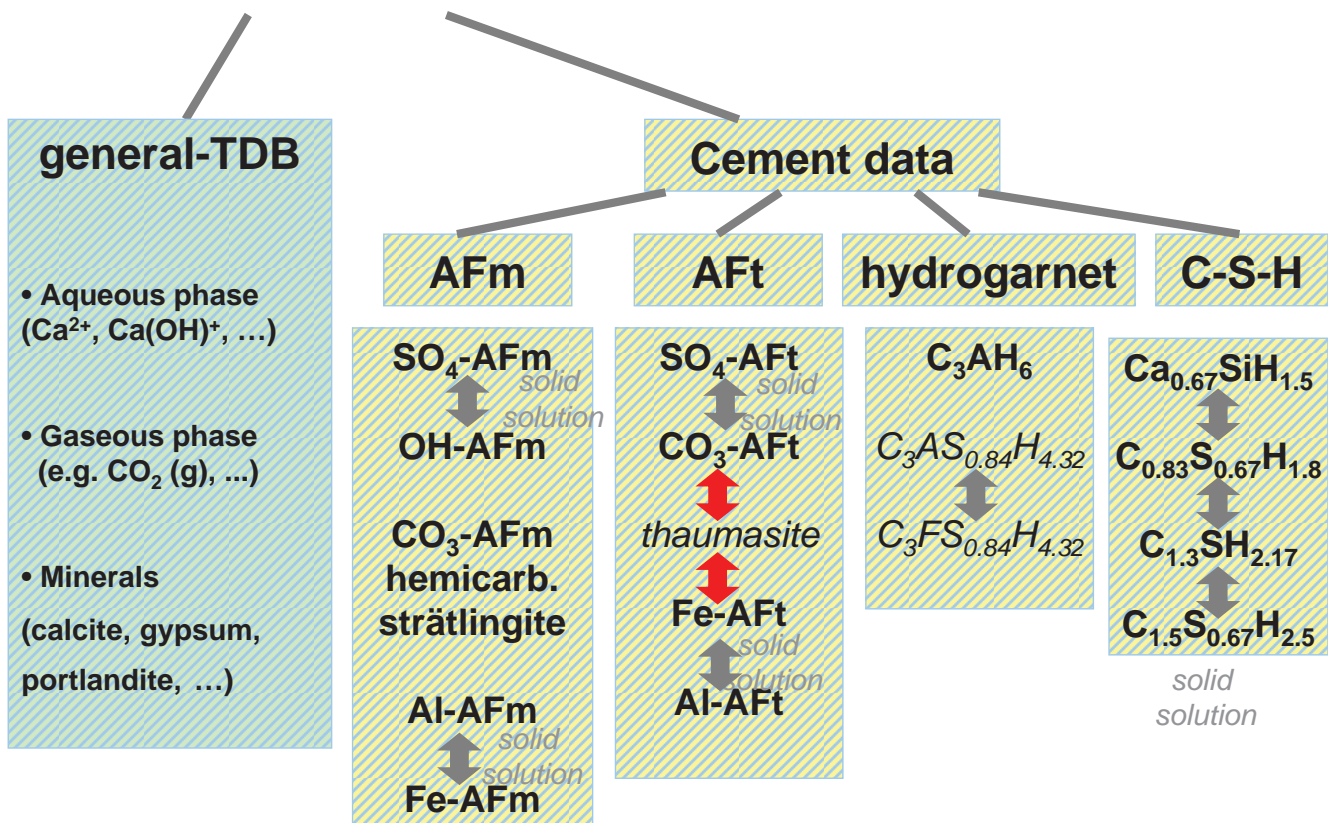




## 3) Database

- Databases available
- Temperature extrapolation
- Database contents

## Thermodynamic databases



# Database 1

- **Geochemical database** (generally integrated in software)
  - Complex formation:  $\text{CaOH}^+$ ,  $\text{CaHCO}_3^+$ , ...
  - Solubility products: gypsum, 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.
    - **CEM DATA07**: 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

3

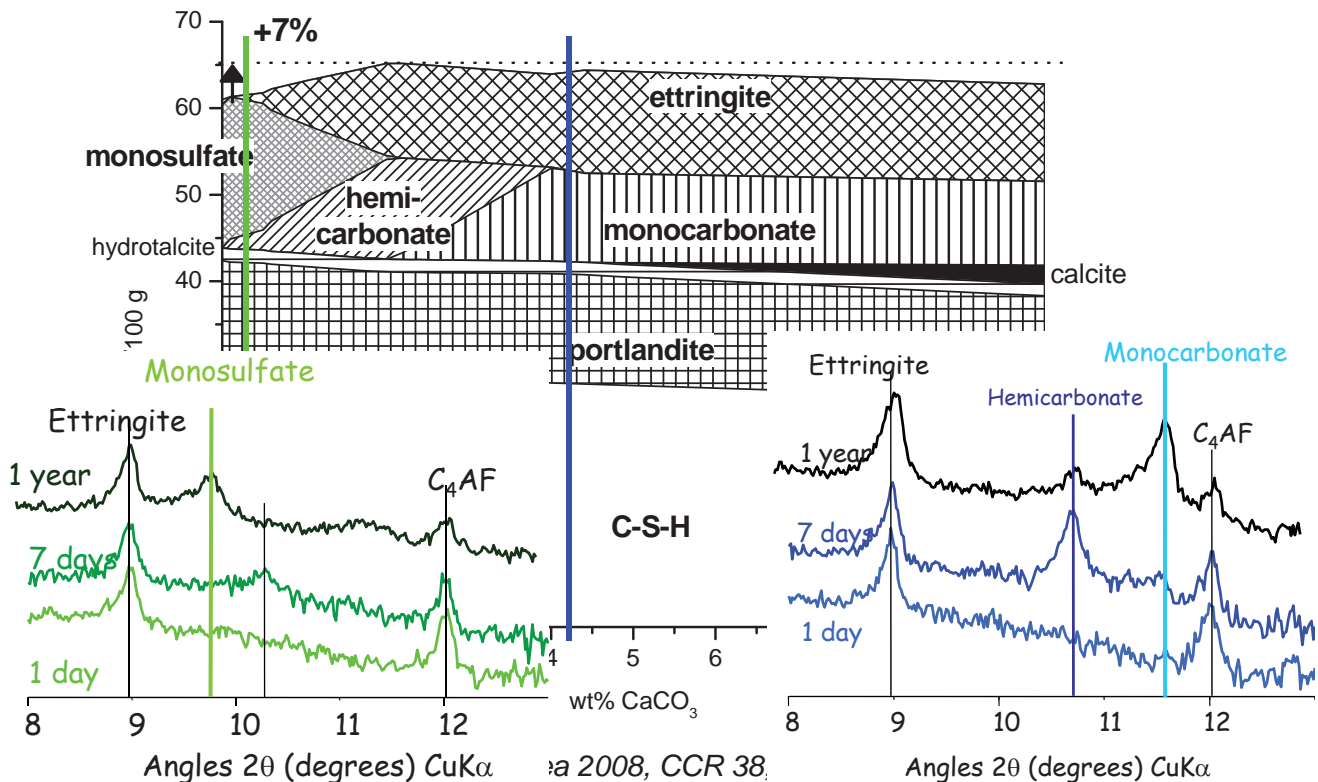
# Database 2

- 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, ...)
  - $\Delta G_f^\circ$  (Gibbs free energy of formation) (GEMS, MTDATA, ...)

– convertible: 
$$K = e^{-\frac{\Delta G_r^\circ}{RT}}$$

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ$$

4



## Different databases

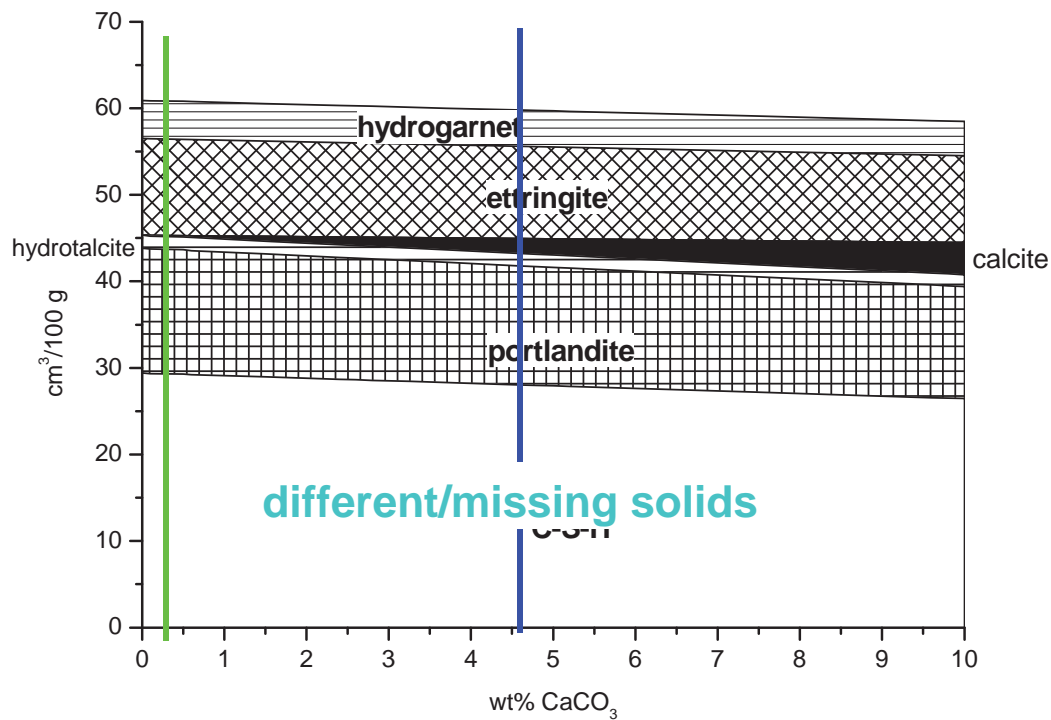
	Reardon 1992	Cemdata 2007	Blanc 2011
Ettringite $\Leftrightarrow 6\text{Ca}^{2+} + 2\text{AlO}_2^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 30\text{H}_2\text{O}$	-43.9	-44.9	-44.8
Monosulfate $\Leftrightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{SO}_4^{2-} + 4\text{OH}^- + 10\text{H}_2\text{O}$	-29.3	-29.3	-28.7
C <sub>3</sub> AH <sub>6</sub> $\Leftrightarrow 3\text{Ca}^{2+} + 2\text{AlO}_2^- + 4\text{OH}^- + 4\text{H}_2\text{O}$	-23.1	-20.8	-21.4
Monocarb. $\Leftrightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CO}_3^{2-} + 4\text{OH}^- + 10\text{H}_2\text{O}$	n.a.	-31.5	-31.5
Ca-carbo. $\Leftrightarrow 2\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CO}_3^{2-} + 11\text{H}_2\text{O}$	-19.5	n.a.	n.a.

## different/missing solids

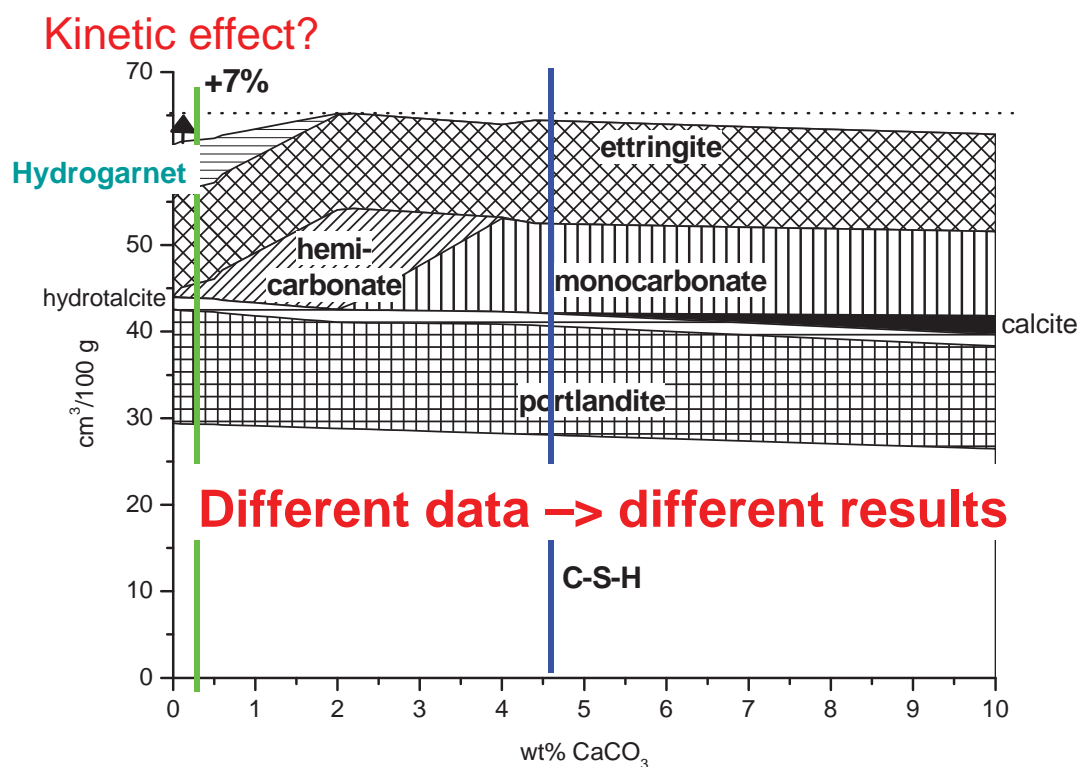
Reardon Waste Management 12, 1992

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



Reardon 1992, Waste Management 12



Blanc ea 2010, CCR 40

Ettringite  $\Leftrightarrow 6\text{Ca}^{2+} + 2\text{AlO}_2^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 30\text{H}_2\text{O}$   
 Monosulfate  $\Leftrightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{SO}_4^{2-} + 4\text{OH}^- + 10\text{H}_2\text{O}$   
 $\text{C}_3\text{AH}_6 \Leftrightarrow 3\text{Ca}^{2+} + 2\text{AlO}_2^- + 4\text{OH}^- + 4\text{H}_2\text{O}$   
 Monocarb.  $\Leftrightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CO}_3^{2-} + 4\text{OH}^- + 10\text{H}_2\text{O}$

Cemdata	Blanc	
2007	2011	$\Delta$
-44.9	-44.8	
-29.3	-28.7	+0.6
-20.8	-21.4	-0.6
-31.5	-31.5	

