Database development for the HotVeGas project

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GTT Users' Meeting 2019, June 26 - June 28, Herzogenrath, Germany

Oxide database

HotVeGas Project

HOTVEGAS
Hochtemperaturvergasung und Gasreinigung

Basic experiments and thermochemical modelling

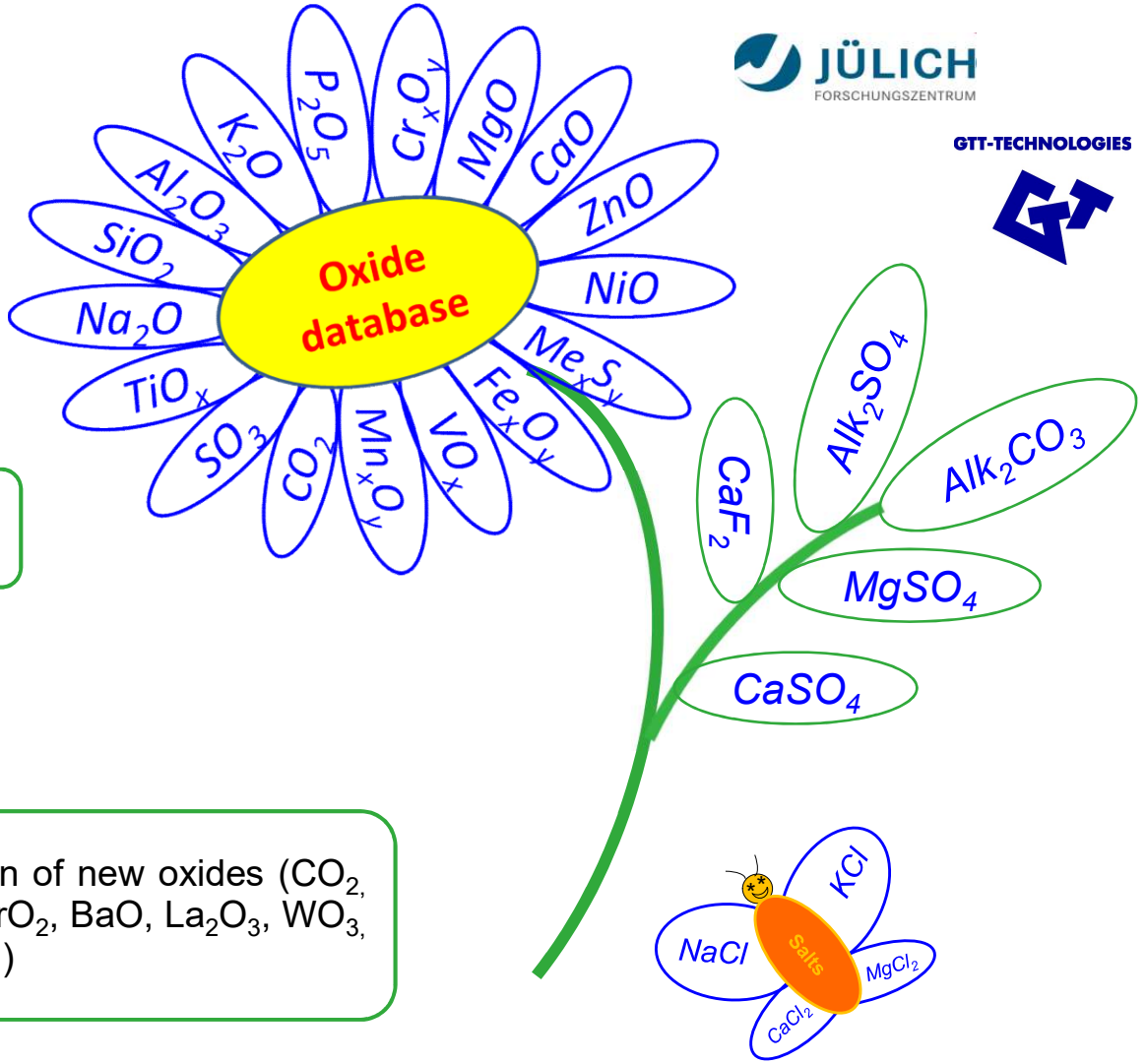
Experiments

(slag, membranes, trace elements, etc.; with TA, XRD, KEMS, MBMS, Visco, etc.)

Database development

Work on various sub-systems for the purpose of database` completeness (ZnO, NiO, SO_3, TiO_2, V_2O_5)

Addition of new oxides (CO_2, SrO, ZrO_2, BaO, La_2O_3, WO_3, H_2O….)



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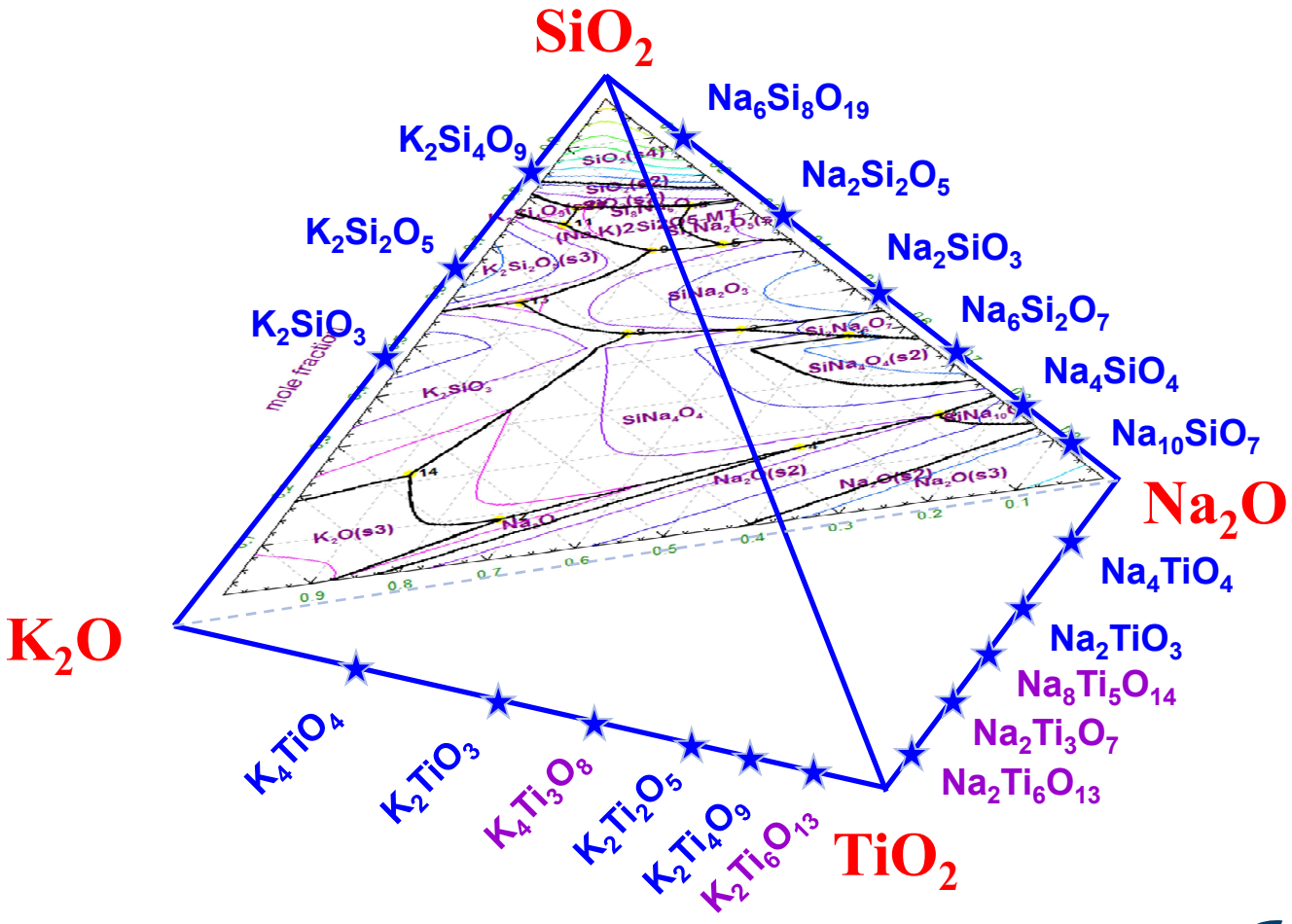
GTT-TECHNOLOGIES

