3) Database

a. **Databases available**
b. **Temperature extrapolation**
c. **Database contents**

Thermodynamic databases

EMPA

general-TDB

- Aqueous phase (Ca^{2+}, $Ca(OH)^{+}$, …)
- Gaseous phase (e.g. CO_2 (g), ...)
- Minerals (calcite, gypsum, portlandite, …)

Cement data

AFm

SO_4-AFm — *solid solution* — OH-AFm

CO_3-AFm
hemicarb.
strätlingite

Al-AFm — *solid solution* — Fe-AFm

AFt

SO_4-AFt — *solid solution* — CO_3-AFt

thaumasite

Fe-AFt — *solid solution* — Al-AFt

hydrogarnet

C_3AH_6

$C_3AS_{0.84}H_{4.32}$

$C_3FS_{0.84}H_{4.32}$

C-S-H

$Ca_{0.67}SiH_{1.5}$

$C_{0.83}S_{0.67}H_{1.8}$

$C_{1.3}SH_{2.17}$

$C_{1.5}S_{0.67}H_{2.5}$

solid solution

Database 1

- **Geochemical database** (generally integrated in software)
  - Complex formation: $CaOH^+$, $CaHCO_3^+$, …
  - Solubility products: gyspum, calcite, ….
- **Specific cement database**
  - Solubility hydration products (ettringite, monosulphate, …)
    - Babushkin et al. (1985) Thermodynamics of Silicates, Springer
    - Reardon, E.J. (1992) Waste Management 12, 221-239.
    - Atkins et al. (1992) CCR 22, 241-246.
    - **CEMDATA07**: Matschei et al. (2007) CCR, Lothenbach et al. (2008) CCR
    - **Blanc et al. (2010**) CCR 40, 851-866; 1360-1374
  - Recent additions:
    - Friedel's salt: Balonis ea (2010) CCR 40,1009-1022
    - Hydrotalcite: Rozov ea (2010, 2011)
    - New C-S-H model: Kulik (2011) CCR 41, 477-495
    - Fe-hydrates: Dilnesa ea (2011, 2012, 2014a, 2014b)
    - Thaumasite: Matschei ea (2014) Materials & Structures, in press
  - Current work (GEMS): L'Hopital ea, …: C-S-H and aluminium / alkali uptake…
    Nied, Bernard ea: M-S-H
    «nea cement database» project: started in 2014

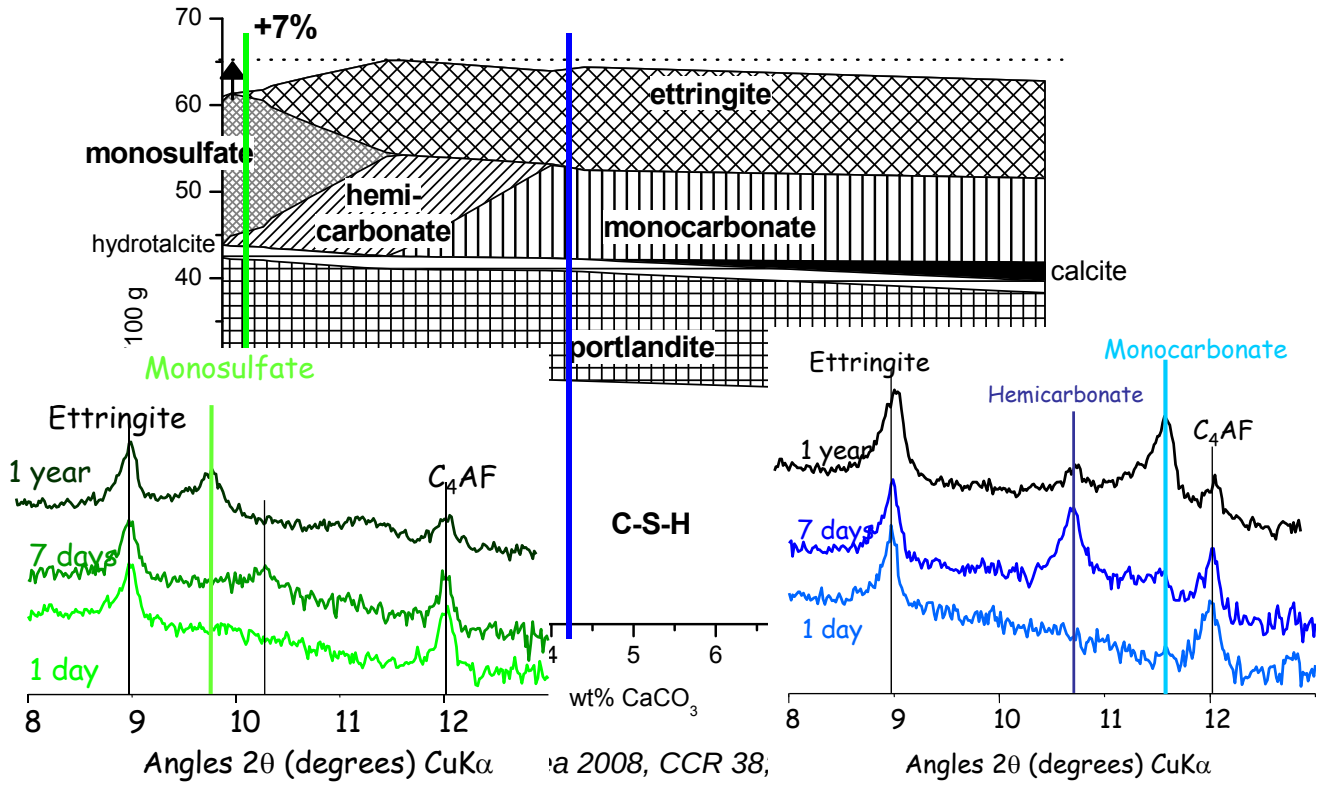
Database 2

- Geochemical database and specific cement database have to be consistent!
- Use the specific cement database only with the correct geochemical database!

- Data formats:
  - Log K values (PHREEQC, GEMS, MINEQL, …)
  - $\Delta G_f°$ (Gibbs free energy of formation) (GEMS, MTDATA, …)
  - convertible: $K = e^{-\frac{\Delta G_r°}{RT}}$

$$\Delta G_r° = \sum_i \nu_i \Delta G_f°$$

Database Cemdata 2007



a 2008, CCR 38,

Different databases

	Reardon 1992	*Cemdata 2007*	*Blanc 2011*
Ettringite ⇔ $6Ca^{2+} + 2AlO_2^- + 3SO_4^{2-} + 4OH^- + 30H_2O$	**-43.9**	**-44.9**	**-44.8**
Monosulfate ⇔ $4Ca^{2+} + 2AlO_2^- + SO_4^{2-} + 4OH^- + 10H_2O$	**-29.3**	**-29.3**	**-28.7**
C_3AH_6 ⇔ $3Ca^{2+} + 2AlO_2^- + 4OH^- + 4H_2O$	**-23.1**	**-20.8**	**-21.4**
Monocarb. ⇔ $4Ca^{2+} + 2AlO_2^- + CO_3^{2-} + 4OH^- + 10H_2O$	*n.a.*	**-31.5**	**-31.5**
Ca-carbo. ⇔ $2Ca^{2+} + 2AlO_2^- + CO_3^{2-} + 11H_2O$	**-19.5**	*n.a.*	*n.a.*

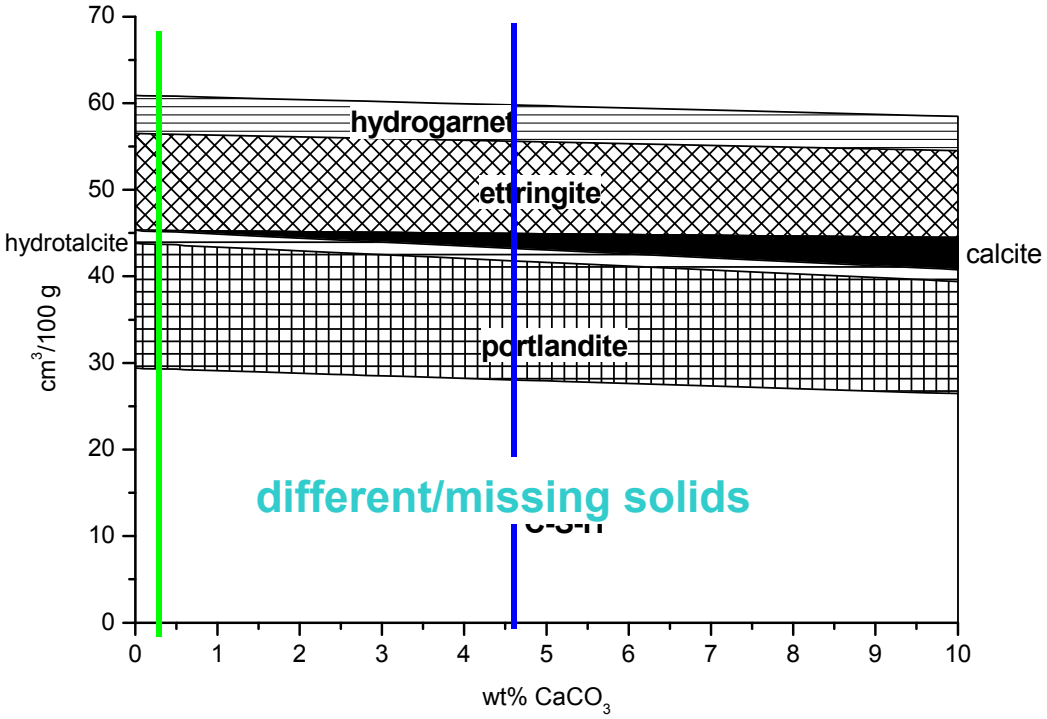
different/missing solids

Reardon Waste Management 12, 1992

Cemdata07: Lothenbach Winnefeld CCR 36 2006; Matschei ea CCR 37, 2007; Lothenbach ea CCR 38, 2008; Möschner ea CCR 39, 2009; Schmidt ea CCR 38, 2008

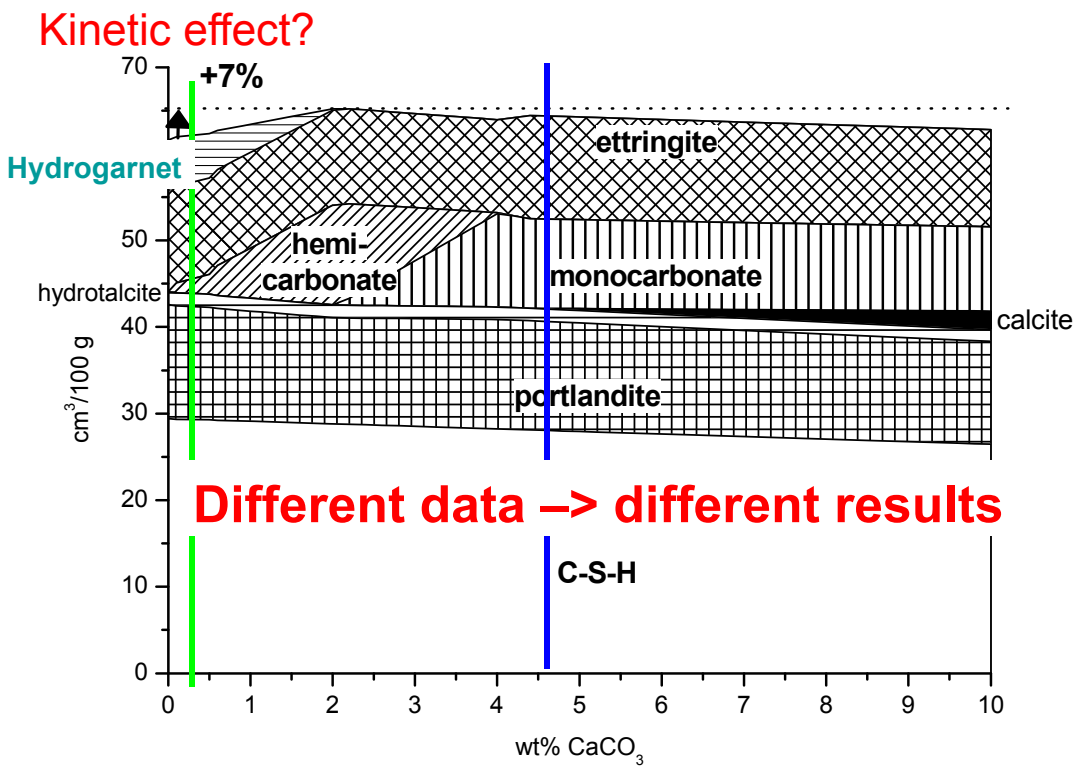
Blanc ea CCR 40, 2010

Databases: Reardon



Reardon 1992, Waste Management 12

Databases: Blanc



Blanc ea 2010, CCR 40

Different databases

	Cemdata 2007	Blanc 2011	Δ
Ettringite ⇔ $6Ca^{2+} + 2AlO_2^- + 3SO_4^{2-} + 4OH^- + 30H_2O$	-44.9	-44.8	
Monosulfate ⇔ $4Ca^{2+} + 2AlO_2^- + SO_4^{2-} + 4OH^- + 10H_2O$	-29.3	-28.7	+0.6
C_3AH_6 ⇔ $3Ca^{2+} + 2AlO_2^- + 4OH^- + 4H_2O$	-20.8	-21.4	-0.6
Monocarb. ⇔ $4Ca^{2+} + 2AlO_2^- + CO_3^{2-} + 4OH^- + 10H_2O$	-31.5	-31.5	

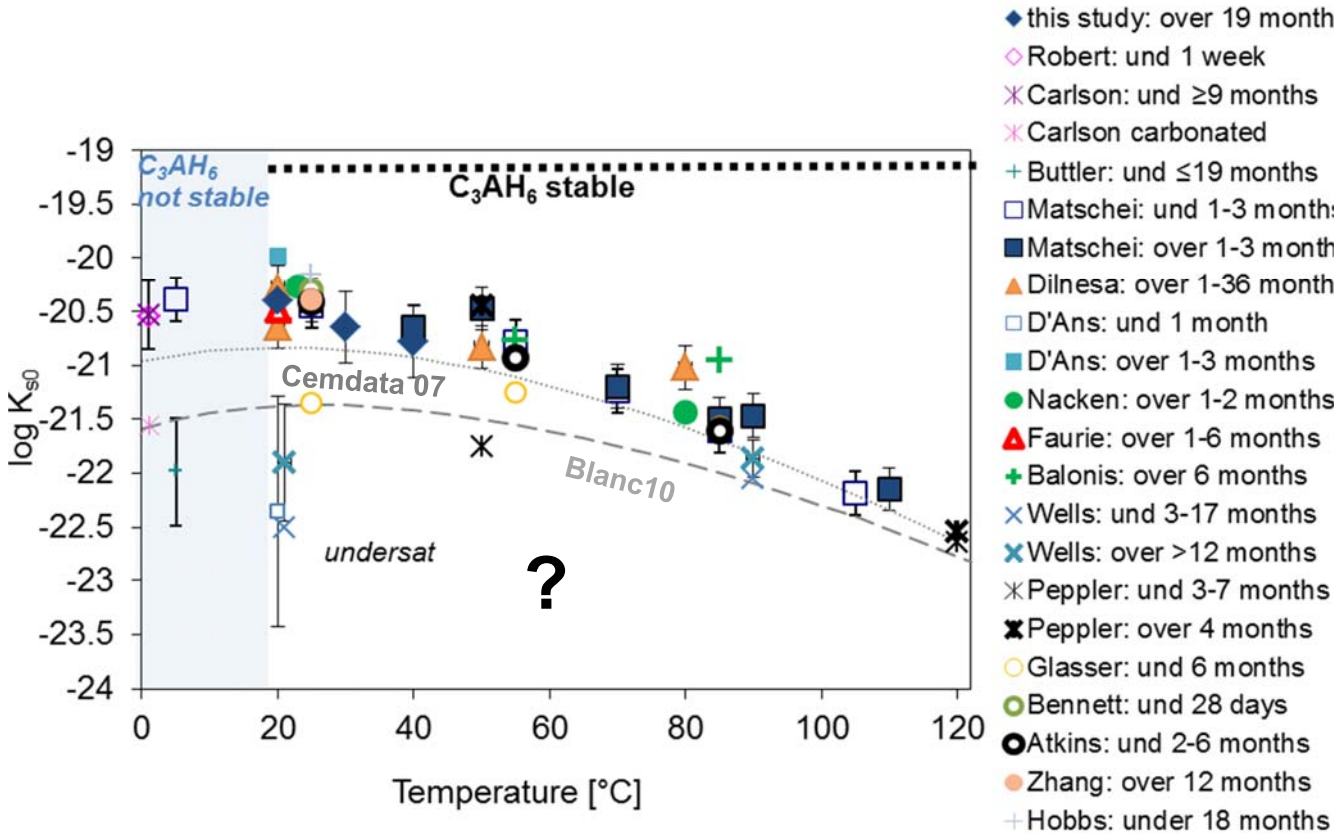
Analytical error ± 0.5 - 1

Reardon Waste Management 12, 1992

Cemdata07: Lothenbach Winnefeld CCR 36 2006; Matschei ea CCR 37, 2007; Lothenbach ea CCR 38, 2008; Möschner ea CCR 39, 2009; Schmidt ea CCR 38, 2008

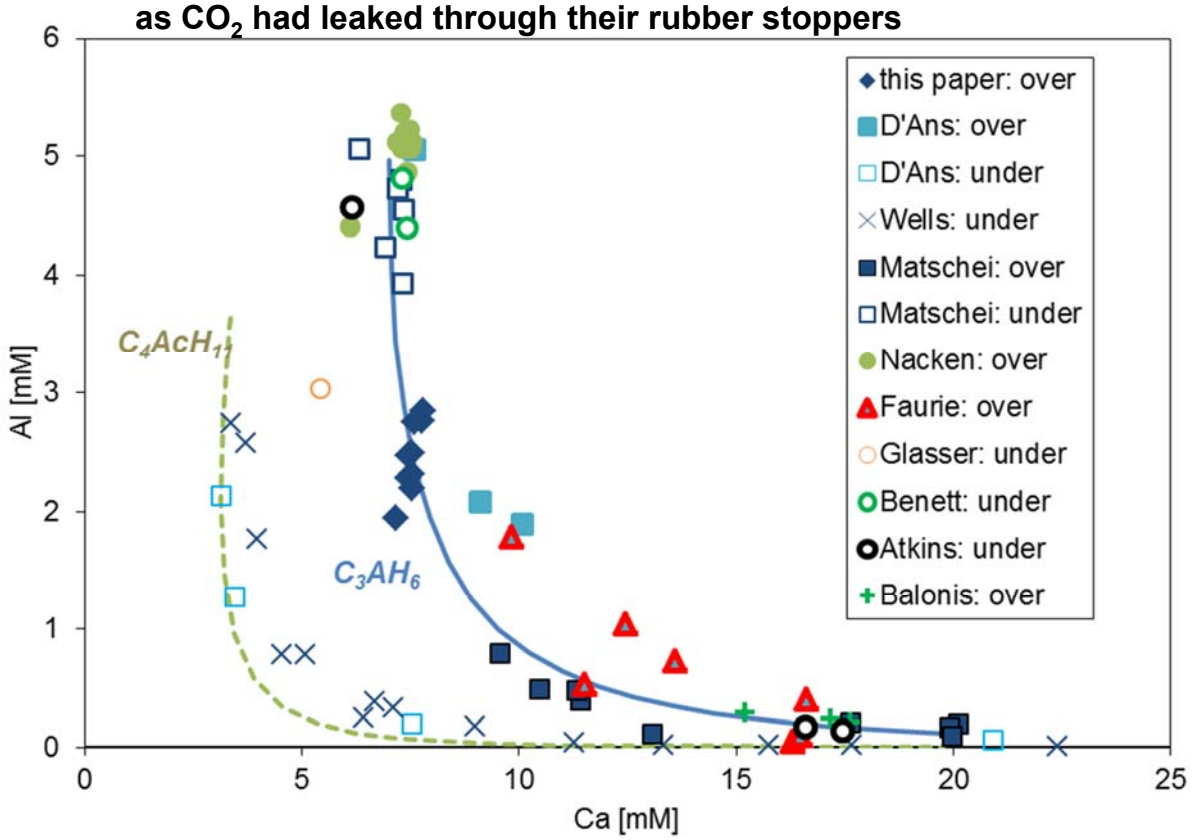
Blanc ea CCR 40, 2010

Solubility of C_3AH_6



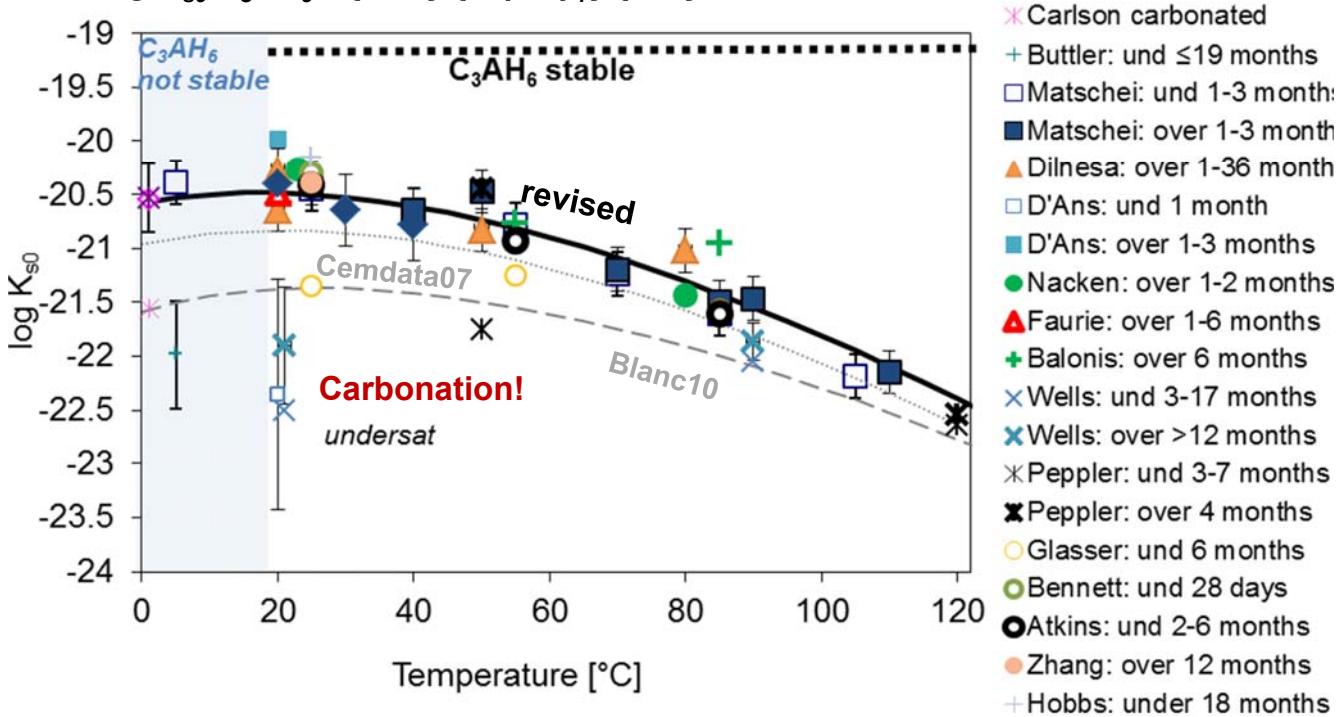
Carbonation!

