Oregon State University

Empa
Materials Science and Technology

Lecture 9
How to calculate

solubility products

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Software development/fitting tools/kinetic:

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PAUL SCHERRER INSTITUT
PSI

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Solubility products

1. **General considerations**
2. Measured concentrations ⇔ log K_s
3. Estimation of C_p and S
4. Calculation of log K_s at different temperatures

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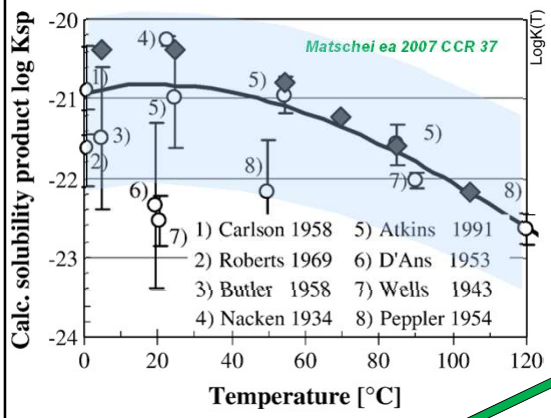
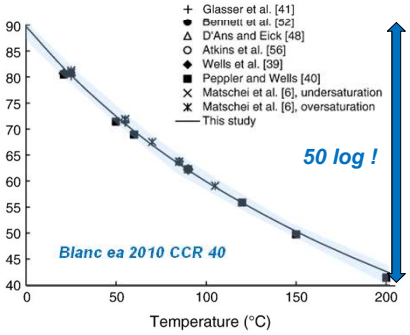
Katoite $(CaO)_3Al_2O_3\ 6H_2O$: C_3AH_6

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





Log K_{s0}, C_3AH_6 = $\{Ca^{2+}\}^3\{Al^{3+}\}^2\{H_2O\}^{12}\ \{H^+\}^{-12}$ = 80.3

Log K_{s0} C_3AH_6 = -21.4±1

Relatively large scatter; -20.8±1

monosulfate predicted in hydrated cements

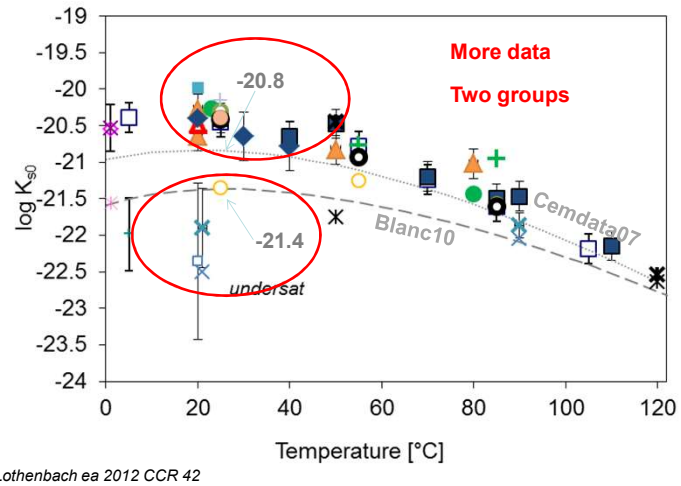
C_3AH_6 predicted instead of monosulfate in hydrated cements

⇔ **contradicts cement experiments (monosulfate is obseverved)**

Why?

3

Solubility of C_3AH_6



this study: over 19 months
Robert: und 1 week
Carlson: und ≥9 months
Carlson carbonated
Buttler: und ≤19 months
Matschei: und 1-3 months
Matschei: over 1-3 months
Dilnesa: over 1-36 month
D'Ans: und 1 month
D'Ans: over 1-3 months
Nacken: over 1-2 months
Faurie: over 1-6 months
Balonis: over 6 months
Wells: und 3-17 months
Wells: over >12 months
Peppler: und 3-7 months
Peppler: over 4 months
Glasser: und 6 months
Bennett: und 28 days
Atkins: und 2-6 months
Zhang: over 12 months
Hobbs: under 18 months

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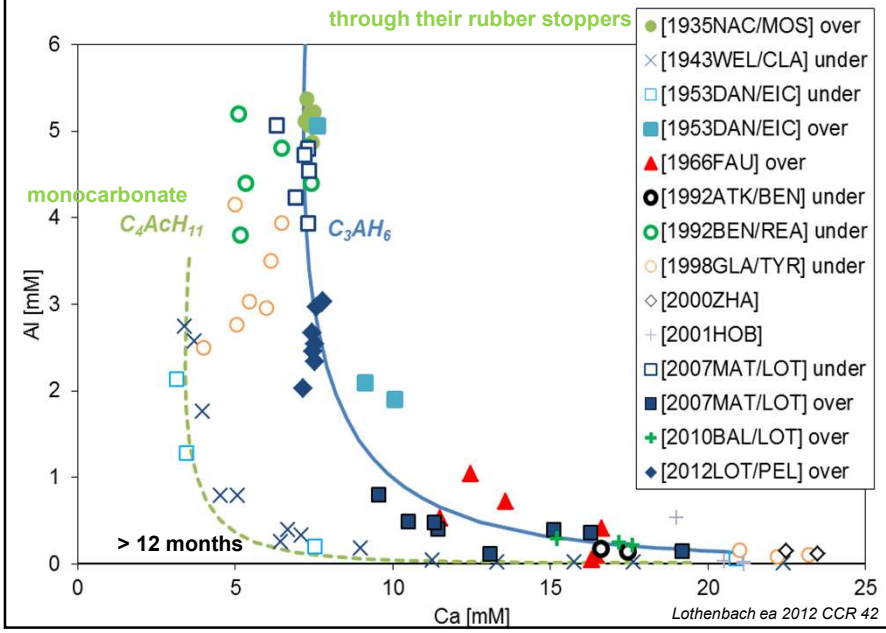
Solubility of C_3AH_6

Carbonation!

Wells ea reported calcite as CO_2 had leaked through their rubber stoppers



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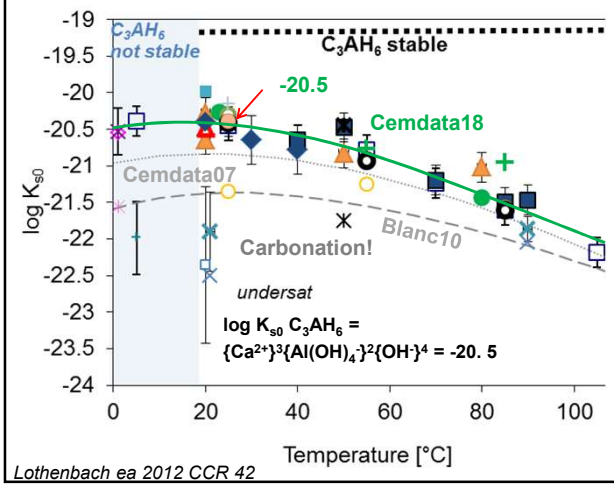
Solubility of C_3AH_6

	log K_{s0}	$\Delta_f G$ kJ/mol	$\Delta_f H$ kJ/mol	S J/mol/K	C_p J/mol/K
C_3AH_6	-20.50	-5008.2	-5537	422	446

Old K_{S0} too low, carbonation



monosulfate predicted in hydrated cements

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Solubility products

1. General considerations
2. **Measured concentrations ⇔ log K_s**
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4. Calculation of log K_s at different temperatures

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Solubility of C_3AH6

Matschei ea 2007 CCR 37

Table 5
Solubility data for C_3AH_6 at different temperatures and ages

Age [Day]	Temperature [°C]	Ca [mmol/l]	Al [mmol/l]	pH	Log_K_{sp}	Phases
C_3AH_6 (samples cooled down from initially ~ 105 °C)						
28	25	6.91	4.24	11.91 (11.98[1])	−20.52	n.d.
56	25	7.29	4.80	11.92 (11.90[2])	−20.34	n.d.
84	25	6.31	5.07	11.81 (11.79[3])	−20.84	C_3AH_6
C_3AH_6 (from undersaturation)						
28	25	7.20	4.73	11.91 (11.96[1])	−20.38	n.d.
56	25	7.34	4.55	11.93 (11.90[2])	−20.32	n.d.
84	25	7.31	3.94	11.95 (11.91[3])	−20.36	C_3AH_6

undersaturation

Table 3
Experimental data and calculated values of pH and log ion activity product (IAP) for hydrogarnet. Concentrations in mmol dm^{-3}