Alkali +TiO_2

Database development: $Si^{4+}O_2$ replaced by $Ti^{4+}O_2$



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Alk_2O-TiO_2

Thermodynamic data

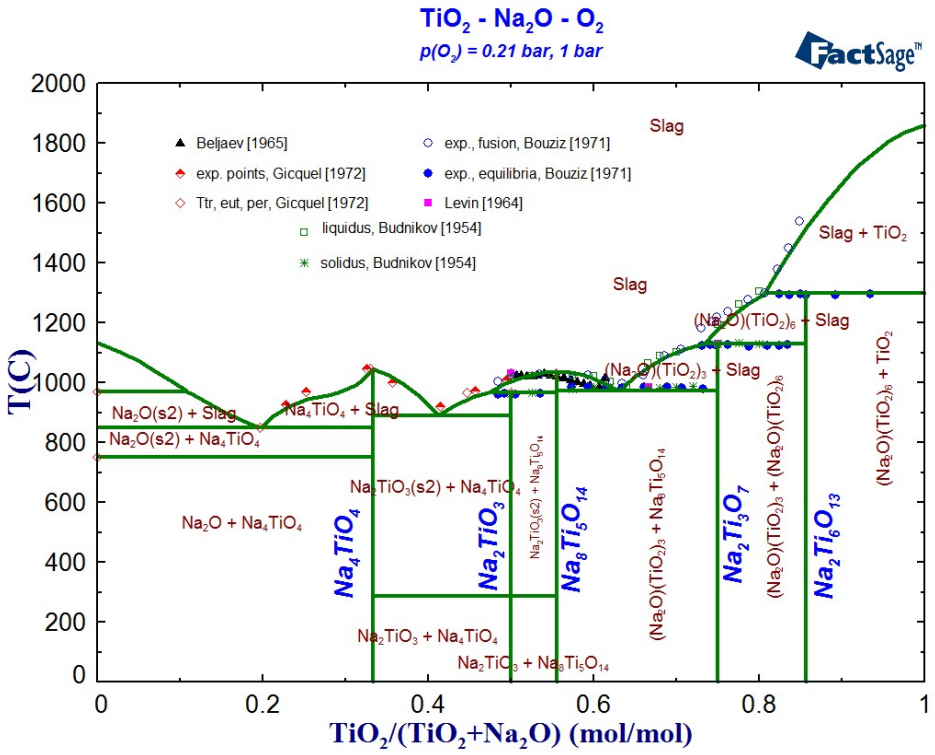
mole% TiO_2	Compound	Cp	ΔH_f^0, S^0	Compound	Cp	ΔH_f^0, S^0
0.333	**Na_4TiO_4**	FTox [1]	S [1]; H_f, ΔH_m optimised	**K_4TiO_4**	FTox [1]	S as [1] for Na_4TiO_4 H optimised; ΔH_m – [1]
0.5	**Na_2TiO_3**	SGPS [2,3]	S [SGPS]; H - exp. [4]	**K_2TiO_3**	FTox [1]	S as [1] for Na_2TiO_3; H exp. [4]
0.555	**$Na_8Ti_5O_{14}$**	FTox [1]	H, S-optimised			
0.6				**$K_4Ti_3O_8$**	NK	H,S optimised; confirmed in [5,6]
0.667	**$Na_2Ti_2O_5$***	SGPS	Not stable	**$K_2Ti_2O_5$***	FTox [1]	S as [1] for $Na_2Ti_2O_5$; H opt.
0.75	**$Na_2Ti_3O_7$**	FTox [1]	S-[1], H- optimised	**$K_2Ti_3O_7$**	*It was not considered, because its existence is not confirmed in literature*	
0.8				**$K_2Ti_4O_9$**	NK	H,S optimised; confirmed in [7,8]
0.857	**$Na_2Ti_6O_{13}$**	FTox [1]	S– exp. [9]; H–optimised	**$K_2Ti_6O_{13}$**	FTox [1]	H,S optimised

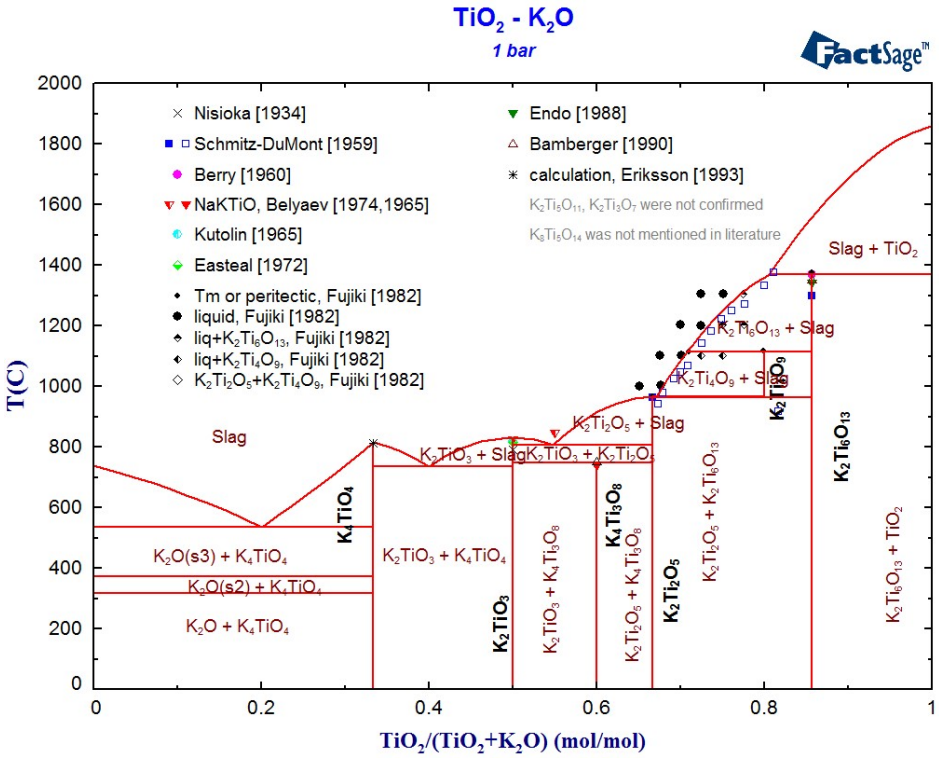
[1] G. Eriksson, A.D. Pelton, Metal. Trans. B 24 (1993) 795-805.
[2] SGPS - SGTE pure substances database (v13.1) 2017.
[3] I. Barin, Thermochemical Data of Pure Substances, 1995.
[4] B.I. Panfilov, Zh. Neorg. Khim. 10(8) (1965) 1844-1847.
[5] E.K. Belyaev et al., Neorg. Mater. 10(3) (1974) 460-464.
[6] C.E. Bamberger et al., Applied Spectroscopy 44(1) (1990) 30-37.
[7] A.J. Easteal, D.J. Udy, High Temp. Sci. 4 (1972) 487-495.
[8] F. Yoshinori, Yogyo Kyokai-Shi 90(10) (1982) 76-78
[9] J.M. Stuve, J. Chem. Eng. Chem. 27 (1982) 391-392

Alk_2O-TiO_2

Calculated phase equilibria

phase	description (Alk=Na, K)
slag	**Alk_2O**, Ti, Ti_2O_2, Ti_2O_3, **Ti_2O_4**, **Alk_4TiO_4/2.5**
$Alk_xTi_yO_z$	stoichiometric





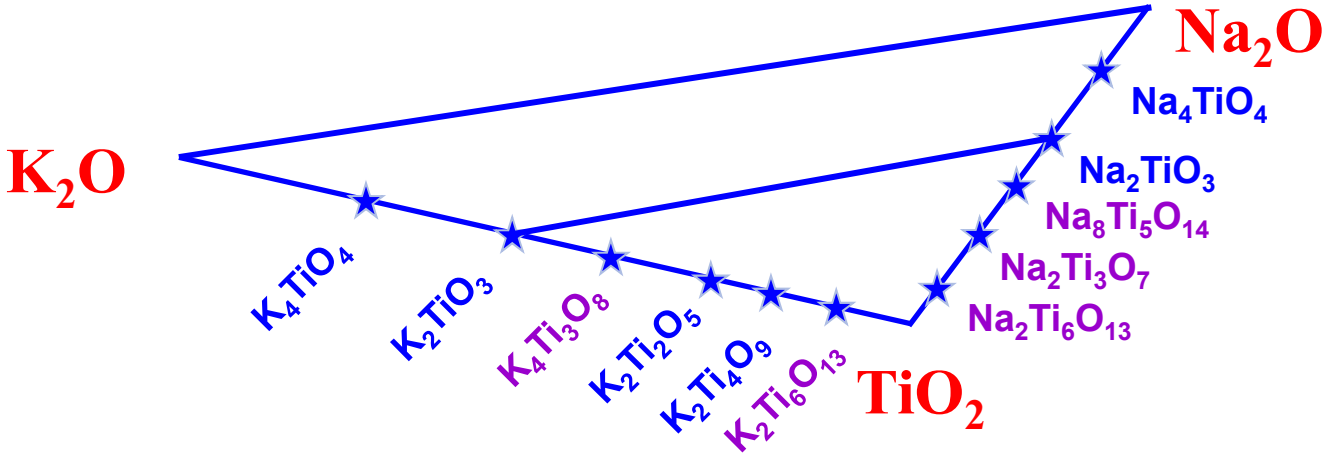
Phase equilibrium data for system with K_2O are scarce. The assessment was done based on additional data regarding formation, structure and thermodynamics of the titanates

Na_2O-K_2O-TiO_2

Thermodynamic modelling

phase	model	description	data
slag	Non-ideal associate model	**Alk_2O**, Ti, Ti_2O_2, Ti_2O_3, Ti_2O_4, Alk_4TiO4_3/2.5	FZJ, GTT
(K_2TiO_3):(Na_2TiO_3)=1:1	stoichiometric	Cp – NK; H,S - optimised	FZJ
(K_2TiO_3):(Na_2TiO_3)=2:1	stoichiometric	Cp – NK; H,S - optimised	FZJ

Ternary system was modelled/extrapolated based on the experimental data the pseudo-binary section K_2TiO_2-Na_2TiO_3.



