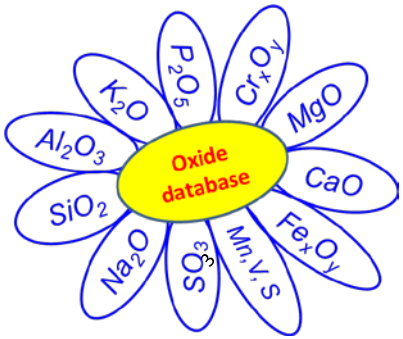
On behalf of all co-authors:

Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Благодарю за внимание!

HOTVEGAS



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