Determination	Ca	Al	OH	pH	log IAP
1	7.43	4.40	23.4	11.66	80.45
2	7.31	4.81	27.0	11.80	81.02
3	5.11	5.20	23.3	11.32	78.89
4	5.16	3.80	23.4	11.83	80.54
5	6.49	4.80	29.6	11.93	81.34
6	5.33	4.40	28.1	11.95	81.12
Average					80.55
Model results	5.75	3.83		11.80	80.55

Bennet ea 1992 J. Nucl Mat 190
redispersion

$\log K_{s0} = \{Ca^{2+}\}^3\{Al(OH)_4^-\}^2\{OH^-\}^4$

$= -20.8$

$\log K_{s0}\ C_3AH_6 = \{Ca^{2+}\}^3\{Al^{3+}\}^2\{H_2O\}^{12}\ \{H^+\}^{-12}$

$= 80.3$

Differenz = $-(2*Al(OH)_4^- + 4*OH^-) = -(2*-22.9 +4*-14) = 101.8$

Product Substance	Reaction	$\log_{10}K^\circ_{298}$
Al+3	AlO2- + 4H + = Al+3 + 2H2O@	22.9
OH-	H2O@ = OH– + H+	−14.0

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Solubility of C_3AH6

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undersaturation

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Average					80.55
Model results	5.75	3.83		11.80	80.55

Bennet ea 1992 J. Nucl Mat 190
redispersion

Oversaturation

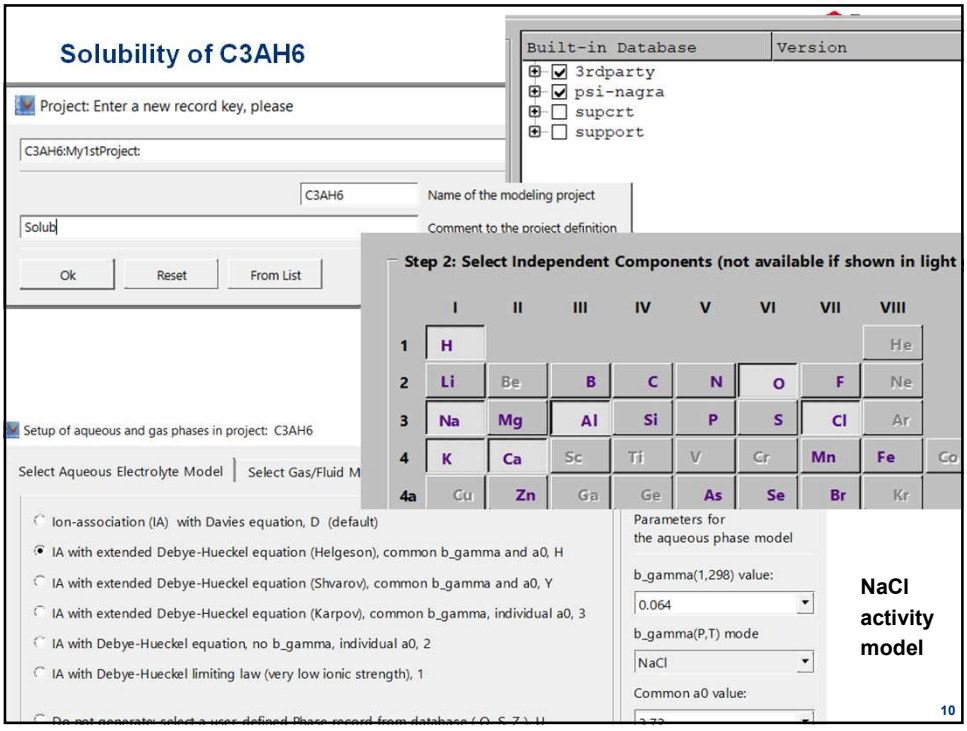
Thesis Matschei 2008

Table A.7: Solubility data of nominally hydroxy-AFm (C_4AH_{13}) at 25 °C

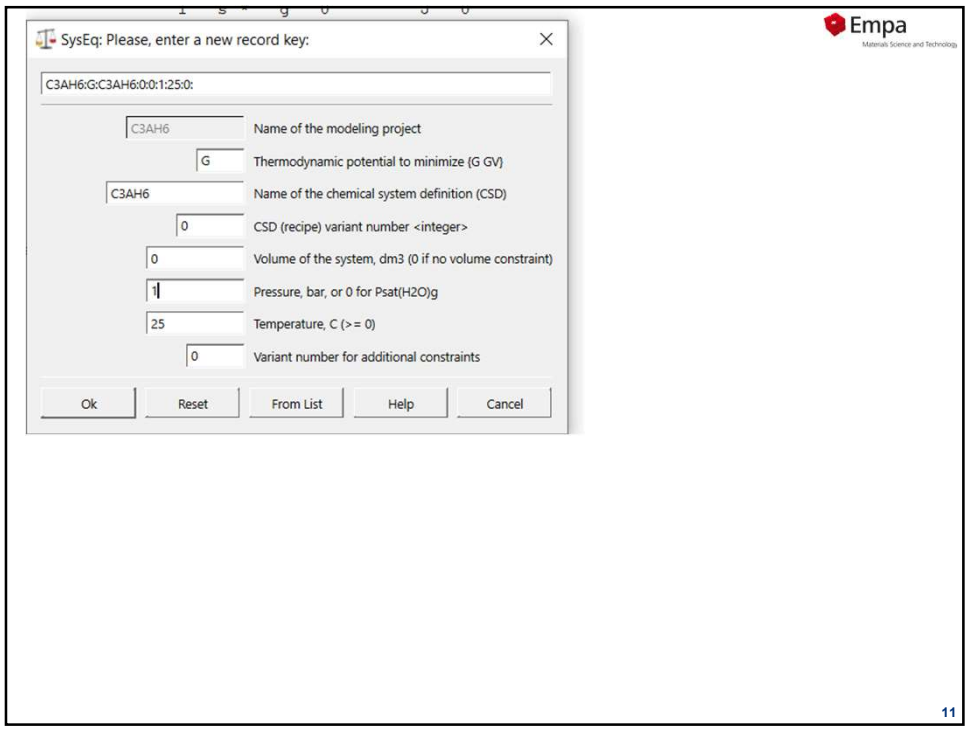
C_4AH_{13} (from supersaturation)

Age [d]	Temp. [°C]	Ca [mmol/l]	Al [mmol/l]	pH	Log_K_{sp}	Phases
28	25	17.64	0.21	12.44(12.40)	-25.60	C_4AH_{13}, C_3AH_6
56	25	20.11	0.20	12.49(12.46)	-25.21	C_4AH_{13}, C_3AH_6
373	25	19.91	0.17	12.48(12.43)	(-25.38)	C_3AH_6 $Ca(OH)_2$, C_4AH_{13} traces
750	25	19.96	0.09	12.49(12.49)	(-25.93)	C_3AH_6 $Ca(OH)_2$, C_4AH_{13} traces