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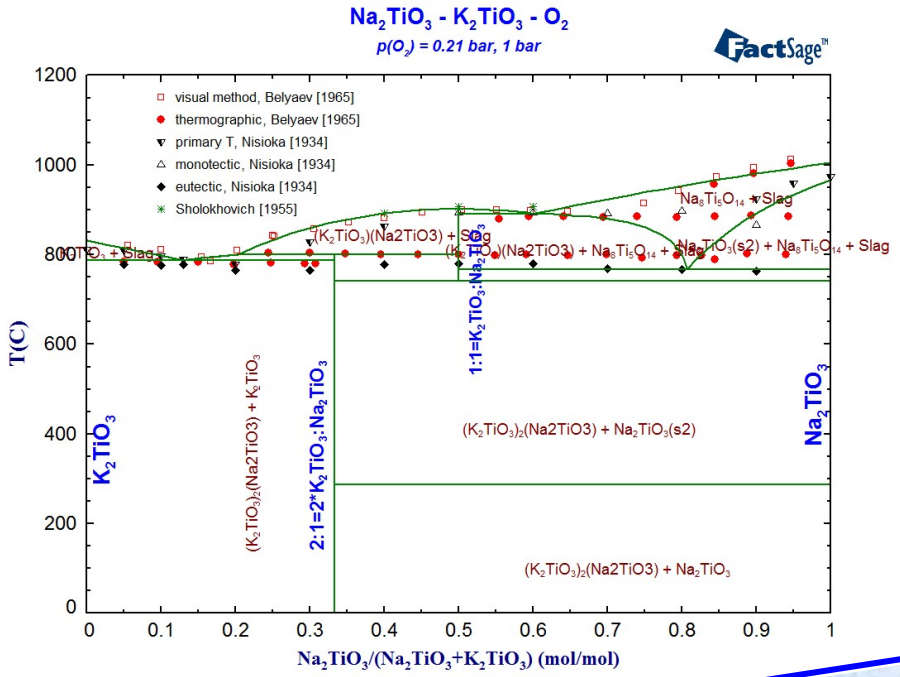
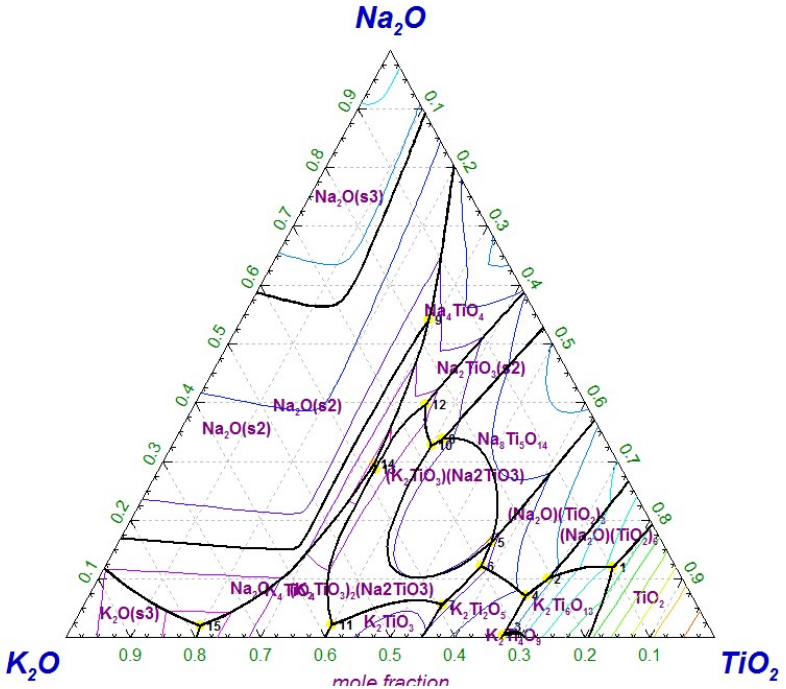
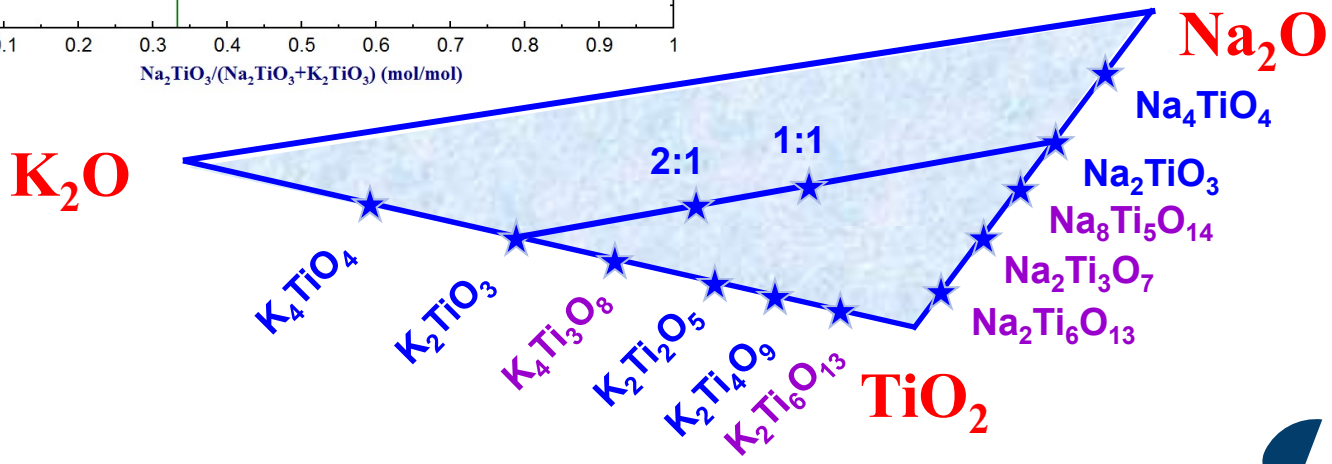
Na_2O-K_2O-TiO_2

Calculated phase equilibria







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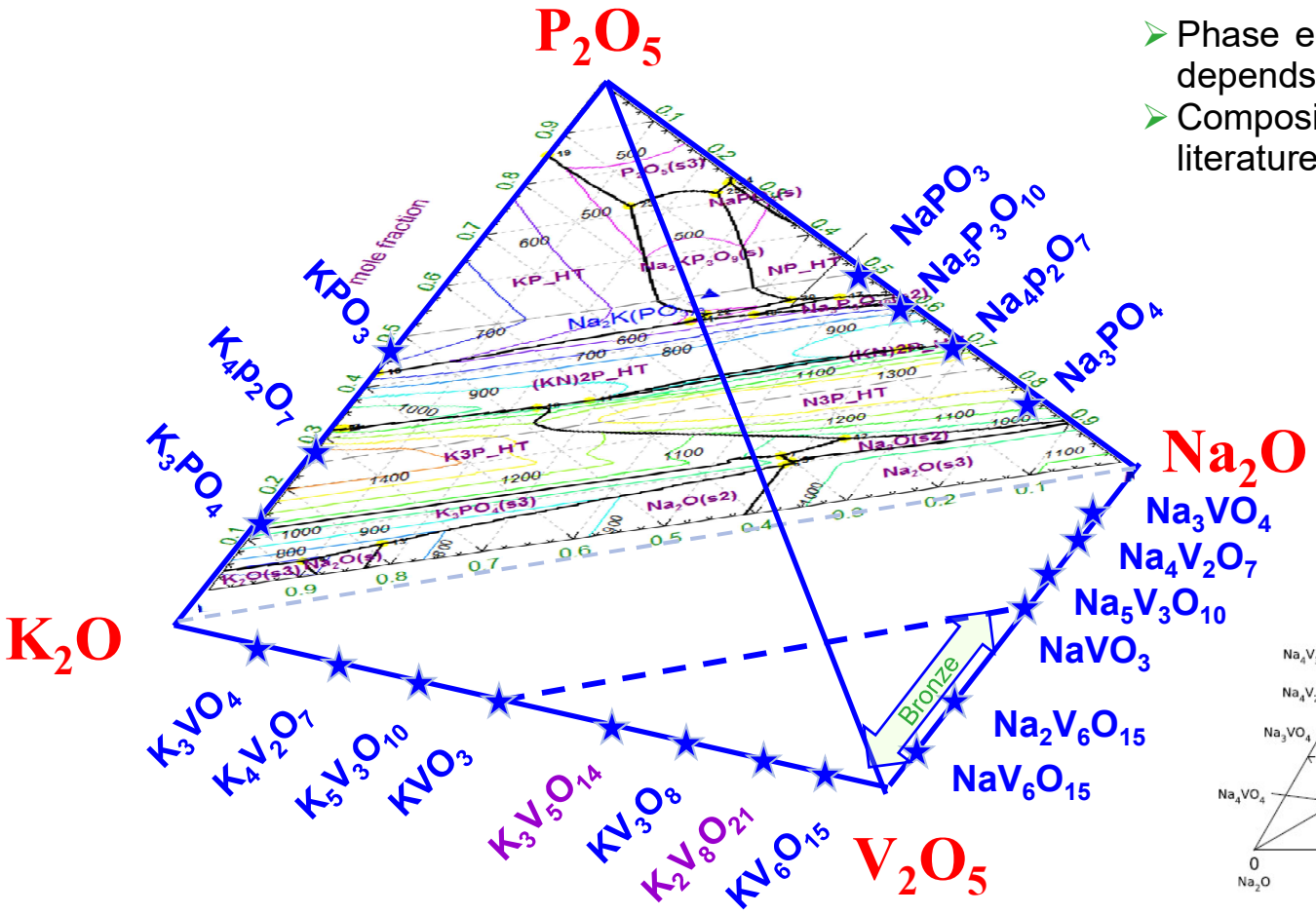
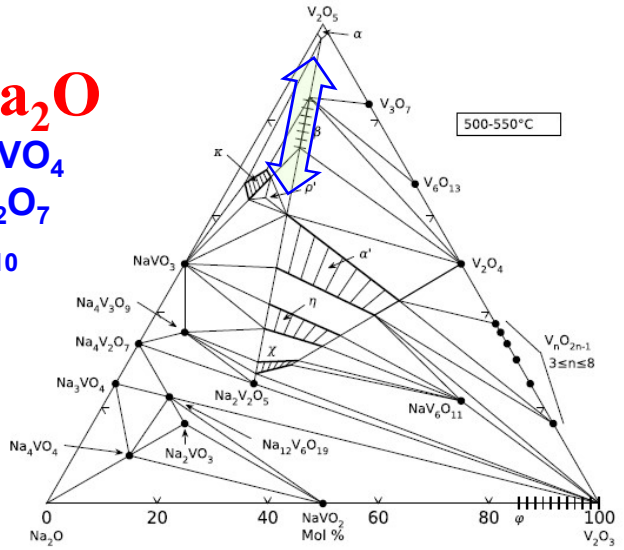
Alkali +V_2O_5