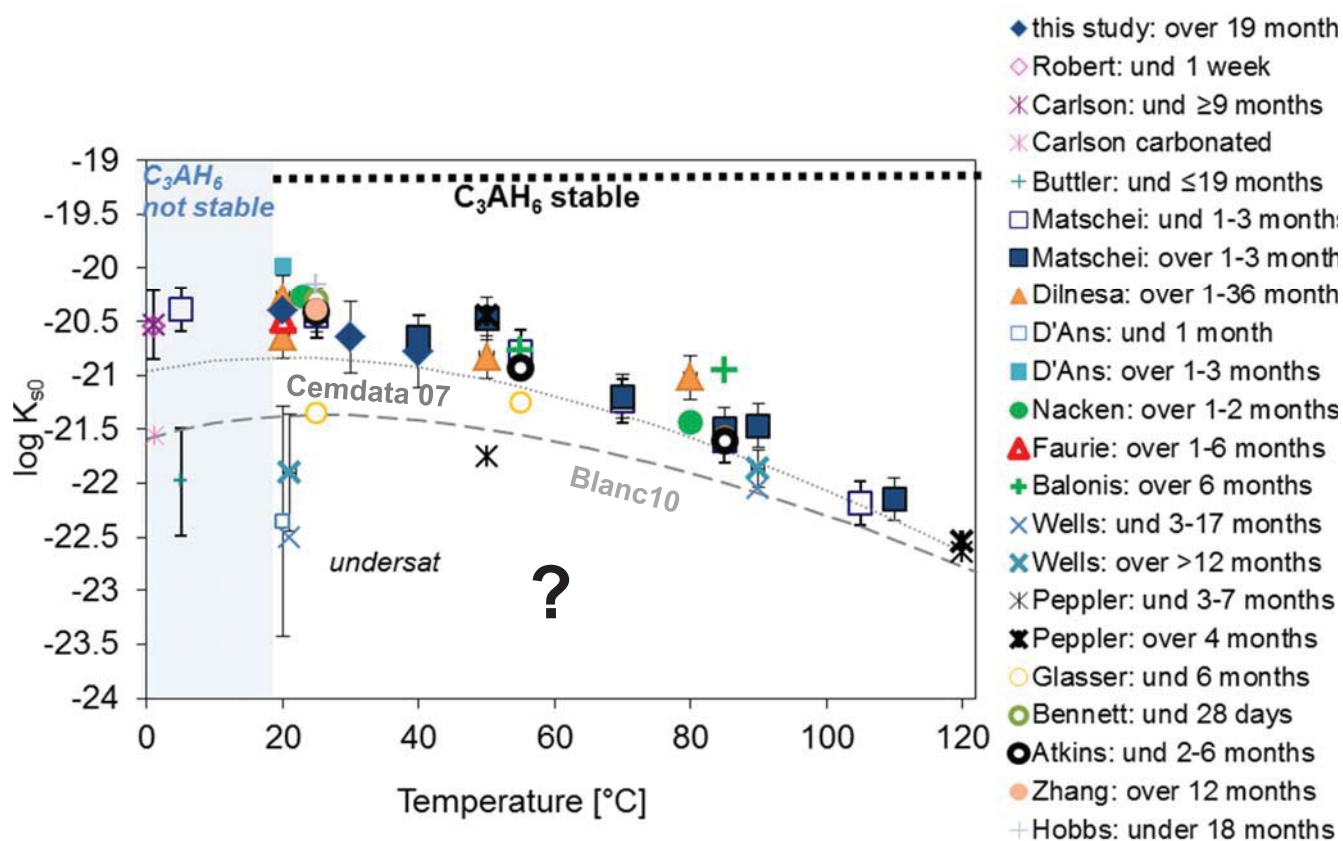
Analytical error  $\pm 0.5 - 1$

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

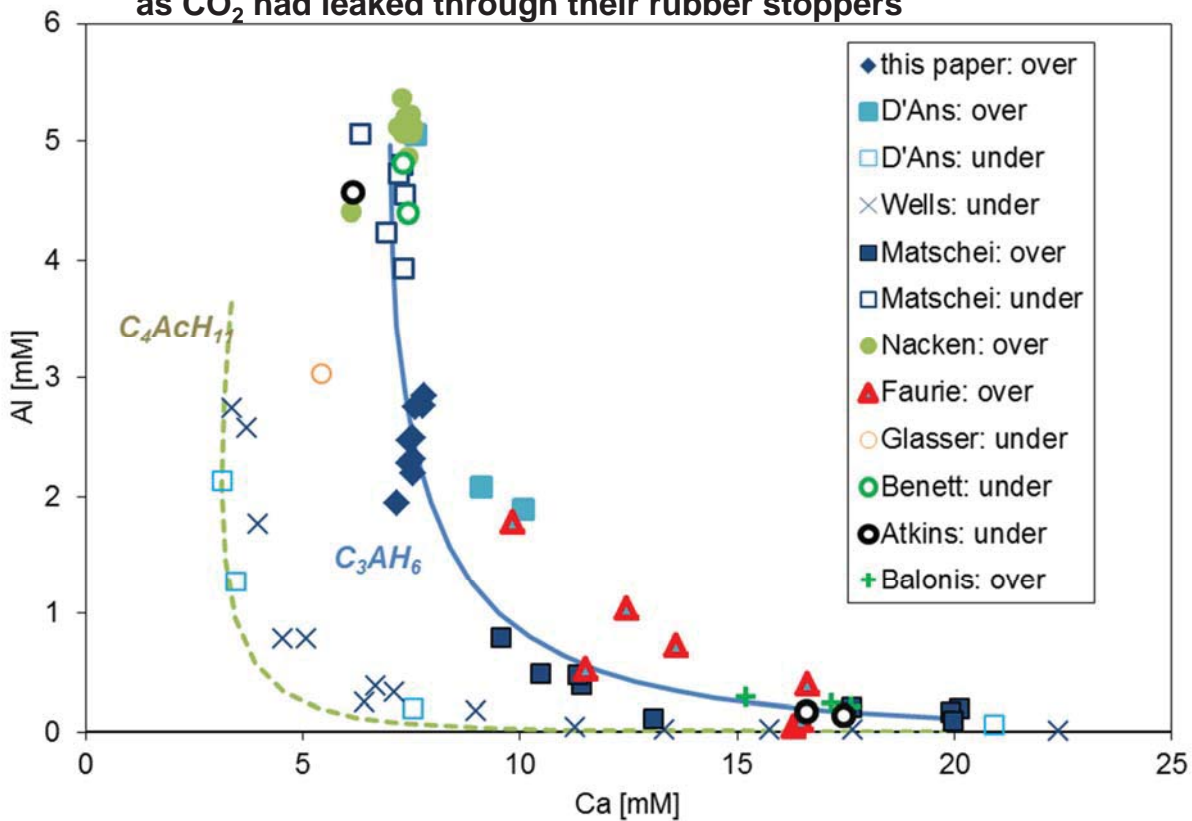
## Solubility of $\text{C}_3\text{AH}_6$





## Carbonation!

Peppler and Wells observed in some samples calcite  
as  $\text{CO}_2$  had leaked through their rubber stoppers

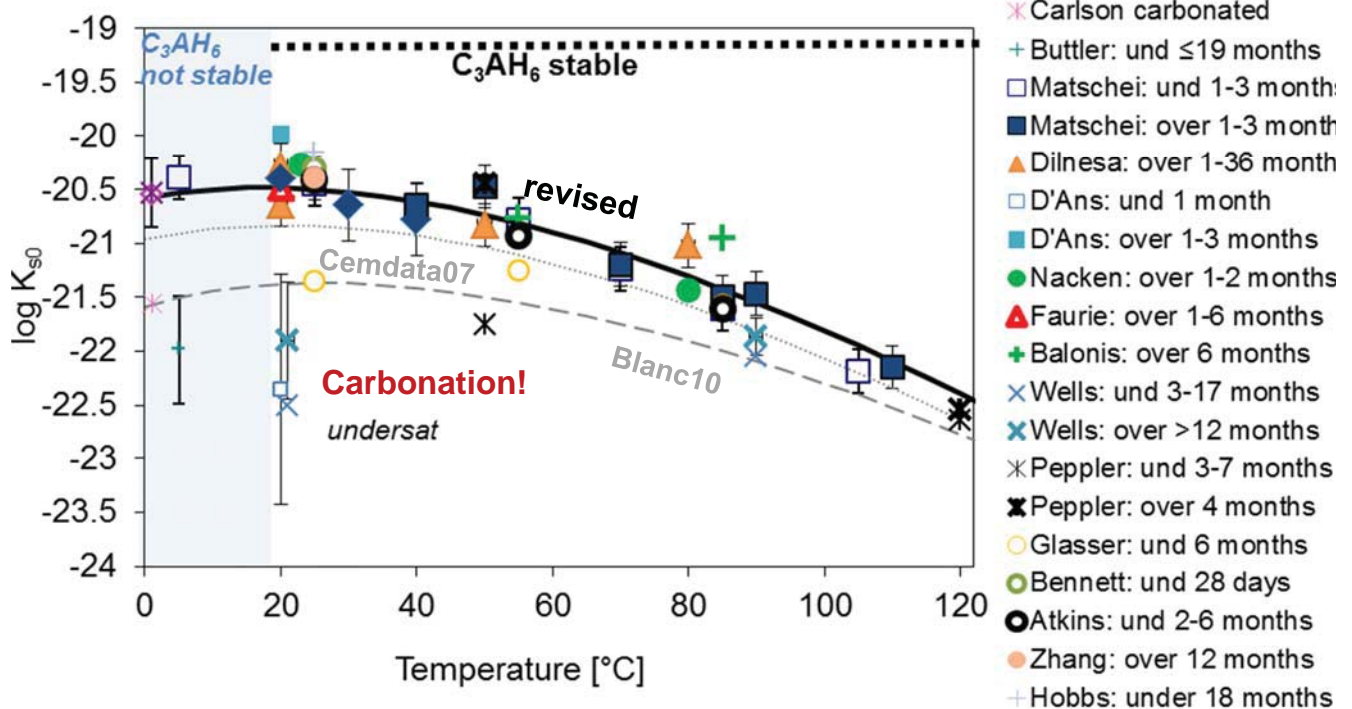


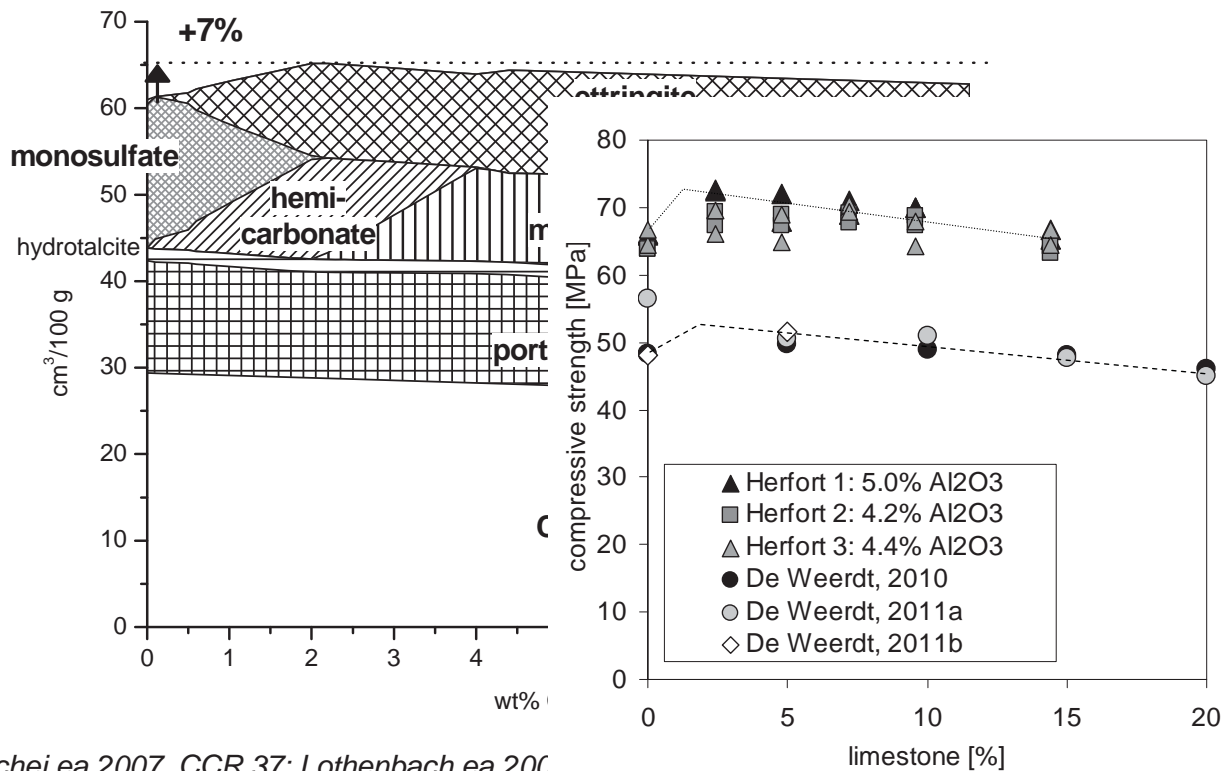
11

## Solubility of $\text{C}_3\text{AH}_6$



$$\text{Log } K_{s0} \text{ C}_3\text{AH}_6 = \{\text{Ca}^{2+}\}^3 \{\text{Al}(\text{OH})_4\}^2 \{\text{OH}\}^4 = -20.5$$