Peppler and Wells observed in some samples calcite as CO_2 had leaked through their rubber stoppers

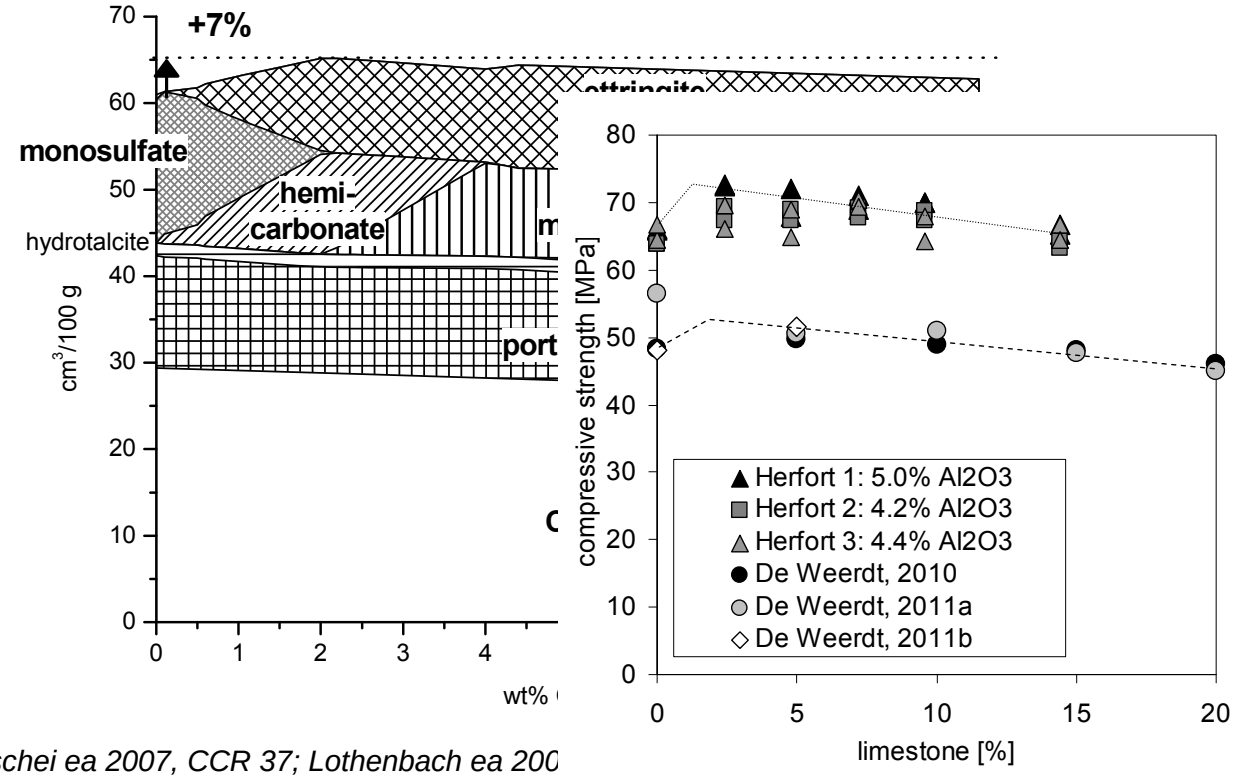


Solubility of C_3AH_6

Log K_{s0} C_3AH_6 = $\{Ca^{2+}\}^3\{Al(OH)_4^-\}^2\{OH^-\}^4$ = -20. 5



Influence of limestone



Matschei ea 2007, CCR 37; Lothenbach ea 200

Thermodynamic modelling: limits

- **Thermodynamic data**
  - **Small differences in data -> other solids stable**
  - **Gaps in database: siliceous hydrogarnets, hydrotalcites, Fe-hydrates, Al-K-Na uptake in C-S-H, …**
- **Kinetics: some phases are metastable**
  - **C-S-H metastable (jennite, tobermorite, …)**
  - **Hydrated cement thermodynamically unstable**

Cemdata14

Cemdata14 data base, to be used with general PSI-Nagra TDB only! [6,7,7a]
Version 14.01: May 2014
Based on the CEMDATA07 data base [1-8]. New data [9-19] are indicated **in bold**

	log K_{s0}	$\Delta_r G°$ [kJ/mol]	$\Delta_r H°$ [kJ/mol]	$S°$ [J/K/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	$V°$ [cm^3/mol]	Ref
(Al-)ettringite[a,b]	-44.9	-15205.94	-17535	1900	1939	0.789			707	[1,2]
tricarboaluminate[a]	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78e6		650	[2,1]
Fe-ettringite[b]	-44.0	-14282.36	-16600	1937	1922	0.855	2.02e6		717	[3,1]
Thaumasite	**-24.75**	**-7564.52**	**-8700**	**897.1**	**1031**	**0.263**	**-3.40e6**		330	**[9]**
C_3AH_6[c]	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25e6		150	[10]
$C_3AS_{0.41}H_{5.18}$[c]	*-25.35*	*-5192.9*	*-5699*	*399*	*310*	*0.566*	*-4.37e6*		*146*	*[11]*
$C_3AS_{0.84}H_{4.32}$[e]	*-26.70*	*-5365.2*	*-5847*	*375*	*331*	*0.484*	*-5.55e6*		*142*	*[11]*
C_3FH_6[d,***]	*-26.30*	*-4122.8*	*-4518*	*870*	*330*	*1.237*	*-4.74e6*		*155*	*[11]*
$C_3FS_{0.84}H_{4.32}$[d,e]	-32.50	-4479.9	-4823	840	371	0.478	-7.03e6		149	[11]
$C_3FS_{1.34}H_{3.32}$	-34.20	-4681.1	-4994	820	395	0.383	-8.39e6		145	[11]
C_4AH_{19}[f]	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	371	[10]
C_4AH_{13}	-25.00	-7324.3	-8300.2	700	711	1.047		-1600	274	[10]
$C_2AH_{7.5}$	-13.80	-4695.5	-5277.6	450	323	0.728			180	[10]
C_4AsH_{12}[f,g]	-29.26	-7778.50	-8750	821	594	1.168			309	[2,1]
C_4AcH_{11}	-31.47	-7337.46	-8250	657	618	0.982	-2.59e6		262	[2,1]
$C_4Ac_{0.5}H_{12}$	-29.13	-7335.97	-8270	713	664	1.014	-1.30e6	-800	285	[2,1]
C_2ASH_8	-19.70	-5705.15	-6360	546	438	0.749	-1.13e6	-800	216	[2,1]
$C_4ACl_2H_{10}$	-27.27	-6810.90	-7604	731	498	0.895	-2.04e6	1503	272	[15,16]
$C_4As_{0.5}ClH_{12}$	-28.53	-7533.97	-8472[***]	820	557	1.141	-1.02e6	751	289	[16,17]
C_4FH_{13}[**]	*-30.75*	*-6438.6*	*-7435*	*630*	*694*	*1.113*	*2.02e6*	*-1600*	*286*	*[11]*
C_4FsH_{12}[g]	-31.57	-6873.2	-7663	1430	577	1.234	2.02e6		321	[12]
C_4FcH_{12}	-34.59	-6674.0	-7485	1230	612	1.157	-5.73e5		292	[13]
$C_4Fc_{0.5}H_{10}$	-30.83	-5952.9	-6581	1270	308	1.201	-9.08e5	3200	273	[13]
CAH_{10}	-7.60	-4623.0	-5288.2	610	151	1.113		3200	193	[10]
M_4AH_{10}[**]	*-56.02*	*-6394.56*	*-7196*	*549*	*-364*	*4.21*	*3.75e6*	*629*	*220*	*[1,4]*
$1/2M_8A\overline{C}H_{13}$[h]	-33.29[v]	-4339.85	-4875.89	411	512.6				115	[18]
$1/2M_8F\overline{C}H_{13}$[h]	-33.64[v]	-3882.60	-4415.09	423	521.7				119	[18]
Cs (anhydrite)	-4.357	-1322.12	-1434.60	106.7	70.2	-0.099			46	[6,7]

Cemdata14

Changes in Cemdata14 (compared to Cemdata07)

- Addition of data for
  - $C_3AS_{0.84}H_{4.32}$, $C_3AS_{0.41}H_{5.18}$, (formation kinetically hindered at room temp.),
  - $FH_{0.5}$, $C_3FS_{0.84}H_{4.32}$, $C_3FS_{1.34}H_{3.32}$
  - Friedel's salt, Kuzel's salt
  - CO_3-hydrotalcite, pyroaurite
  - hemihydrate, $C_{12}A_7$, CA, and CA_2
- Updated data for
  - $AH_{3,mic}$, CAH_{10}, $C_2AH_{7.5}$, C_3AH_6, C_4AH_{13}, C_4AH_{19},
  - Fe-monocarbonate, Fe-hemicarbonate, Fe-monosulfate, C_3FH_6, C_4FH_{13}
  - thaumasite
- Changes in water content: $C_2AH_{7.5}$, $C_4Fc_{0.5}H_{10}$
- Removal $AH_{3,am}$, C_2FH_8, C_2FSH_8 and Fe-hydrotalcite
- Use of the quarternary C-S-H model from Kulik (2011) instead of the "tobermorite-jennite" model used in cemdata07.
- Rescaling within GEMS for all Al-Fe solid solution to 1Al: 1Fe

b) Influence of temperature

$$K_T = e^{-\frac{\Delta_r G_T^\circ}{RT}}$$

K ↔ Gibbs free energy

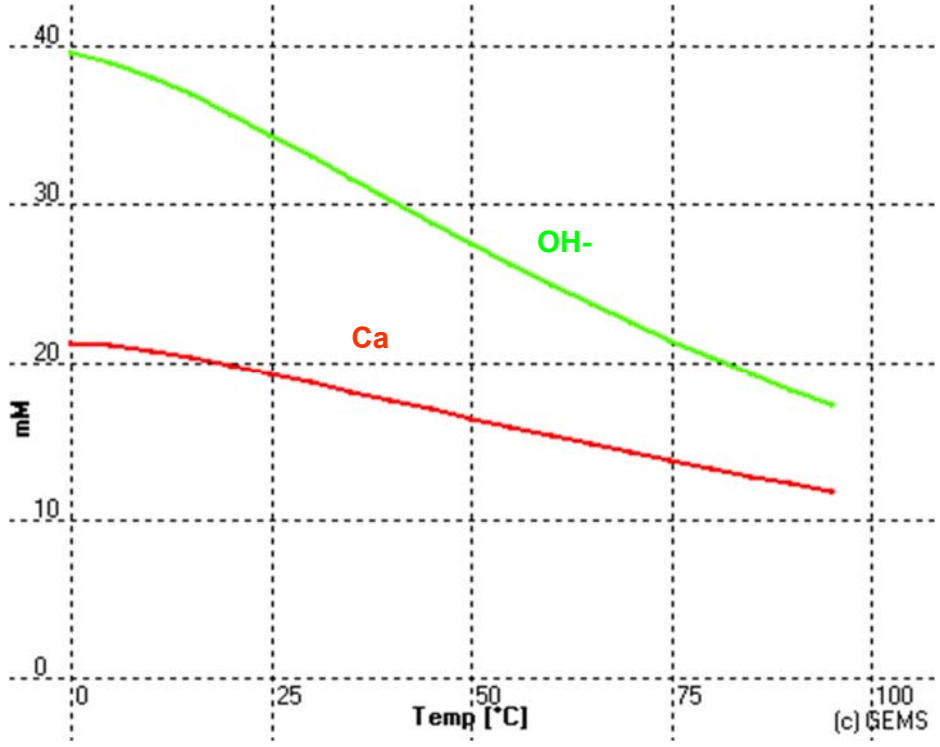
$$\Delta_r G_T^\circ = \sum_i \nu_i \Delta_f G_T^\circ$$

ν_i: $Ca(OH)_2$ (reaction); $\Delta_f G_T^\circ$: Ca^{2+}, OH^- (components)

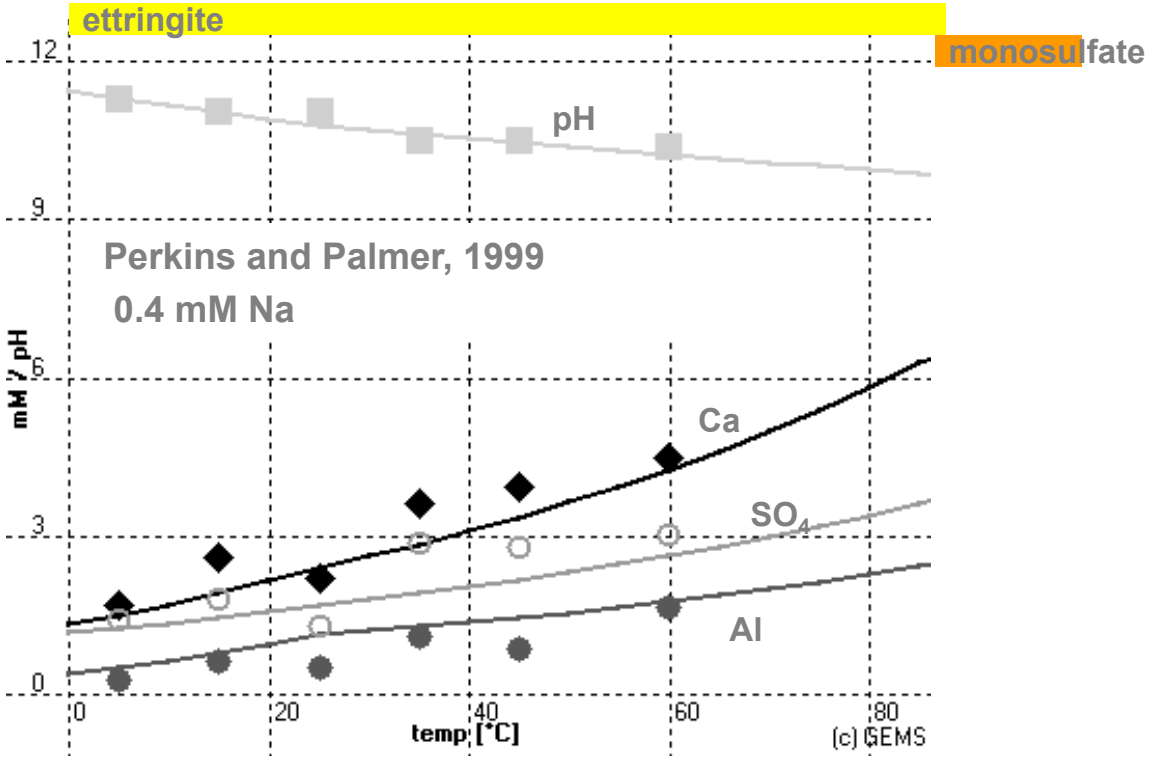
Portlandite solubility: $Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^-$

log K = {Ca^{2+}}*{OH^-}^{2}/{$Ca(OH)_2$}; K = 10^{Ca^{2+}}*{OH^-}^{2}/{$Ca(OH)_2$}

General database: Decrease of portlandite solubility with temperature



Solubility of ettringite as f(T)



Temperature corrections: G°

$\Delta_a G^\circ$ (apparent Gibbs free energy of formation at T); e.g. for a solid $Ca(OH)_2$

T_0 = Reference Temperature: 25 °C

T = Temperature of interest

C_p = Heat capacity:

$C_p = a_0 + a_1 T + a_2 T^{-2} + a_3 T^{0.5} + \ldots$

$$\Delta_a G^o_T = \Delta_f G^o_{T_0} - \int_{T_0}^{T} S^o_T dT$$

$$\Delta_a G^o_T = \Delta_f G^o_{T_0} - S^o_{T_0}(T - T_0) - \int_{T_0}^{T}\int_{T_0}^{T} \frac{C^o_p}{T} dT dT$$

$$= \Delta_f G^o_{T_0} - S^o_{T_0}(T - T_0) - a_0\left(T \ln\frac{T}{T_0} - T + T_0\right)$$

$$- 0.5a_1(T - T_0)^2 - a_2\frac{(T - T_0)^2}{2T \cdot T_0^{\,2}} - a_3\frac{2\left(\sqrt{T} - \sqrt{T_0}\right)^2}{\sqrt{T_0}} - \ldots$$

cf. C:\Selektor2014\Gems3-app\Resources\doc\pdf\T-corrections.pdf;

G Anderson, Cerar (1993): Thermodynamics in Geochemistry

Temperature corrections: log K

$$K_T = e^{-\frac{\Delta_r G_T^\circ}{RT}}$$

$$\Delta_r G_T^\circ = \sum_i \nu_i \Delta_f G_T^\circ$$

$$\log K_T = A_0 + A_1 T + \frac{A_2}{T} + A_3 \ln T + \frac{A_4}{T^2} + A_5 T^2 + \frac{A_6}{T^{0.5}}$$

7 terms

More details:
C:\Selektor2014\Gems3-app\Resources\doc\pdf\T-corrections-Reac.pdf;
Anderson, Cerar: Thermodynamics in Geochemistry
Damidot ea 2011, CCR 41

Temperature corrections: log K

3-term extrapolation
up to 150 °C; > 150 °C isoelectric reactions

$$\Delta Cp_T = \Delta Cp_{T_0} = const$$

$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

$$A_0 = \frac{0.4343}{R} \cdot \left[\Delta_r S^0_{T_0} - \Delta_r Cp_{T_0} (\ln T_0 + 1)\right]$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H^0_{T_0} - \Delta_r Cp_{T_0} T_0)$$

$$A_3 = \frac{0.4343}{R} \cdot \Delta_r Cp_{T_0}$$

2-term extrapolation
(for isoelectric reactions only)

$$\Delta Cp_T = \Delta Cp_{T_0} = 0$$

$$\log K_T = \frac{0.4343}{R}\left(\Delta_r S^0_{T_0} - \frac{\Delta_r H^0_{T_0}}{T}\right)$$