Database development: $P^{5+}{}_2O_5$ replaced by $V^{5+}{}_2O_5$



- Phase equilibria in system Alk_2O-V_2O_5 depends on $P(O_2)$
- Composition of „bronze“ is varied in literature → not considered yet



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Na-V-O

Thermodynamic data

$Na_2O:V_2O_x$	Compound	Cp	ΔH_f^0, S^0	Slag	Remarks
1:6	NaV_6O_{15}	NK	optimised		Bronze, ½(Na_2O+V_2O_4+5V_2O_5) or ½(Na_2O+xV_2O_4+(6-x)V_2O_5) x=1
1:3	$Na_2V_6O_{15}$	NK	optimised		Bronze: as (Na_2O+xV_2O_4+(3-x)V_2O_5) x=1
2:5	$Na_4V_{10}O_{27}$	-	-		Reported in [1,2], but later not confirmed
5:12	$Na_5V_{12}O_{32}$	-	-		Reported in [3] as (5Na_2O+xV_2O_4+ (12-x)V_2O_5), but later not confirmed
1:1	$NaVO_3$	[4]	[4]	$NaVO_3$	Liq. species $\underline{AlkMO_3}$ (Alk=Na, K; M=P, V)
5:3	$Na_5V_3O_{10}$	NK	S–optimised; H-exp.[5]		
2:1	$Na_4V_2O_7$	[4]	[4]	$Na_4V_2O_7$/3	Liq. species $\underline{Alk_4M_2O_7}$ (Alk=Na, K; M=P, V)
3:1	Na_3VO_4	FTox	optimised	Na_3VO_4/2	Liq. species $\underline{Alk_3MO_4}$ (Alk=Na, K; M=P, V)

[1] V. Danek, J. Balajka, K. Matiasovsky, Chem. Zvesti 27(6) (1973) 748-751.
[2] M.P. Glazyrin, A.A. Fotiev, Inorg. Mater. (Engl. Transl.) 4(1) (1968) 67-70.
[3] R.C. Kerby, J.R. Wilson, Can. J. Chem. 51(7) (1973) 1032-1040.
[4] I. Barin, Thermochemical Data of Pure Substances, In: VCH Verlagsgeselschaft mbH, 1995.
[5] B.G. Golovkin, L.V. Kristallov, M.V. Kruchinina, Russ. J. Inorg. Chem. 40(3) (1995) 496-500.

K-V-O

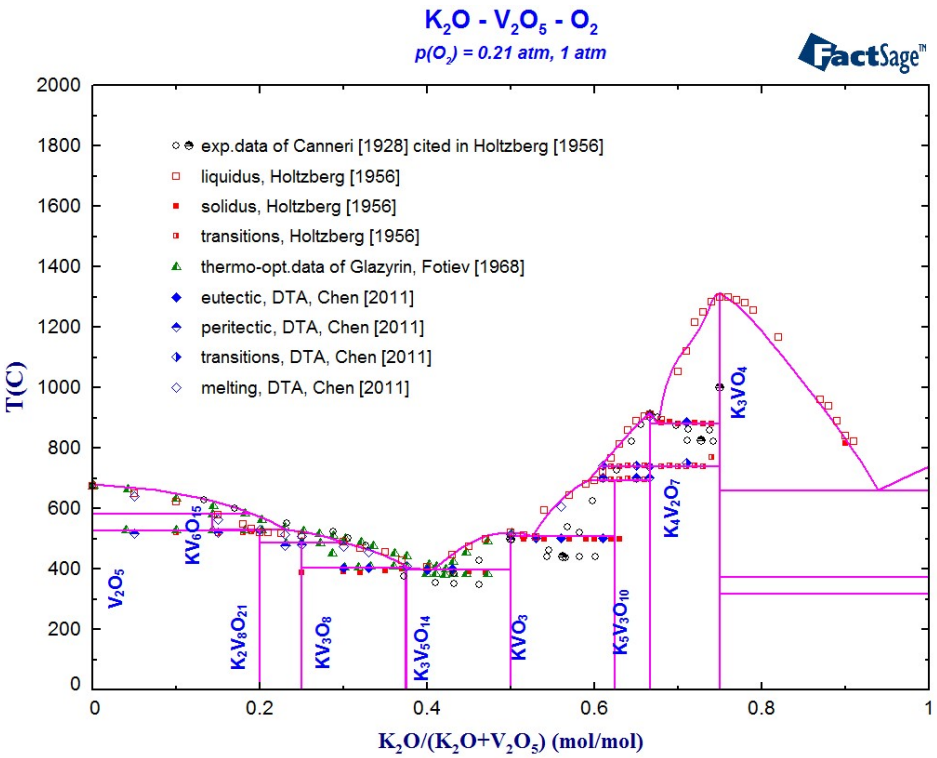
Thermodynamic data

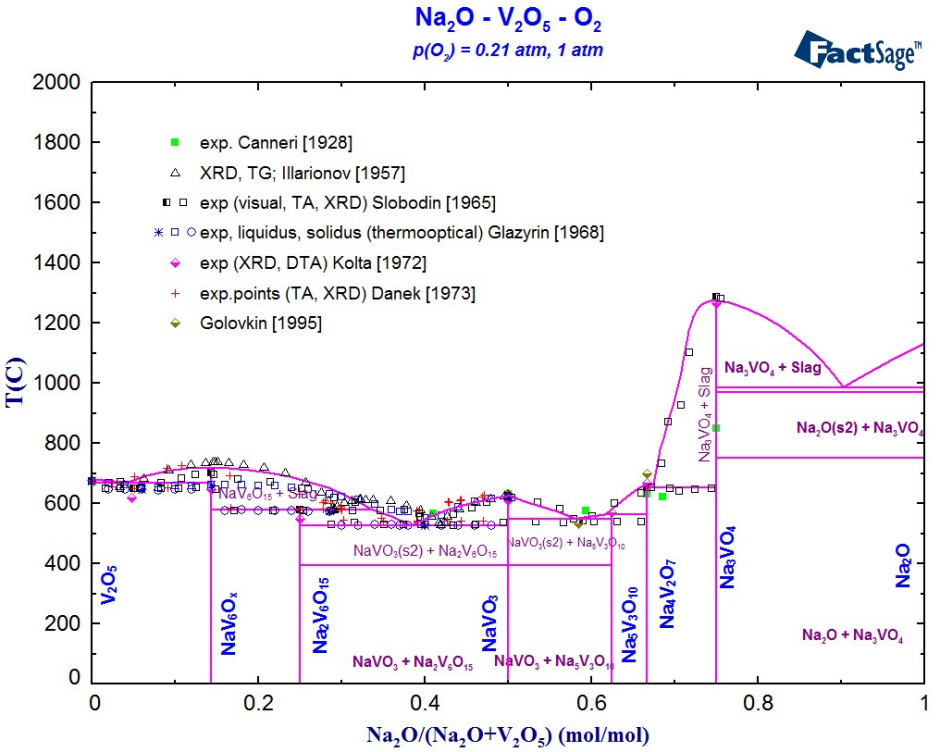
$K_2O:V_2O_x$	Compound	Cp	ΔH_f^0, S^0	Slag	Remarks
1:6	KV_6O_{15}	NK	optimised		Bronze ½(K_2O+V_2O_4+5V_2O_5), stable in air [1]
1:4	$K_2V_8O_{21}$	NK	optimised		Bronze, reported in [1-3], confirmed in [4]
1:3	KV_3O_8	NK	H–exp.[5]; S-opt.		Bronze, but currently was modelled as ½ (K_2O+3V_2O_5)
3:5	$K_3V_5O_{14}$	NK	H–exp.[5]; S-optimised		Reported in [3], later confirmed in [4]
1:1	KVO_3	NK (mod.)	S–[6]; H–exp. [5]; ΔHm –$NaVO_3$	KVO_3	Liq. species $\underline{AlkMO_3}$ (Alk=Na,K; M=P, V)
5:3	$K_5V_3O_{10}$	NK	optimised		Reported in [4]
2:1	$K_4V_2O_7$	NK (mod.)	S–[6]; H–exp.[5]; ΔHm – $Na_4V_2O_7$	$K_4V_2O_7$/3	Liq. species $\underline{Alk_4M_2O_7}$ (Alk=Na, K; M=P, V)
3:1	K_3VO_4	NK (mod.)	S, H – [6]; ΔHm – Na_3VO_4	K_3VO_4/2	Liq. species $\underline{Alk_3MO_4}$ (Alk=Na, K; M=P, V)

[1] V.V. Illarionov, R.P. Ozerov, E.V. Kil`disheva, Zh. Neorg. Khim. 1(4) (1956) 777-782.
[2] A.A. Fotiev, M.P. Glazyrin, S.I. Alyamovskii, Russ. J. Inorg. Chem. 12(5) (1967) 701-703.
[3] M.P. Glazyrin, A.A. Fotiev, Russ. J. Phys. Chem. 42(10) (1968) 1288-1290.
[4] C. Ye-Qing et al., Chin. Phys. B 20(7) (2011) 076401-076407.
[5] M.Y. Khodos et al., Neorg. Mater. 16(3) (1980) 502-504
[6] T.B. Lindemer, T.M. Besmann, C.E. Johnson, J. Nucl. Mater. 100(1-3) (1981) 176-226.