Matschei et al 2007, CCR 37; Lothenbach et al 2006

## 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 <sub>50</sub>	Δ <sub>r</sub> G° [kJ/mol]	Δ <sub>r</sub> H° [kJ/mol]	S° [J/K/mol]	a <sub>0</sub> [J/K/mol]	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	V° [cm <sup>3</sup> /mol]	Ref
(Al-)ettringite <sup>a,b</sup>	-44.9	-15205.94	-17535	1900	1939	0.789			707	[1,2]
tricarboaluminate <sup>a</sup>	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78e6		650	[2,1]
Fe-ettringite <sup>b</sup>	-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 <sub>3</sub> AH <sub>6</sub> <sup>o</sup>	-20.50	-5008.2	-5537.3	422	290	0.644	-3.25e6		150	[10]
C <sub>3</sub> AS <sub>0.41</sub> H <sub>5.18</sub> <sup>a,c</sup>	-25.35	-5192.9	-5699	399	310	0.566	-4.37e6		146	[11]
C <sub>3</sub> AS <sub>0.84</sub> H <sub>4.32</sub> <sup>a,e</sup>	-26.70	-5365.2	-5847	375	331	0.484	-5.55e6		142	[11]
C <sub>3</sub> FH <sub>6</sub> <sup>d,m</sup>	-26.30	-4122.8	-4518	870	330	1.237	-4.74e6		155	[11]
C <sub>3</sub> FS <sub>0.84</sub> H <sub>4.32</sub> <sup>d,e</sup>	-32.50	-4479.9	-4823	840	371	0.478	-7.03e6		149	[11]
C <sub>3</sub> FS <sub>1.34</sub> H <sub>3.32</sub>	-34.20	-4681.1	-4994	820	395	0.383	-8.39e6		145	[11]
C <sub>4</sub> AH <sub>19</sub> <sup>f</sup>	-25.45	-8749.9	-10017.9	1120	1163	1.047		-1600	371	[10]
C <sub>4</sub> AH <sub>13</sub>	-25.00	-7324.3	-8300.2	700	711	1.047		-1600	274	[10]
C <sub>2</sub> AH <sub>7.5</sub>	-13.80	-4695.5	-5277.6	450	323	0.728			180	[10]
C <sub>4</sub> AsH <sub>12</sub> <sup>f,g</sup>	-29.26	-7778.50	-8750	821	594	1.168			309	[2,1]
C <sub>4</sub> AcH <sub>11</sub>	-31.47	-7337.46	-8250	657	618	0.982	-2.59e6		262	[2,1]
C <sub>4</sub> Ac <sub>0.5</sub> H <sub>12</sub>	-29.13	-7335.97	-8270	713	664	1.014	-1.30e6	-800	285	[2,1]
C <sub>2</sub> ASH <sub>8</sub>	-19.70	-5705.15	-6360	546	438	0.749	-1.13e6	-800	216	[2,1]
C <sub>4</sub> ACl <sub>2</sub> H <sub>10</sub>	-27.27	-6810.90	-7604	731	498	0.895	-2.04e6	1503	272	[15,16]
C <sub>4</sub> As <sub>0.5</sub> ClH <sub>12</sub>	-28.53	-7533.97	-8472 <sup>m</sup>	820	557	1.141	-1.02e6	751	289	[16,17]
C <sub>4</sub> FH <sub>13</sub> <sup>m</sup>	-30.75	-6438.6	-7435	630	694	1.113	2.02e6	-1600	286	[11]
C <sub>4</sub> FsH <sub>12</sub> <sup>o</sup>	-31.57	-6873.2	-7663	1430	577	1.234	2.02e6		321	[12]
C <sub>4</sub> FcH <sub>12</sub>	-34.59	-6674.0	-7485	1230	612	1.157	-5.73e5		292	[13]
C <sub>4</sub> Fc <sub>0.5</sub> H <sub>10</sub>	-30.83	-5952.9	-6581	1270	308	1.201	-9.08e5	3200	273	[13]
CAH <sub>10</sub>	-7.60	-4623.0	-5288.2	610	151	1.113		3200	193	[10]
M <sub>4</sub> AH <sub>10</sub> <sup>m</sup>	-56.02	-6394.56	-7196	549	-364	4.21	3.75e6	629	220	[1,4]
1/2M <sub>8</sub> A <sup>-</sup> Cl <sup>-</sup> H <sub>13</sub> <sup>h</sup>	-33.29 <sup>v</sup>	-4339.85	-4875.89	411	512.6				115	[18]
1/2M <sub>8</sub> F <sup>-</sup> Cl <sup>-</sup> H <sub>13</sub> <sup>h</sup>	-33.64 <sup>v</sup>	-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]

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## Cemdata14



### Changes in Cemdata14 (compared to Cemdata07)

- Addition of data for
  - C<sub>3</sub>AS<sub>0.84</sub>H<sub>4.32</sub>, C<sub>3</sub>AS<sub>0.41</sub>H<sub>5.18</sub>, (formation kinetically hindered at room temp.),
  - FH<sub>0.5</sub>, C<sub>3</sub>FS<sub>0.84</sub>H<sub>4.32</sub>, C<sub>3</sub>FS<sub>1.34</sub>H<sub>3.32</sub>
  - Friedel's salt, Kuzel's salt
  - CO<sub>3</sub>-hydrotalcite, pyroaurite
  - hemihydrate, C<sub>12</sub>A<sub>7</sub>, CA, and CA<sub>2</sub>
- Updated data for
  - AH<sub>3,mic</sub>, CAH<sub>10</sub>, C<sub>2</sub>AH<sub>7.5</sub>, C<sub>3</sub>AH<sub>6</sub>, C<sub>4</sub>AH<sub>13</sub>, C<sub>4</sub>AH<sub>19</sub>,
  - Fe-monocarbonate, Fe-hemicarbonate, Fe-monosulfate, C<sub>3</sub>FH<sub>6</sub>, C<sub>4</sub>FH<sub>13</sub>
  - thaumasite
- Changes in water content: C<sub>2</sub>AH<sub>7.5</sub>, C<sub>4</sub>Fc<sub>0.5</sub>H<sub>10</sub>
- Removal AH<sub>3,am</sub>, C<sub>2</sub>FH<sub>8</sub>, C<sub>2</sub>FSH<sub>8</sub> 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

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

$K \leftrightarrow$  Gibbs free energy

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

$\uparrow$ 
 $\uparrow$ 
 $\uparrow$

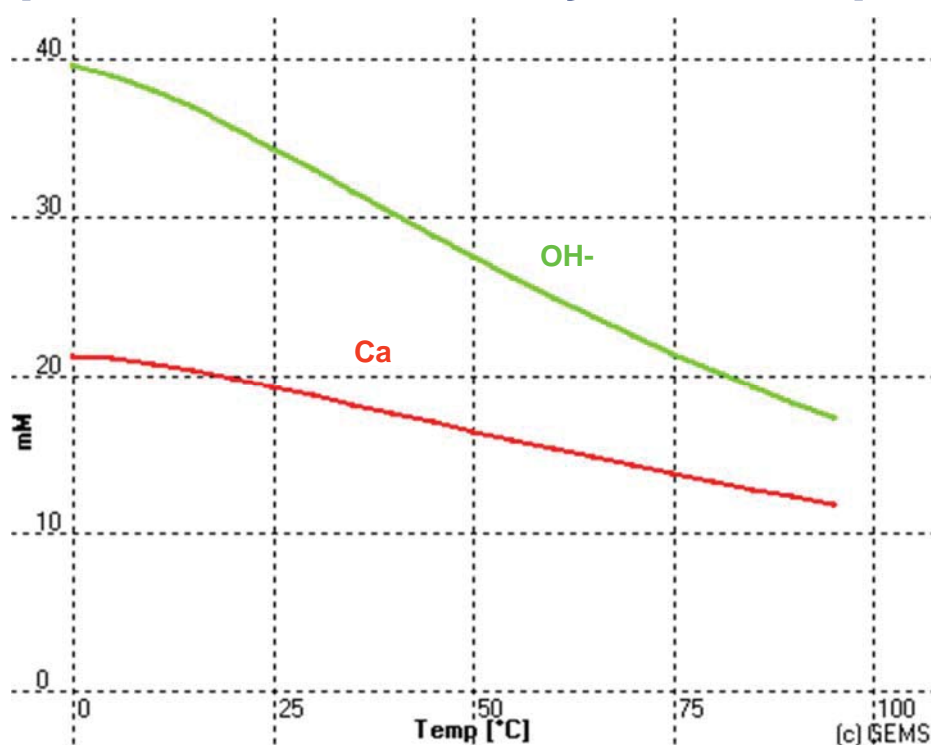
$\text{Ca(OH)}_2$ 
 $\text{OH}^-$ 
 $\text{Ca}^{2+}$

reaction
components

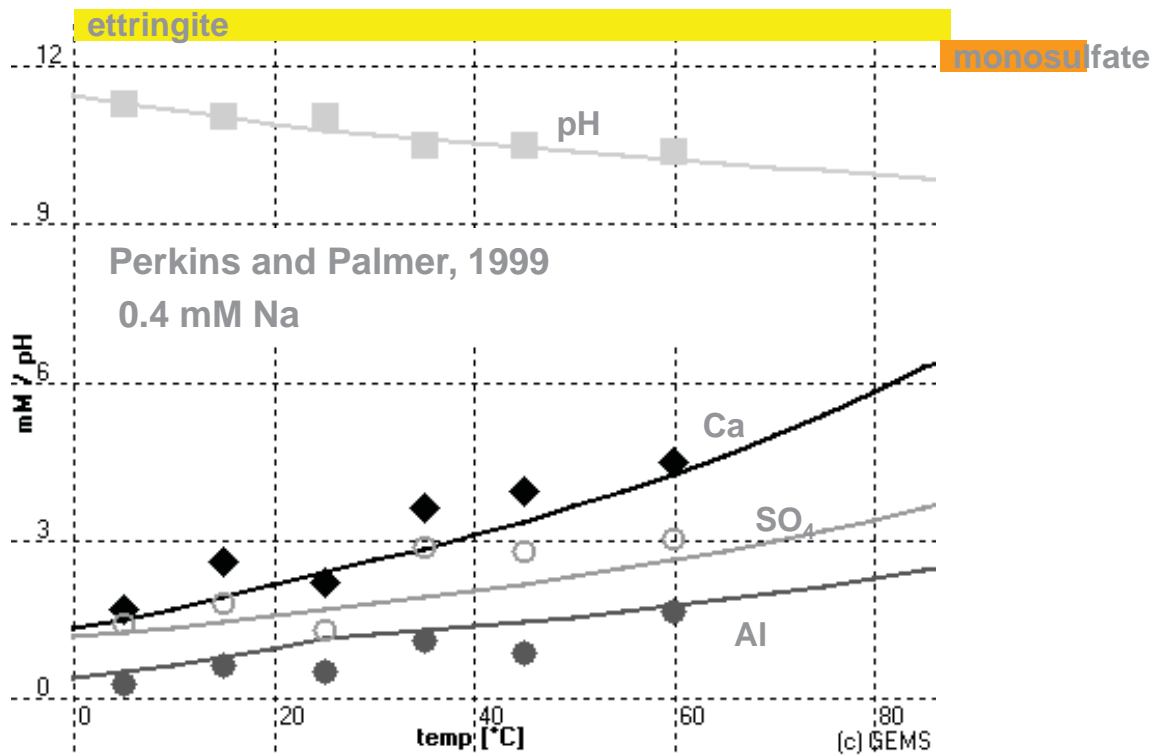
Portlandite solubility:  $\text{Ca(OH)}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^-$

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

## General database: Decrease of portlandite solubility with temperature



# Solubility of ettringite as f(T)



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19

## Temperature corrections: $G^\circ$

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

$T_0$  = Reference Temperature: 25 °C

$$\Delta_a G_T^\circ = \Delta_f G_{T_0}^\circ - \int_{T_0}^T S_T^\circ dT$$

T = Temperature of interest

$C_p$  = Heat capacity:

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

$$\Delta_a G_T^\circ = \Delta_f G_{T_0}^\circ - S_{T_0}^\circ (T - T_0) - \int_{T_0}^T \int_{T_0}^T \frac{C_p^\circ}{T} dT dT$$

$$= \Delta_f G_{T_0}^\circ - S_{T_0}^\circ (T - T_0) - a_0 \left( T \ln \frac{T}{T_0} - T + T_0 \right)$$

$$- 0.5 a_1 (T - T_0)^2 - a_2 \frac{(T - T_0)^2}{2T \cdot T_0^2} - a_3 \frac{2(\sqrt{T} - \sqrt{T_0})^2}{\sqrt{T_0}} - \dots$$

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

Anderson, Cerar (1993): Thermodynamics in Geochemistry

20

# 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 et al 2011, CCR 41

21

# Temperature corrections: log K



3-term extrapolation

up to 150 °C; > 150 °C isoelectric reactions

$$\Delta C p_T = \Delta C p_{T_0} = \text{const}$$

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

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

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H_{T_0}^0 - \Delta_r C p_{T_0} T_0)$$

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

2-term extrapolation

(for isoelectric reactions only)

$$\Delta C p_T = \Delta C p_{T_0} = 0$$

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

Van't Hoff equation

1-term extrapolation

(for isocoulombic reactions)

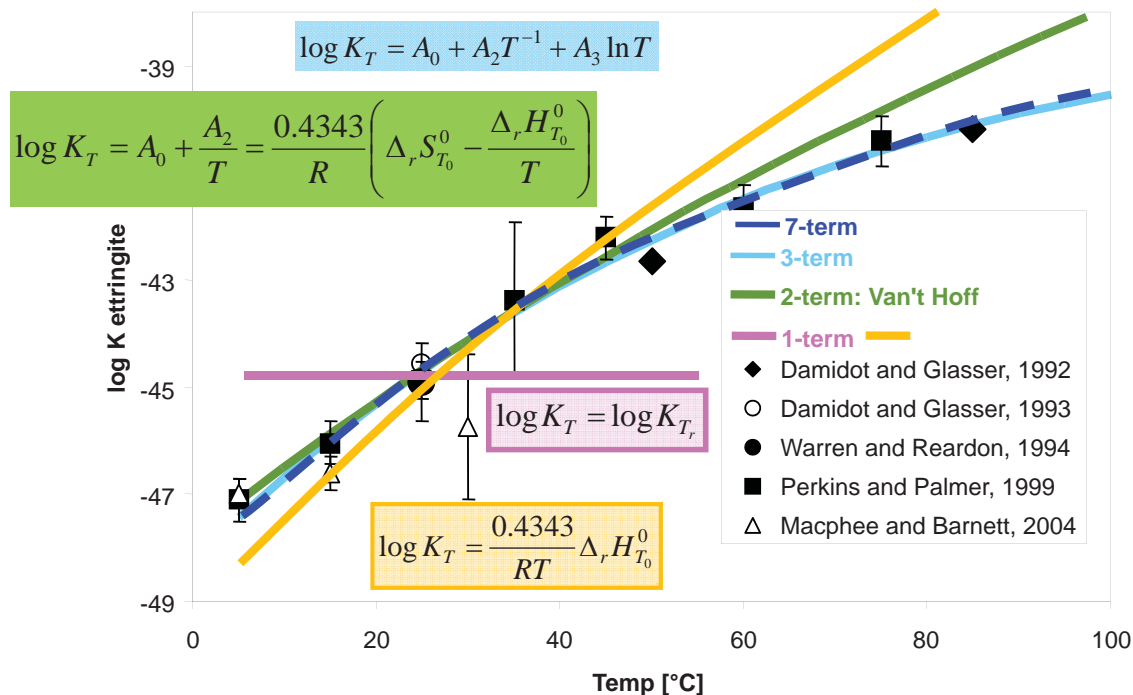
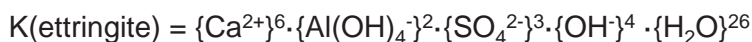
$$\Delta C p_T = 0; \quad \Delta_r H_T^\circ = \Delta_r H_{T_r}^\circ = 0$$

$$\log K_T = \frac{0.4343}{R} (\Delta_r S_{T_0}^0) = \log K_{T_r}$$

# Solubility of ettringite

3-term similar to 7-term

Less parameters



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

23

## GEMS structure

calculations



Thermodynamic database  
for experienced users

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [EqStat: S]

Modules: Record Data Calculate View Print Window Help

SingleSystem

portlandite:\*,\*,\*,\*,\*,\*,\*,\*

	3	4	5	6	7	8
1	CO2	0	0	1	25	0

Input: System Definition Results: Equilibrium State

Phase/species	L	T
aq_gen	22	a
gas_gen	5	g
Graphite	1	s
Aragonite	1	s
Calcite	1	s
lime	1	s
Portlandite	1	s
Anhydrite	1	s
Gypsum	1	s
hemihydrate	1	s
Sulphur	1	s

Single calculation

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [DComp :: Thermochemical/EOS data fo...]