Solubility of C3AH6



NaCl activity model


SysEq: Please, enter a new record key:
C3AH6:G:C3AH6:0:0:1:25:0:
C3AH6
Name of the modeling project
G
Thermodynamic potential to minimize (G GV)
C3AH6
Name of the chemical system definition (CSD)
0
CSD (recipe) variant number <integer>
0
Volume of the system, dm3 (0 if no volume constraint)
1
Pressure, bar, or 0 for Psat(H2O)g
25
Temperature, C (>= 0)
0
Variant number for additional constraints
Ok
Reset
From List
Help
Cancel
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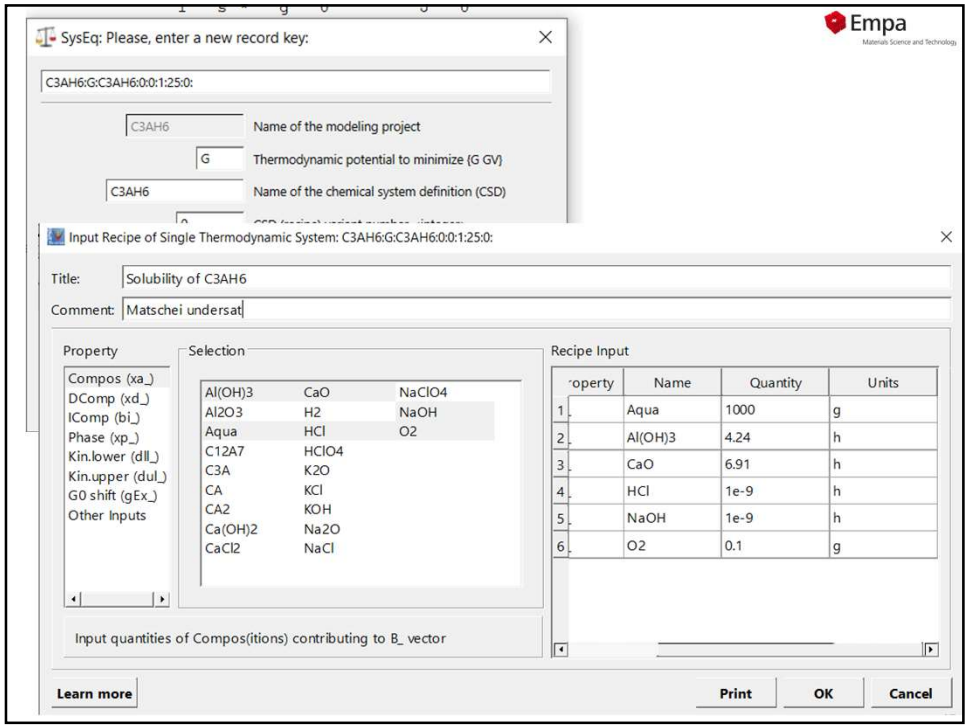
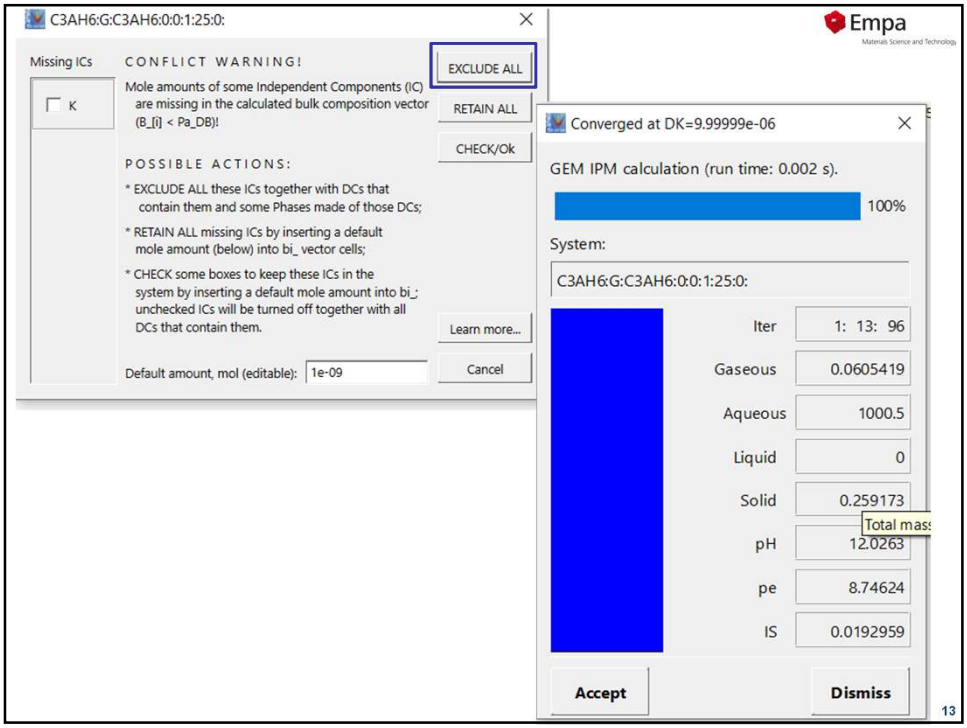

SysEq: Please, enter a new record key:
C3AH6:G:C3AH6:0:0:1:25:0:
C3AH6
Name of the modeling project
G
Thermodynamic potential to minimize (G GV)
C3AH6
Name of the chemical system definition (CSD)
Input Recipe of Single Thermodynamic System: C3AH6:G:C3AH6:0:0:1:25:0:
Title:
Solubility of C3AH6
Comment:
Matschei undersat
Property
Compos (xa_)
DComp (xd_)
IComp (bi_)
Phase (xp_)
Kin.lower (dll_)
Kin.upper (dul_)
G0 shift (gEx_)
Other Inputs
Selection
Al(OH)3
Al2O3
Aqua
C12A7
C3A
CA
CA2
Ca(OH)2
CaCl2
CaO
H2
HCl
HClO4
K2O
KCl
KOH
Na2O
NaCl
NaClO4
NaOH
O2
Recipe Input
Name
Quantity
Units
1 Aqua 1000 g
2 Al(OH)3 4.24 h
3 CaO 6.91 h
4 HCl 1e-9 h
5 NaOH 1e-9 h
6 O2 0.1 g
Input quantities of Compos(itions) contributing to B_ vector
Learn more
Print
OK
Cancel
Empa