K_2O-V_2O_5, Na_2O-V_2O_5

Calculated phase equilibria





The detail description of the „bronze“-phase would be desirable taking into account the phase equilibria under various $p(O_2)$

Na_2O-K_2O-V_2O_5

Thermodynamic modelling

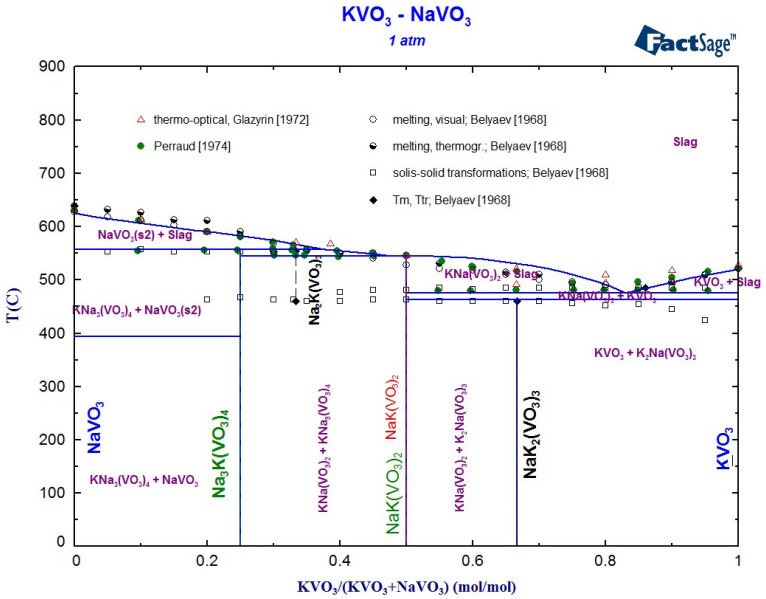
phase	model	description	data	
slag	Non-ideal associate model	V, V_2O_2, V_2O_3, V_2O_4, V_2O_5, Alk_2O, Alk_2O:V_2O_5=1:1, 2:1, 3:1	FZJ, GTT	
($NaVO_3$):(KVO_3)=3:1	stoichiometric	Cp – NK; H,S - optimised	FZJ	reported in [1]
($NaVO_3$):(KVO_3)=2:1	stoichiometric		FZJ	reported in [2], but not confirmed in [1,3]
($NaVO_3$):(KVO_3)=1:1	stoichiometric		FZJ	reported in [1-3]
($NaVO_3$):(KVO_3)=2:1	stoichiometric		FZJ	reported in [2]

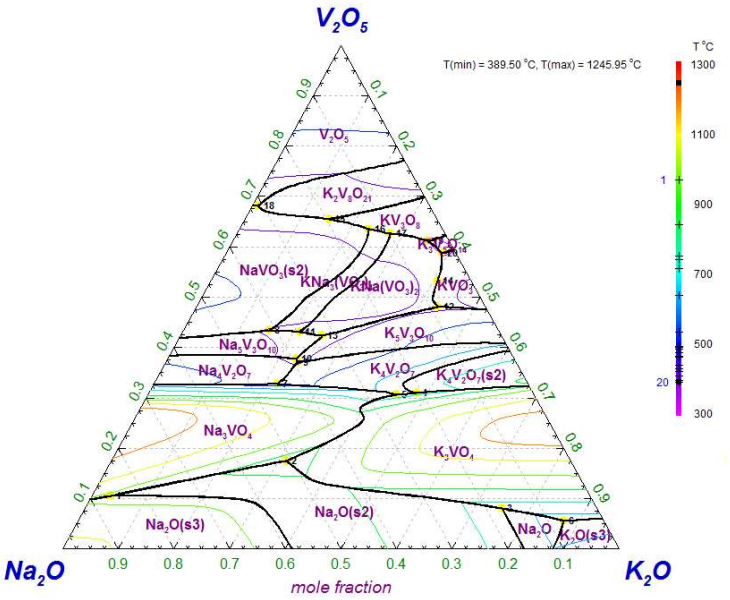
[1] J. Perraud, Rev. Chim. minerale 11(3) (1974) 302-326.
[2] I.N. Belyaev, T.G. Golovanova, Russ. J. Inorg. Chem. 13(6) (1968) 859-860.
[3] M.P. Glazyrin, A.A. Ivakin, A.P. Yatsenko, Russ. J. Inorg. Chem. 17(2) (1972) 280-281.

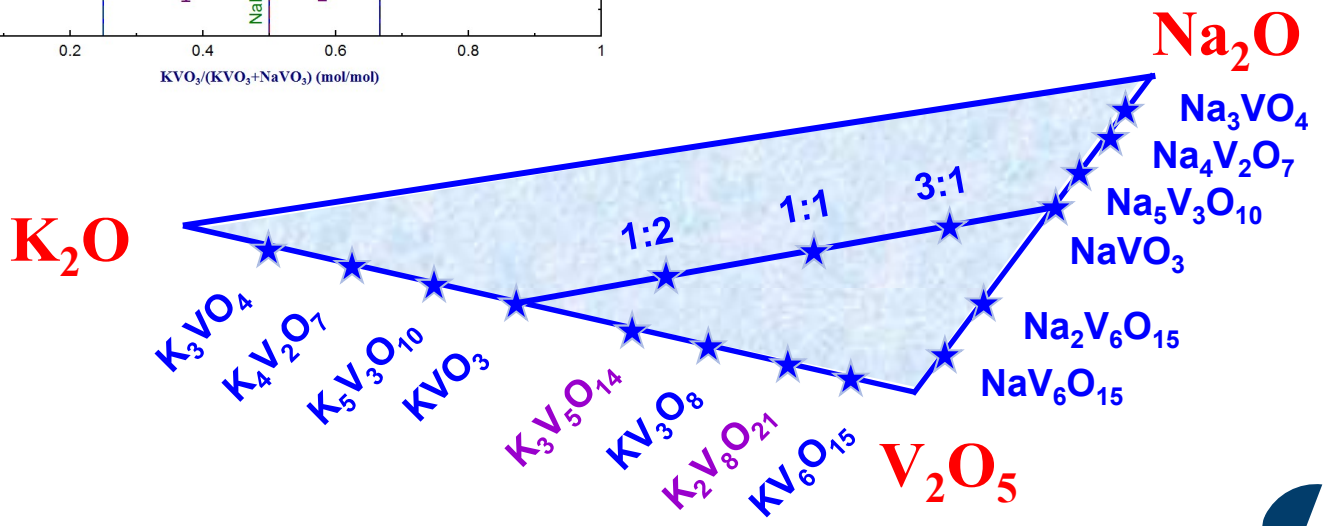
Ternary system was modelled/extrapolated based on the experimental data the pseudo-binary section KVO_3-$NaVO_3$.

Na_2O-K_2O-V_2O_5

Calculated phase diagrams







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Oxide database

HotVeGas Project

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Hochtemperaturvergasung und Gasreinigung

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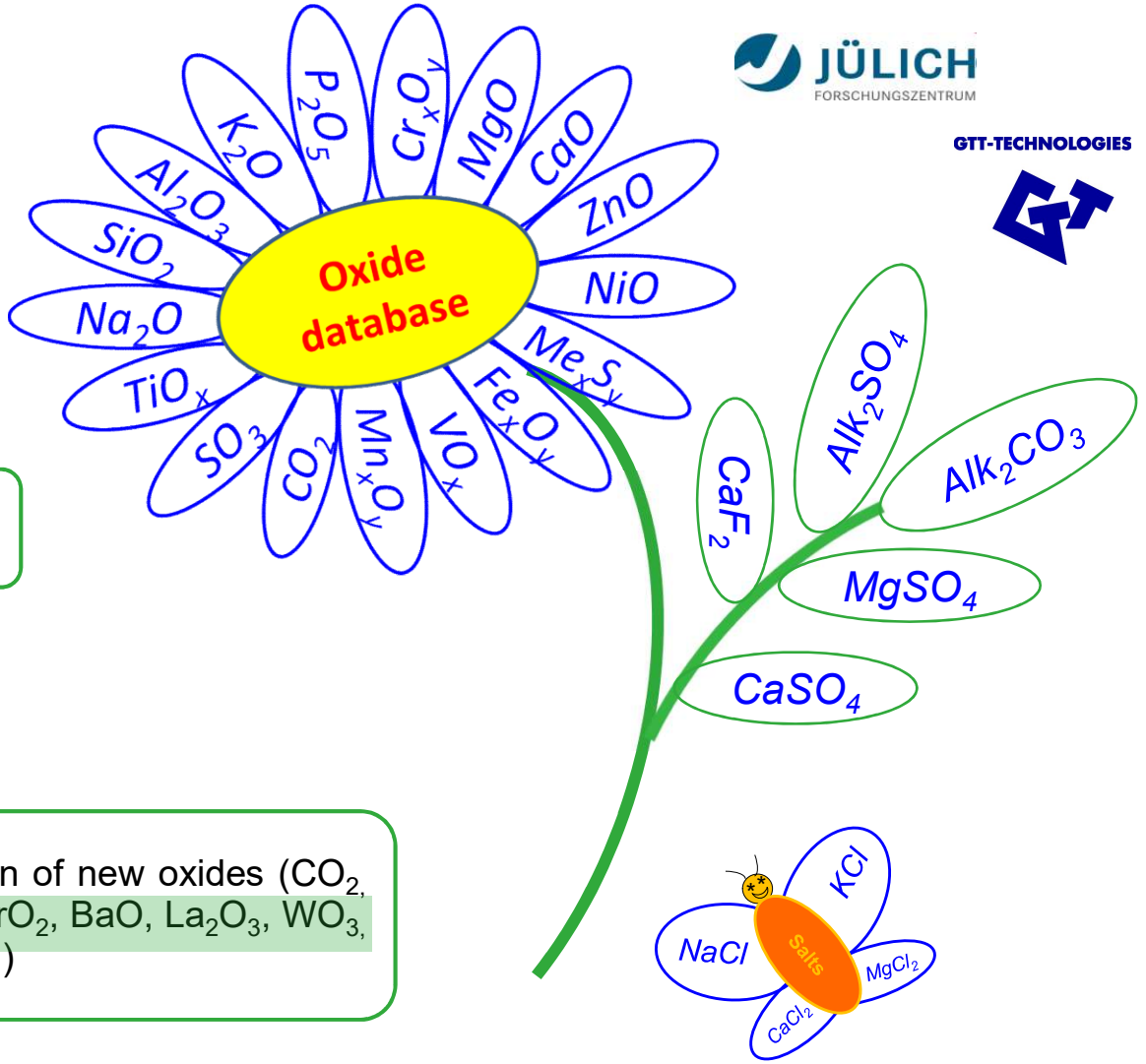
Addition of new oxides (CO_2, SrO, ZrO_2, BaO, La_2O_3, WO_3, H_2O….)