Module: Record Record List Database Files Window Help

DComp

	1	2	3	4
1	g	S-2	H2S	en_
2	s	CO	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_

Page 1 Page 2 29/08/2012, 12:38

Portlandite

Ca (OH) 2

M0	74.0927	Zz	0	ab	--
V0d	3.306		0		
G0d	-897013		---		
H0d	-984675		---		

24

**Independent components**  
(chemical elements: Ca)

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

**2 input options: both equally valid**

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

**Calculation and plotting of T/P dependency**

**Solids phases**  
**single phases / solid solutions**

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

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## 1) GEMS: independent components

**IComp :: Data for Independent Components**

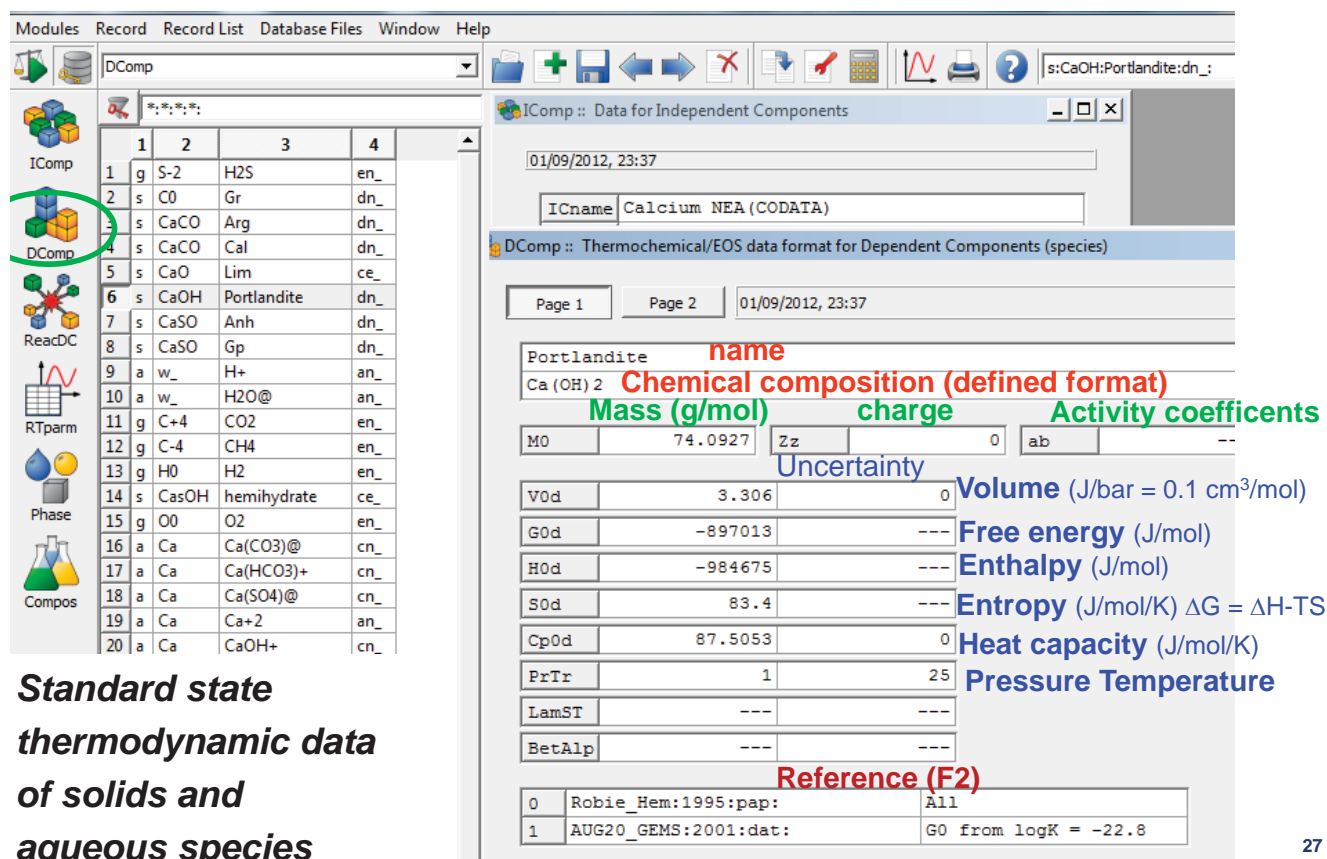
01/09/2012, 23:37

ICname: Calcium NEA (CODATA)  
ICform: Ca  
StdSt: s IC DC: ---

M0i: 40.078 S0i: 41.59 Cp0i: 25.929  
V0i: 25.86 IXi: 1 Valen: 2  
indMT: 20 Ri: --- Zi: ---

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

## 2) GEMS: dependent components (DComp)



**Standard state thermodynamic data of solids and aqueous species**

**Chemical composition (defined format)**

**Mass (g/mol)** **charge** **Activity coefficients**

**Uncertainty** **Volume (J/bar = 0.1 cm<sup>3</sup>/mol)**

**Free energy (J/mol)**

**Enthalpy (J/mol)**

**Entropy (J/mol/K)  $\Delta G = \Delta H - TS$**

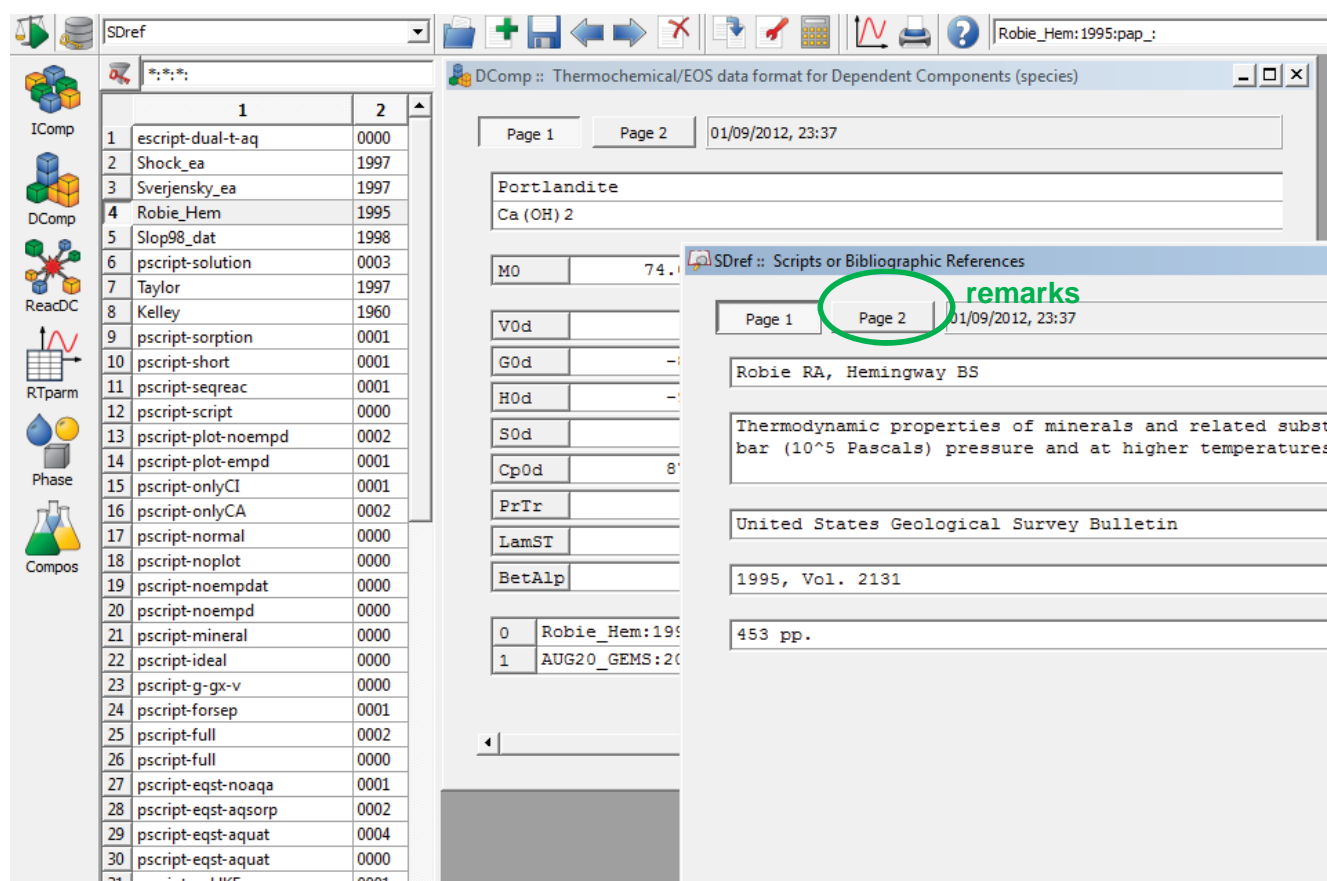
**Heat capacity (J/mol/K)**

**Pressure Temperature**

**Reference (F2)**

27

## GEMS: dependent components (DComp)



**remarks**

**Robie RA, Hemingway BS**

**Thermodynamic properties of minerals and related substances (10<sup>5</sup> Pascals) pressure and at higher temperatures**

**United States Geological Survey Bulletin**

**1995, Vol. 2131**

**453 pp.**

# GEMS: dependent components (DComp)

GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization

Modules Record Record List Database Files Window Help

DComp

IComp

DComp

ReactDC

RTparm

Phase

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\_

Right click: further information/help

DComp :: Thermochemical/EOS data format for Dependent Components (species)

Page 1 Page 2 01/09/2012, 23:37

Temperature/Pressure changes of heat capacity

TCint

0 0

1 426.85

aiCpT

0 186.7

1 -0.02191

2 0

3 -1600

4 0

5 0

6 0

Temperature range where equations are valid

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

Tabulated values

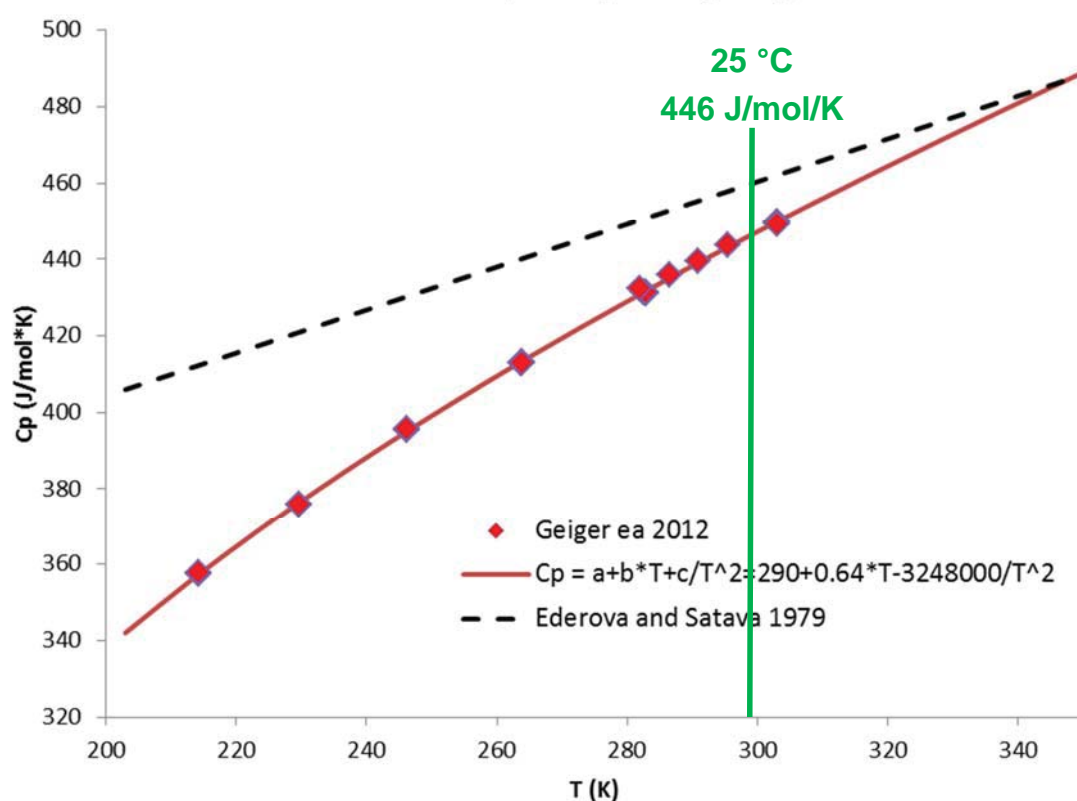
Table 4

Standard thermodynamic properties at 25 °C: Thermo007"

	$\log K_{50}^b$	$\Delta_f G^\circ$ [kJ/mol]	$a_0$ [J/K/mol]	$a_1$	$a_2$	$a_3$	$V^\circ$ [cm <sup>3</sup> ]
(Al-)ettringite	-44.9 <sup>b</sup>	-15205.94 <sup>b</sup>	1939 <sup>f</sup>	0.789 <sup>c</sup>			707 <sup>d</sup>
Tricarboaluminate	-46.5 <sup>f</sup>	-14565.64 <sup>f</sup>	2042 <sup>b</sup>	0.559 <sup>b</sup>	-7.78e6 <sup>b</sup>		650 <sup>d</sup>
Fe-ettringite	-44.0 <sup>b</sup>	-14282.36 <sup>b</sup>	1922 <sup>b</sup>	0.855 <sup>b</sup>	2.02e6 <sup>b</sup>		717 <sup>b</sup>
C <sub>3</sub> AH <sub>6</sub>	-20.84 <sup>f</sup>	-5010.09 <sup>f</sup>	292 <sup>f</sup>	0.561 <sup>c</sup>			150 <sup>d</sup>

# GEMS: dependent components (DComp)

## Heat capacity of C<sub>3</sub>AH<sub>6</sub>



### 3) GEMS: reactions (ReacDC)

**HS<sup>-</sup> = H<sup>+</sup> + S<sup>2-</sup>; log K = -19**  
**{H<sup>+</sup>}{S<sup>2-</sup>}/{HS<sup>-</sup>} = 10<sup>-19</sup>**