Van't Hoff equation

1-term extrapolation
(for isocoulombic reactions)

$$\Delta Cp_T = 0; \quad \Delta_r H_T^\circ = \Delta_r H_{T_r}^\circ = 0$$

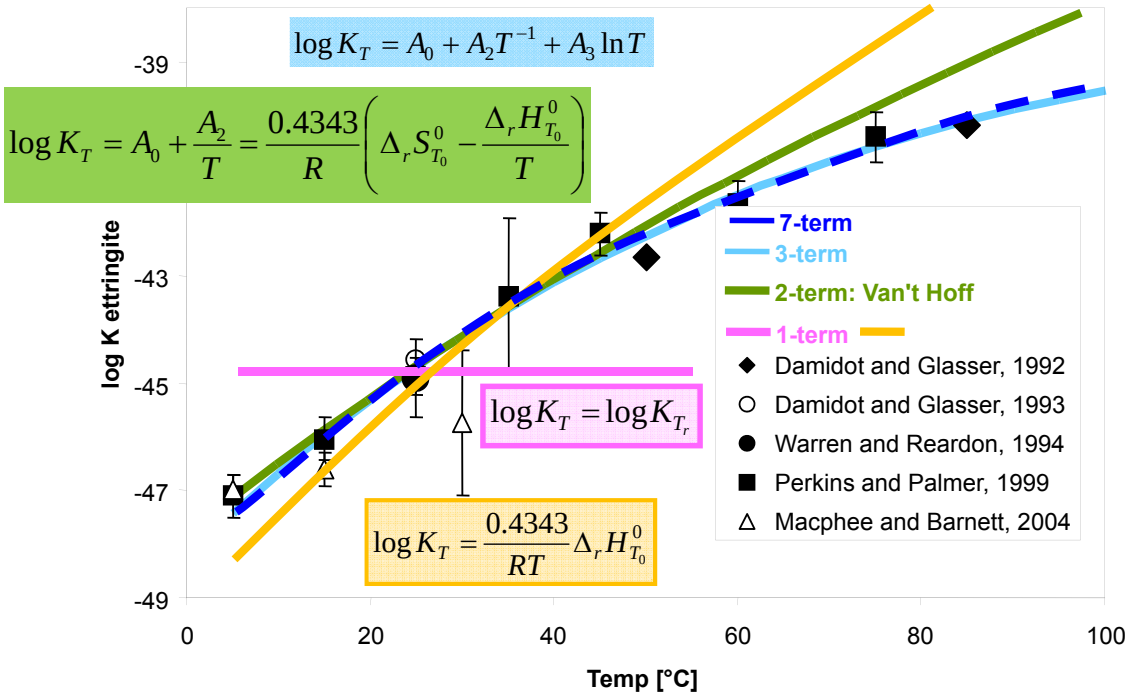
$$\log K_T = \frac{0.4343}{R}\left(\Delta_r S^0_{T_0}\right) = \log K_{T_r}$$

Solubility of ettringite

3-term similar to 7-term

Less parameters

K(ettringite) = $\{Ca^{2+}\}^6 \cdot \{Al(OH)_4^-\}^2 \cdot \{SO_4^{2-}\}^3 \cdot \{OH^-\}^4 \cdot \{H_2O\}^{26}$



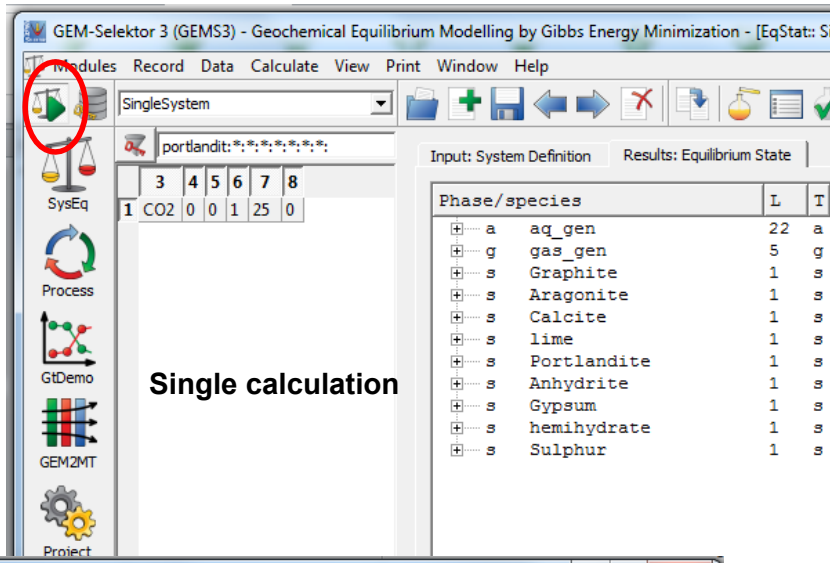
Lothenbach ea CCR 38, 2008; Damidot ea CCR 41, 2011

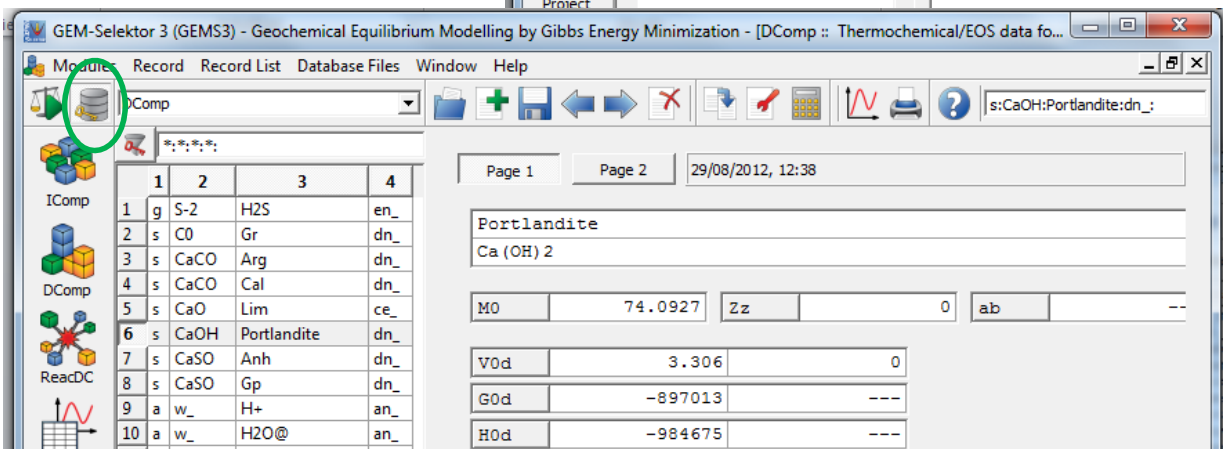
GEMS structure

calculations

Thermodynamic database

for experienced users





Thermodynamic database

Independent components (chemical elements: Ca)

Dependent components: e.g. Ca^{2+}, $Ca(OH)_2$, …

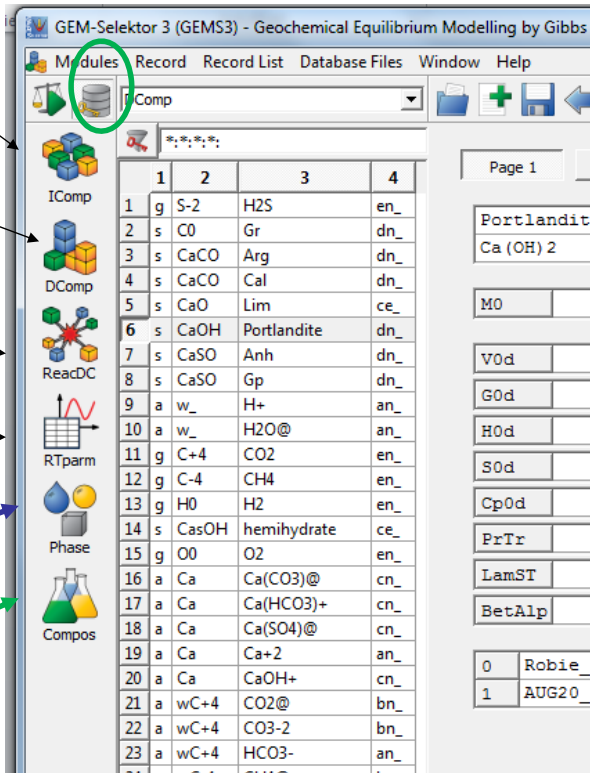
2 input options: both equally valid

Reaction of dependent components (K) e.g. $Ca^{2+} + 2OH^- \Leftrightarrow Ca(OH)_2$

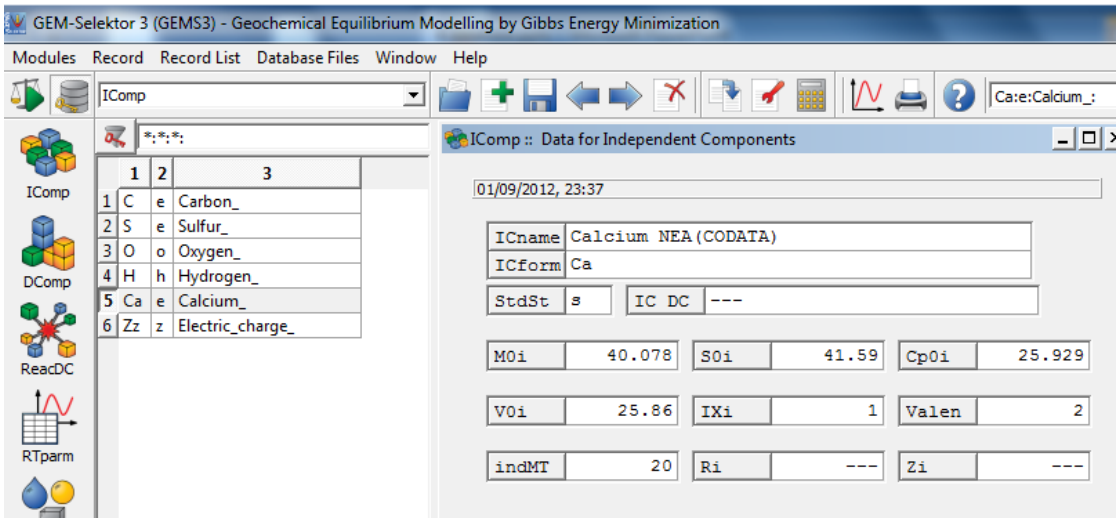
Calculation and plotting of T/P dependency

Solids phases
single phases / solid solutions

Predefined compositions: e.g. air, OPC, slag, …

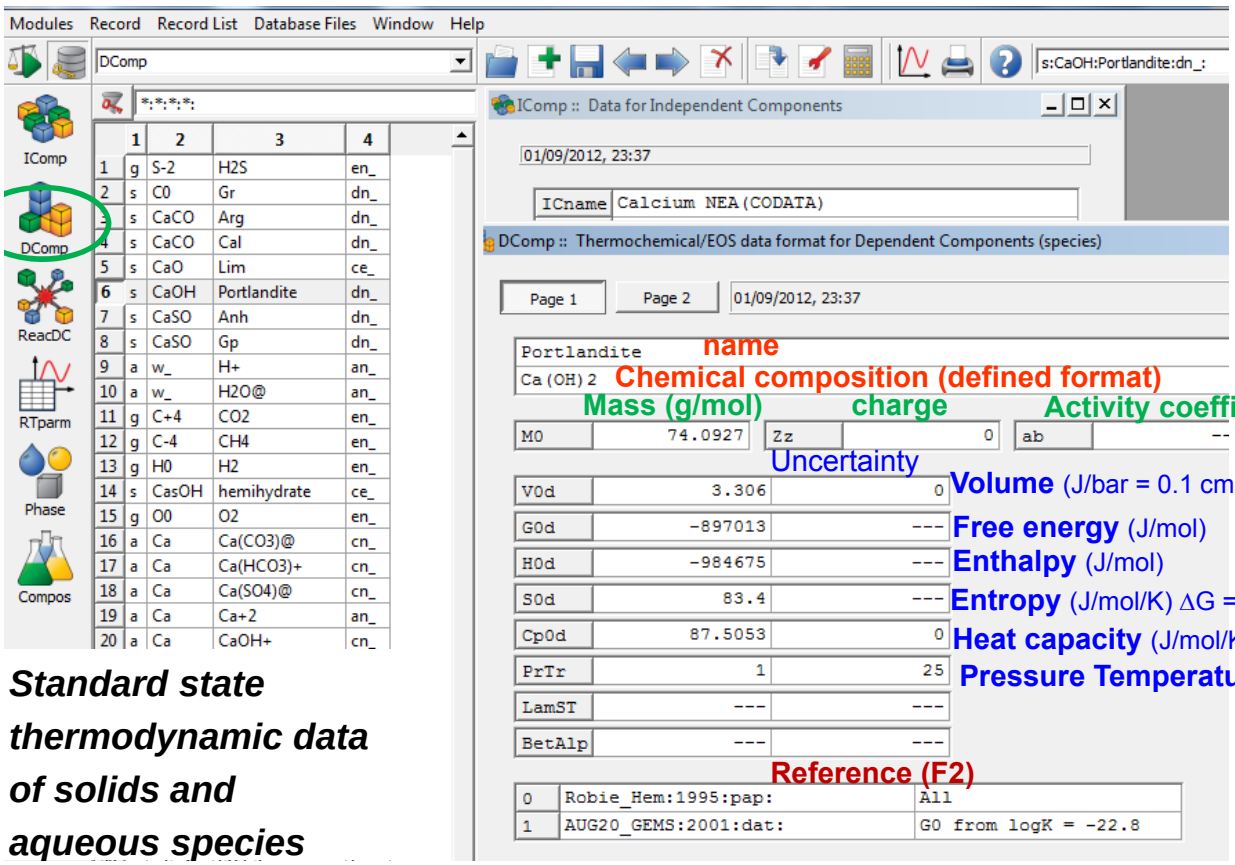


1) GEMS: independent components



Contains basic properties of elements (e.g. molar weight, standard state entropy, valence number)

2) GEMS: dependent components (DComp)



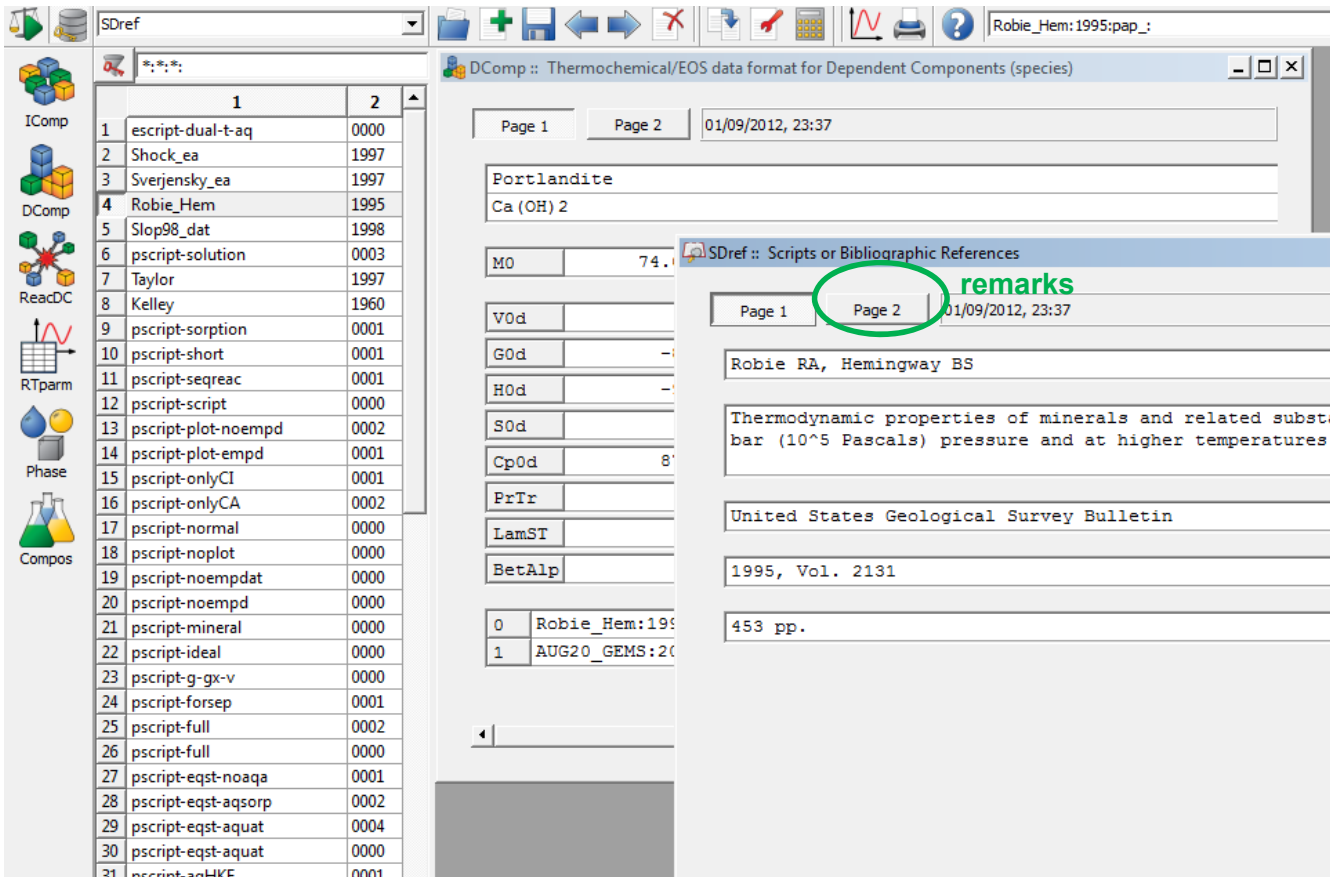
		1	2	3	4
1	g	S-2	H2S		en_
2	s	C0	Gr		dn_
3	s	CaCO	Arg		dn_
4	s	CaCO	Cal		dn_
5	s	CaO	Lim		ce_
6	s	CaOH	Portlandite		dn_
7	s	CaSO	Anh		dn_
8	s	CaSO	Gp		dn_
9	a	w_	H+		an_
10	a	w_	H2O@		an_
11	g	C+4	CO2		en_
12	g	C-4	CH4		en_
13	g	H0	H2		en_
14	s	CasOH	hemihydrate		ce_
15	g	O0	O2		en_
16	a	Ca	Ca(CO3)@		cn_
17	a	Ca	Ca(HCO3)+		cn_
18	a	Ca	Ca(SO4)@		cn_
19	a	Ca	Ca+2		an_
20	a	Ca	CaOH+		cn_

M0	74.0927	
Zz	0	
ab		
V0d	3.306	0
G0d	-897013	---
H0d	-984675	---
S0d	83.4	---
Cp0d	87.5053	0
PrTr	1	25
LamST	---	---
BetAlp	---	---

0	Robie_Hem:1995:pap:	All
1	AUG20_GEMS:2001:dat:	G0 from logK = -22.8

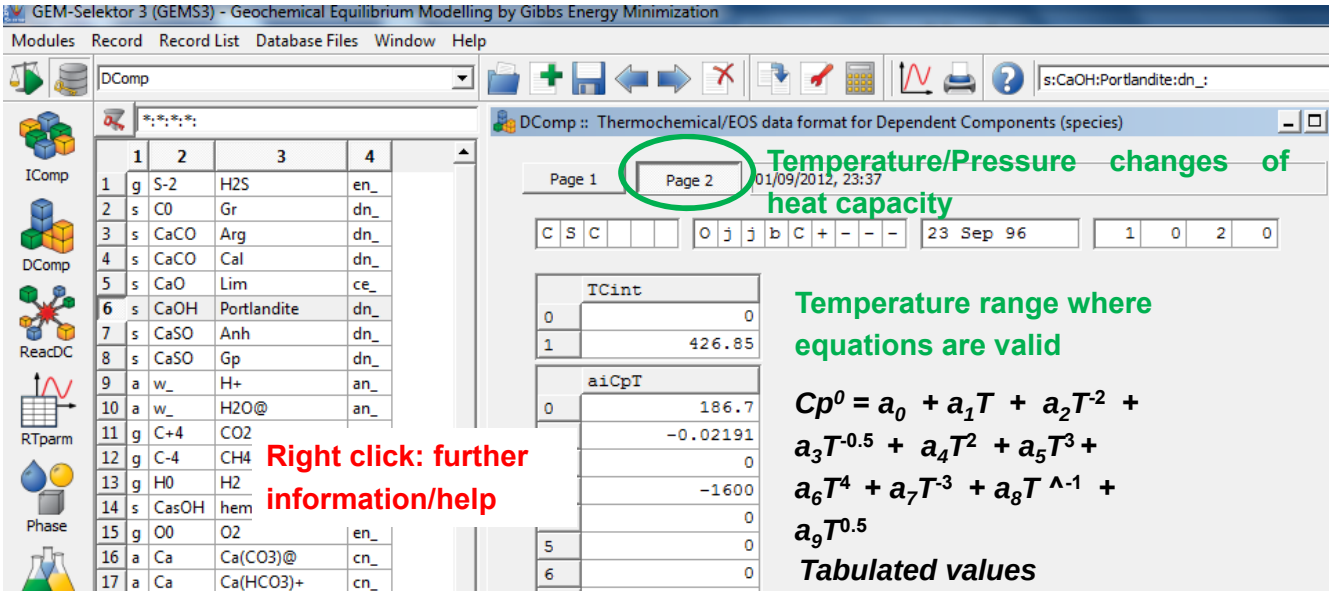
Standard state thermodynamic data of solids and aqueous species