C3AH6:G:C3AH6:0:0:1:25:0:
Missing ICs
K
CONFLICT WARNING!
Mole amounts of some Independent Components (IC) are missing in the calculated bulk composition vector (B_[i] < Pa_DB)!
POSSIBLE ACTIONS:
* EXCLUDE ALL these ICs together with DCs that contain them and some Phases made of those DCs;
* RETAIN ALL missing ICs by inserting a default mole amount (below) into bi_ vector cells;
* CHECK some boxes to keep these ICs in the system by inserting a default mole amount into bi_; unchecked ICs will be turned off together with all DCs that contain them.
Default amount, mol (editable): 1e-09
EXCLUDE ALL
RETAIN ALL
CHECK/Ok
Learn more...
Cancel
Converged at DK=9.99999e-06
GEM IPM calculation (run time: 0.002 s).
100%
System:
C3AH6:G:C3AH6:0:0:1:25:0:
Iter 1: 13: 96
Gaseous 0.0605419
Aqueous 1000.5
Liquid 0
Solid 0.259173
pH 12.0263
pe 8.74624
IS 0.0192959
Accept
Dismiss
Empa
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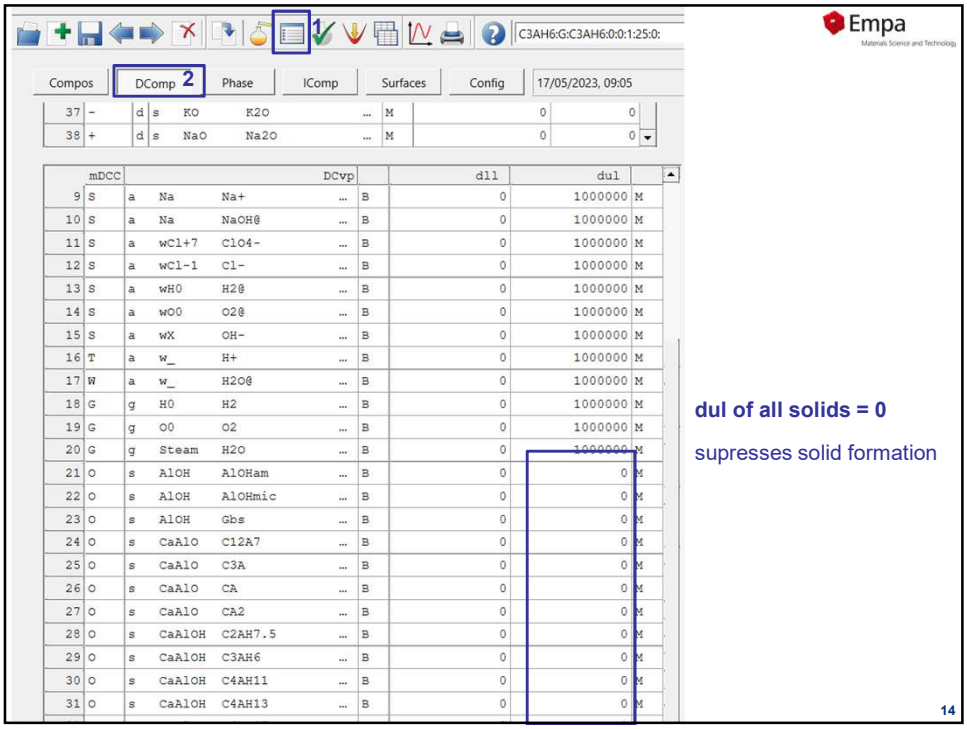
C3AH6:G:C3AH6:0:0:1:25:0:
Compos
DComp
2
Phase
IComp
Surfaces
Config
17/05/2023, 09:05
37 - d s KO K2O ... M 0 0
38 + d s NaO Na2O ... M 0 0
mDCC DCvp dll dul
9 S a Na Na+ ... B 0 1000000 M
10 S a Na NaOH@ ... B 0 1000000 M
11 S a wCl+7 ClO4- ... B 0 1000000 M
12 S a wCl-1 Cl- ... B 0 1000000 M
13 S a wH0 H2@ ... B 0 1000000 M
14 S a wO0 O2@ ... B 0 1000000 M
15 S a wX OH- ... B 0 1000000 M
16 T a w_ H+ ... B 0 1000000 M
17 W a w_ H2O@ ... B 0 1000000 M
18 G g H0 H2 ... B 0 1000000 M
19 G g O0 O2 ... B 0 1000000 M
20 G g Steam H2O ... B 0 1000000 M
21 O s AlOH AlOHam ... B 0 0 M
22 O s AlOH AlOHmic ... B 0 0 M
23 O s AlOH Gbs ... B 0 0 M
24 O s CaAlO C12A7 ... B 0 0 M
25 O s CaAlO C3A ... B 0 0 M
26 O s CaAlO CA ... B 0 0 M
27 O s CaAlO CA2 ... B 0 0 M
28 O s CaAlOH C2AH7.5 ... B 0 0 M
29 O s CaAlOH C3AH6 ... B 0 0 M
30 O s CaAlOH C4AH11 ... B 0 0 M
31 O s CaAlOH C4AH13 ... B 0 0 M
dul of all solids = 0
supresses solid formation
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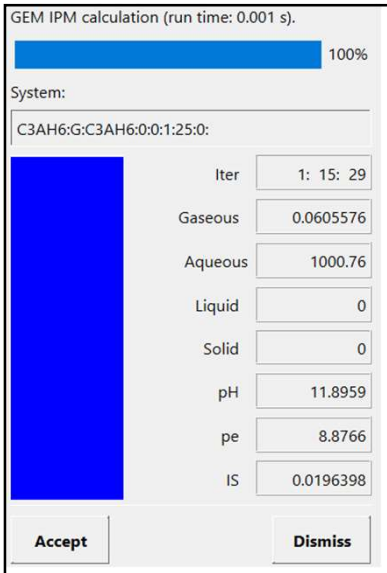

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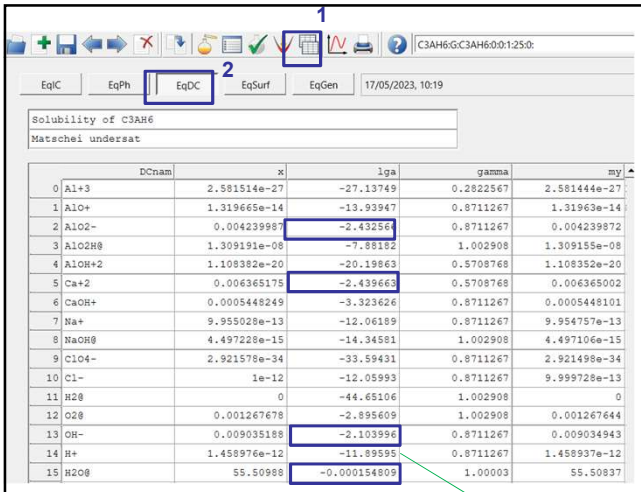
Age [Day]	Temperature [°C]	Ca [mmol/l]	Al [mmol/l]	pH	Log_K_{sp}	Phases
C_3AH_6 (samples cooled down from initially ~ 105 °C)						
28	25	6.91	4.24	11.91 (11.98[1])	−20.52	n.d.

Experimental data: pH ±0.1 ☺

15



	DCnam	x	lga	gamma	my
0	Al+3	2.581514e-27	-27.13749	0.2822567	2.581444e-27
1	AlO+	1.319665e-14	-13.93947	0.8711267	1.31963e-14
2	AlO2-	0.004239987	-2.43256	0.8711267	0.004239872
3	AlO2H@	1.309191e-08	-7.88182	1.002908	1.309155e-08
4	AlOH+2	1.108382e-20	-20.19863	0.5708768	1.108352e-20
5	Ca+2	0.006365175	-2.439663	0.5708768	0.006365002
6	CaOH+	0.0005448249	-3.323626	0.8711267	0.0005448101
7	Na+	9.955028e-13	-12.06189	0.8711267	9.954757e-13
8	NaOH@	4.497228e-15	-14.34581	1.002908	4.497106e-15
9	ClO4-	2.921578e-34	-33.59431	0.8711267	2.921498e-34
10	Cl-	1e-12	-12.05993	0.8711267	9.999728e-13
11	H2@	0	-44.65106	1.002908	0
12	O2@	0.001267678	-2.895609	1.002908	0.001267644
13	OH-	0.009035188	-2.103996	0.8711267	0.009034943
14	H+	1.458976e-12	-11.89595	0.8711267	1.458937e-12
15	H2O@	55.50988	-0.000154809	1.00003	55.50837

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$K_{s0} = \{Ca^{2+}\}^3 * \{Al(OH)_4^-\}^2 * \{OH^-\}^4$

Convention from SUPCRT used in GEMS

$Al(OH)_4^{-2} = AlO_2^- + 2H_2O^0$

Experimental data: pH 11.98 ☺

$K_{s0} = \{Ca^{2+}\}^3 * \{AlO_2^-\}^2 \{H_2O^0\}^4 * \{OH^-\}^4$

$\log K_{s0} = 3*\log aCa^{2+} + 2*\log aAlO_2^- + 4*\log aH_2O^0 + 4*\log a\ OH^-$