**Volume** (J/bar = 0.1 cm<sup>3</sup>/mol)  
**Constant K** (-)  
**Free energy** (J/mol)  
**Enthalpy** (J/mol)  
**Entropy** (J/mol/K)  $\Delta G = \Delta H - TS$   
**Heat capacity** (J/mol/K)

**Standard state**  
**thermodynamic data of**  
**solids and aqueous species:**  
**Reaction data are known**

**ReacDC :: Reaction-defined data format for Dependent Components (species)**

Page 1 Page 2 01/09/2012, 23:37

**S-2 name**  
**S|-2|-2 Chemical composition (defined format)**

SC	DC	REsDC
0	-1 d	a wS-2 HS- bnp
1	1 d	a w_ H+ anp
2	1 n	a wS-2 S-2 cnp

**Reaction component Uncertainty**

Property	Value	Uncertainty
V0r	0	2.02095
logKr	1e-019	-19
G0r	108452.8	120422
H0r	108452.8	92236
S0r	0	68.1992
Cp0r	0	-93.927
NisoX	---	---
PrTr	1	25 M0 32.067 -2
BetAl	---	ab 4

**Pressure Temperature Mass (g/mol) charge**  
**Activity coefficients**

**Reference (F2)**  
 AUG20\_GEMS:2001:dat: logK

31

### 5.) Thermodynamic Phases

**GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization**

Modules Record Record List Database Files Window Help

Phase

**Phase :: Definition of thermodynamic phase**

Page 1 Page 2 Page 3 01/09/2012, 23:37

Portlandite Ca (OH)<sub>2</sub> cryst.  
 nagra-psi

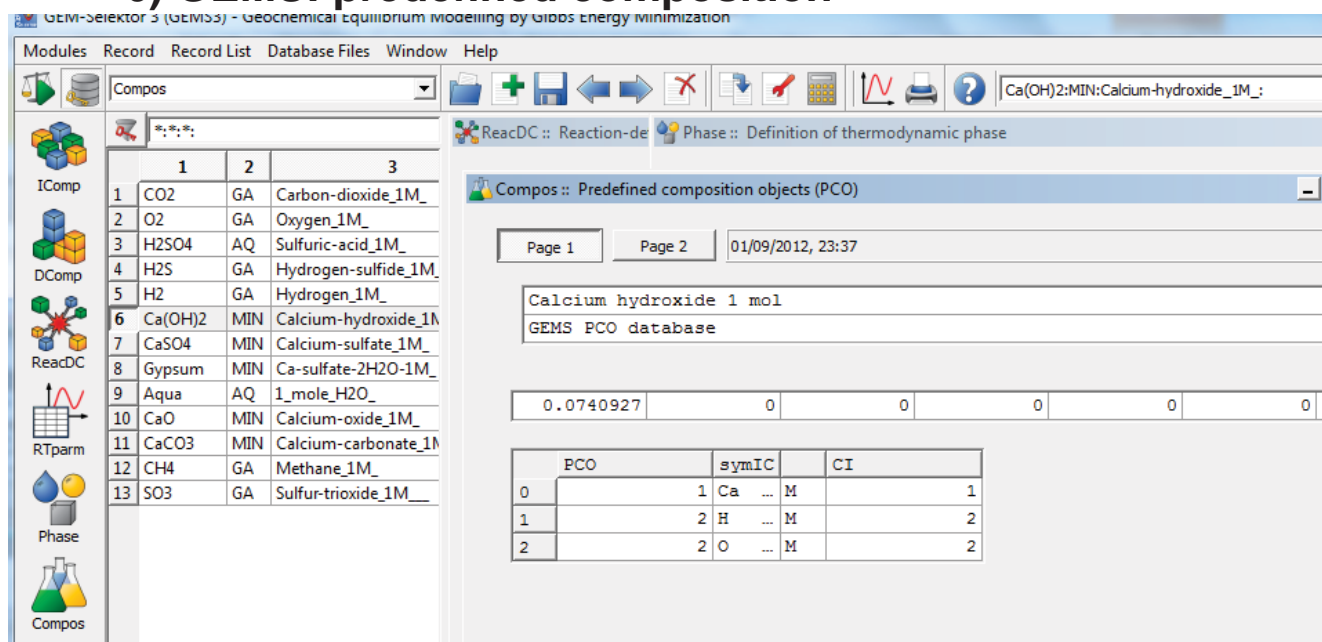
Property	Value
0	0 0 0 0 0 0

**O: single solid d: DComp**

**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



The screenshot shows the GEMS-Selektor 3 software interface. The 'Compos' module is active, displaying a list of predefined composition objects (PCO) in a table. The table has columns for the object name, its chemical formula, and its phase. The objects listed are:

Object Name	Chemical Formula	Phase
1	CO2	GA
2	O2	GA
3	H2SO4	AQ
4	H2S	GA
5	H2	GA
6	Ca(OH)2	MIN
7	CaSO4	MIN
8	Gypsum	MIN
9	Aqua	AQ
10	CaO	MIN
11	CaCO3	MIN
12	CH4	GA
13	SO3	GA

The right-hand pane shows the 'Predefined composition objects (PCO)' for 'Calcium hydroxide 1 mol'. It displays the GEMS PCO database and a table of the object's composition:

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

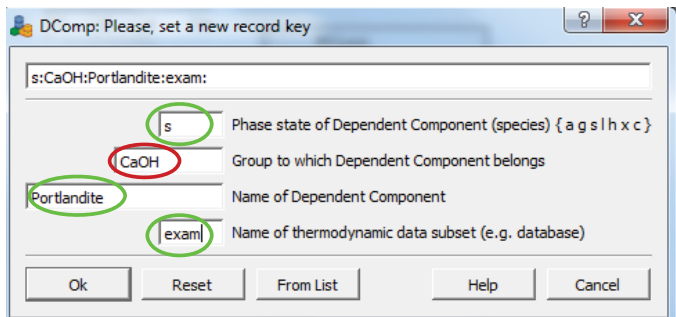
**Contains chemical compositions of input  
(e.g. OPC, slag, Ca(OH)2, HCl, ...)**

**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: Please, set a new record key

s:CaOH:Portlandite:exam:

s Phase state of Dependent Component (species) { a g s l h x c }

CaOH Group to which Dependent Component belongs

Portlandite Name of Dependent Component

exam Name of thermodynamic data subset (e.g. database)

Ok Reset From List Help Cancel

Phase state (s ... solid; a ... aqueous; g ... gaseous; l ... liquid; h ... hexagonal; c ... cubic)

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  
**Optional:** Choice of mixing model if a non ideal solid solution is included

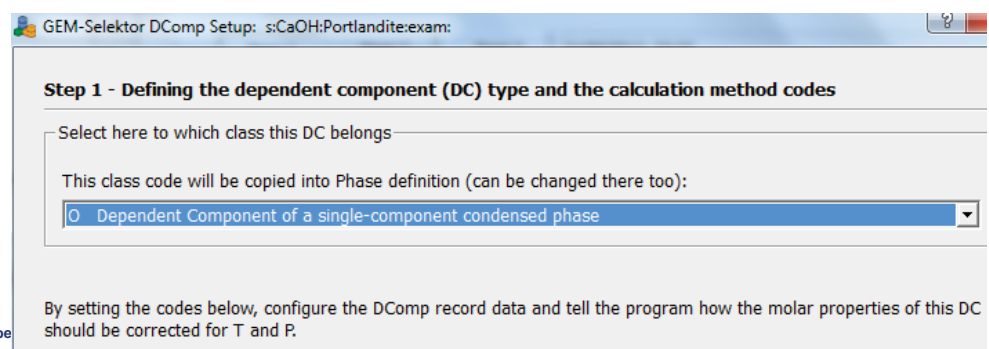
O: solid phase

S: Aqueous species

M: Major end-member  
(solvent)

J: Junior end-member  
(solute)

GEMS-Workshop May 2014, Düren



GEM-Selektor DComp Setup: s:CaOH:Portlandite:exam:

Step 1 - Defining the dependent component (DC) type and the calculation method codes

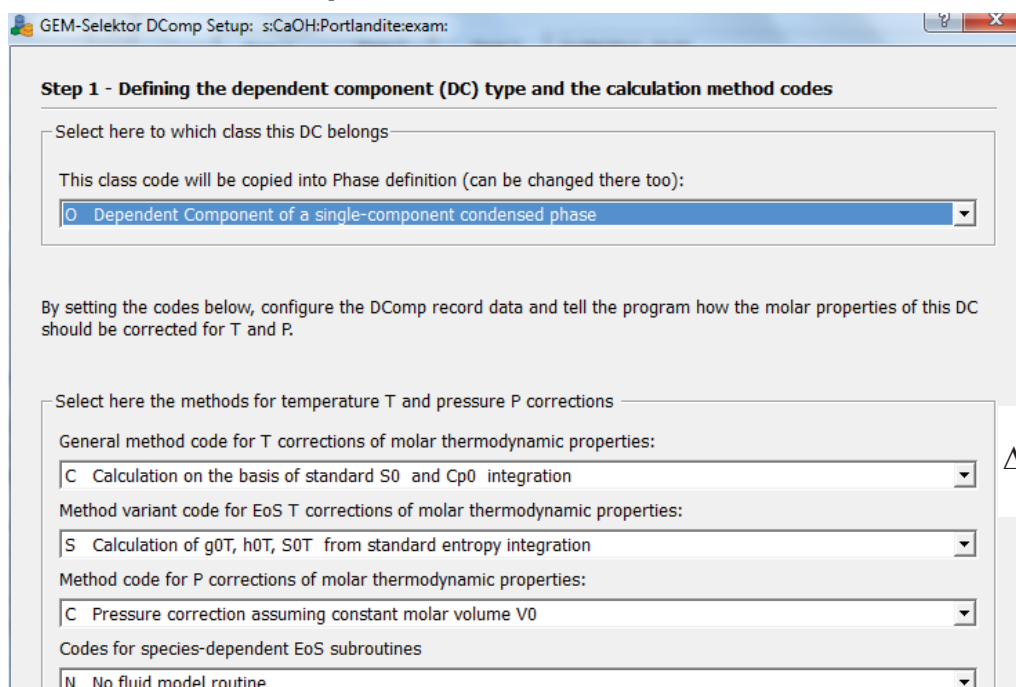
Select here to which class this DC belongs

This class code will be copied into Phase definition (can be changed there too):

0 Dependent Component of a single-component condensed phase

By setting the codes below, configure the DComp record data and tell the program how the molar properties of this DC should be corrected for T and P.

## DComp– creation of new entries



GEM-Selektor DComp Setup: s:CaOH:Portlandite:exam:

Step 1 - Defining the dependent component (DC) type and the calculation method codes

Select here to which class this DC belongs

This class code will be copied into Phase definition (can be changed there too):

0 Dependent Component of a single-component condensed phase

By setting the codes below, configure the DComp record data and tell the program how the molar properties of this DC should be corrected for T and P.

Select here the methods for temperature T and pressure P corrections

General method code for T corrections of molar thermodynamic properties:

C Calculation on the basis of standard S0 and Cp0 integration

Method variant code for EoS T corrections of molar thermodynamic properties:

S Calculation of g0T, h0T, S0T from standard entropy integration

Method code for P corrections of molar thermodynamic properties:

C Pressure correction assuming constant molar volume V0

Codes for species-dependent EoS subroutines

N No fluid model routine

Optional parameters for experienced users, else leave default values

Default: "CS"

$$\Delta_a G_T^o = \Delta_f G_{T_0}^o - \int_{T_0}^T S_T^o dT$$

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];

**Step 2 - Specific dimensions and settings**

Dimensions to change only in special cases

Number of Cp(T) equations can be changed here if Cp(T) coefficients are available for more than one temperature interval. Default is 1, maximum 5 intervals.

Number of phase transitions can be changed here, if necessary (usually one less than the number of Cp=f(T) equations). Default is 0, maximal 4.

Number of EoS coefficients can be set here if certain EoS models for fluids will be used (default: 0). The coefficients will be collected automatically into Phase record.

☐ Check here to allocate the Vm=f(P, T) vector of coefficients (reserved)

Units of measurement (cannot be changed in this version of GEMS)

Units of energy (default: j)

Units of volume (default: j)

Units of pressure (default: b)

Units of temperature (default: C)

[Learn more](#) < Back Next > Cancel

*Optional parameters for experienced users, else leave default values*

## 3) GEMS: reactions (ReacDC): new

**Portlandite solubility:**



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

**Elements:ordering**  
**Component name**  
**Data base: «example»**

ReacDC: Reaction-defined data format for Dependent Components (species)

Page 1 Page 2 01/09/2012, 23:37

ReacDC: Please, set a new record key

s:CaOH:portland:exa:

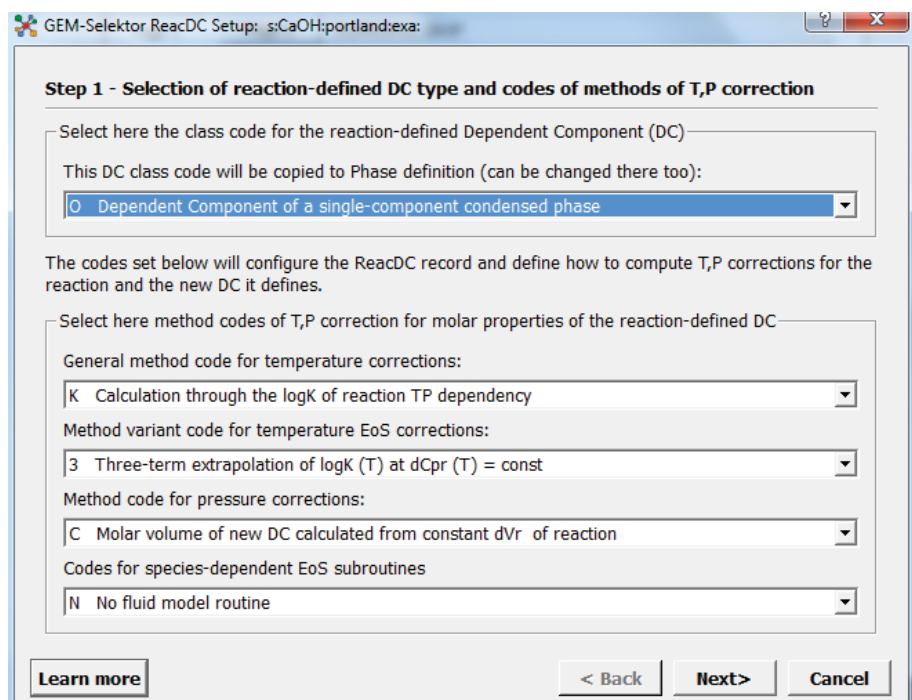
**s: solid** Phase state of new (reaction-defined) Dependent Component

CaOH Group to which Dependent Component belongs

portland Name of new Dependent Component

exa Name of thermodynamic data subset (e.g. database)

Ok Reset From List Help Cancel



**Step 1 - Selection of reaction-defined DC type and codes of methods of T,P correction**

Select here the class code for the reaction-defined Dependent Component (DC)

This DC class code will be copied to Phase definition (can be changed there too):

0 Dependent Component of a single-component condensed phase

The codes set below will configure the ReacDC record and define how to compute T,P corrections for the reaction and the new DC it defines.