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$BaO\text{-}ZrO_2$

Revision of thermodynamic data on $BaZrO_3$: heat capacity, entropy

Cp, J/mol·K	S^0, J/mol·K	T, K	Method	[Ref]
Cp_{298}=101.71	124.68	53-297	AC	[King 1960]
Cp_{298}^{*}=101.71		296-1606	H-H_{298},C	[Levitskii 1976]**
Cp_{298}^{*}=101.71		1030-1687	H-H_{298}, DSC	[Nagarajan 1985]
Cp_{298}^{*}=101.71		407-775	H-H_{298}, DROP	[Cordfunke 1989]
		298-1200	STA	[Vassen 2000]
Cp_{298}=107.71		400-1400	DSC	[Yamanaka 2003]
Cp_{298}=107.0	125.5	1.6-298	AC	[Ahrens 2006]
$Cp_{304.4}$=106.4	126.0	1.8-305	PPMS***	[Kurosaki 2006]
	124.68			Fact PS
	125.5			SGPS
Cp_{298}=101.71	**124.68**			**our database**

$$H(T) = \Delta H^{0}_{f,298.15} + \int_{298.15}^{T} c_P(T)dT$$

$$S(T) = S^{o}_{298.15} + \int_{298.15}^{T} \frac{c_P(T)}{T} dT$$

AC- adiabatic calorimetry; C-calorimetry
**derivative of H-H_{298}; **transitions were reported: at 758, 1175K with ΔH=0, 1.38;*
****-hybrid adiabatic relaxation method*

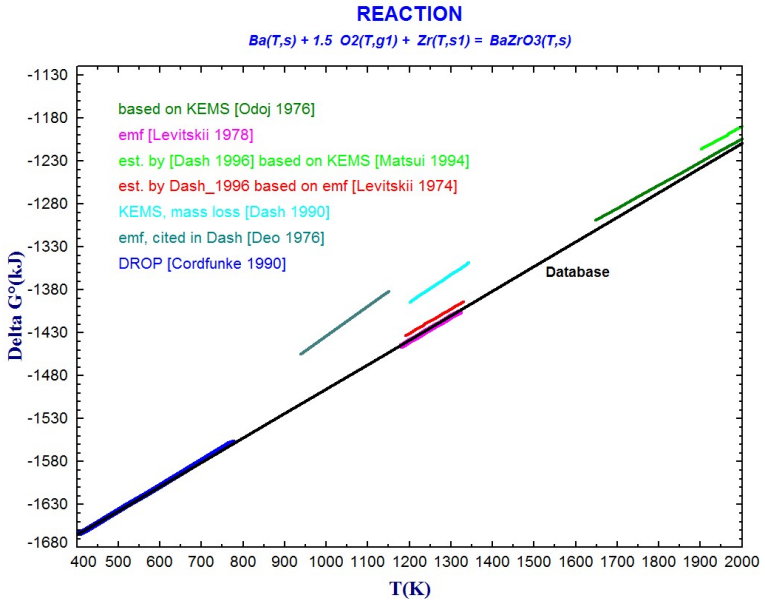
$BaO\text{-}ZrO_2$

Revision of thermodynamic data on $BaZrO_3$: heat content

ΔH_f^0, J/mol	T, K	Method	[Ref]
-1745.0		E	[Shibanov 1969]
-1779.5		E	[Parker 1971]
-1769.0			[Kubashevski 1993]
-1694.0		evaluated[1] on KEMS	[Odoj 1976]
-1761.9	1673-1873	CB	[L`vova 1964]
-1771.4	1068	SC	[Takayama 1988]
-1785.4[2] -1779.5[3] -1765.4[1]	1180-1320	EMF	[Levitskii 1978]
-1776.1 (-1721.7[4])	1203-1347	P(Ba), KML[5]	[Dash 1990]
-1767.7	1203-1347	P(Ba), KML[5]	[Dash 1994]
-1774.8		DROP	[Cordfunke 1990]
-1779.45			Fact PS
-1770.0			SGPS
-1779.45			**our database**

$$H(T) = \Delta H^0_{f,298.15} + \int_{298.15}^{T} c_P(T)dT$$

$$S(T) = S^o_{298.15} + \int_{298.15}^{T} \frac{c_P(T)}{T} dT$$



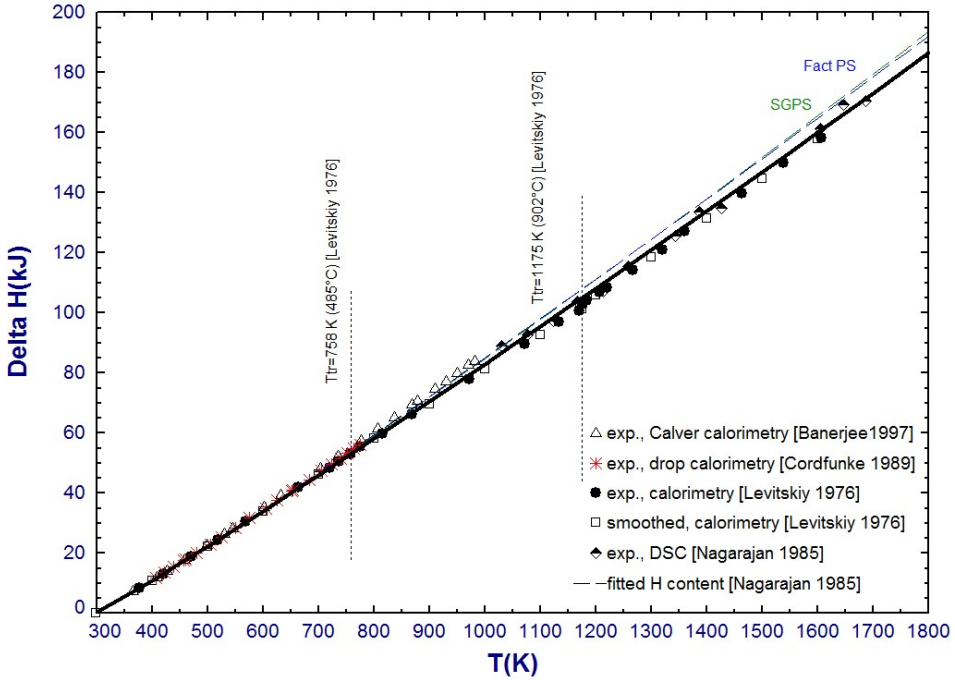
E-evaluation; CB-calorimtric bomb; SC-solution calorimetry
1-evaluated in the book [Cordfunke 1990]; 2-mean value; 3-value from calorimetry;
4-third-law value; 5-Knudsen mass-loss technique

$BaO\text{-}ZrO_2$

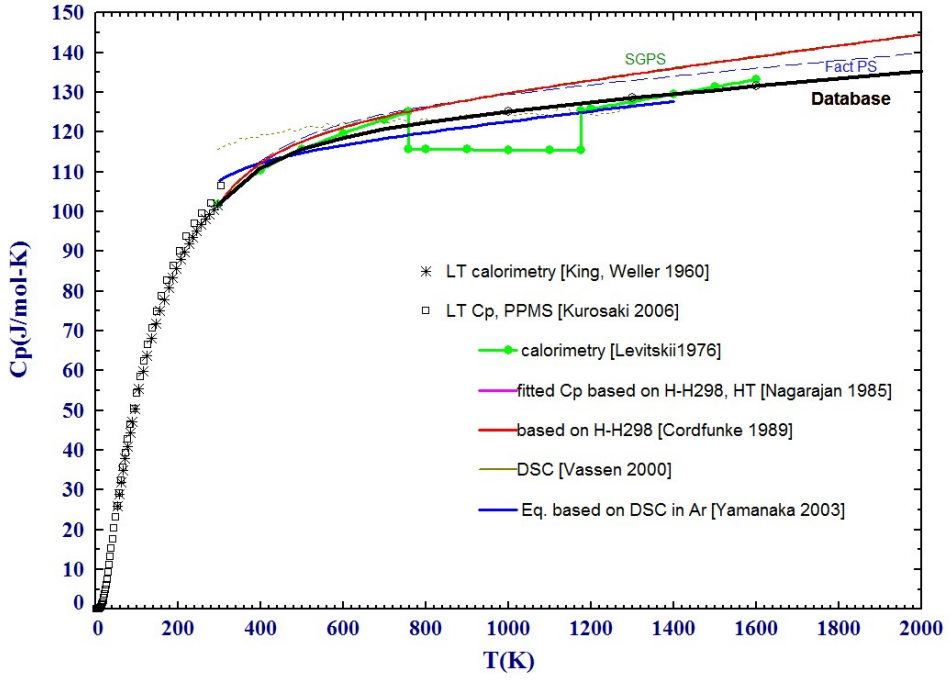
Revised thermodynamic data on $BaZrO_3$

$BaZrO_3$	taken from
Cp, $H\text{-}H_{298}$	[Nagarajan 1985]
ΔH_f^0=-1779.45 kJ/mol	[Levitskii 1978]
S^0=124.68 J/mol*K	[King 1960]