GEMS: dependent components (DComp)



		1	2
1		escript-dual-t-aq	0000
2		Shock_ea	1997
3		Sverjensky_ea	1997
4		Robie_Hem	1995
5		Slop98_dat	1998
6		pscript-solution	0003
7		Taylor	1997
8		Kelley	1960
9		pscript-sorption	0001
10		pscript-short	0001
11		pscript-seqreac	0001
12		pscript-script	0000
13		pscript-plot-noempd	0002
14		pscript-plot-empd	0001
15		pscript-onlyCI	0001
16		pscript-onlyCA	0002
17		pscript-normal	0000
18		pscript-noplot	0000
19		pscript-noempdat	0000
20		pscript-noempd	0000
21		pscript-mineral	0000
22		pscript-ideal	0000
23		pscript-g-gx-v	0000
24		pscript-forsep	0001
25		pscript-full	0002
26		pscript-full	0000
27		pscript-eqst-noaqa	0001
28		pscript-eqst-aqsorp	0002
29		pscript-eqst-aquat	0004
30		pscript-eqst-aquat	0000

GEMS: dependent components (DComp)



		1	2	3	4
1	g	S-2	H2S		en_
2	s	C0	Gr		dn_
3	s	CaCO	Arg		dn_
4	s	CaCO	Cal		dn_
5	s	CaO	Lim		ce_
6	s	CaOH	Portlandite		dn_
7	s	CaSO	Anh		dn_
8	s	CaSO	Gp		dn_
9	a	w_	H+		an_
10	a	w_	H2O@		an_
11	g	C+4	CO2		
12	g	C-4	CH4		
13	g	H0	H2		
14	s	CasOH	hem		
15	g	O0	O2		en_
16	a	Ca	Ca(CO3)@		cn_
17	a	Ca	Ca(HCO3)+		cn_

	TCint
0	0
1	426.85

	aiCpT
0	186.7
	-0.02191
	0
	-1600
	0
5	0
6	0

$Cp^0 = a_0 + a_1T + a_2T^{-2} + a_3T^{-0.5} + a_4T^2 + a_5T^3 + a_6T^4 + a_7T^{-3} + a_8T^{\wedge -1} + a_9T^{0.5}$

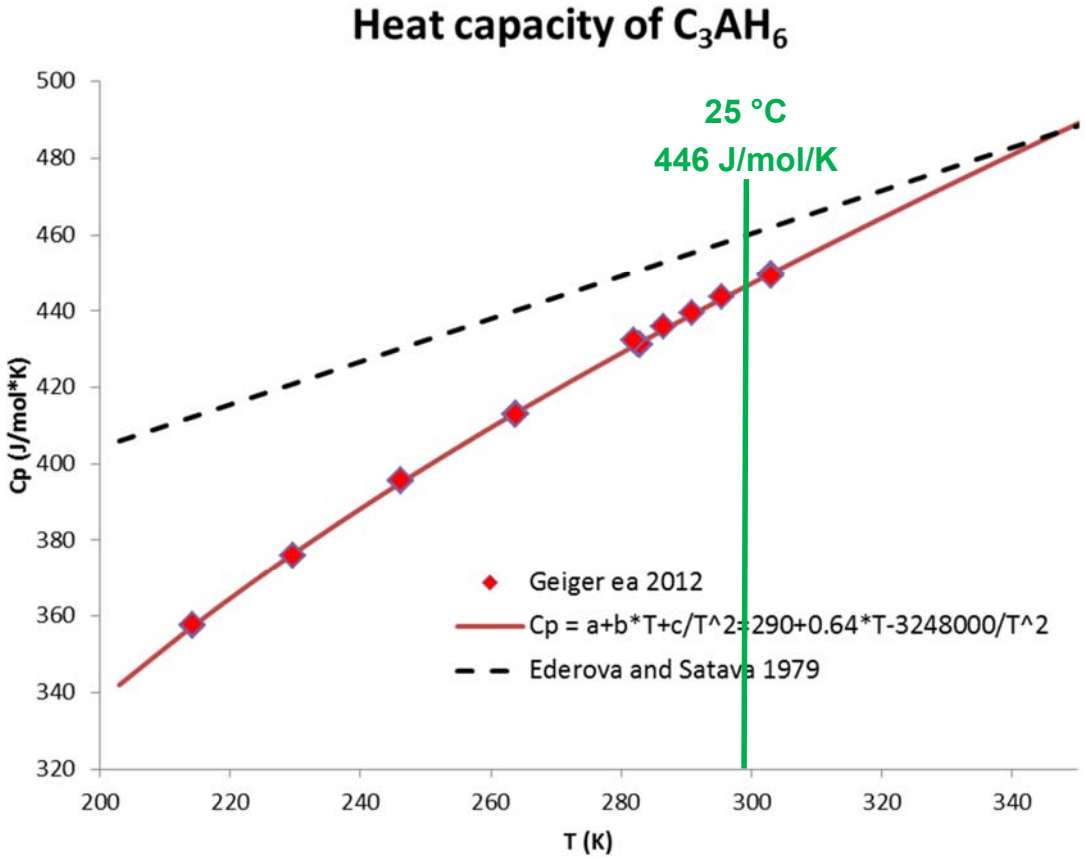
Tabulated values

Table 4

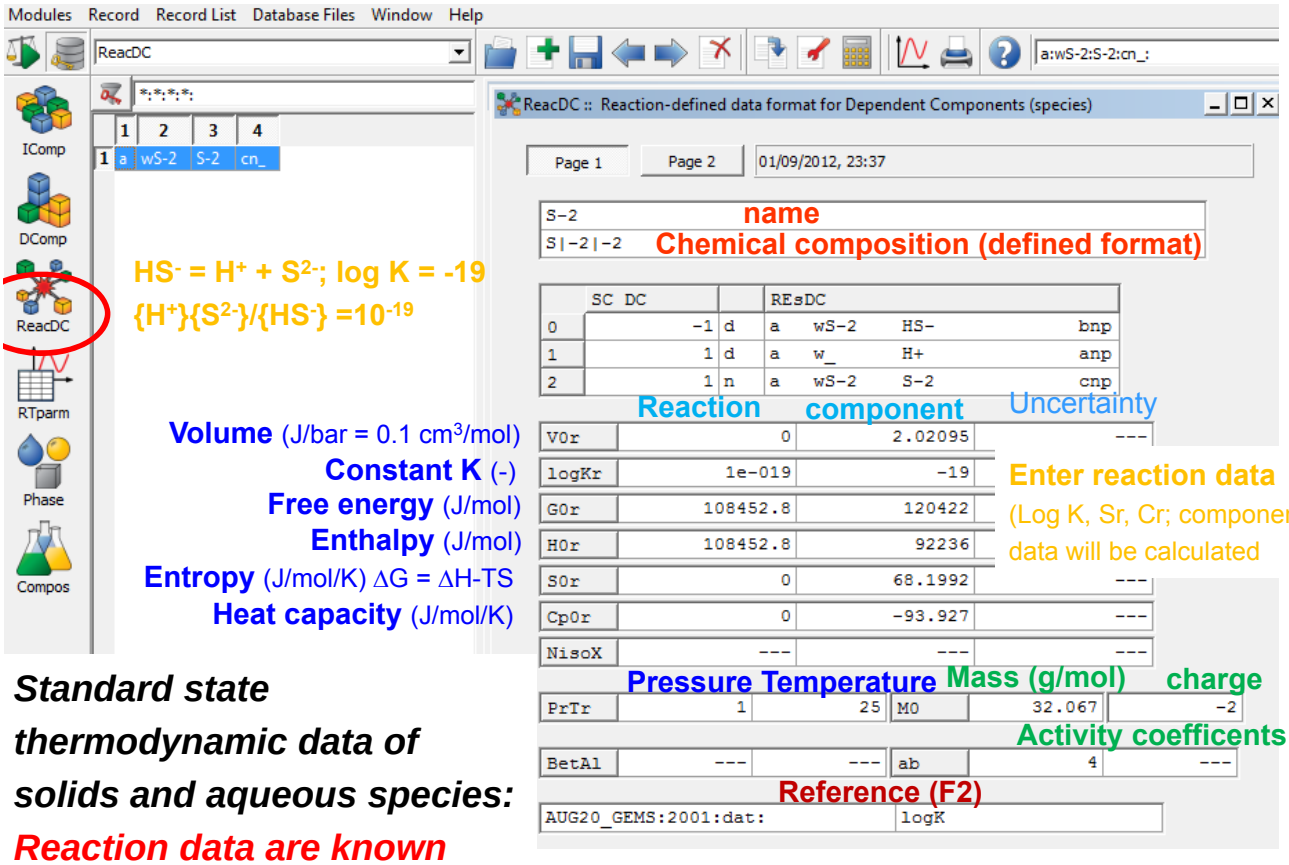
Standard thermodynamic properties at 25 °C: Thermo007[m]

	log K^a_{50}	$\Delta_f G°$ [kJ/mol]	a_0 [J/K/mol]	a_1	a_2	a_3	$V°$ [cm^3
(Al-)ettringite	−44.9[b]	−15205.94[b]	1939[c]	0.789[c]			707[d]
Tricarboaluminate	−46.5[f]	−14565.64[f]	2042[b]	0.559[b]	−7.78e6[b]		650[d]
Fe-ettringite	−44.0[g]	−14282.36[g]	1922[g]	0.855[g]	2.02e6[g]		717[h]
C_3AH_6	−20.84[f]	−5010.09[f]	292[c]	0.561[c]			150[d]

GEMS: dependent components (DComp)



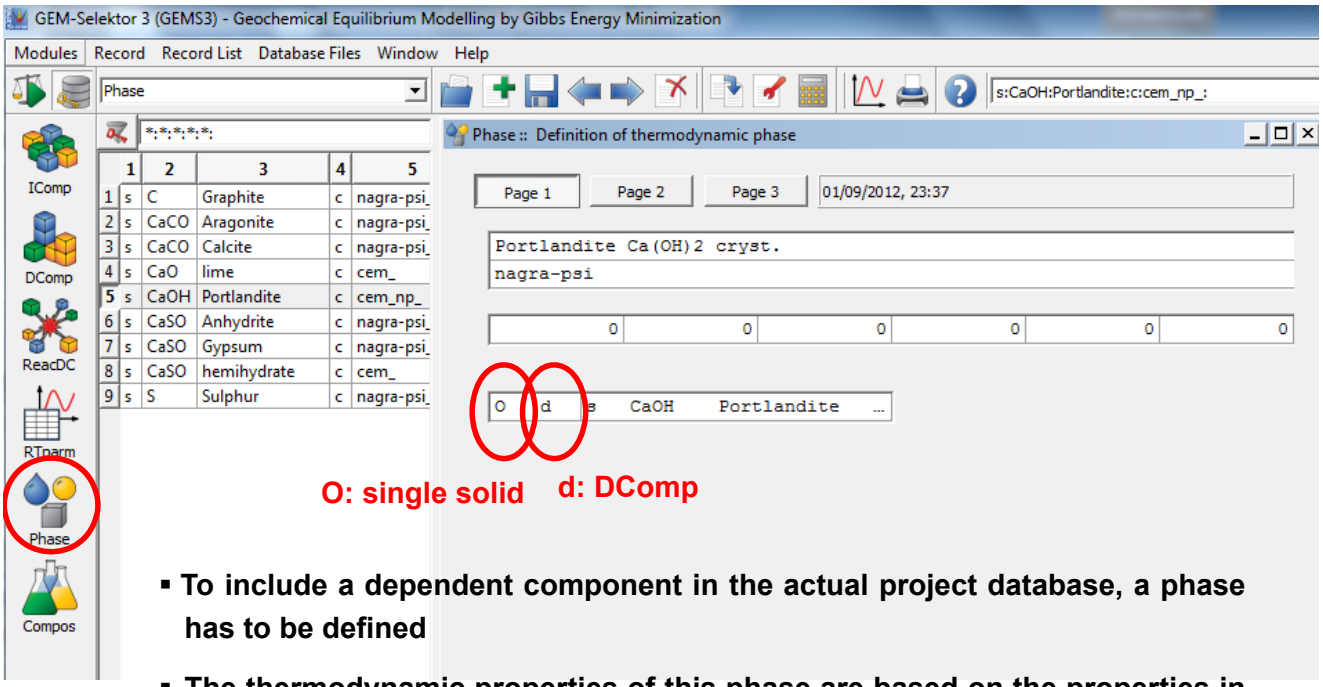
3) GEMS: reactions (ReacDC)



Standard state thermodynamic data of solids and aqueous species:

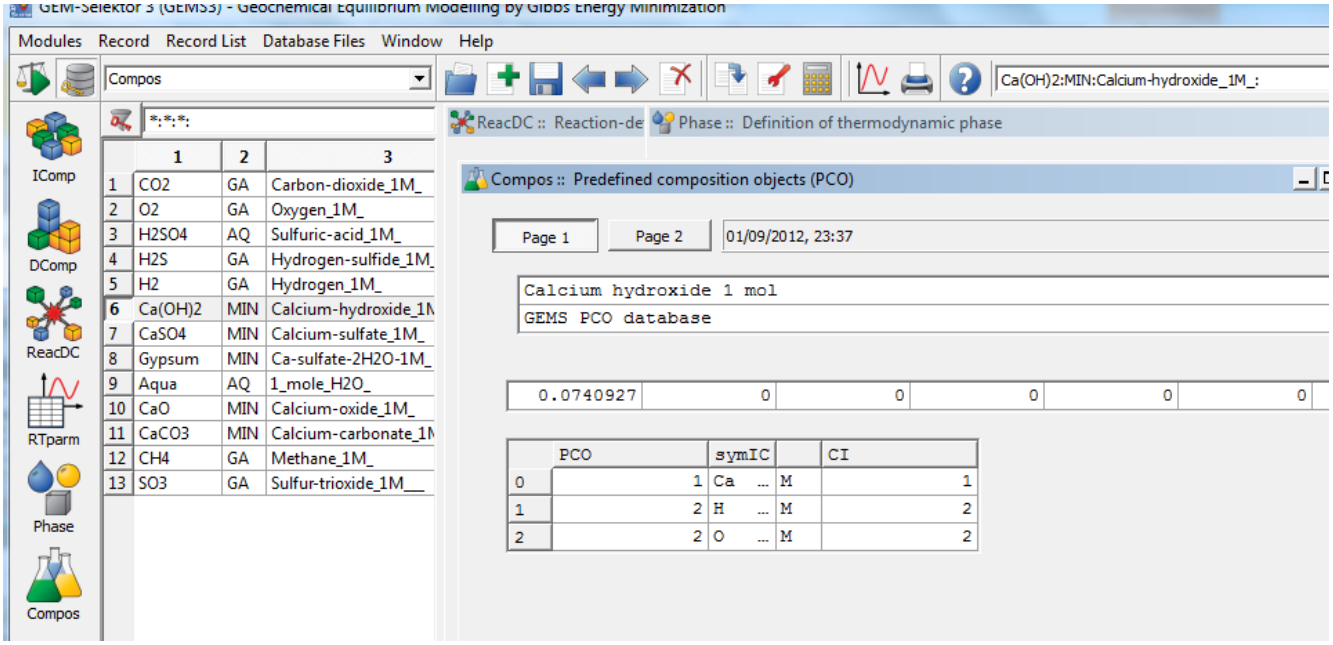
Reaction data are known

5.) Thermodynamic Phases



- **To include a dependent component in the actual project database, a phase has to be defined**
- **The thermodynamic properties of this phase are based on the properties in the dependent component entry of the database and possible additional data e.g. mixing parameters for solid solutions**

6) GEMS: predefined composition



	1	2	3
1	CO2	GA	Carbon-dioxide_1M_
2	O2	GA	Oxygen_1M_
3	H2SO4	AQ	Sulfuric-acid_1M_
4	H2S	GA	Hydrogen-sulfide_1M_
5	H2	GA	Hydrogen_1M_
6	Ca(OH)2	MIN	Calcium-hydroxide_1M
7	CaSO4	MIN	Calcium-sulfate_1M_
8	Gypsum	MIN	Ca-sulfate-2H2O-1M_
9	Aqua	AQ	1_mole_H2O_
10	CaO	MIN	Calcium-oxide_1M_
11	CaCO3	MIN	Calcium-carbonate_1M
12	CH4	GA	Methane_1M_
13	SO3	GA	Sulfur-trioxide_1M__

	PCO	symIC		CI
0	1	Ca ...	M	1
1	2	H ...	M	2
2	2	O ...	M	2

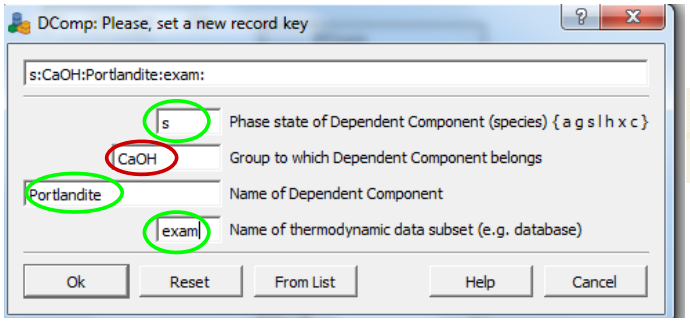
Contains chemical compositions of input (e.g. OPC, slag, Ca(OH)2, HCl, …)

Alternative way of input, no thermodynamic properties needed

Further tutorials for database management

- **Creation of new entries**
  - **DComp**
  - **ReacDC**
  - **Temperature and pressure plots**
  - **Thermodynamic phases**

DComp– creation of new entries



Phase state (s … solid; a … aqueous; g … gaseous

Group id (e.g. elements of chem composition

name

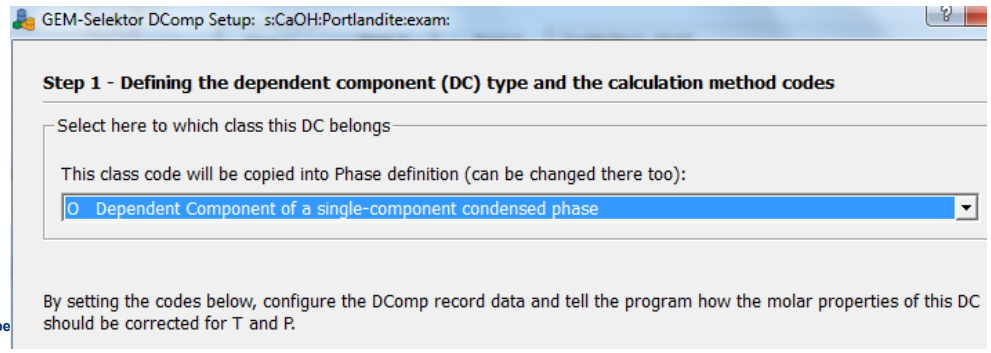
Comment (e.g. cem … cement; Exam: Example)

Leave default values if including a single phase or an ideal solid solution
<u>Optional:</u> Choice of mixing model if a non ideal solid solution is included