Select here method codes of T,P correction for molar properties of the reaction-defined DC

General method code for temperature corrections:

K Calculation through the logK of reaction TP dependency

Method variant code for temperature EoS corrections:

3 Three-term extrapolation of logK (T) at dCpr (T) = const

Method code for pressure corrections:

C Molar volume of new DC calculated from constant dVr of reaction

Codes for species-dependent EoS subroutines

N No fluid model routine

Learn more < Back Next> Cancel

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

(K) 3

Three-term extrapolation of  $\log K(T)$  at  $dCpr(T) = \text{const}$  (preferable). Enter non-[empty] values into the [Cp0x\[0,0\]](#) cell, and into either [H0x\[0,0\]](#) or [S0x\[0,0\]](#) cells (another must contain [empty]); enter a non-empty value in either [logKx\[0,0\]](#), [logKx\[0,1\]](#) or [G0x\[0,0\]](#) cells (the other two cells and [G0x\[0,1\]](#) must contain [empty]). Then re-calculate and save the record. Use this code combination also for the [PRONSPREP calculation](#).

C

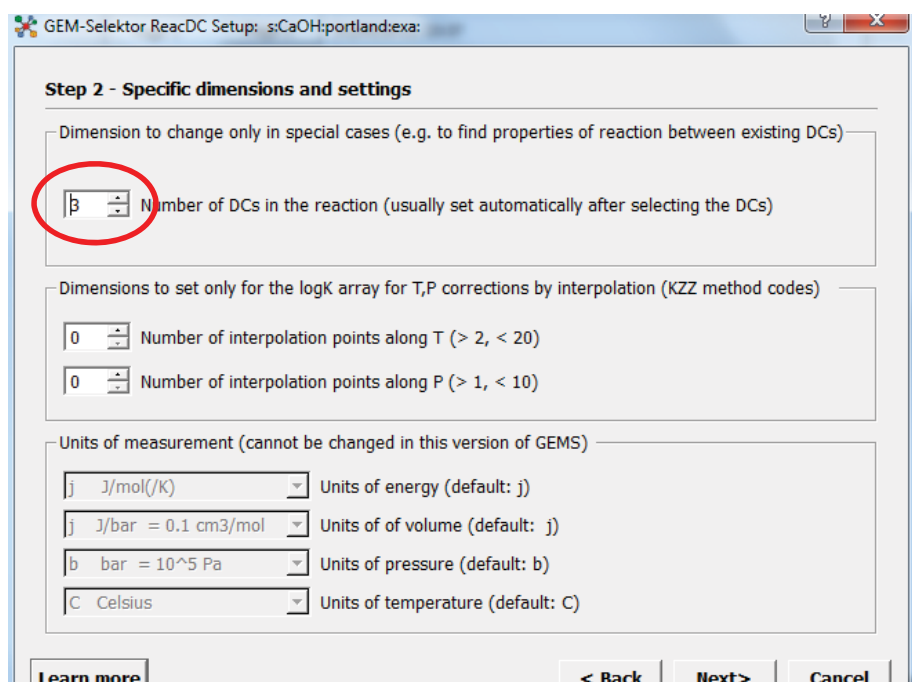
Molar volume of species  $V^P$  (in [DComp](#)) or  $dVr$  of reaction (in [ReacDC](#)) is assumed to be constant, independent of  $P$  and  $T$  (may be used for minerals up to a 1-2 kbar pressures at low-to-moderate temperatures).

### 3) GEMS: reactions (ReacDC): new

Portlandite solubility:



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

**Step 2 - Specific dimensions and settings**

Dimension to change only in special cases (e.g. to find properties of reaction between existing DCs)

3 Number of DCs in the reaction (usually set automatically after selecting the DCs)

Dimensions to set only for the logK array for T,P corrections by interpolation (KZZ method codes)

0 Number of interpolation points along T (> 2, < 20)

0 Number of interpolation points along P (> 1, < 10)

Units of measurement (cannot be changed in this version of GEMS)

j J/mol/(K) Units of energy (default: j)

j J/bar = 0.1 cm<sup>3</sup>/mol Units of of volume (default: j)

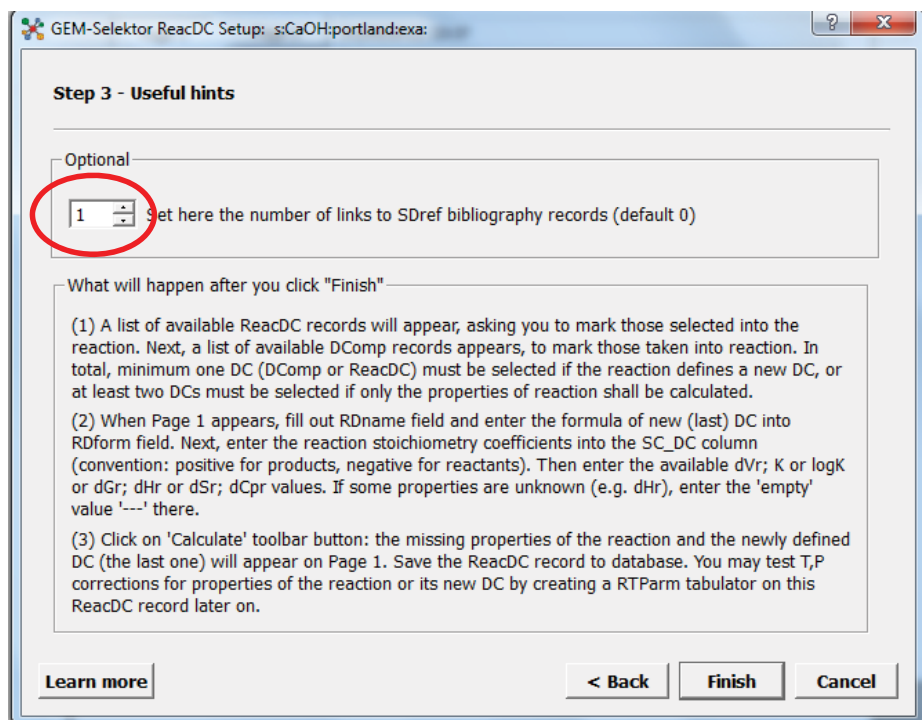
b bar = 10<sup>5</sup> Pa Units of pressure (default: b)

C Celsius Units of temperature (default: C)

Learn more < Back Next> Cancel

### 3) GEMS: reactions (ReacDC)

Portlandite solubility:

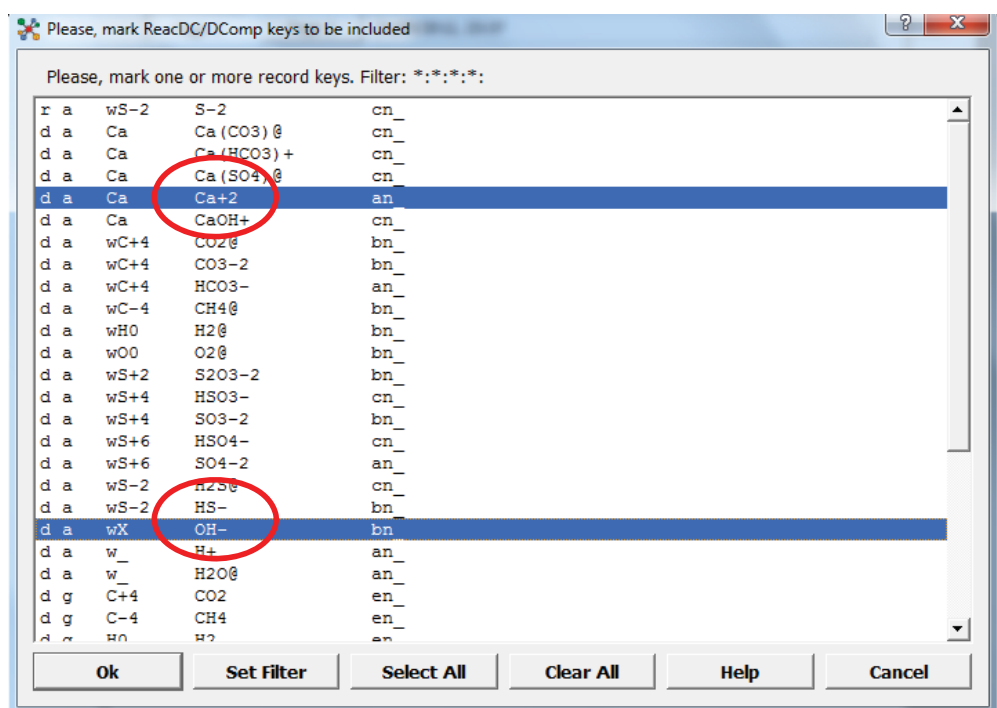


Literature reference

41

### 3) GEMS: reactions (ReacDC)

Portlandite solubility:



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

42

### 3) GEMS: reactions (ReacDC)

Portlandite solubility:



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

DComp :: Thermochemical/EOS data format for De

Page 1 Page 2 01/09/2012, 23:37

Portlandite  
Ca (OH) 2

M0 74.0927 Zz

V0d 3.306

G0d -897013

H0d -984675

S0d 83.4

Cp0d 87.5053

PrTr 1

LamST ---

BetAlp ---

0 Robie\_Hem:1995:pap:  
1 AUG20\_GEMS:2001:dat:

ReacDC :: Remake finished OK. It is recommended to re-calculate the data.

Page 1 Page 2 03/09/2012, 14:14

portlandite  
Ca (OH) 2

	SC	DC		REsDC
0	1	d	a	Ca Ca+2 an_
1	2	d	a	wX OH- bn_
2	-1	r	s	CaOH portland exa

V0r -6.0914 3.30596 ---

logKr --- -5.2 ---

G0r --- --- ---

H0r --- --- ---

S0r -161.306 --- ---

Cp0r -391.104 --- ---

NisoX --- --- ---

PrTr 1 25 M0 74.0927 0

BetAl --- --- ab --- ---

Reaction coefficient

New component

Volume changes

Log K

S reaction

Cp reaction

43

### 3) GEMS: reactions (ReacDC)

Portlandite solubility:



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

DComp :: Thermochemical/EOS data format for De

Page 1 Page 2 01/09/2012, 23:37

Portlandite  
Ca (OH) 2

M0 74.0927 Zz

V0d 3.306

G0d -897013

H0d -984675

S0d 83.4

Cp0d 87.5053

PrTr 1

LamST ---

BetAlp ---

0 Robie\_Hem:1995:pap:  
1 AUG20\_GEMS:2001:dat:

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1 Page 2 03/09/2012, 14:14

portlandite  
Ca (OH) 2

	SC	DC		REsDC
0	1	d	a	Ca Ca+2 an_
1	2	d	a	wX OH- bn_
2	-1	r	s	CaOH portland exa

V0r -6.0914 3.30596 ---

logKr 6.3095734e-006 -5.2 ---

G0r 29681.819 -897011.82 ---

H0r -18411.597 -984675.4 ---

S0r -161.306 83.4 ---

Cp0r -391.104 87.5053 ---

NisoX --- --- ---

PrTr 1 25 M0 74.0927 0

BetAl --- --- ab --- ---

Reaction coefficient

New component

Volume changes

Log K

S reaction

Cp reaction

44

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1   Page 2   03/09/2012, 14:14

portlandite  
Ca(OH)<sub>2</sub>

	SC DC		REsDC
0	1 d	a	Ca Ca+2 an_
1	2 d	a	wX OH- bn_
2	-1 n	s	CaOH portland exa

V0r	-6.0914	3.30596	--
logKr	6.3095734e-006	-5.2	--
G0r	29681.819	-897011.82	--
H0r	-18411.597	-984675.4	--
S0r	-161.306	83.4	--
Cp0r	-391.104	87.5053	--

ReacDC :: Calculation finished OK (elapsed time: 0 s).

Page 1   Page 2   03/09/2012, 14:14

K 3 C N   O j j b C   + - - - - -

03/09/12   3   0   0   0   0   0   0   1

	TCint	P int	aiLgKr
0	0	0	128.397
1	426.85	1	0
2			-5129.11
3			-20.4287
4			0
5			0
6			0
7			0
8			0
9			0
10			0

**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>

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3-term extrapolation  $\Delta C p_T = \Delta C p_{T_0} = const$

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

$$A_0 = \frac{0.4343}{R} \cdot [\Delta_r S_{T_0}^0 - \Delta_r C p_{T_0} (\ln T_0 + 1)]$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H_{T_0}^0 - \Delta_r C p_{T_0} T_0)$$

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

#### 4.) Plot of temperature/pressure dependent thermodynamic data



Modules   Record   Record List   Database Files   Window   Help

RTParm

IComp

DComp

ReacDC

RTParm

Phase

Compos

**new**

RTParm :: Tabulation/plot of thermodynamic data for one DC (species)

Scripts   Tables   TPwork   Setup   16/06/2005, 14:16

logKsp = f(TC) of ettringite

Please, change the script and/or remake, if necessary

Please, select a source record from:

DComp   **ReacDC**   Cancel

rpMode 2   rpNpT 1   17

tExpr

```
xT[jTP] =: twTC;
xP[jTP] =: twP;
yF[jTP][0] =: tlogK;
```

**Helps to determine S or H for Temperature extrapolations**

## Temperature/pressure dependent thermodynamic data



ReacDC: Select one key of a source ReacDC record

Please, select one record key. Filter: \*

a	wS-2	S-2	cn
s	CaOH	portland	exa

Ok Set Filter

RTParm: Please, set a new record key

s:CaOH:portland:exa:r:001:

s Phase state of source Dependent Component (DComp or ReacDC)

CaOH Group to which source Dependent Component belongs

portland Name of source Dependent Component

exa Code of source thermodynamic data set

r Source of input data for DC { r d }

001 Variant number of this RTParm calculation task <integer>

Ok Reset From List Help Cancel

*number*

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## Temperature/pressure dependent thermodynamic data



RTParm :: Calculation finished OK (elapsed time: 0.358 s).

Scripts Tables TPwork Setup 05/09/2012, 14:50

T (and P) corrections: g0 function of portland

Please, change the script and/or remake, if necessary

rpPi		rpTi		rpMode	rpNpI	1	15	15
0	1	0	0					
1	1	1	350					
2	0	2	25					

*Start value*  
*Stop value*  
*Step*

calc. values

RTParm :: Calculation finished OK (elapsed time: 0.39 s).