$= 3*-2.44 + 2*-2.43 + 4*-0.0002 + 4*-2.10 = -20.58$

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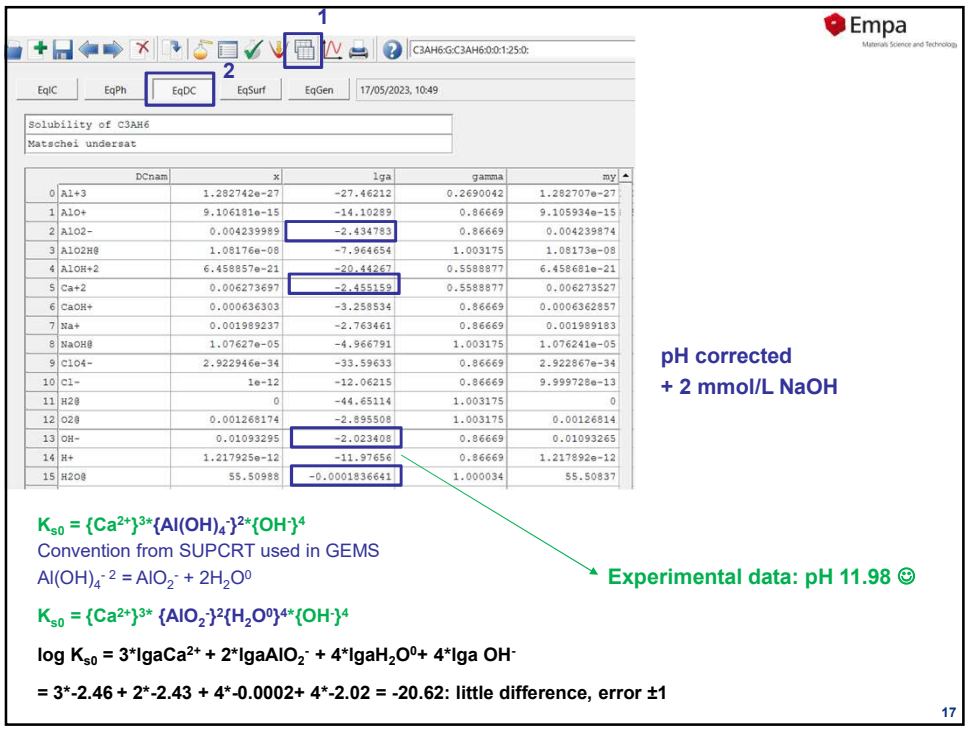


pH corrected
+ 2 mmol/L NaOH

$K_{s0} = \{Ca^{2+}\}^{3*}\{Al(OH)_4^-\}^{2*}\{OH^-\}^4$

Convention from SUPCRT used in GEMS

$Al(OH)_4^{-2} = AlO_2^- + 2H_2O^0$

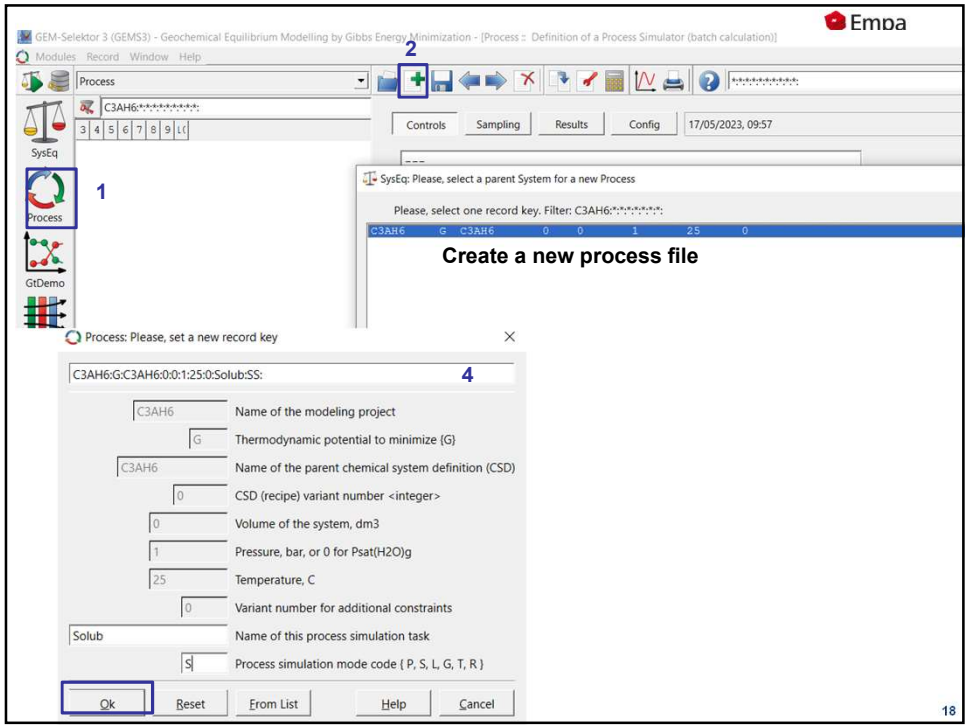
Experimental data: pH 11.98 ☺

$K_{s0} = \{Ca^{2+}\}^{3*}\{AlO_2^-\}^2\{H_2O^0\}^{4*}\{OH^-\}^4$

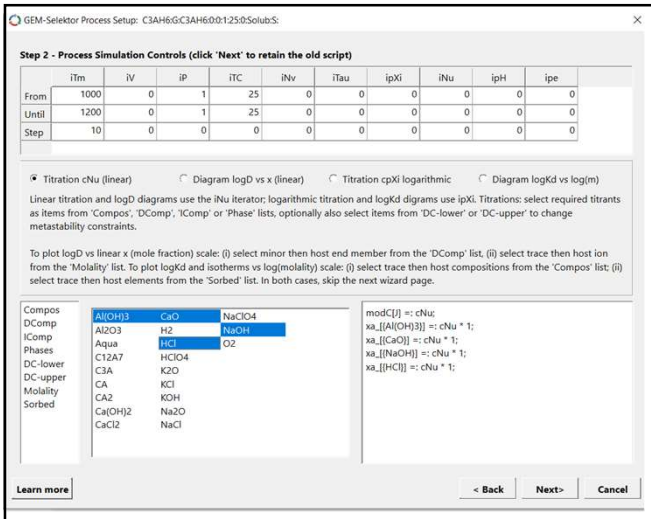
$\log K_{s0} = 3*\log aCa^{2+} + 2*\log aAlO_2^- + 4*\log aH_2O^0 + 4*\log a\ OH^-$

= 3*-2.46 + 2*-2.43 + 4*-0.0002+ 4*-2.02 = -20.62: little difference, error ±1

17



18



Select Al(OH)3 and CaO as input for measured total Al and Ca (in mM)

NaOH and HCl in case you need to correct the pH

Experimental data: pH ±0.1 ☺

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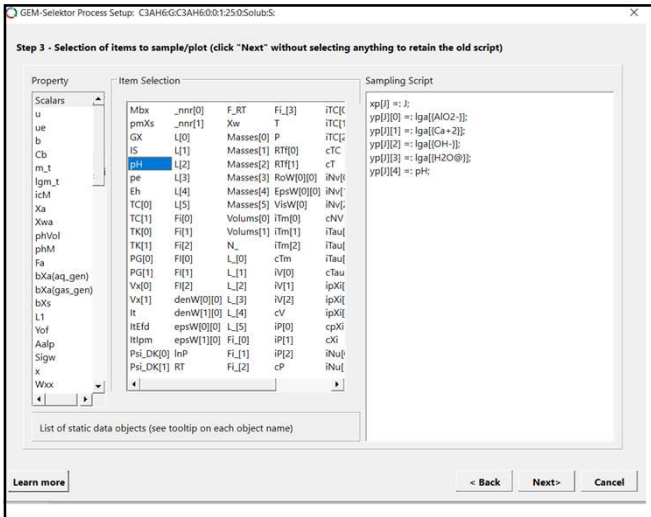

Collect lga[{AlO-2}], lga[{Ca+2}], lga[{OH-}], lga[{H2O@}] and pH needed to formulate equation