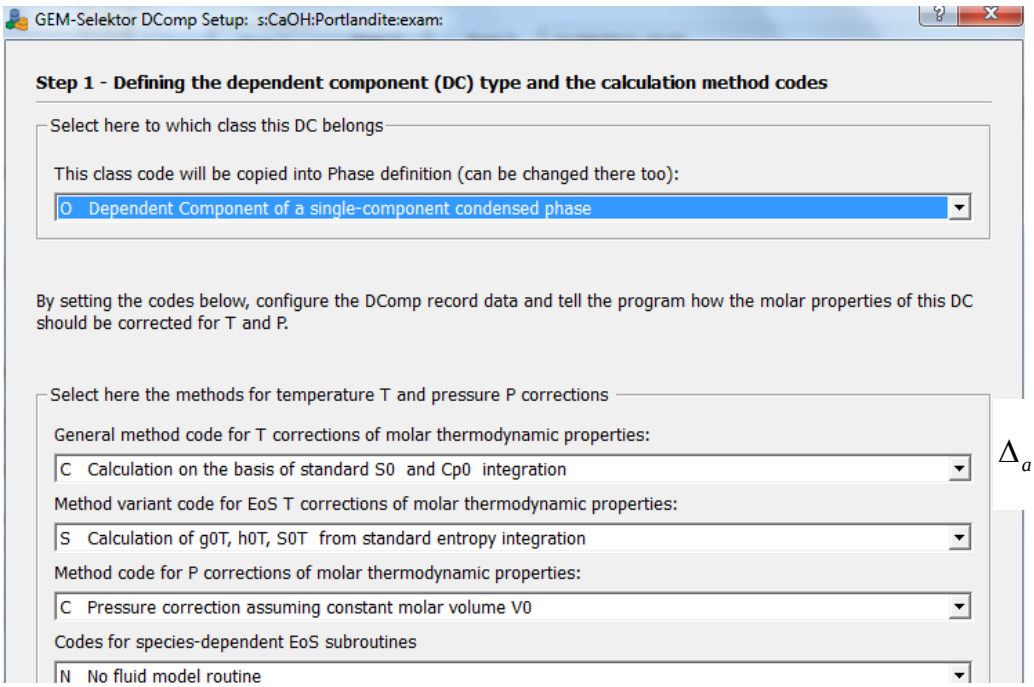
O: solid phase

S: Aqueous species

M: Major end-member *(solvent)*
J: Junior end-member *(solute)*



DComp– creation of new entries



Optional parameters for experienced users, else leave default values

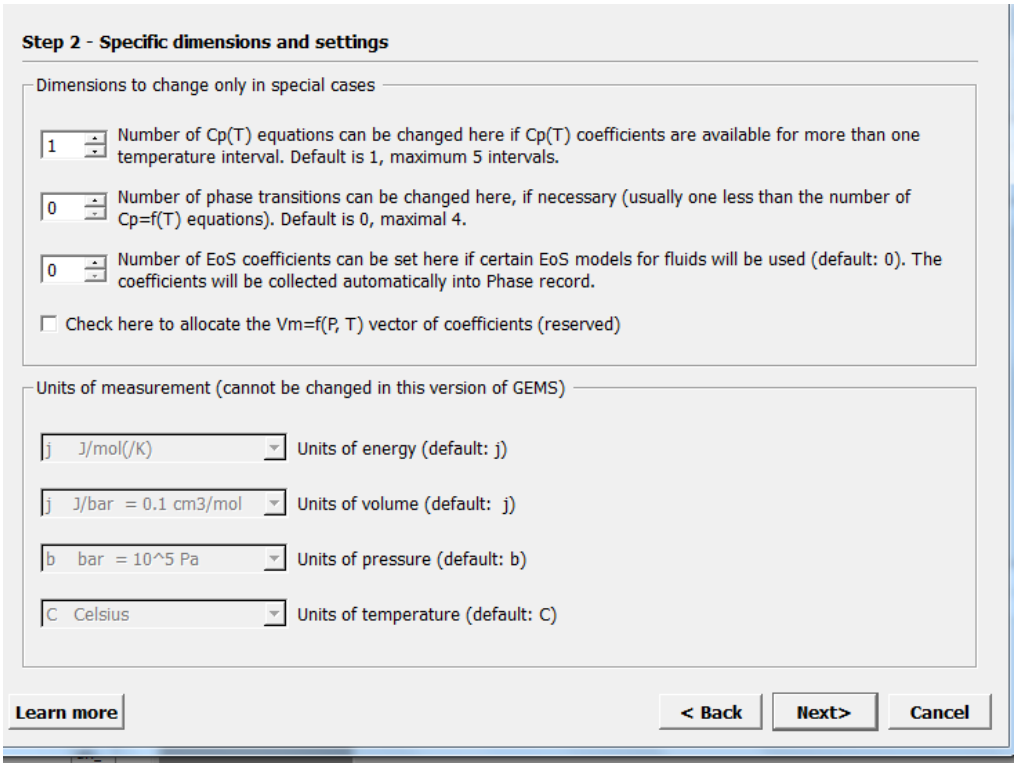
Default: "CS"

$$\Delta_a G^o_T = \Delta_f G^o_{T_0} - \int_{T_0}^{T} S^o_T dT$$

and "C"

Alternatively, the "HKF" is used for aqueous species. *This optional vector contains empirical parameters of revised Helgeson- Kirkham- Flowers equation of state for calculation of standard partial molal properties of aqueous species up to 1000 oC and 5000 bar [1981HEL/KIR; 1997SHO/SAS]. The coefficients were imported from SPRONS92.DAT file [1992JOH/OEL] and its latest extension, SLOP98.DAT [1997SHO/SAS;*

DComp– creation of new entries



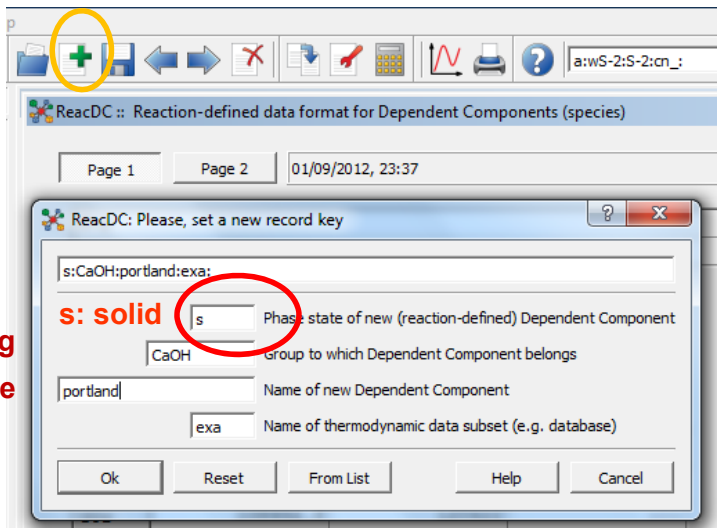
Optional parameters for experienced users, else leave default values

3) GEMS: reactions (ReacDC): new

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

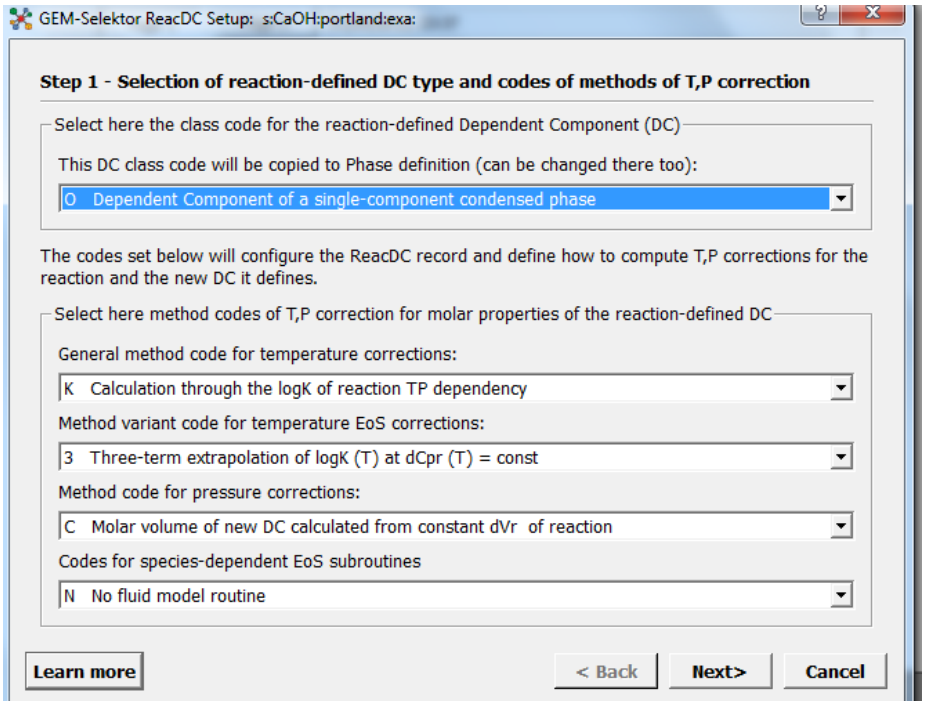
$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$



Elements:ordering

Component name

Data base: «example»



$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

(K) 3

Three-term extrapolation of log*K (T)* at *dCpr(T)* = const (preferable). Enter non-[empty] values into the `Cp0r[0,0]` cell, and into either `H0r[0,0]` or `S0r[0,0]` cells (another must contain [empty]); enter a non-empty value in either `logKr[0,0]`, `logKr[0,1]` or `G0r[0,0]` cells (the other two cells and `G0r[0,1]` must contain [empty]). Then re-calculate and save the record. Use this code combination also for the PRONSPREP calculation.

C

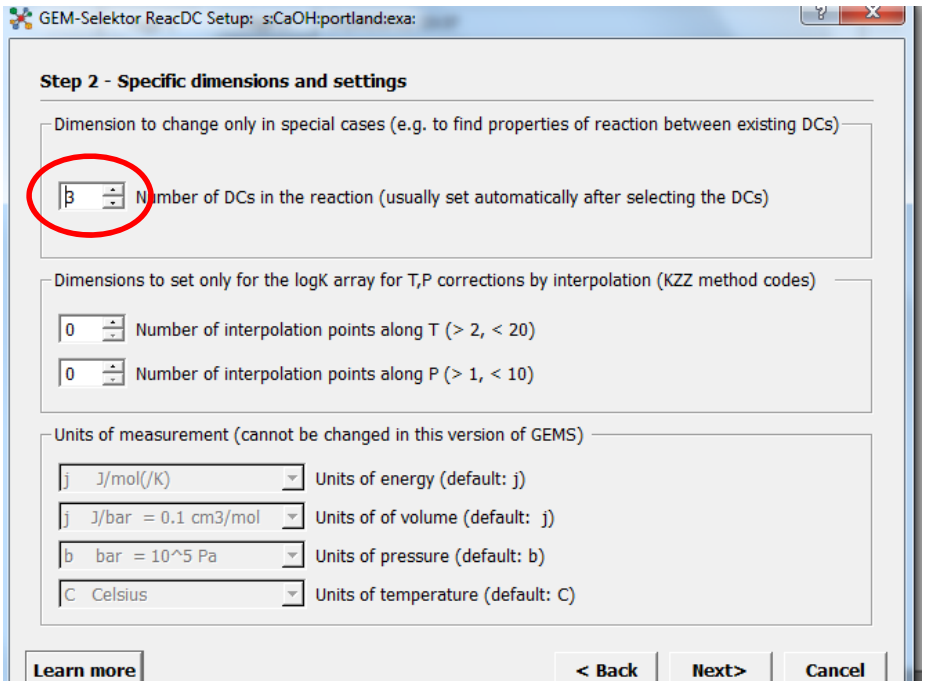
Molar volume of species V^o (in DComp) or dVr of reaction (in ReacDC) is assumed to be constant, independent of P and T (may be used for minerals up to a 1-2 kbar pressures at low-to-moderate temperatures).

3) GEMS: reactions (ReacDC): new

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

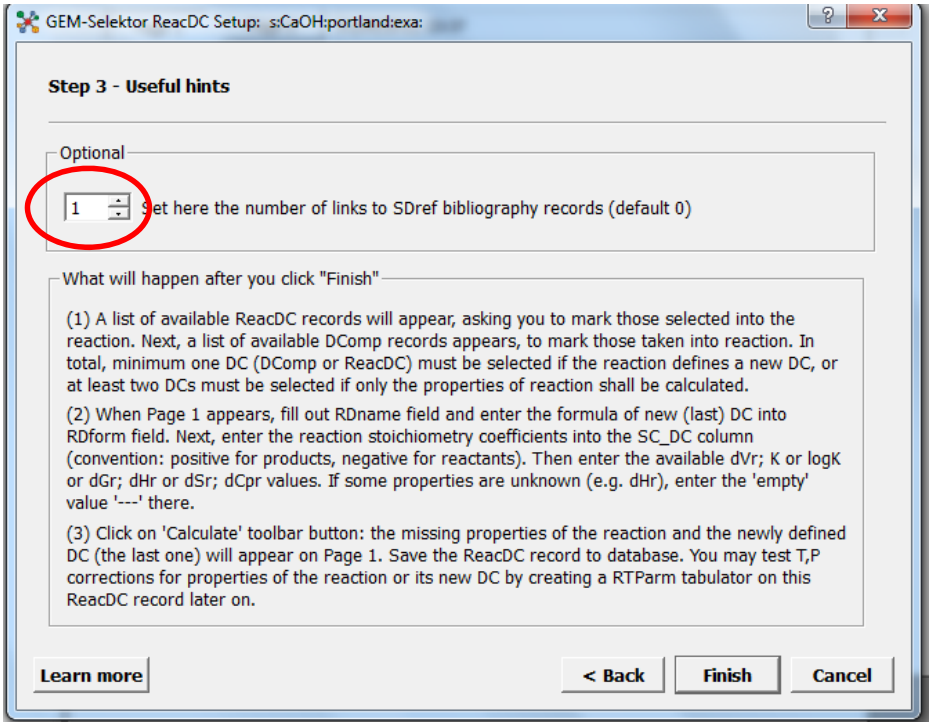
$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$



Ca^{2+}, OH^-, $Ca(OH)_2$

3) GEMS: reactions (ReacDC)

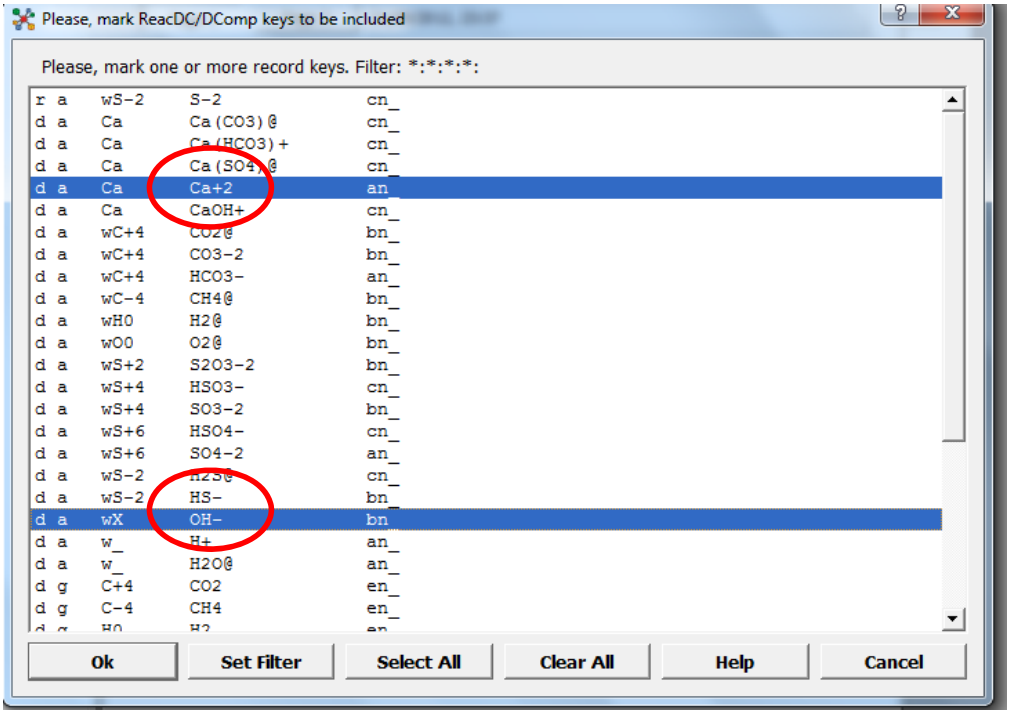
Portlandite solubility:
$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2
$\{Ca^{2+}\}\{OH^-\}/\{Ca(OH)_2\} = 10^{-5.2}$



Literature reference

3) GEMS: reactions (ReacDC)

Portlandite solubility:
$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2
$\{Ca^{2+}\}\{OH^-\}/\{Ca(OH)_2\} = 10^{-5.2}$



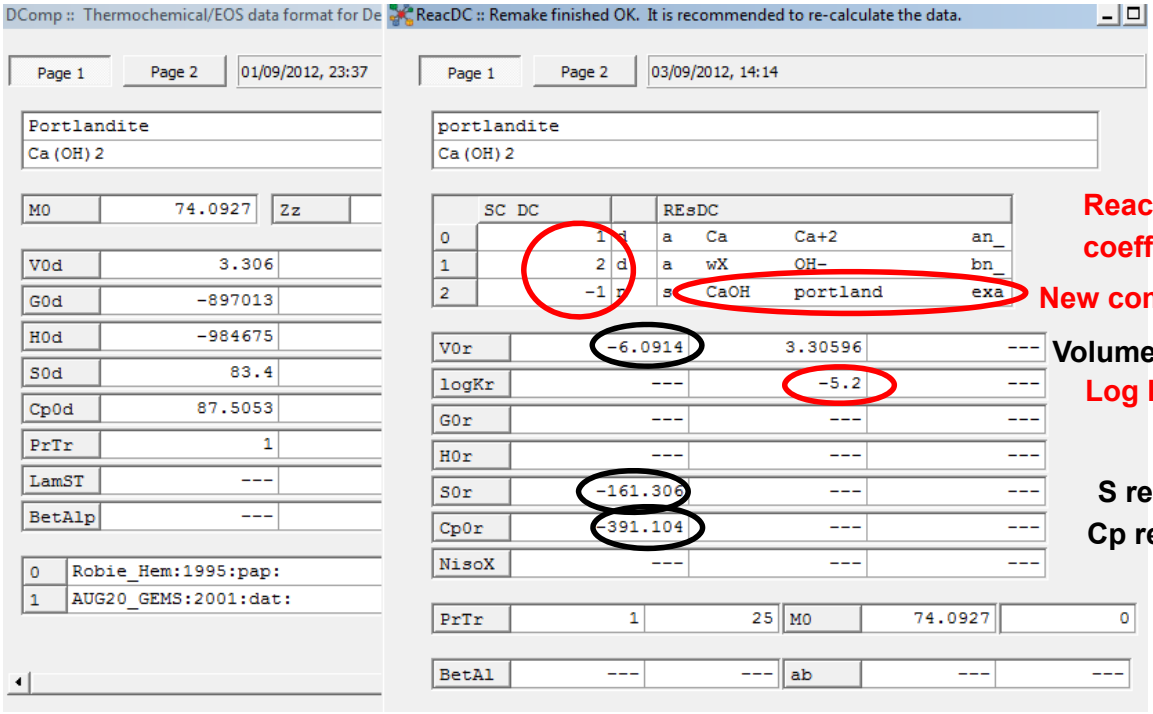
Chose existing compounds;
New compound will be made by the programme

3) GEMS: reactions (ReacDC)

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

$\{Ca^{2+}\}\{OH^-\}^2/\{Ca(OH)_2\} = 10^{-5.2}$



Reaction coefficient

New component

Volume changes

Log K

S reaction

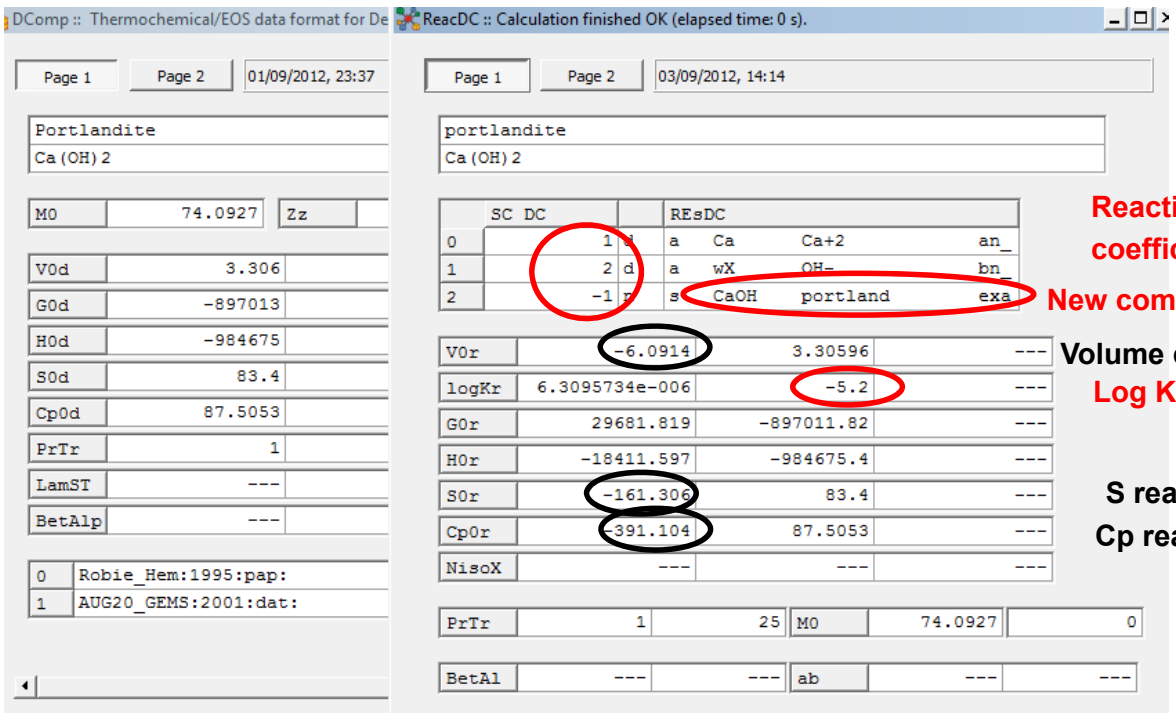
Cp reaction

3) GEMS: reactions (ReacDC)

Portlandite solubility:

$Ca(OH)_2 = Ca^{2+} + 2OH^-$; log K = -5.2

$\{Ca^{2+}\}\{OH^-\}/\{Ca(OH)_2\} = 10^{-5.2}$



Reaction coefficient

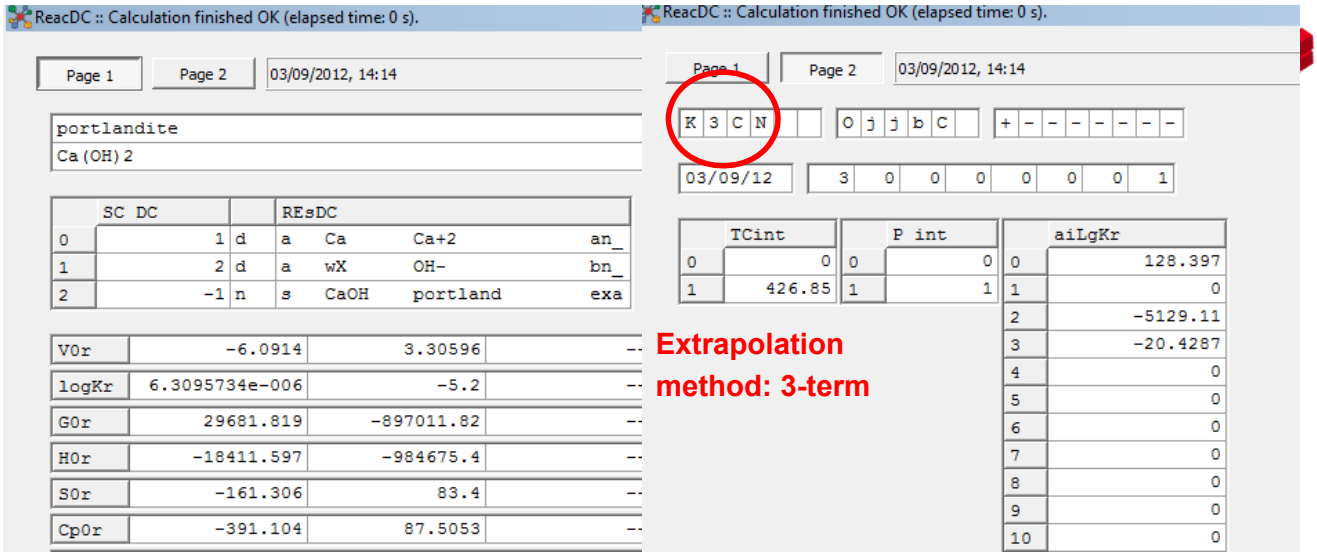
New component

Volume changes

Log K

S reaction

Cp reaction



Extrapolation method: 3-term

Calculates automatically temperature dependent function of the solubility product, depending on the initial data input

see C:\Selektor\Gems3-app\Resources\doc\pdf\T-corrections-Reac.pdf

3-term extrapolation $\Delta Cp_T = \Delta Cp_{T_0} = const$

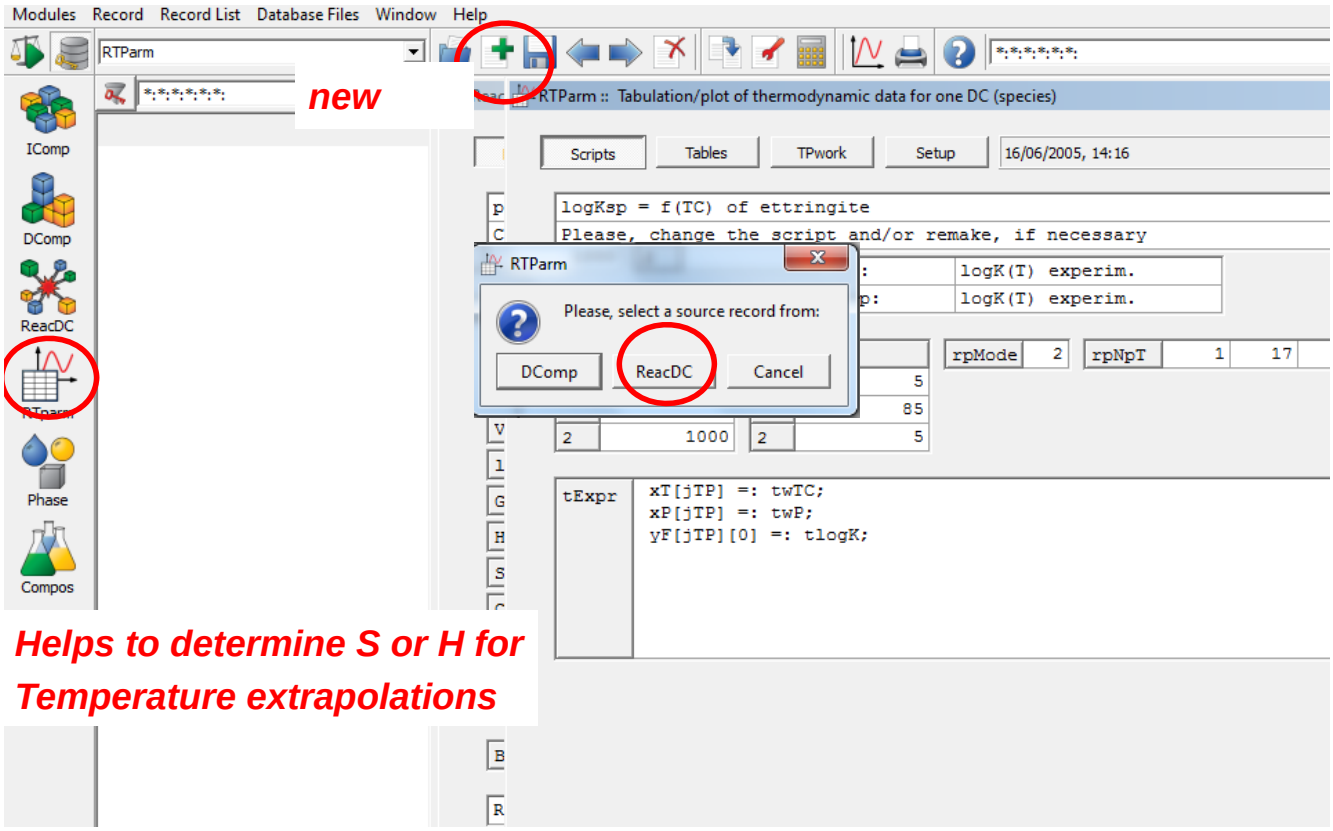
$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T$$

$$A_0 = \frac{0.4343}{R} \cdot \left[\Delta_r S^0_{T_0} - \Delta_r Cp_{T_0} (\ln T_0 + 1)\right]$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H^0_{T_0} - \Delta_r Cp_{T_0} T_0)$$

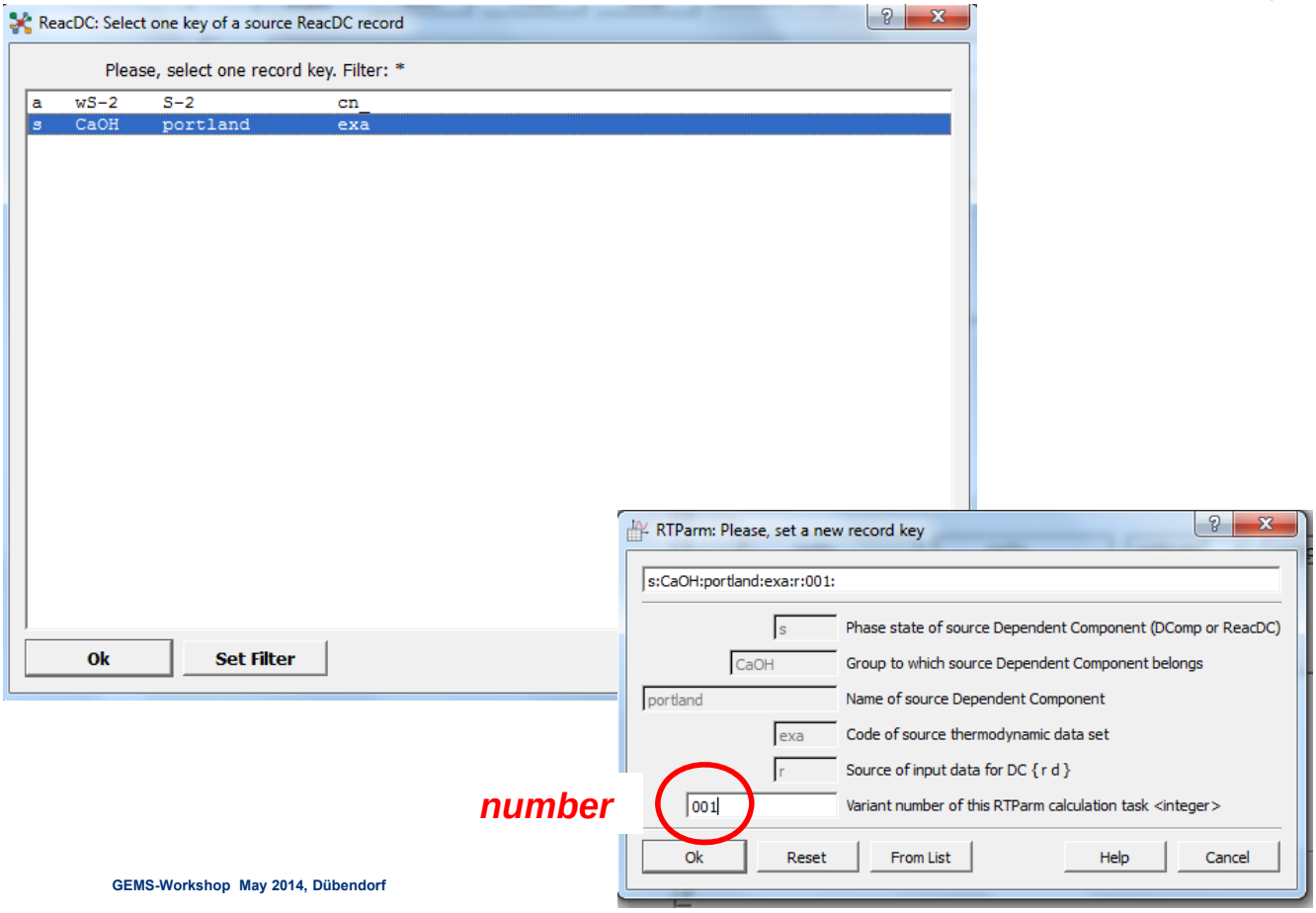
$$A_3 = \frac{0.4343}{R} \cdot \Delta_r Cp_{T_0} = \frac{0.4343}{8.3145} \cdot -391.1 = -20.43$$

4.) Plot of temperature/pressure dependent thermodynamic data

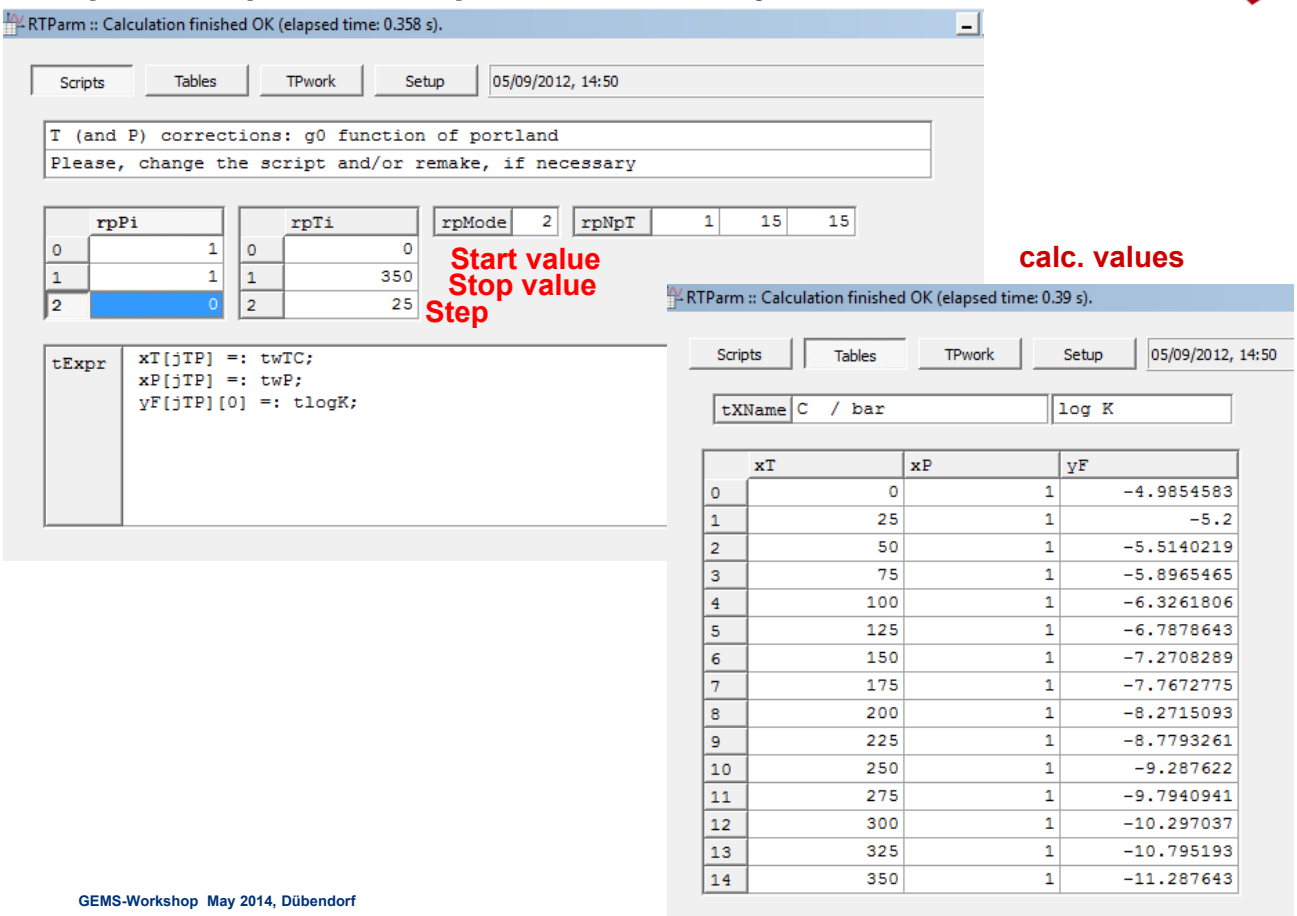


Helps to determine S or H for Temperature extrapolations

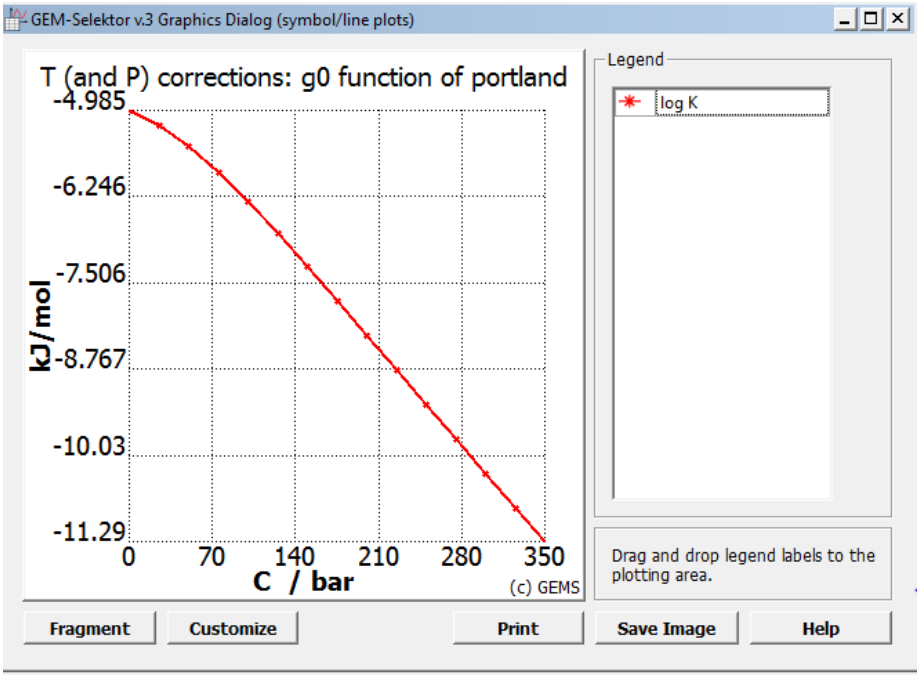
Temperature/pressure dependent thermodynamic data



Temperature/pressure dependent thermodynamic data



	xT	xP	yF
0	0	1	-4.9854583
1	25	1	-5.2
2	50	1	-5.5140219
3	75	1	-5.8965465
4	100	1	-6.3261806
5	125	1	-6.7878643
6	150	1	-7.2708289
7	175	1	-7.7672775
8	200	1	-8.2715093
9	225	1	-8.7793261
10	250	1	-9.287622
11	275	1	-9.7940941
12	300	1	-10.297037
13	325	1	-10.795193
14	350	1	-11.287643

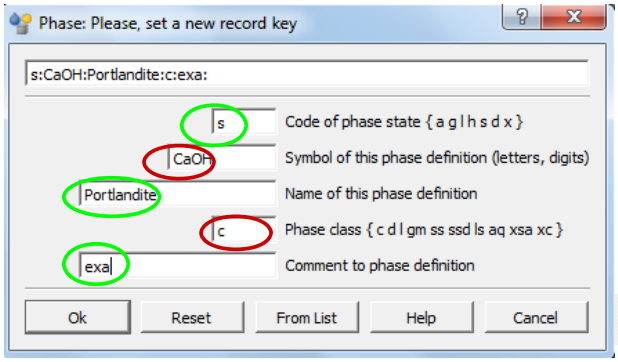


Graphical output

Comparison between extrapolated $LogK_T$ function and experimental values:

Good tool for visual data fitting, e.g. estimation of ΔH_0^r based on experimental data

5.) Thermodynamic Phases – creation of entries



Phase state (s … solid; a … aqueous; g … gaseous)

Group id (e.g. elements of chem composition name

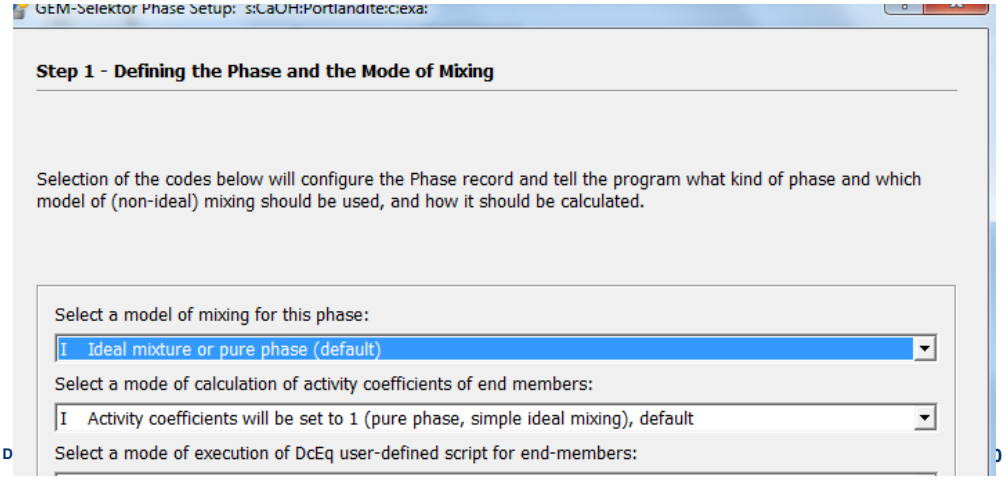
c: condensed solid (single compound); ss: solid solution; aq: Aqueous

Comment (e.g. cem: cement; exa: example)

Leave default values if including a single phase or an ideal solid solution

<u>Optional:</u> Choice of mixing model if a non ideal solid solution is included

I for Single phase or ideal solid solution:

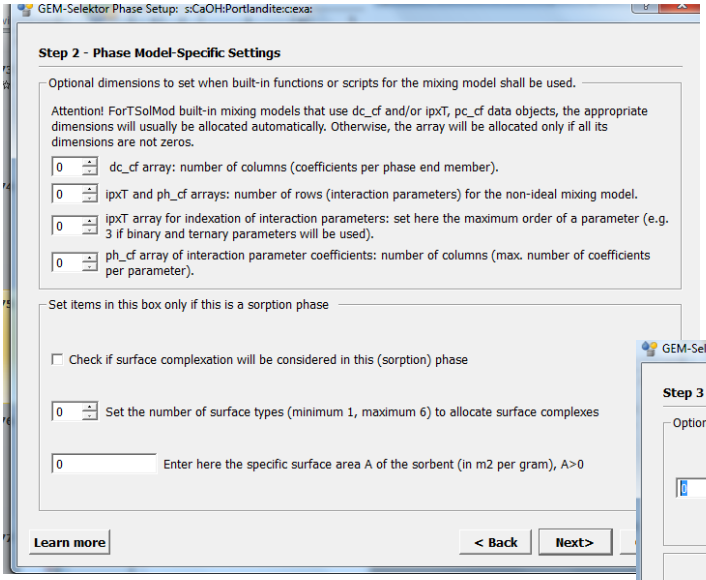


5.) Thermodynamic Phases – creation of entries

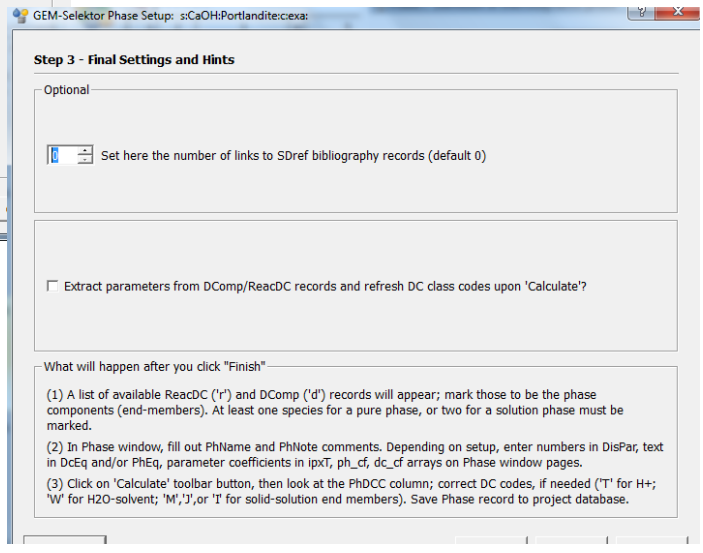
I	Ideal mixture (also multi-site) or pure phase, default
M	Binary subregular Margules solid-solution model
G	Binary Redlich-Kister solid-solution model
T	Ternary regular Margules solid-solution model
R	Regular multicomponent solid- or liquid solution model
V	Van Laar multicomponent solid- or liquid solution model
K	Redlich-Kister multicomponent solid- or liquid solution model
B	Microscopic a(symmetric) multicomponent solid-solution model (reserved)
L	NRTL multicomponent liquid solution model
W	Wilson multicomponent liquid solution (or ion exchange) model

Optional parameters only for experienced users, otherwise leave default value "I" !