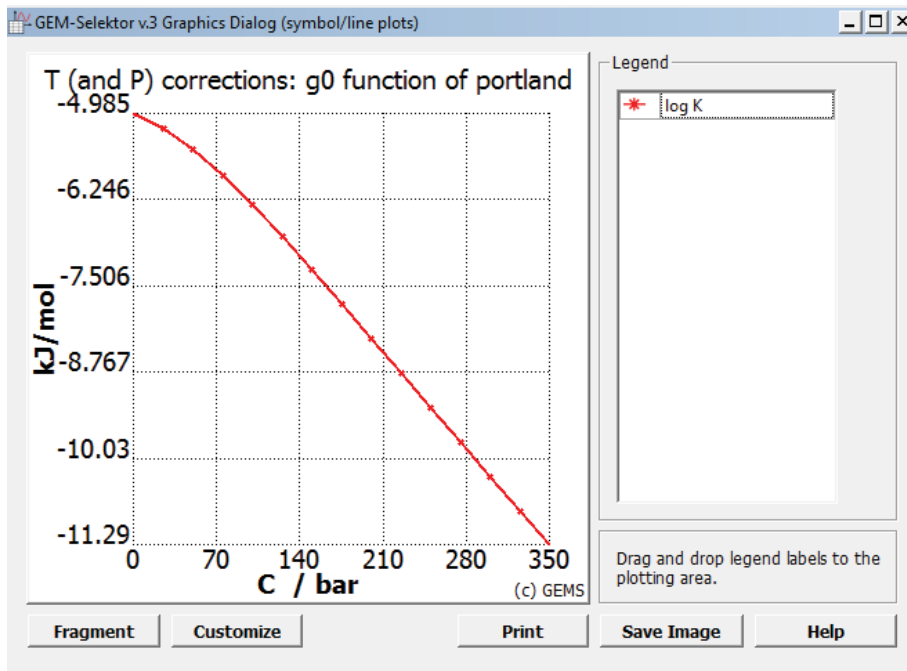
Scripts Tables TPwork Setup 05/09/2012, 14:50

tXName C / bar log K

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

tExpr xI[jTP] =: twTC;  
xP[jTP] =: twP;  
yF[jTP][0] =: tlogK;

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Comparison between extrapolated  $\log K_T$  function and experimental values:

Good tool for visual data fitting, e.g. estimation of  $\Delta H_0^r$  based on experimental data

Graphical output

## 5.) Thermodynamic Phases – creation of entries

Phase: Please, set a new record key

s:CaOH:Portlandite:c:exa:

s Code of phase state { a g l h s d x }

CaOH Symbol of this phase definition (letters, digits)

Portlandite Name of this phase definition

c Phase class { c d l gm ss ssd ls aq xsa xc }

exa Comment to phase definition

Ok Reset From List Help Cancel

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

Optional: Choice of mixing model if a non ideal solid solution is included

I for Single phase or ideal solid solution:

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

Step 1 - Defining the Phase and the Mode of Mixing

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of (non-ideal) mixing should be used, and how it should be calculated.

Select a model of mixing for this phase:

I Ideal mixture or pure phase (default)

Select a mode of calculation of activity coefficients of end members:

I Activity coefficients will be set to 1 (pure phase, simple ideal mixing), default

Select a mode of execution of DcEq user-defined script for end-members:

## 5.) Thermodynamic Phases – creation of entries

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

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

**Step 2 - Phase Model-Specific Settings**

Optional dimensions to set when built-in functions or scripts for the mixing model shall be used.

Attention! ForTSolMod built-in mixing models that use dc\_cf and/or ipxT, pc\_cf data objects, the appropriate dimensions will usually be allocated automatically. Otherwise, the array will be allocated only if all its dimensions are not zeros.

0 dc\_cf array: number of columns (coefficients per phase end member).

0 ipxT and ph\_cf arrays: number of rows (interaction parameters) for the non-ideal mixing model.

0 ipxT array for indexation of interaction parameters: set here the maximum order of a parameter (e.g. 3 if binary and ternary parameters will be used).

0 ph\_cf array of interaction parameter coefficients: number of columns (max. number of coefficients per parameter).

Set items in this box only if this is a sorption phase

☐ Check if surface complexation will be considered in this (sorption) phase

0 Set the number of surface types (minimum 1, maximum 6) to allocate surface complexes

0 Enter here the specific surface area A of the sorbent (in m<sup>2</sup> per gram), A>0

[Learn more](#) [< Back](#) [Next>](#)

**Optional parameters only for experienced users, otherwise leave default values**

GEM-Selektor Phase Setup: s:CaOH:Portlandite:c:exa:

**Step 3 - Final Settings and Hints**

Optional

0 Set here the number of links to SDref bibliography records (default 0)

☐ Extract parameters from DComp/ReacDC records and refresh DC class codes upon 'Calculate'?

What will happen after you click "Finish"

(1) A list of available ReacDC ('r') and DComp ('d') records will appear; mark those to be the phase components (end-members). At least one species for a pure phase, or two for a solution phase must be marked.

(2) In Phase window, fill out PhName and PhNote comments. Depending on setup, enter numbers in DisPar, text in DcEq and/or PhEq, parameter coefficients in ipxT, ph\_cf, dc\_cf arrays on Phase window pages.

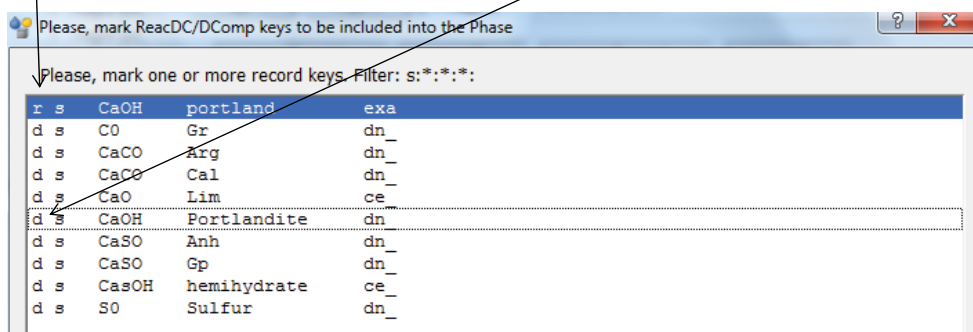
(3) Click on 'Calculate' toolbar button, then look at the PhDCC column; correct DC codes, if needed ('T' for H+; 'W' for H<sub>2</sub>O-solvent; 'M', 'J', or 'I' for solid-solution end members). Save Phase record to project database.

## 5.) Thermodynamic Phases – creation of entries

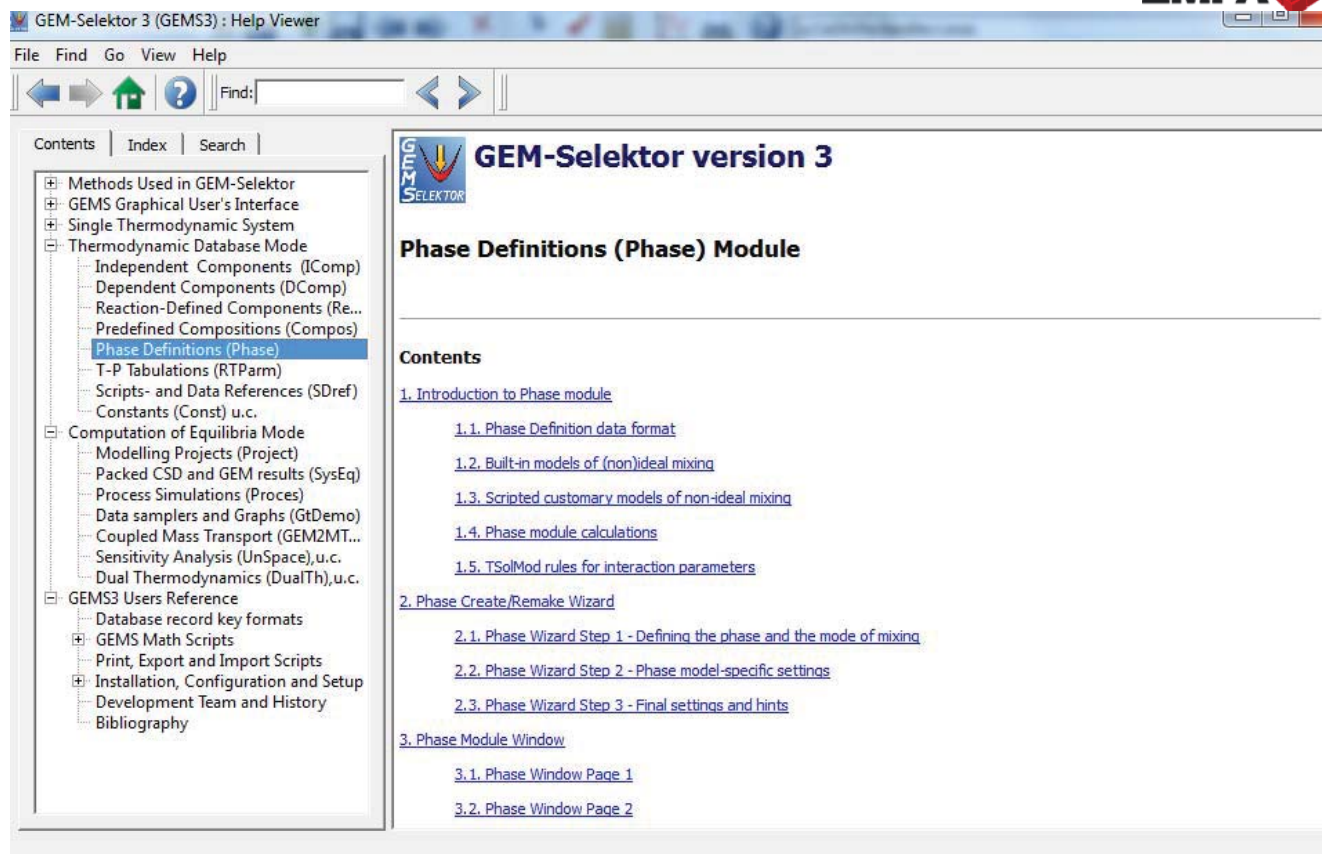
Mark dependent component to be included in the project database

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)

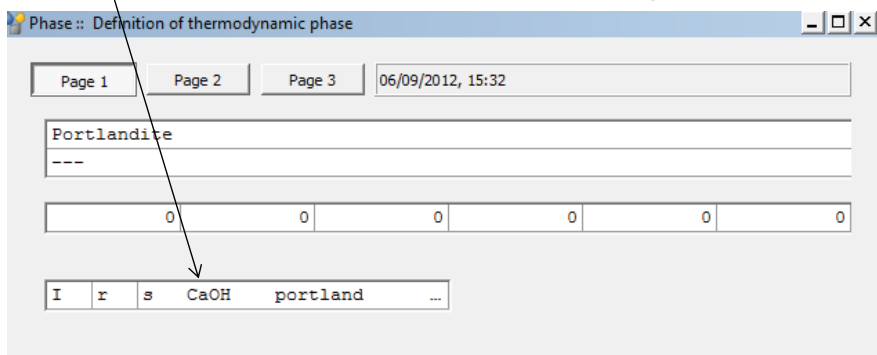


## 5.) Thermodynamic Phases – creation of entries

Mark dependent component to be included in the project database

### a) Single solid phase

### b) Solid solution



Phase: Definition of thermodynamic phase

Page 1 Page 2 Page 3 06/09/2012, 15:32

Portlandite

---

0 0 0 0 0 0

I r s CaOH portland ...

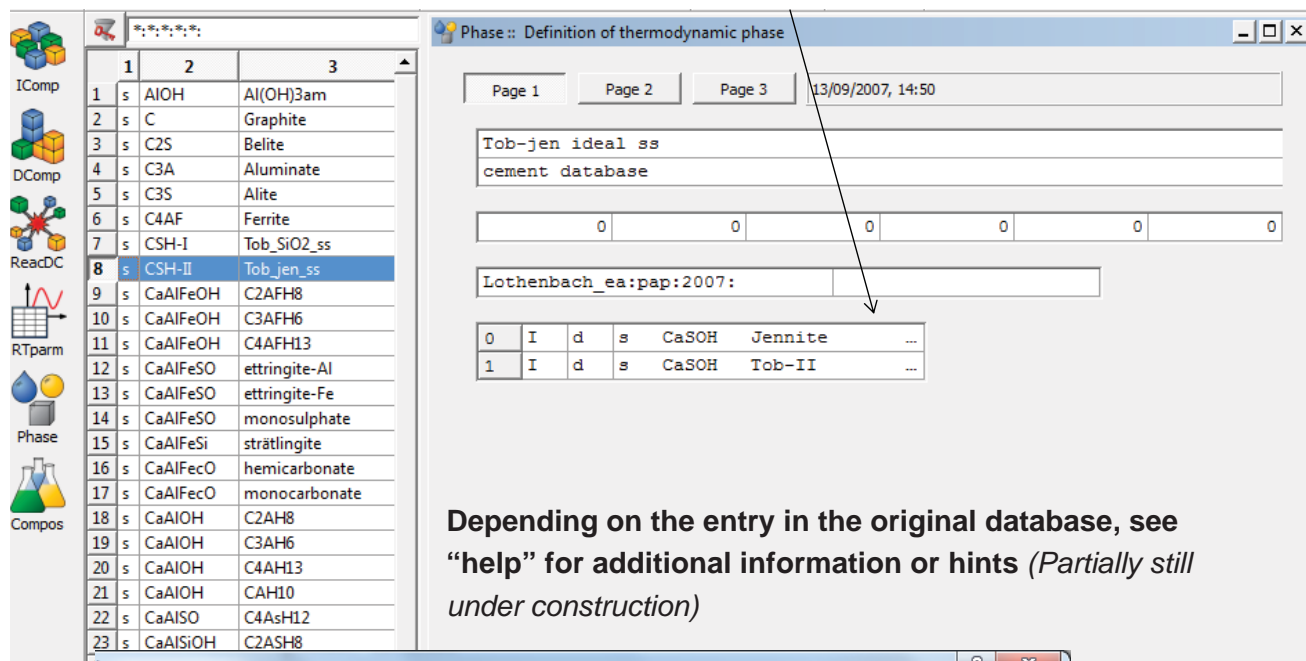
Depending on the entry in the original database, see “help” for additional information or hints (Partially still under construction)

## 5.) Thermodynamic Phases – creation of entries

Mark dependent component to be included in the project database

### a) Single solid phase

### b) Solid solution



Phase: Definition of thermodynamic phase

Page 1 Page 2 Page 3 13/09/2007, 14:50

Tob-jen ideal ss

cement database

0 0 0 0 0 0

Lothenbach\_ea:pap:2007:

0	I	d	s	CaSOH	Jennite	...
1	I	d	s	CaSOH	Tob-II	...

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

	1	2	3
1	s	AlOH	Al(OH)3am
2	s	C	Graphite
3	s	C2S	Belite
4	s	C3A	Aluminate
5	s	C3S	Alite
6	s	C4AF	Ferrite
7	s	CSH-I	Tob_SiO2 ss
8	s	CSH-II	Tob_jen ss
9	s	CaAlFeOH	C2AFH8
10	s	CaAlFeOH	C3AFH6
11	s	CaAlFeOH	C4AFH13
12	s	CaAlFeSO	ettringite-Al
13	s	CaAlFeSO	ettringite-Fe
14	s	CaAlFeSO	monosulphate
15	s	CaAlFeSi	strätlingite
16	s	CaAlFecO	hemicarbonat
17	s	CaAlFecO	monocarbonat
18	s	CaAlOH	C2AH8
19	s	CaAlOH	C3AH6
20	s	CaAlOH	C4AH13
21	s	CaAlOH	CAH10
22	s	CaAlSO	C4AsH12
23	s	CaAlSiOH	C2ASH8
24	s	CaAlSiOH	Si-hydrogarnet
25	s	CaAlcOH	C4Ac0.5H12

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 13/09/2007, 14:50

Tob-jen ideal ss  
cement database

0	0	0	0	0	0
---	---	---	---	---	---

Lothenbach\_ea:pap:2007:

0	I	d	s	CaSOH	Jennite	...
1	I	d	s	CaSOH	Tob-II	...

ss  
solid solution

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

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 13/09/2007, 14:50

p solt I N N I N N Ph Ps s - - - - Ph Nc 2 1 Ph nsc 0

pDC v	
0	s CaSOH Jennite ...
1	s CaSOH Tob-II ...