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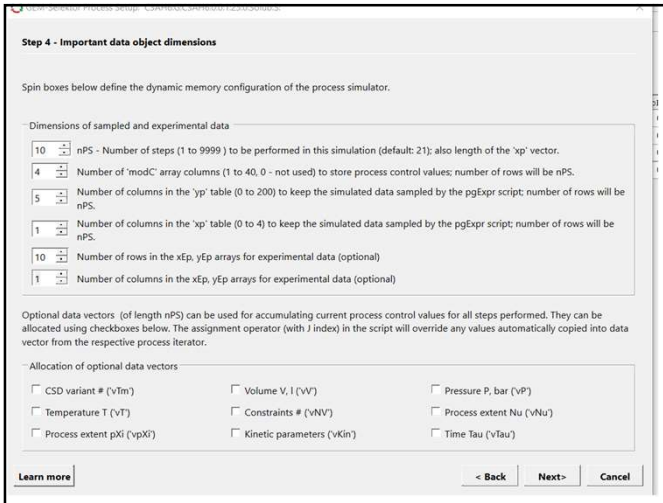
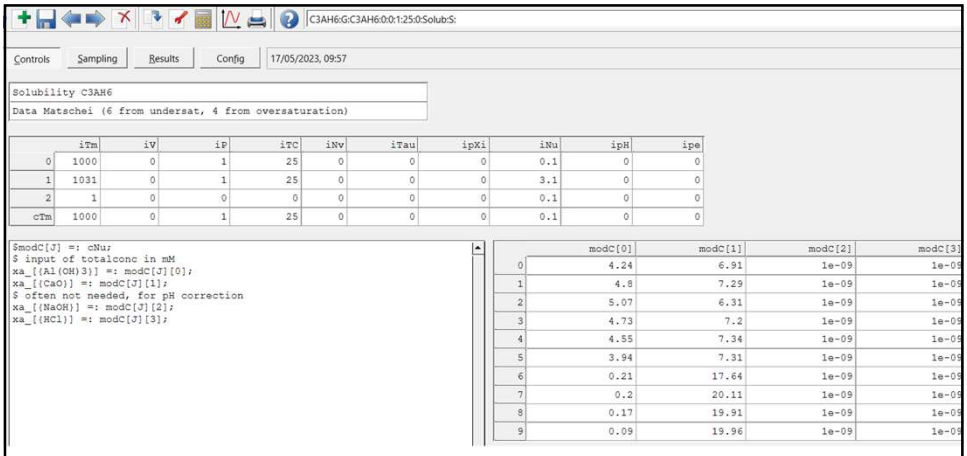


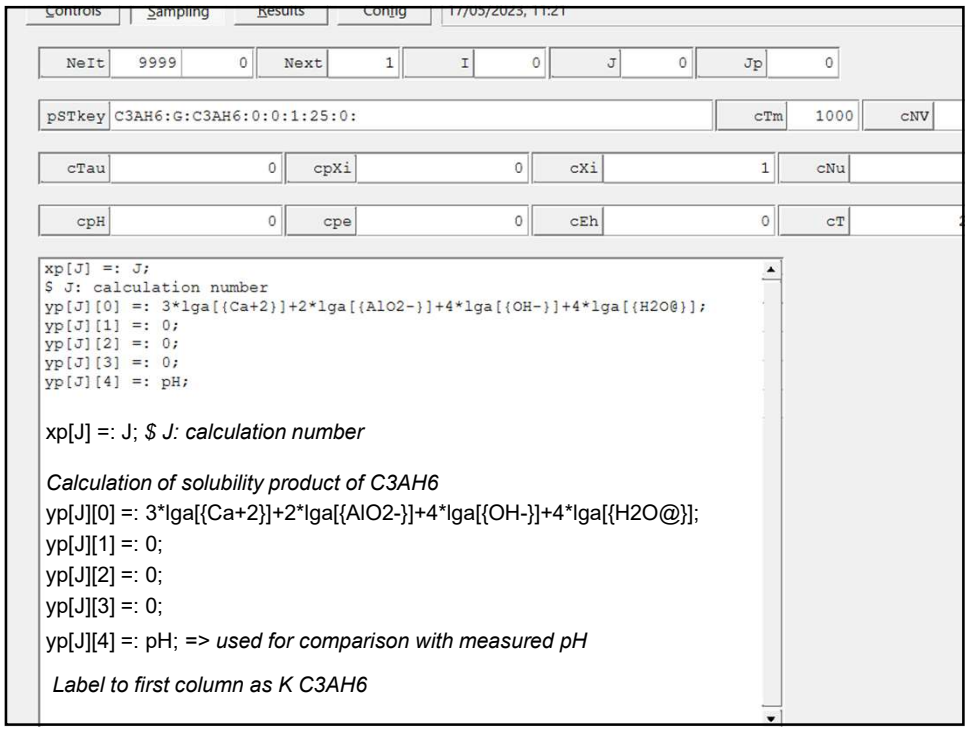
10 experimental data points from Matschei
4 columns for input: Al, Ca, NaOH and HCl
5 output columns
1 X-axis
10 experimental pH values for comparison
1 experimental column for pH values



	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	25	0	0	0	0.1	0	0
1	1031	0	1	25	0	0	0	3.1	0	0
2	1	0	0	0	0	0	0	0.1	0	0
cTm	1000	0	1	25	0	0	0	0.1	0	0

	modC[0]	modC[1]	modC[2]	modC[3]
0	4.24	6.91	1e-09	1e-09
1	4.8	7.29	1e-09	1e-09
2	5.07	6.31	1e-09	1e-09
3	4.73	7.2	1e-09	1e-09
4	4.55	7.34	1e-09	1e-09
5	3.94	7.31	1e-09	1e-09
6	0.21	17.64	1e-09	1e-09
7	0.2	20.11	1e-09	1e-09
8	0.17	19.91	1e-09	1e-09
9	0.09	19.96	1e-09	1e-09

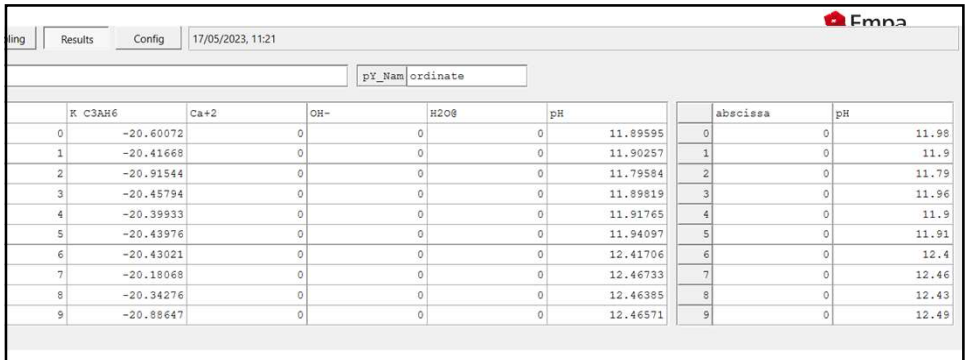
Input in mM
modC[J][0] = total Al measured
modC[J][1] = total Ca measured in mM
modC[J][2], and modC[J][3] = 10^{-9} mM (use small numbers not «0»)



xp[J] =: J; *$ J: calculation number*

Calculation of solubility product of C3AH6
yp[J][0] =: 3*lga[{Ca+2}]+2*lga[{AlO2-}]+4*lga[{OH-}]+4*lga[{H2O@}];
yp[J][1] =: 0;
yp[J][2] =: 0;
yp[J][3] =: 0;
yp[J][4] =: pH; => *used for comparison with measured pH*

Label to first column as K C3AH6



	K C3AH6	Ca+2	OH-	H2O@	pH
0	-20.60072	0	0	0	11.89595
1	-20.41668	0	0	0	11.90257
2	-20.91544	0	0	0	11.79584
3	-20.45794	0	0	0	11.89819
4	-20.39933	0	0	0	11.91765
5	-20.43976	0	0	0	11.94097
6	-20.43021	0	0	0	12.41706
7	-20.18068	0	0	0	12.46733
8	-20.34276	0	0	0	12.46385
9	-20.88647	0	0	0	12.46571

	abscissa	pH
0	0	11.98
1	0	11.9
2	0	11.79
3	0	11.96
4	0	11.9
5	0	11.91
6	0	12.4
7	0	12.46
8	0	12.43
9	0	12.49