5.) Thermodynamic Phases – creation of entries



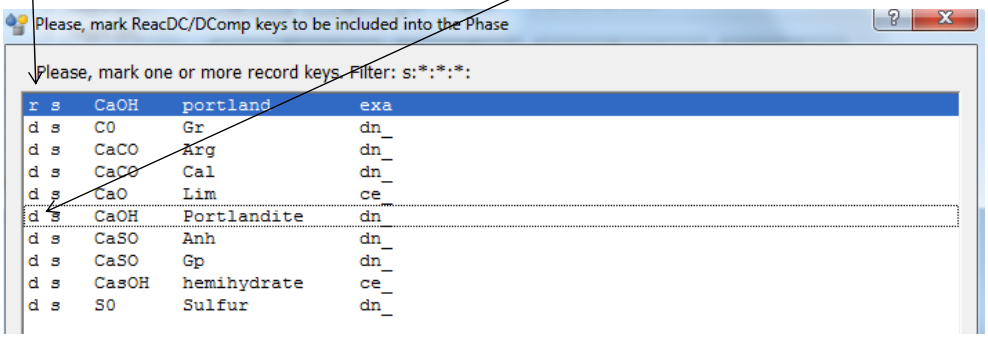
Optional parameters only for experienced users, otherwise leave default values



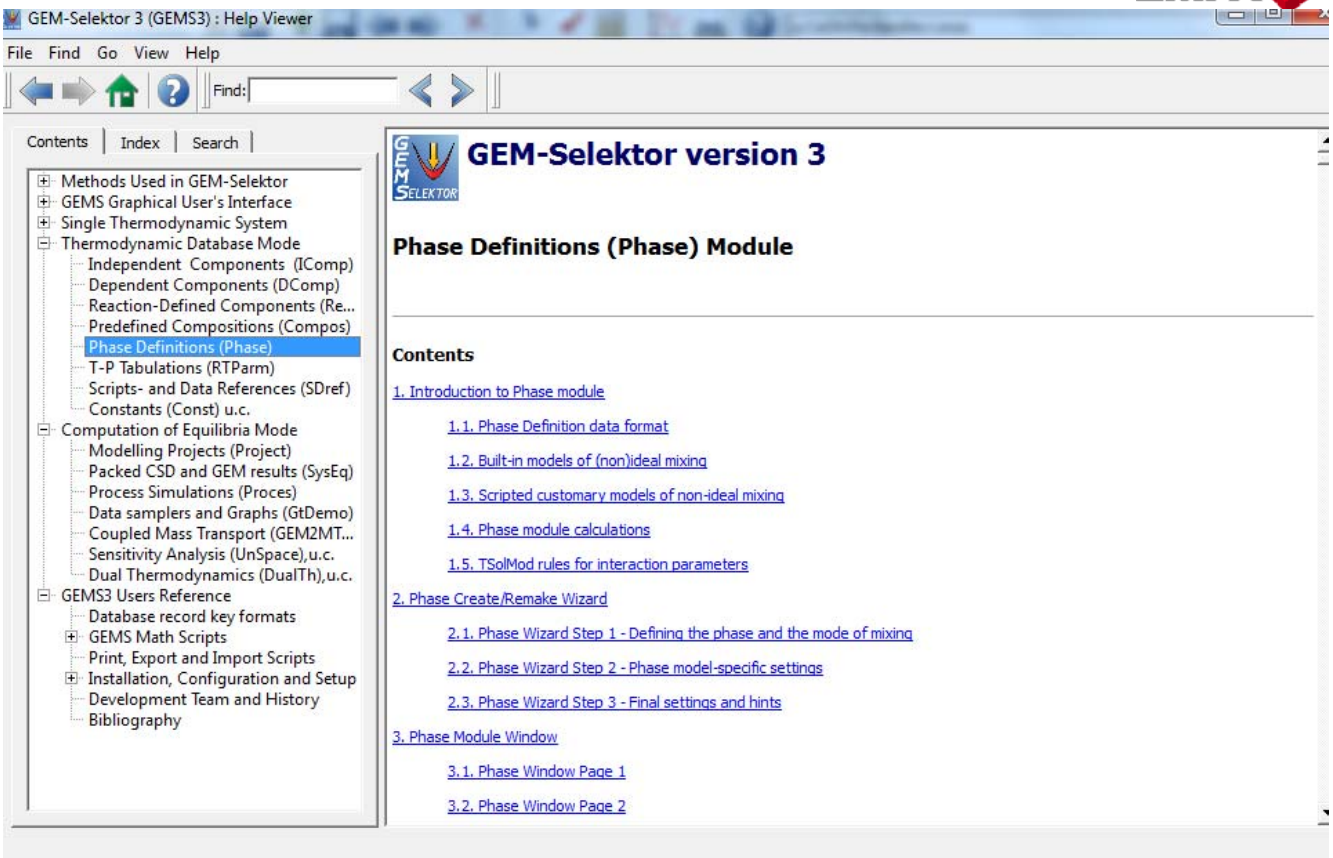
5.) Thermodynamic Phases – creation of entries

Mark dependent component to be included in the project database

a) either from ReacDC **b) or from DComp**



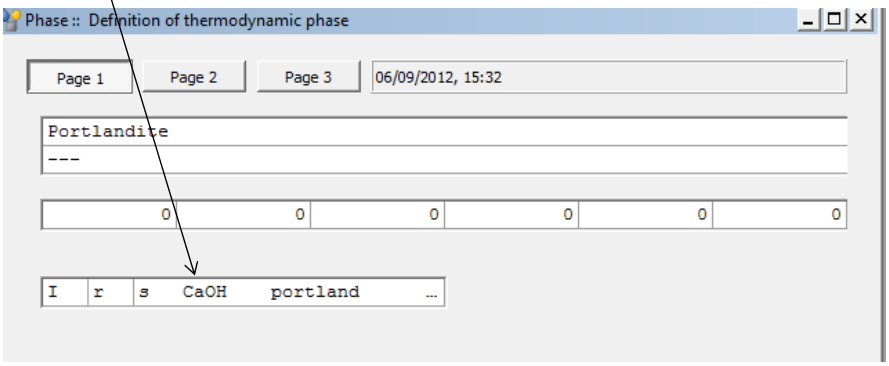
Depending on the entry in the original database, see "help" for additional information or hints *(Partially still under construction)*



5.) Thermodynamic Phases – creation of entries

Mark dependent component to be included in the project database

a) Single solid phase **b) Solid solution**

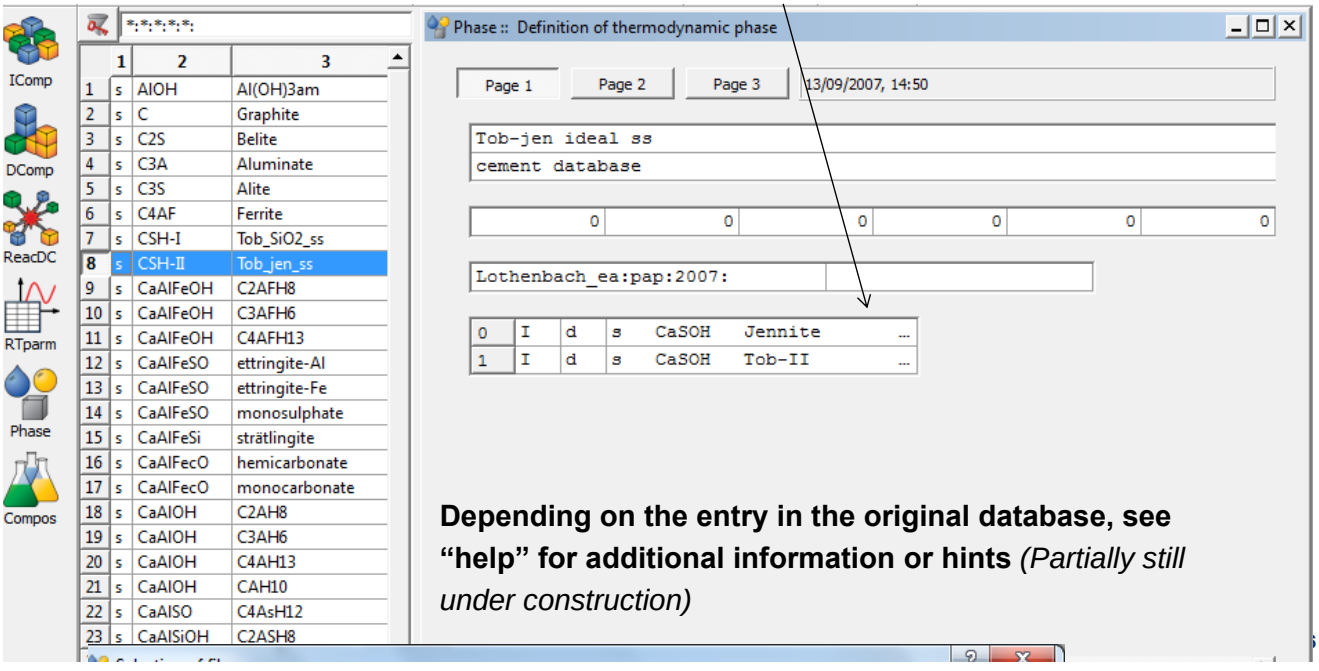


Depending on the entry in the original database, see "help" for additional information or hints *(Partially still under construction)*

5.) Thermodynamic Phases – creation of entries

Mark dependent component to be included in the project database

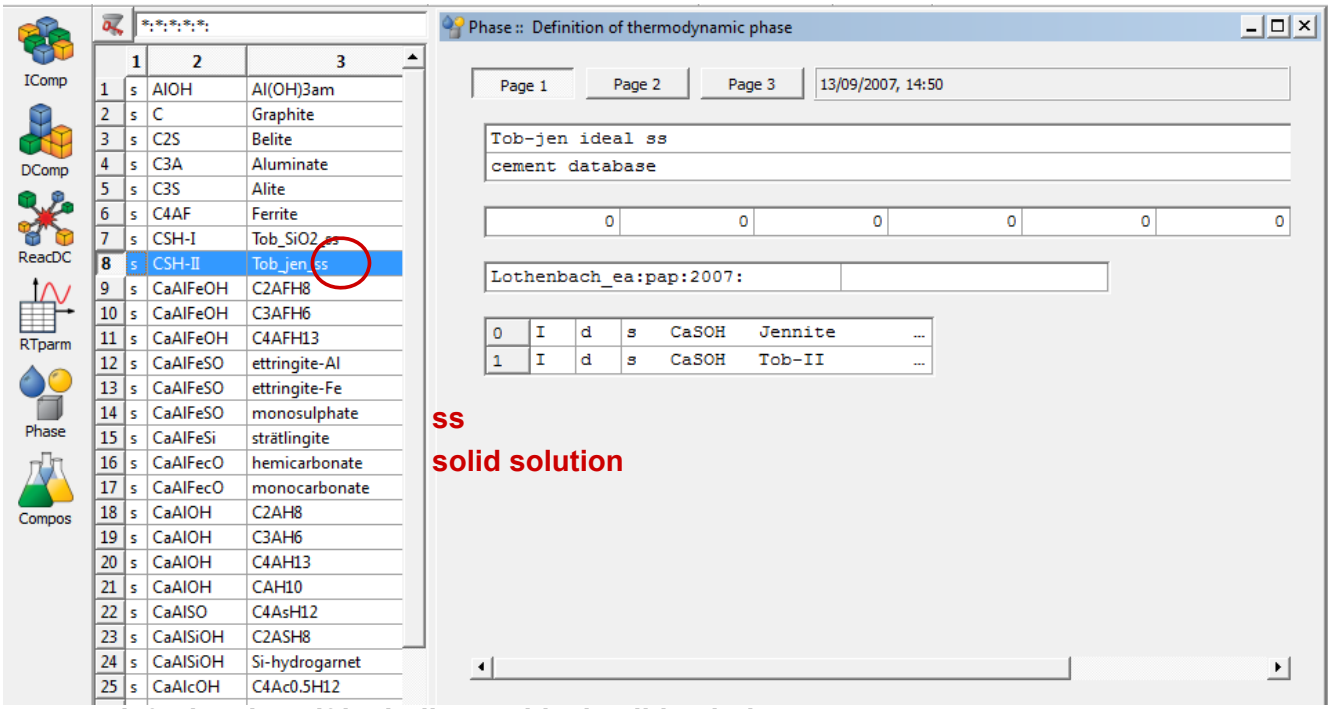
a) Single solid phase **b) Solid solution**



Depending on the entry in the original database, see "help" for additional information or hints *(Partially still under construction)*

5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H



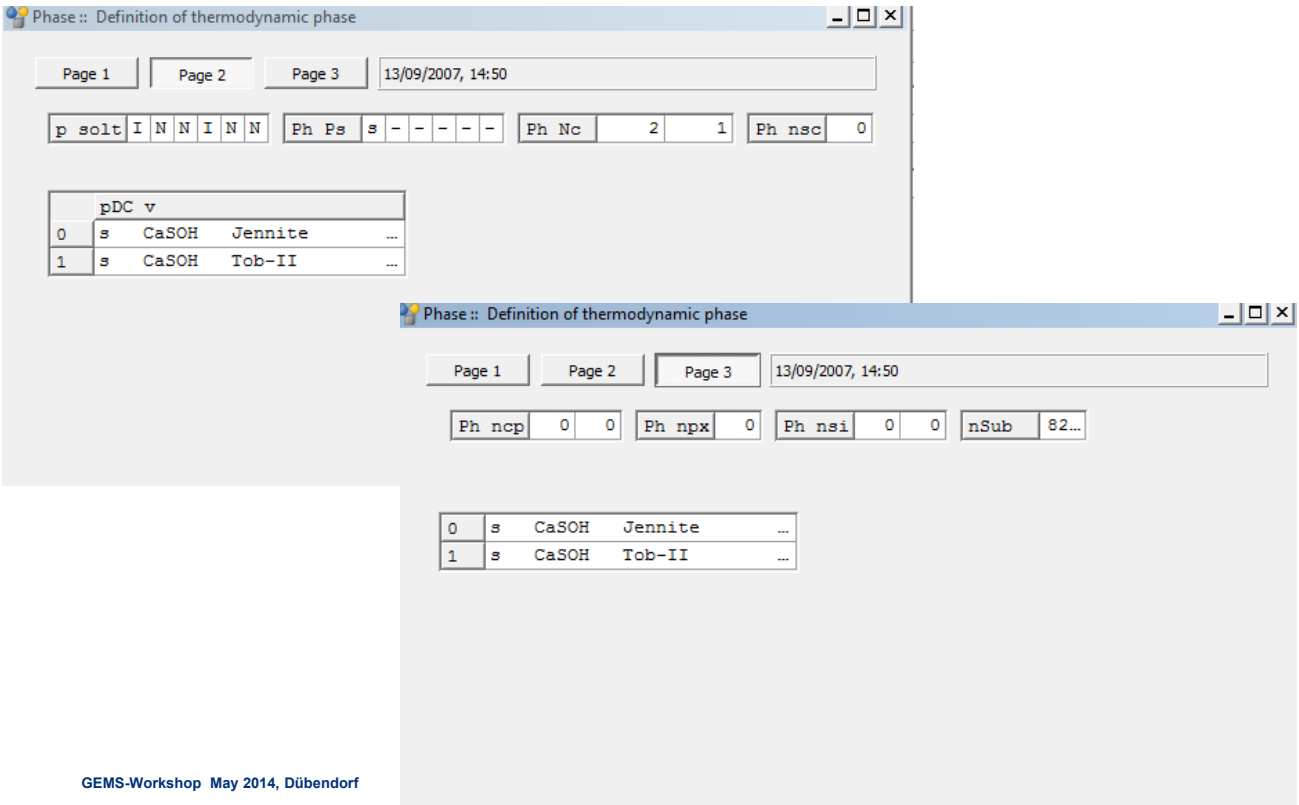
Leave default values if including an ideal solid solution

See Kulik et al. for background information on the used C-S-H model

Kulik D.A. and Kersten M.: Aqueous solubility diagrams for cementitious waste stabilization systems: II, End-member stoichiometries of ideal calcium silicate hydrate solid solutions. *Journal of the American Ceramic Society*, 2001, **84**, 3017-3026

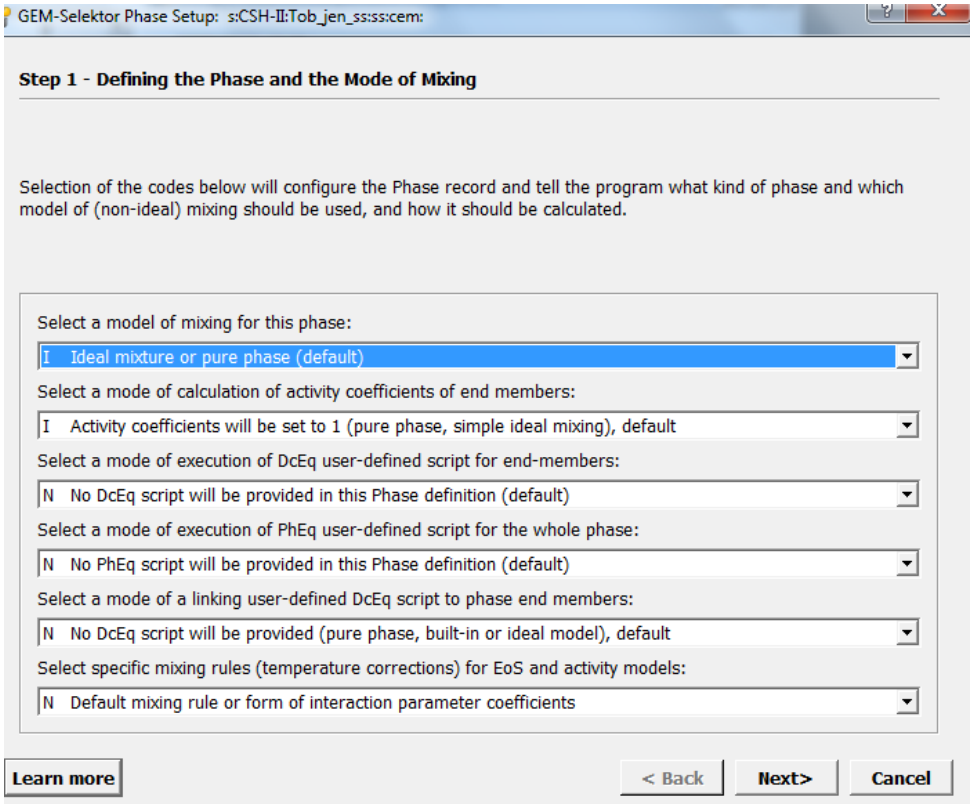
5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H



5.) Thermodynamic Phases – Treatment of solid solutions

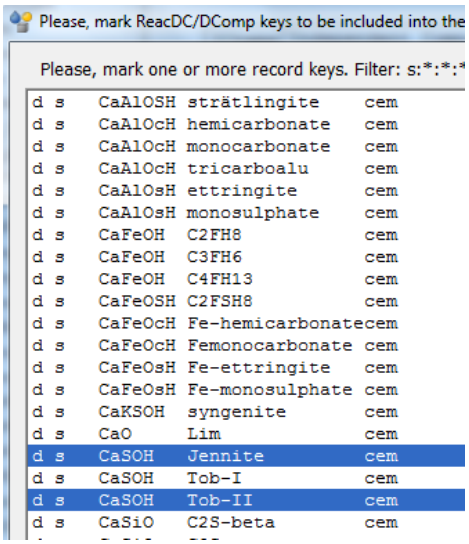
a) Ideal solid solutions, e.g. C-S-H

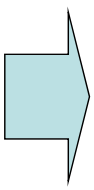


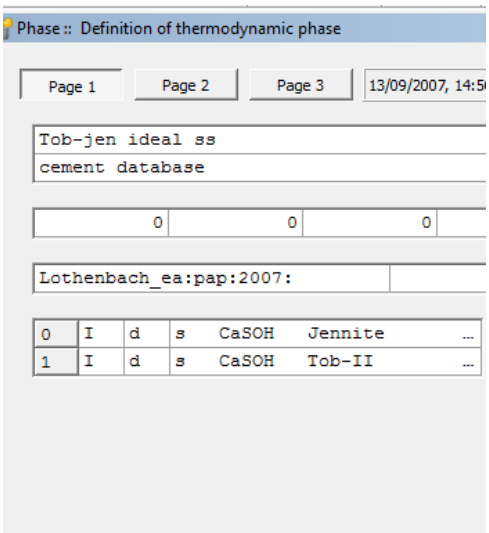
GEMS – Database management

5.) Thermodynamic Phases – Treatment of solid solutions

a) Ideal solid solutions, e.g. C-S-H







Mark the end members of the solid solution series

Ideal solid solution phase as defined previously

5.) Thermodynamic Phases – Treatment of solid solutions

b) Non-ideal solid solutions, e.g. SO_4-OH-AFm

Phase :: Definition of thermodynamic phase

Page 1 | Page 2 | Page 3 | 09/11/2007, 08:09

SO4_OH_AFm nonideal ss

nonideal ss monosulfat_C4AH13; cement database

0	0	0	0	0

Matschei_ea:2007:pap:	a0=0.188, a1=2.49

0	J	d	s	CaAlOH C4AH13	...
1	M	d	s	CaAlOsH monosulphate	

Choose corresponding solid solution model e.g. Binary Redlich-Kister model

Phase :: Definition of thermodynamic phase

Page 1 | Page 2 | Page 3 | 09/11/2007, 08:09

p solt	G	N	N	S	N	N	Ph Ps	s	+	-	-	-	-	Ph Nc	2	1	Ph nsc	0

	pDC v	
0	s	CaAlOH C4AH13 ...
1	s	CaAlOsH monosulphate ...