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 13/09/2007, 14:50

Ph ncp 0 0 Ph npv 0 Ph nsi 0 0 nSub 82...

0	s	CaSOH	Jennite	...
1	s	CaSOH	Tob-II	...

## 5.) Thermodynamic Phases – Treatment of solid solutions

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

GEM-Selektor Phase Setup: s:CSH-II:Tob\_jen\_ss:ss:cem:

**Step 1 - Defining the Phase and the Mode of Mixing**

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of (non-ideal) mixing should be used, and how it should be calculated.

Select a model of mixing for this phase:

☐ Ideal mixture or pure phase (default)

Select a mode of calculation of activity coefficients of end members:

☐ Activity coefficients will be set to 1 (pure phase, simple ideal mixing), default

Select a mode of execution of DcEq user-defined script for end-members:

☐ No DcEq script will be provided in this Phase definition (default)

Select a mode of execution of PhEq user-defined script for the whole phase:

☐ No PhEq script will be provided in this Phase definition (default)

Select a mode of a linking user-defined DcEq script to phase end members:

☐ No DcEq script will be provided (pure phase, built-in or ideal model), default

Select specific mixing rules (temperature corrections) for EoS and activity models:

☐ Default mixing rule or form of interaction parameter coefficients

[Learn more](#)

59

## GEMS – Database management

### 5.) Thermodynamic Phases – Treatment of solid solutions

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

Please, mark ReacDC/DComp keys to be included into the

Please, mark one or more record keys. Filter: s:\*:\*:\*

d	s	CaAlOSH	strätlingite	cem
d	s	CaAlOcH	hemicarbonat	cem
d	s	CaAlOcH	monocarbonat	cem
d	s	CaAlOcH	tricarboalu	cem
d	s	CaAlOsH	ettringite	cem
d	s	CaAlOsH	monosulphate	cem
d	s	CaFeOH	C2FH8	cem
d	s	CaFeOH	C3FH6	cem
d	s	CaFeOH	C4FH13	cem
d	s	CaFeOSH	C2FSH8	cem
d	s	CaFeOcH	Fe-hemicarbonat	cem
d	s	CaFeOcH	Femonocarbonat	cem
d	s	CaFeOsH	Fe-ettringite	cem
d	s	CaFeOsH	Fe-monosulphate	cem
d	s	CaKSOH	syngenite	cem
d	s	CaO	Lim	cem
d	s	CaSOH	Jennite	cem
d	s	CaSOH	Tob-I	cem
d	s	CaSOH	Tob-II	cem
d	s	CaSiO	C2S-beta	cem

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 13/09/2007, 14:5

Tob-jen ideal ss  
cement database

0 0 0

Lothenbach\_ea:pap:2007:

0	I	d	s	CaSOH	Jennite	...
1	I	d	s	CaSOH	Tob-II	...

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. $\text{SO}_4\text{-OH-AFm}$

Phase :: Definition of thermodynamic phase

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

SO<sub>4</sub>\_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 npv 0 Ph nsi 0 1 nSub 0

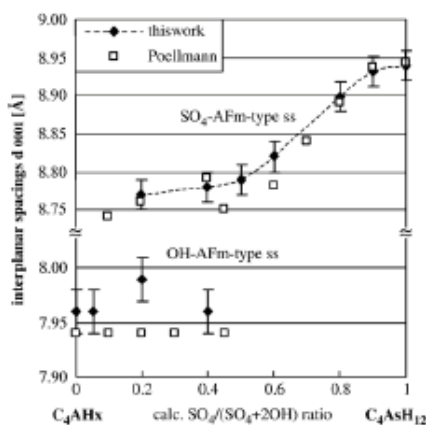
ph cf 0.188 2.49 0

61

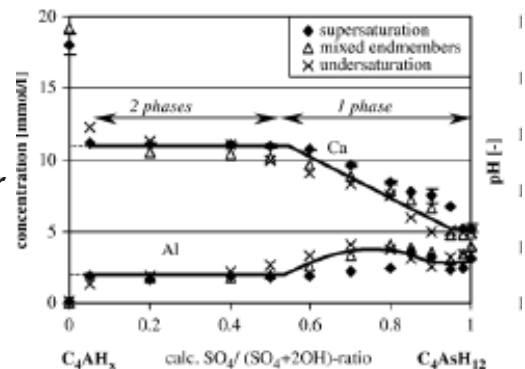
## 5.) Thermodynamic Phases – Treatment of solid solutions



### b) Non-ideal solid solutions, e.g. $\text{SO}_4\text{-OH-AFm}$



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 npv 0 Ph nsi 0 1 nSub 0

ph cf 0.188 2.49 0

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

62

## 5.) Thermodynamic Phases – Treatment of solid solutions



### b) Non-ideal solid solutions, e.g. $\text{SO}_4\text{-OH-AFm}$

GEM-Selektor Phase Setup: s:CaAl<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>:OH<sub>2</sub>:AFm:cm

Step 1 - Defining the Phase and the Mode of Mixing

Selection of the codes below will configure the Phase record and tell the program what kind of phase and which model of (non-ideal) mixing should be used, and how it should be calculated.

Select a model of mixing for this phase:  
G Binary Redlich-Kister solid-solution model

Select a mode of calculation of activity coefficients of end members:  
S Activity coefficients will be calculated using a built-in mixing model selected above

Select a mode of execution of DcEq user-defined script for end-members:  
N No DcEq script will be provided in this Phase definition (default)

Select a mode of execution of PhEq user-defined script for the whole phase:  
N No PhEq script will be provided in this Phase definition (default)

Select a mode of a linking user-defined DcEq script to phase end members:  
N No DcEq script will be provided (pure phase, built-in or ideal model), default

Select specific mixing rules (temperature corrections) for EoS and activity models:  
N Default mixing rule or form of interaction parameter coefficients

Learn more < Back Next> Cancel

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. $\text{SO}_4\text{-OH-AFm}$

GEM-Selektor Phase Setup: s:CaAl<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>:OH<sub>2</sub>:AFm:cm

Step 2 - Phase Model-Specific Settings

Optional dimensions to set when built-in functions or scripts for the mixing model shall be used.

Attention! ForTsolMod built-in mixing models that use dc\_cf and/or ipxT, pc\_cf data objects, the appropriate dimensions will usually be allocated automatically. Otherwise, the array will be allocated only if all its dimensions are not zeros.

0 dc\_cf array: number of columns (coefficients per phase end member).

1 ipxT and ph\_cf arrays: number of rows (interaction parameters) for the non-ideal mixing model.

0 ipxT array for indexation of interaction parameters: set here the maximum order of a parameter (e.g. 3 if binary and ternary parameters will be used).

3 ph\_cf array of interaction parameter coefficients: number of columns (max. number of coefficients per parameter).

Set items in this box only if this is a sorption phase

☐ Check if surface complexation will be considered in this (sorption) phase

0 Set the number of surface types (minimum 1, maximum 6) to allocate surface complexes

0 Enter here the specific surface area A of the sorbent (in m<sup>2</sup> per gram), A>0

Learn more < Back Next> Cancel

leave default values, GEMS generates needed additional arrays automatically

GEM-Selektor Phase Setup: s:CaAl<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>:OH<sub>2</sub>:AFm:cm

Step 3 - Final Settings and Hints

Optional

1 Set here the number of links to Sdref bibliography records (default 0)

☐ Extract parameters from DComp/ReacDC records and refresh DC class codes upon 'Calculate'?

What will happen after you click "Finish"

(1) A list of available ReacDC ('r') and DComp ('d') records will appear; mark those to be the phase components (end-members). At least one species for a pure phase, or two for a solution phase must be marked.

(2) In Phase window, fill out PhName and PhNote comments. Depending on setup, enter numbers in DisPar, text in DcEq and/or PhEq, parameter coefficients in ipxT, ph\_cf, dc\_cf arrays on Phase window pages.

(3) Click on 'Calculate' toolbar button, then look at the PhDCC column; correct DC codes, if needed ('T' for H+; 'W' for H<sub>2</sub>O-solvent; 'M','J', or 'I' for solid-solution end members). Save Phase record to project database.

Learn more < Back Finish Cancel

## 5.) Thermodynamic Phases – Treatment of solid solutions

### a) Non-ideal solid solutions, e.g. $\text{SO}_4\text{-OH-AFm}$

Please, mark one or more record keys. Filter: s:\*:

d	s	AlO	Crn	s98c
d	s	AlOH	AlOHAm	cem
d	s	CaAlFeO	C4AF	cem
d	s	CaAlO	C3A	cem
d	s	CaAlOH	C2AH8	cem
d	s	CaAlOH	C3AH6	cem
d	s	CaAlOH	C3ASO.8H4.4	cem
d	s	CaAlOH	C4AH13	cem
d	s	CaAlOH	CAH10	cem
d	s	CaAlOSH	strätlingite	cem
d	s	CaAlOCH	hemcarbonate	cem
d	s	CaAlOCH	monocarbonate	cem
d	s	CaAlOCH	tricarboalu	cem
d	s	CaAlOsH	ettringite	cem
d	s	CaAlOsH	monosulphate	cem
d	s	CaFeOH	C2FH8	cem
d	s	CaFeOH	C3FH6	cem
d	s	CaFeOH	C4FH13	cem
d	s	CaFeOSH	C2FSH8	cem
d	s	CaFeOCH	Fe-hemicarbonate	cem
d	s	CaFeOCH	Femonocarbonate	cem
d	s	CaFeOSH	Fe-ettringite	cem
d	s	CaFeOSH	Fe-monosulphate	cem
d	s	CaKSOH	syngenite	cem
d	s	CaO	Tim	cem

Ok Set Filter Select A

Phase :: Remake finished OK. It is recommended to re-calculate the data.

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	...

J ... junior end member  
M ... major end member

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

Mark the end members of the solid solution series

Phase

1	2	3	4
7	s	CSH-II	Tob_jen_ss
8	s	CaAlFeOH	C2AFH8
9	s	CaAlFeOH	C3AFH6
10	s	CaAlFeOH	C4AFH13
11	s	CaAlFeSO	ettringite-Al
12	s	CaAlFeSO	ettringite-Fe
13	s	CaAlFeSO	monosulphate
14	s	CaAlFeSi	strätlingite
15	s	CaAlFecO	hemcarbonate
16	s	CaAlFecO	monocarbonate
17	s	CaAlOH	C2AH8
18	s	CaAlOH	C3AH6
19	s	CaAlOH	C4AH13
20	s	CaAlOH	CAH10
21	s	CaAlSO	C4AsH12
22	s	CaAlSiOH	C2ASH8
23	s	CaAlSiOH	Si-hydrogarnet
24	s	CaAlcOH	C4Ac0.5H12
25	s	CaAlcOH	C4AcH11
26	s	CaAlsOH	ettringite
27	s	CaAlsOH1	SO4_OH_AFm
28	s	CaAlsOH2	OH_SO4_AFm
29	s	CaAlscH1	SO4_CO3_Aft
30	s	CaAlscH2	CO3_SO4_Aft

Phase :: Remake finished OK. It is recommended to re-calculate the data.

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	...

Solid solution 1 (SO4\_OH\_AFm)

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 06/11/2007, 16:55

OH\_SO4\_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	M	d	s	CaAlOH	C4AH13	...
1	J	d	s	CaAlOsH	monosulphate	...

Solid solution 2 (OH\_SO4\_AFm)

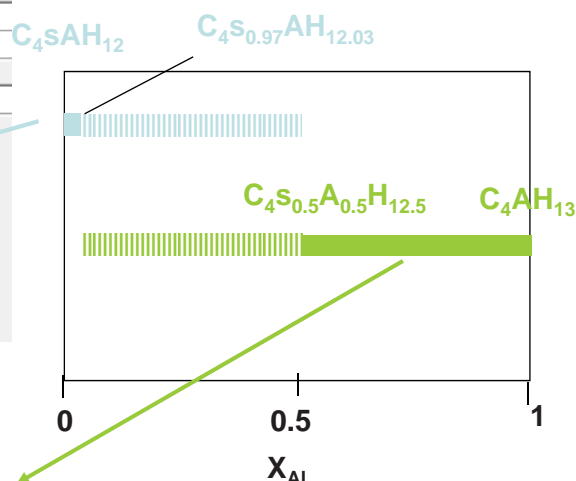
Page 1 Page 2 Page 3 09/11/2007, 08:09

SO4\_OH\_AfM nonideal ss  
nonideal ss monosulfat\_C4AH13; cement database

0	0	0	0	0	0
---	---	---	---	---	---

Matschei\_ea:2007:pap: a0=0.188, a1=2.49

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



2nd phase: identical, M and J changed

Phase :: Definition of thermodynamic phase

Page 1 Page 2 Page 3 06/11/2007, 16:55

OH\_SO4\_AfM nonideal ss  
nonideal ss monosulfat\_C4AH13; cement database

0	0	0	0	0	0
---	---	---	---	---	---

Matschei\_ea:2007:pap: a0=0.188, a1=2.49

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

GEMS-Workshop

6<sup>67</sup>

## 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)