K C3AH6 = *solubility product of C3AH6*
yp[J][0] =: 3*lga[{Ca+2}]+2*lga[{AlO2-}]+4*lga[{OH-}]+4*lga[{H2O@}];
Varies from -20.2 to -20.9

Calculated pH comparable to measured pH
Δ pH ± 0.1
⇒ *No pH correction needed*

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Error on solubility products (assuming normal distribution)

see also https://www.oecd-nea.org/jcms/pl_37493/tdb-3-guidelines-for-the-assignment-of-uncertainties

Measurement error

Standarddeviation: in excel use **STDEV.S**

$$s_X = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \overline{X})^2}$$

Uncertainity (includes also systematic errors, s_j

$$\sigma_{\overline{X}} = \sqrt{s_X^2 + \sum_j (s_j^2)}$$

95% confidence interval

$$95\%\ \text{Confidence Interval} = \bar{x} \pm t(\sigma / \sqrt{n})$$

	-20.60
	-20.42
	-20.92
	-20.46
	-20.40
	-20.44
	-20.43
	-20.18
	-20.34
	-20.89
Mean	**-20.51**
Standard deviation	**0.23**
confidence interval (95%, 2 sided)	**0.17**

T value for n-1 from table

One-sided	75%	80%	85%	90%	95%	97.5%	99%	99.5%	99.75%	99.9%	99.95%
Two-sided	50%	60%	70%	80%	90%	95%	98%	99%	99.5%	99.8%	99.9%
1	1.000	1.376	1.963	3.078	6.314	12.706	31.821	63.657	127.321	318.309	636.619
2	0.816	1.061	1.386	1.886	2.920	4.303	6.965	9.925	14.089	22.327	31.599
3	0.765	0.978	1.250	1.638	2.353	3.182	4.541	5.841	7.453	10.215	12.924
4	0.741	0.941	1.190	1.533	2.132	2.776	3.747	4.604	5.598	7.173	8.610
5	0.727	0.920	1.156	1.476	2.015	2.571	3.365	4.032	4.773	5.893	6.869
6	0.718	0.906	1.134	1.440	1.943	2.447	3.143	3.707	4.317	5.208	5.959
7	0.711	0.896	1.119	1.415	1.895	2.365	2.998	3.499	4.029	4.785	5.408
8	0.706	0.889	1.108	1.397	1.860	2.306	2.896	3.355	3.833	4.501	5.041
9	0.703	0.883	1.100	1.383	1.833	2.262	2.821	3.250	3.690	4.297	4.781
10	0.700	0.879	1.093	1.372	1.812	2.228	2.764	3.169	3.581	4.144	4.587

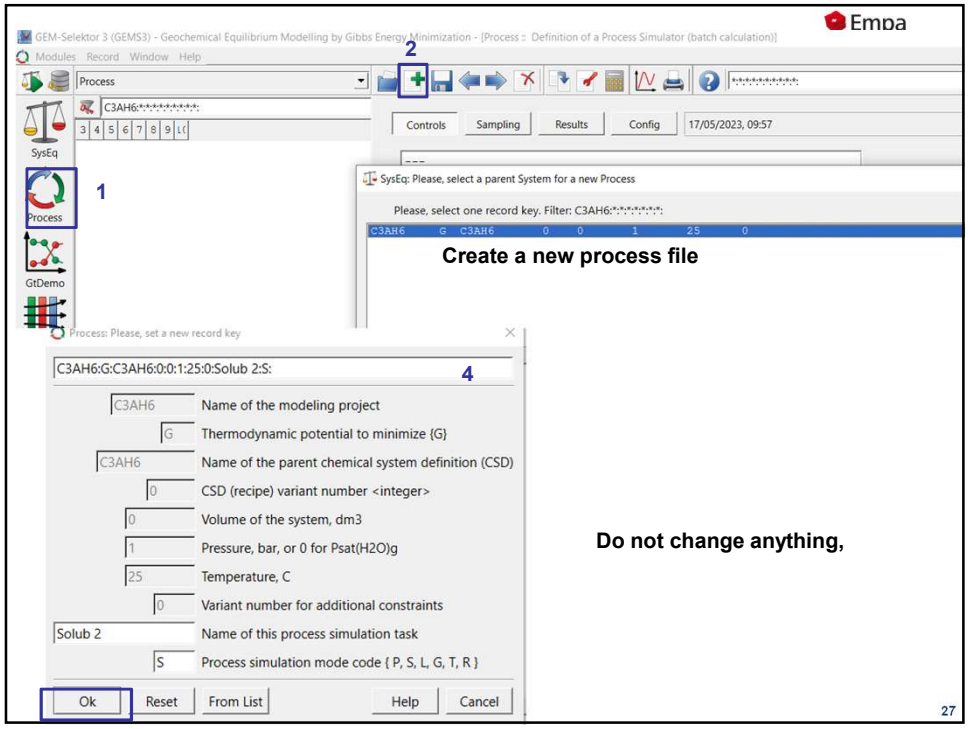
Do and do nots

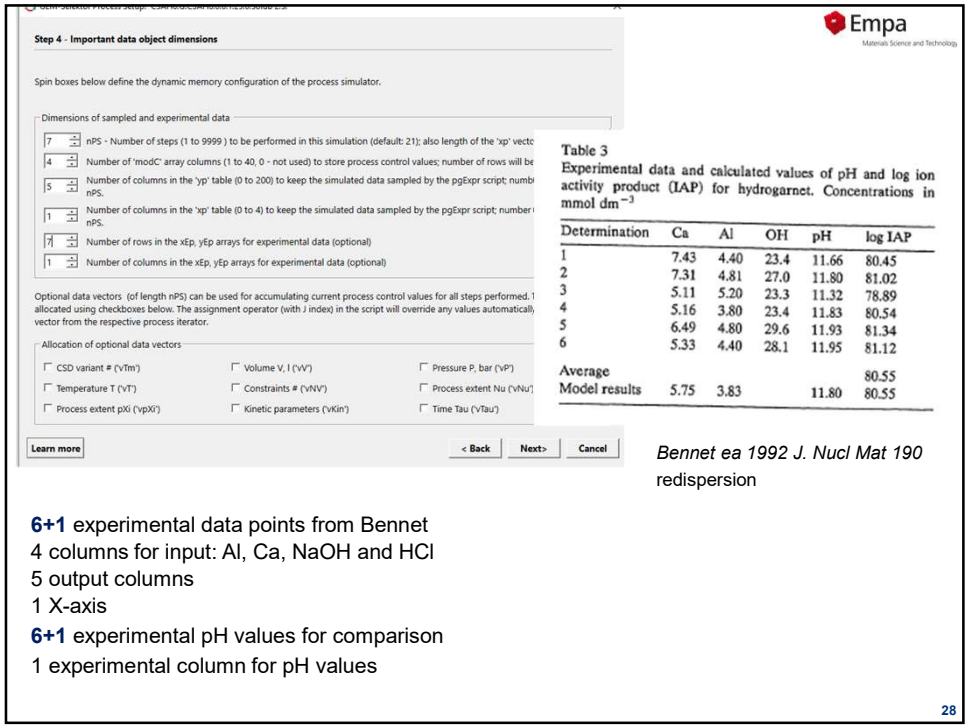
- Do not use the mean of all measurements to calculate one solubility product

	Al	Ca		
Undersat	4.24	6.91		
	4.8	7.29		
	5.07	6.31		
	4.73	7.2		
	4.55	7.34		
	3.94	7.31		
Oversat	0.21	17.64		
	0.2	20.11		
	0.17	19.91		
	0.09	19.96		
mean				
undersat	**4.56**	**7.06**	**-20.52**	*1.5*
oversat	**0.17**	**19.41**	**-20.40**	*3.5*
all	**2.8**	**12.00**	**-19.25**	*14.2*
standard dev	*2.3*	*6.4*		