BaZrO3



$BaZrO_3$ - Cp vs T(K)



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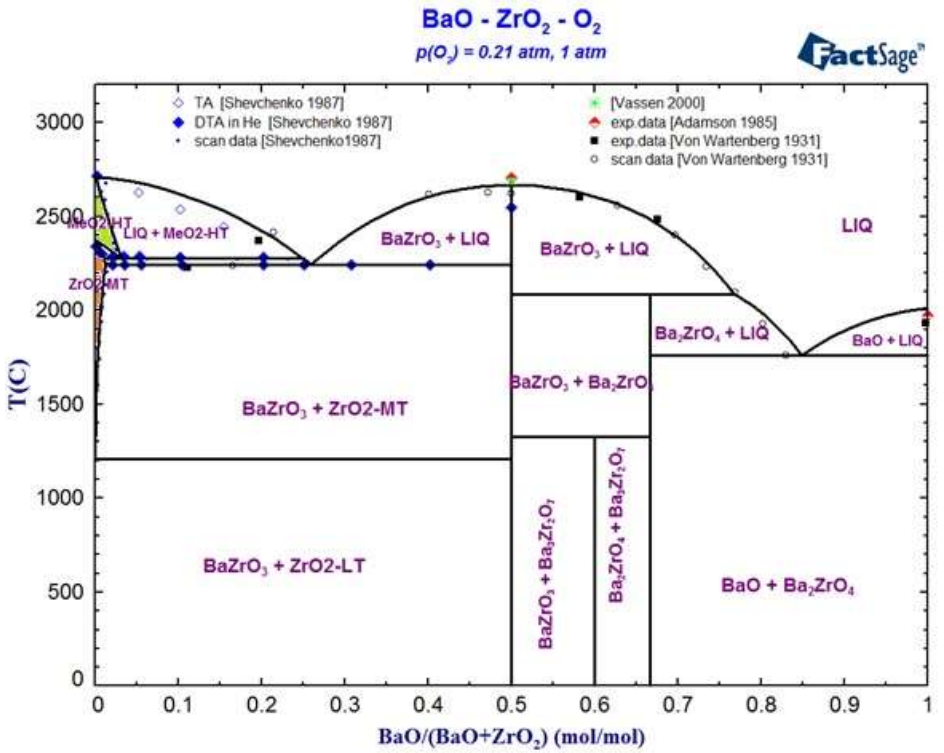
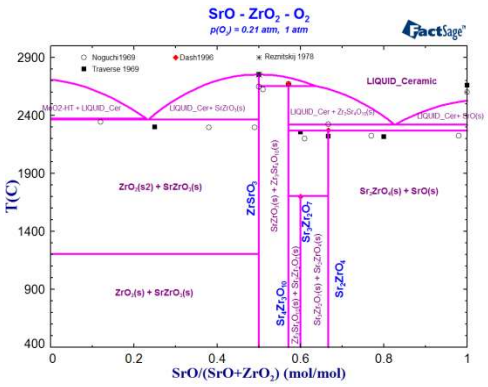
$BaO-ZrO_2$

Calculated phase equilibria

ZrO_2-HT $(Zr^{4+}, Zr^{2+}, \mathbf{Ba^{2+}})(\underline{O^{2-}}, Va)_2$
ZrO_2-MT $(ZrO_2, \mathbf{BaO_2})_1$



phase	model	description	data
Liquid	Modified associate species	Ba, Zr, $\mathbf{Ba_2O_2}$, $\mathbf{Zr_2O_4}$, O	FZJ
MeO2-HT	Sublattice model	$(Zr^{2+},Zr^{4+},Ba^{2+})(O^{2-},Va)_2$	GTT-FZJ
ZrO2-MT	Sublattice model	(ZrO_2, BaO_2)	GTT-FZJ
gas	ideal		SGPS
$BaZrO_3$	Stoichiometric, thermodynamic data are revised based on the literature	$BaO:ZrO_2$=1:1	FZJ
$Ba_3Zr_2O_7$		$BaO:ZrO_2$=3:2	FZJ
Ba_2ZrO_4		$BaO:ZrO_2$=2:1	FZJ



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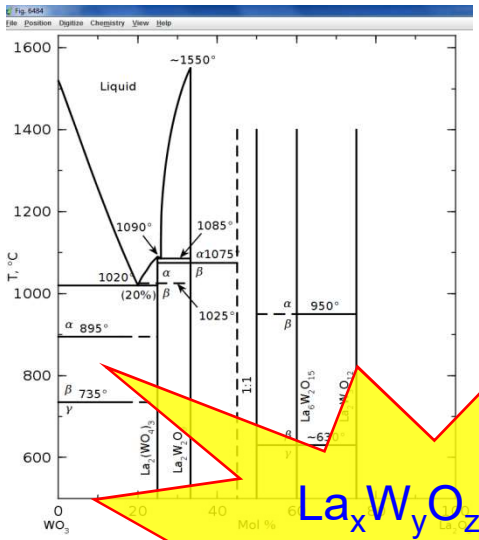
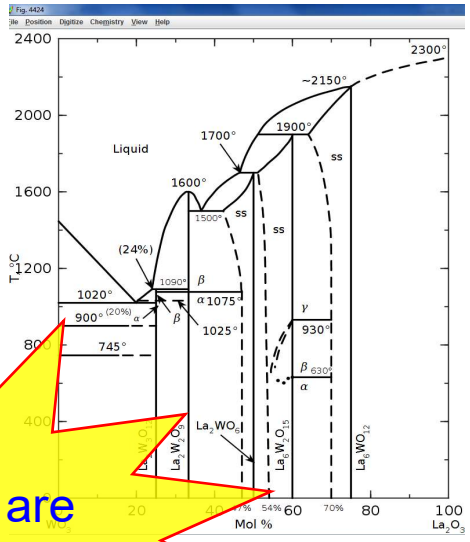
La_2O_3-WO_3

Literature review

Exp.:
DTA, XRD, CA[1], DA [2]

E. Ya. Rode et al., Zh. Neorg. Khim., 13 [5] 1451-1456 (1968);

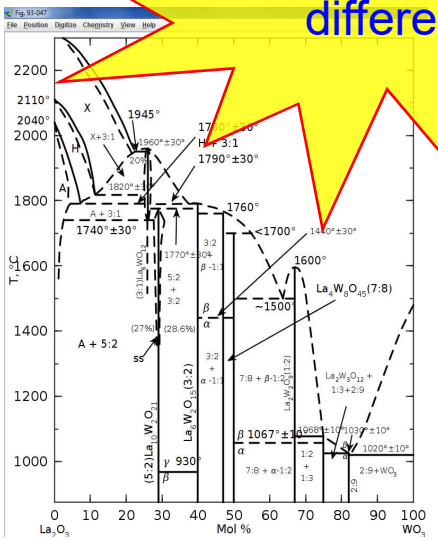


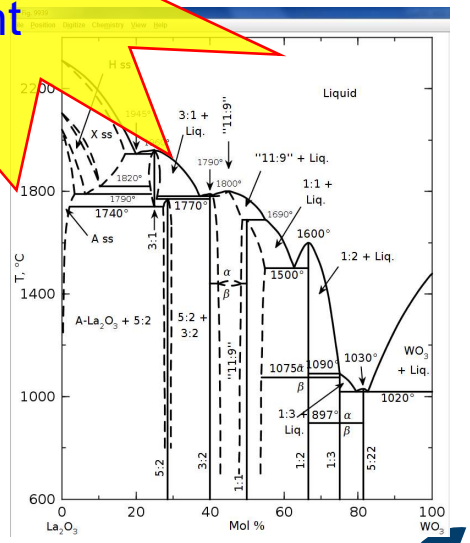


$La_xW_yO_z$ are different

Exp.:
DTA, XRD, DA [2],
VP[3], HSM[4]

M. M. Ivanova et al., Izv. Akad. Nauk SSSR, Neorg. Mater., 6 [5] 914-919 (1970);





Exp.:
XRD

V.K. Yanovskii, V.I. Voronkova, Izv. Akad. Nauk SSSR, Neorg. Mater., 19 [3] 416-421 (1983);

Exp.:
TA, HT-XRD

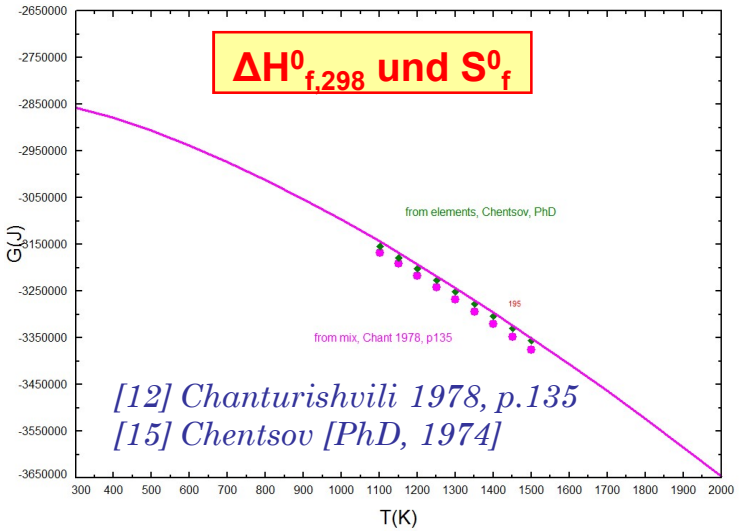
*M. Yoshimura and A. Rouanet, Mater. Res. Bull., 11 [2] 151-158 (**1976**)*