Phase :: Definition of thermodynamic phase

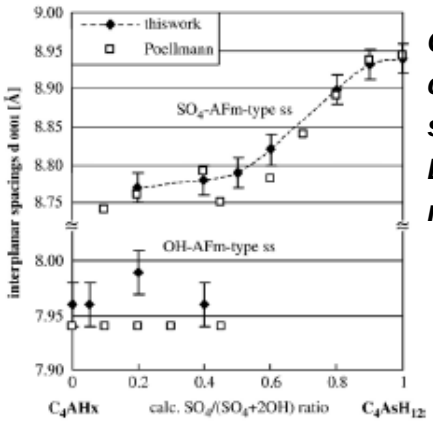
Page 1 | Page 2 | Page 3 | 09/11/2007, 08:09

Ph ncp	1	3	Ph npx	0	Ph nsi	0	1	nSub	0		

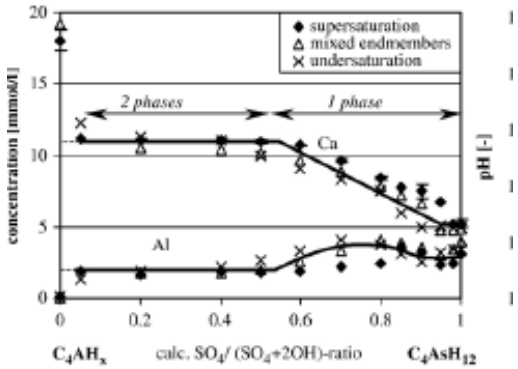
ph cf	0.188	2.49	0

5.) Thermodynamic Phases – Treatment of solid solutions

b) Non-ideal solid solutions, e.g. SO_4-OH-AFm



Choose corresponding solid solution model e.g. Binary Redlich-Kister model



miscibility gap 0.03-0.5 =>
Guggenheim parameters a0=0.188 and a1=2.49
(see Matschei ea 2007, CCR 37)

Phase :: Definition of thermodynamic phase

Page 1 | Page 2 | Page 3 | 09/11/2007, 08:09

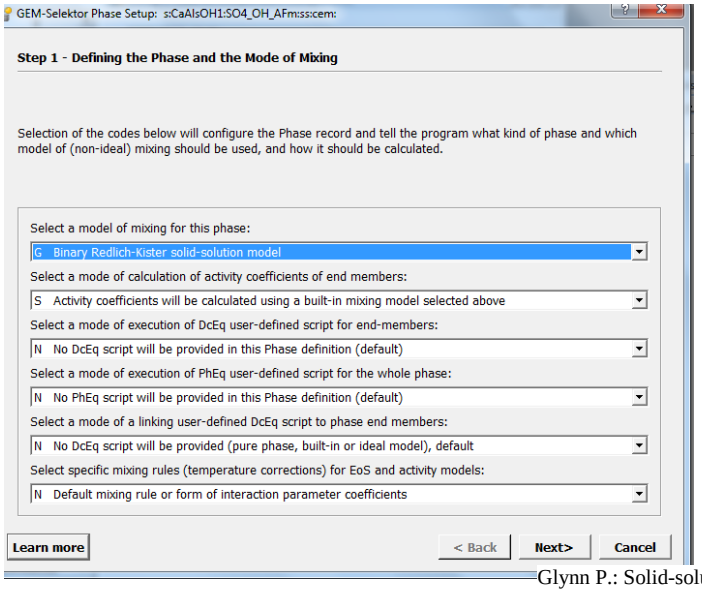
Ph ncp	1	3	Ph npx	0	Ph nsi	0	1	nSub	0		

ph cf	0.188	2.49	0

0	0	s	CaAlOH C4AH13 ...
1	0	s	CaAlOsH monosulphate ...

5.) Thermodynamic Phases – Treatment of solid solutions

b) Non-ideal solid solutions, e.g. SO_4-OH-AFm



Choose corresponding solid solution model e.g. Binary Redlich-Kister model;

S: Activity expressions built in

Guggenheim parameter can be calculated from the measured miscibility gap using MBSSAS

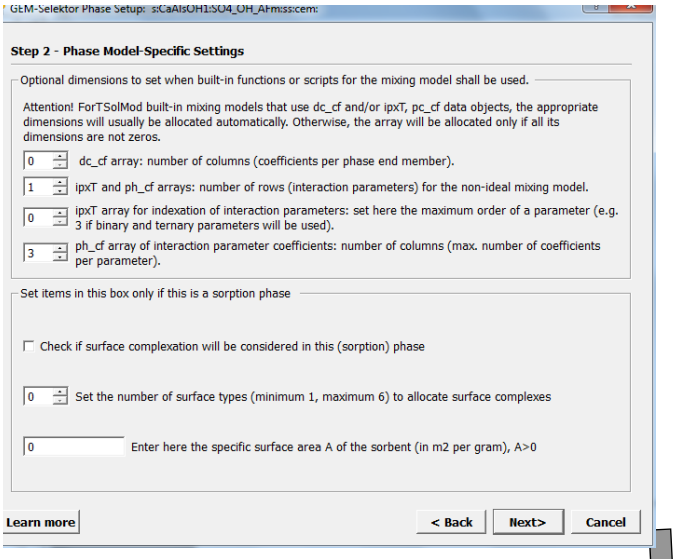
Glynn P.: Solid-solution solubilities and thermodynamics: sulfates, carbonates and halides. In: *Sulfate Minerals: Crystallography, Geochemistry and Environmental Significance*, Alpers C.N., Jambor J.L. and Nordstrom D.K. (eds.), Mineralogical Society of America and Geochemical Society, Reviews in Mineralogy and Geochemistry, 2000, v. **40**, 481-511

Glynn, P.D.: MBSSAS: A code for the computing of margules parameters and equilibrium relations in binary solid-solutions aqueous-solution systems. *Computers & Geoscience*, **17**, 1991, 907-966

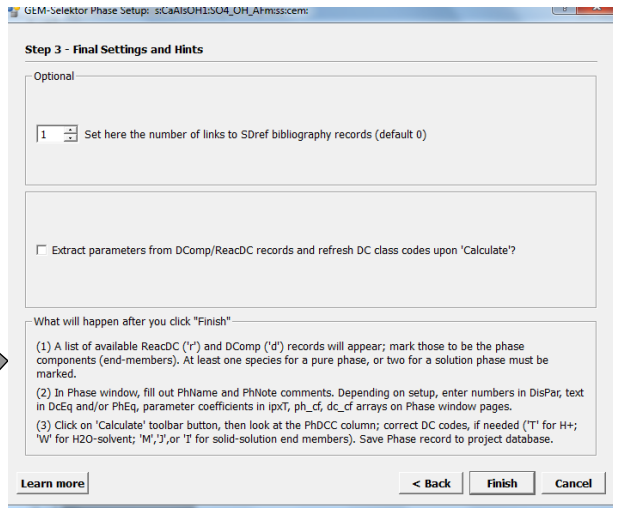
Kulik D.A.: Dual-thermodynamic estimation of stoichiometry and stability of solid solution end members in aqueous–solid solution systems. *Geochemical Geology*, 2006, **225**, 189-212

5.) Thermodynamic Phases – Treatment of solid solutions

a) Non-ideal solid solutions, e.g. SO_4-OH-AFm

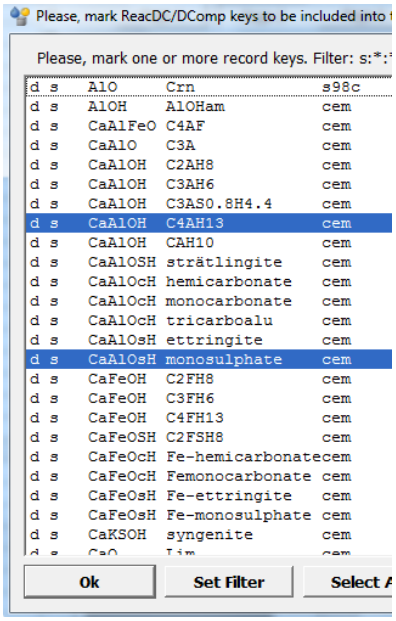


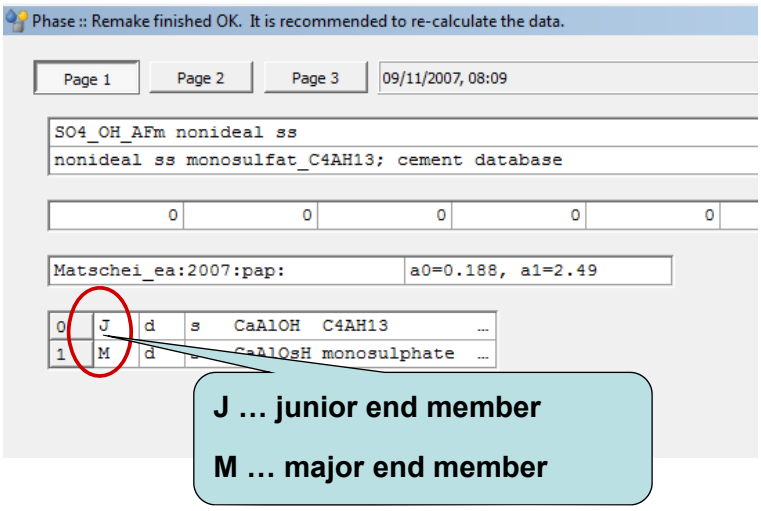
leave default values, GEMS generates needed additional arrays automatically



5.) Thermodynamic Phases – Treatment of solid solutions

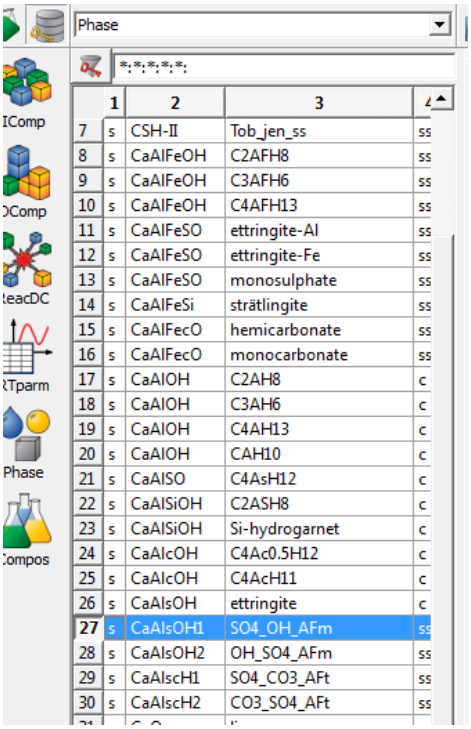
a) Non-ideal solid solutions, e.g. SO_4-OH-AFm

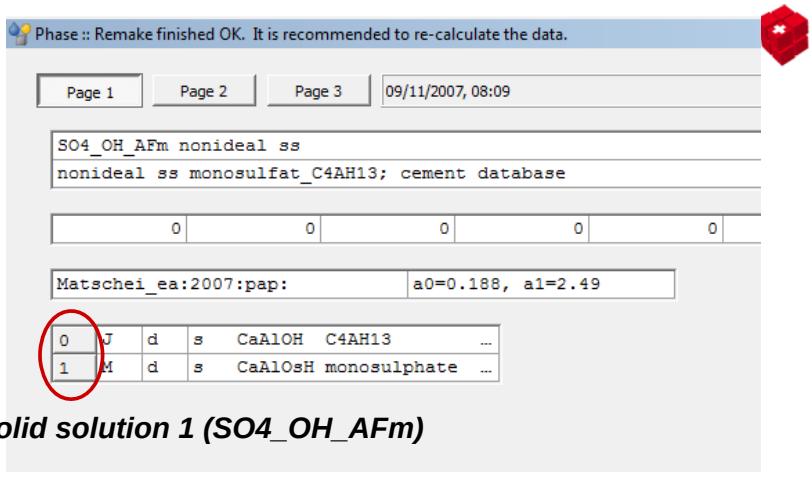




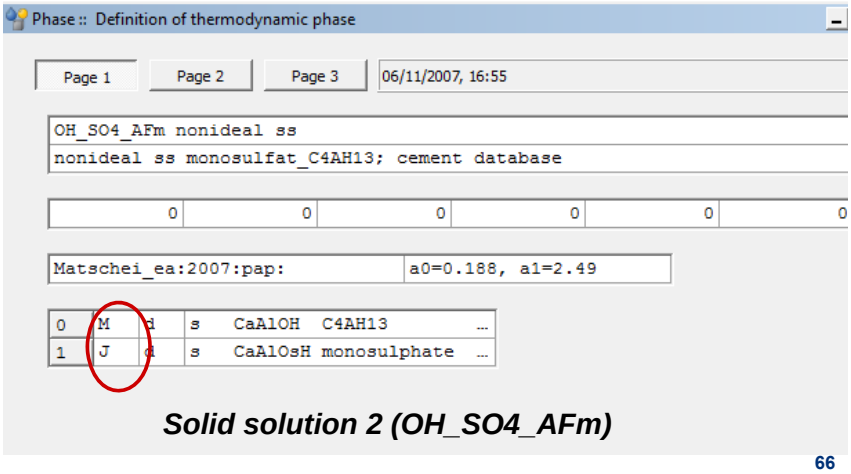
Explanations see Activity_Coeffs.pdf in C:\Selektor\Gems3-app\Resources\doc\pdf

Mark the end members of the solid solution series

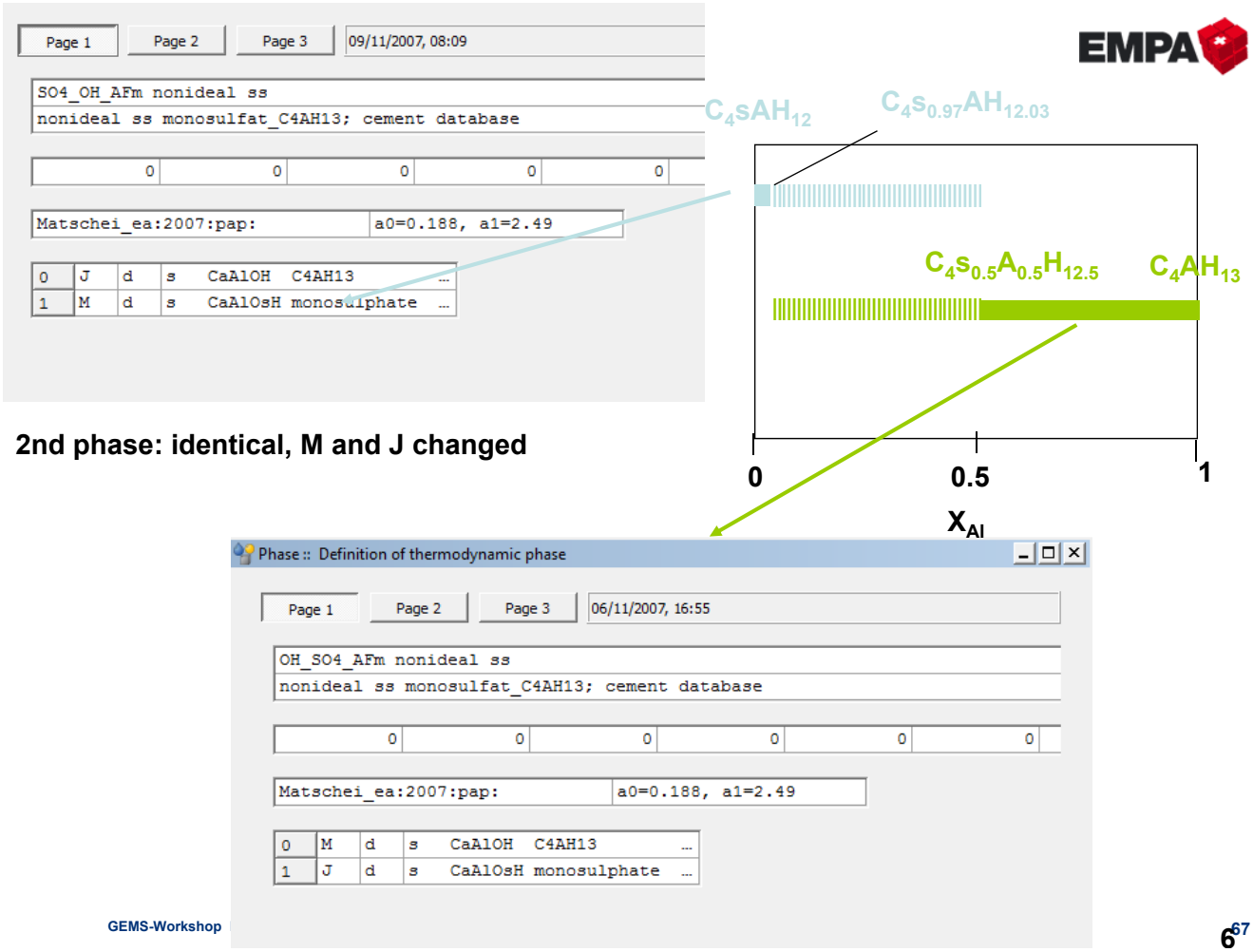




Solid solution 1 (SO4_OH_AFm)



Solid solution 2 (OH_SO4_AFm)



2nd phase: identical, M and J changed

GEMS – solid solutions

Further information see help and tutorials;

For theoretical information: C:\Selektor\Gems3-app\Resources\doc\pdf

Ideal solid solution in cements:

- **C-S-H:** Kulik (2011)
- **Fe-Al Hydrogarnet**: Dilnesa ea (2014)
- **Hydrotalcite pyroaurite** (Fe, Al): Rozov ea (2011)
- *Cl-OH Afm and Cl-CO3-AFm: Balonis ea (2010) (not activated in Cemdata2014)*

Non-ideal solid solution in cements:

- **OH-SO4 AFm:** Matschei ea (2007);
- **CO3-SO4 AFt:** Matschei ea (2007);
- **Fe-Al AFt:** Möschner ea (2009);
- **Fe-Al monosulfate**: Dilnesa ea (2012)
- *CrO4-SO4 AFt and –AFm: Leisinger ea 2010, 2012 (not included in Cemdata2014)*