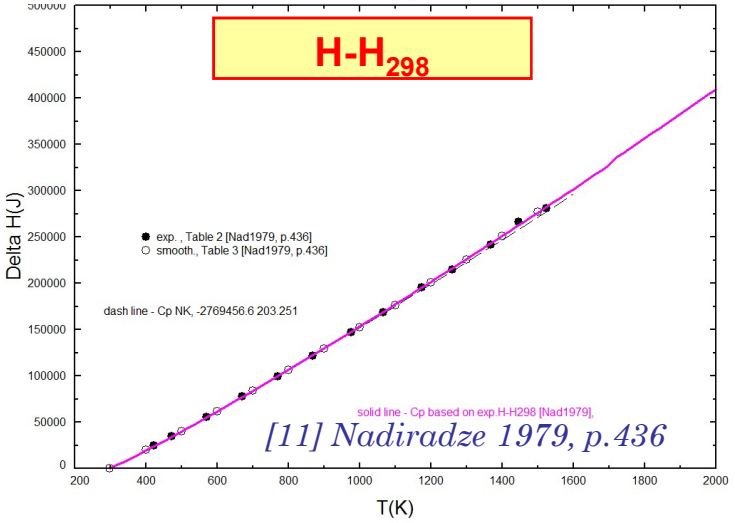
[1]-Chemische Analyse; [2]-Densitometrie; [3]-Visuell Polythermal Analyse; [4]-Hot Stage Mikroskopie

La_2O_3-WO_3

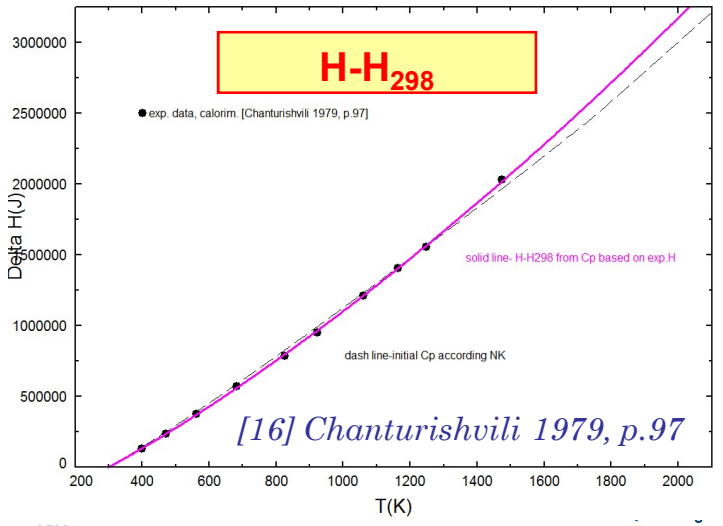
Cp is modelled based on the available H-H_{298} data;
H and S are optimised based on thermodynamics and phase equilibria

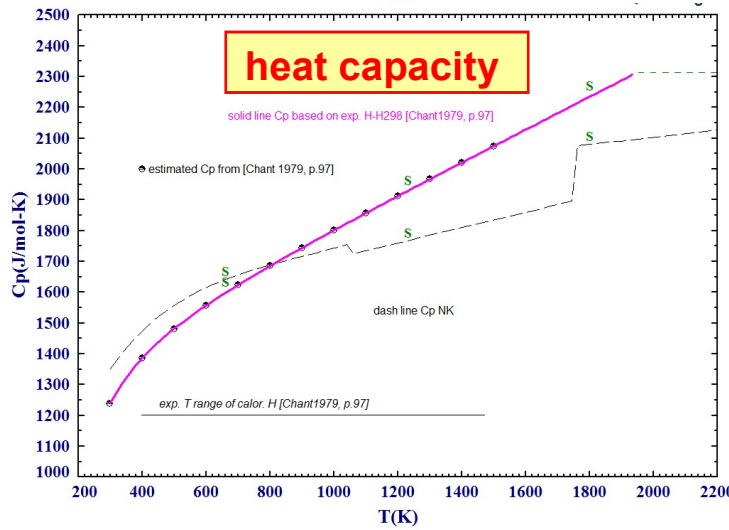
La_2O_3:WO_3=1:1, La_2WO_6





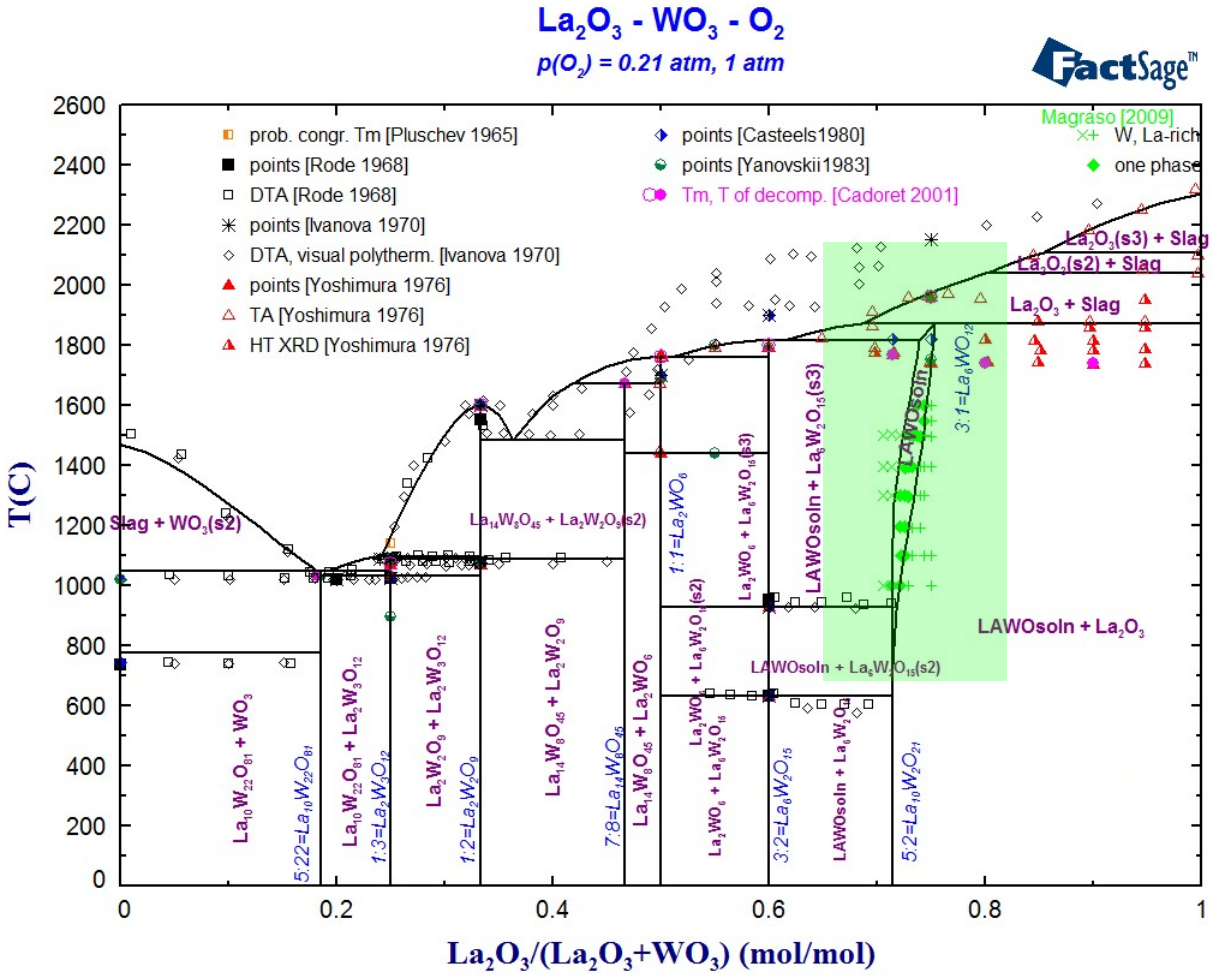
La_2O_3:WO_3=7:8, $La_{14}W_8O_{45}$





La_2O_3-WO_3

Calculated phase equilibria



- Thermodynamic data are included along with phase equilibria – ☺
- Solid solubility is modelled based on 5:2 (La/W=5) - ☺

Conclusions

HOTVEGAS
Hochtemperaturvergasung und Gasreinigung

Basic experiments and thermochemical modelling

Experiments

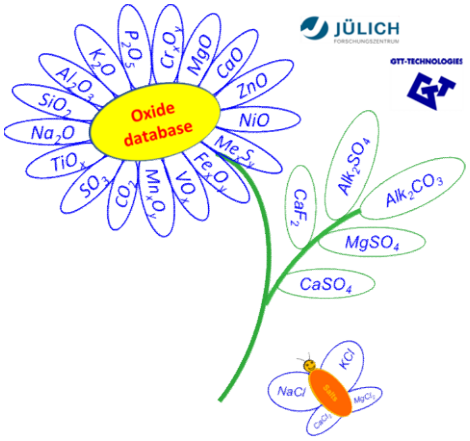
(slag, membranes, trace elements, etc.; with TA, XRD, KEMS, MBMS, Visco, etc.)

Database development

Work on various sub-systems for the purpose of database` completeness (ZnO, NiO, SO_3, TiO_2, V_2O_5)

Addition of new oxides (CO_2, SrO, ZrO_2, BaO, La_2O_3, WO_3, H_2O….)

Oxide database	Atlas (14.0) Dec. 2018
Binary systems	171
Ternary systems	141
Quaternaries	7
Slag components	199
Solid solution phases	112
Stoichiometric compounds	596



On behalf of all co-authors:

Thank you for your attention!

Vielen Dank für Ihre Aufmerksamkeit!

Благодарю за внимание!