- Use the log of the individual solubility products to calculate the mean

	-20.60
	-20.42
	-20.92
	-20.46
	-20.40
	-20.44
	-20.43
	-20.18
	-20.34
	-20.89
Mean	**-20.51**
Standard deviation	**0.23**
confidence interval (95%, 2 sided)	**0.17**


Empa
GEM-Selektor 3 (GEMS3) - Geochemical Equilibrium Modelling by Gibbs Energy Minimization - [Process :: Definition of a Process Simulator (batch calculation)]
Modules Record Window Help
Process
C3AH6:**********:
SysEq
Process
GtDemo
1
2
Controls Sampling Results Config 17/05/2023, 09:57
SysEq: Please, select a parent System for a new Process
Please, select one record key. Filter: C3AH6:*:*:*:*:*:*:
C3AH6 G C3AH6 0 0 1 25 0
Create a new process file
Process: Please, set a new record key
C3AH6:G:C3AH6:0:0:1:25:0:Solub 2:S:
4
C3AH6 Name of the modeling project
G Thermodynamic potential to minimize {G}
C3AH6 Name of the parent chemical system definition (CSD)
0 CSD (recipe) variant number <integer>
0 Volume of the system, dm3
1 Pressure, bar, or 0 for Psat(H2O)g
25 Temperature, C
0 Variant number for additional constraints
Solub 2 Name of this process simulation task
S Process simulation mode code { P, S, L, G, T, R }
Ok Reset From List Help Cancel
Do not change anything,
27


Empa
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Step 4 - Important data object dimensions
Spin boxes below define the dynamic memory configuration of the process simulator.
Dimensions of sampled and experimental data
7 nPS - Number of steps (1 to 9999) to be performed in this simulation (default: 21); also length of the 'xp' vecto
4 Number of 'modC' array columns (1 to 40, 0 - not used) to store process control values; number of rows will be
5 Number of columns in the 'yp' table (0 to 200) to keep the simulated data sampled by the pgExpr script; numb
nPS.
1 Number of columns in the 'xp' table (0 to 4) to keep the simulated data sampled by the pgExpr script; number
nPS.
7 Number of rows in the xEp, yEp arrays for experimental data (optional)
1 Number of columns in the xEp, yEp arrays for experimental data (optional)
Optional data vectors (of length nPS) can be used for accumulating current process control values for all steps performed.
allocated using checkboxes below. The assignment operator (with J index) in the script will override any values automatically
vector from the respective process iterator.
Allocation of optional data vectors
CSD variant # ('vTm')
Volume V, l ('vV')
Pressure P, bar ('vP')
Temperature T ('vT')
Constraints # ('vNV')
Process extent Nu ('vNu')
Process extent pXi ('vpXi')
Kinetic parameters ('vKin')
Time Tau ('vTau')
Learn more
< Back
Next>
Cancel
Table 3
Experimental data and calculated values of pH and log ion activity product (IAP) for hydrogarnet. Concentrations in mmol dm^{-3}
Determination Ca Al OH pH log IAP
1 7.43 4.40 23.4 11.66 80.45
2 7.31 4.81 27.0 11.80 81.02
3 5.11 5.20 23.3 11.32 78.89
4 5.16 3.80 23.4 11.83 80.54
5 6.49 4.80 29.6 11.93 81.34
6 5.33 4.40 28.1 11.95 81.12
Average 80.55
Model results 5.75 3.83 11.80 80.55
Bennet ea 1992 J. Nucl Mat 190
redispersion
6+1 experimental data points from Bennet
4 columns for input: Al, Ca, NaOH and HCl
5 output columns
1 X-axis
6+1 experimental pH values for comparison
1 experimental column for pH values
28

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Solubility C3AH6
Data Bennet (6 from undersat redispersion, 1 mean)

	iTm	iV	iP	iTC	iNv	iTau	ipXi	iNu	ipH	ipe
0	1000	0	1	25	0	0	0	0.1	0	0
1	1031	0	1	25	0	0	0	3.1	0	0
2	1	0	0	0	0	0	0	0.1	0	0
cTm	1000	0	1	25	0	0	0	0.1	0	0

```
$modC[J] =: cNu;
$ input of totalconc in mM
xa_[{Al(OH)3}] =: modC[J][0];
xa_[{CaO}] =: modC[J][1];
$ often not needed, for pH correction
xa_[{NaOH}] =: modC[J][2];
xa_[{HCl}] =: modC[J][3];

$ last is mean, for comparison only
```

	modC[0]	modC[1]	m
0	4.4	7.43	
1	4.81	7.31	
2	5.2	5.11	
3	3.8	5.16	
4	4.8	6.49	
5	4.4	5.33	
6	3.83	5.75	

Input in mM
modC[J][0] = total Al measured
modC[J][1] = total Ca measured in mM
modC[J][2], and modC[J][3] = 10^{-9} mM (use small numbers not «0»)

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ols | Sampling | Results | Config | 17/05/2023, 17:44

bility C3AH6 | pY_Nam ordinate

am	abscissa	K C3AH6	Ca+2	OH-	H2O@	pH
0	0	-20.36573	0	0	0	11.93112
1	1	-20.40765	0	0	0	11.90379
2	2	-21.75347	0	0	0	11.62643
3	3	-21.57668	0	0	0	11.74005
4	4	-20.80627	0	0	0	11.82964
5	5	-21.49081	0	0	0	11.72102
6	6	-21.20783	0	0	0	11.80663

	abscissa	pH
0	0	11.66
1	0	11.8
2	0	11.32
3	0	11.83
4	0	11.93
5	0	11.95
6	0	11.8

K C3AH6 = *solubility product of C3AH6*
yp[J][0] =: 3*lga[{Ca+2}]+2*lga[{AlO2-}]+4*lga[{OH-}]+4*lga[{H2O@}];
Varies from -20.3 to -21.8
Decreases with time. Carbonation!

Calculated pH ≈ comparable to measured pH
Δ pH ± 0.3 => No pH correction done
(pH difficult to measure, least reliable, avoid if difference not too large
With pH correction -20.6 to -23.0)

ility C3AH6 | pY_Nam ordinate

m	abscissa	K C3AH6	Ca+2	OH-	H2O@	pH
0	0	-21.45787	0	0	0	11.64714
1	1	-20.78876	0	0	0	11.80412
2	2	-22.99794	0	0	0	11.30874
3	3	-21.36384	0	0	0	11.80088
4	4	-20.55935	0	0	0	11.90139
5	5	-20.76407	0	0	0	11.93134

	abscissa	pH
0	0	
1	0	
2	0	
3	0	
4	0	
5	0	

Comparison with literature data

Bennet ea 1992 J. Nucl Mat 190

Redispersion (28 days

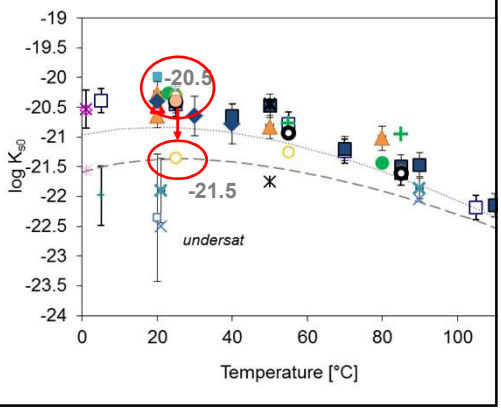
After 28 days	-20.37
56	-20.41
84	-21.75
112	-21.58
140	-20.81
168 days	-21.49
Mean	**-21.07**
Standard deviation	**0.62**
confidence interval (95%, 2 sided)	**0.65**

~~*Mean conc* **-21.21**~~

Matschei ea 2007 CCR 37

Mean	**-20.51**
Standard deviation	**0.23**
confidence interval (95%, 2 sided)	**0.17**

- Check for trends with time
- Carbonation during exposure?



- Use the log of the individual solubility products to calculate the mean
- Do not use the mean of all measurements to calculate one solubility product

Solubility products

1. General considerations
2. Measured concentrations ⇔ log K_s
3. **Estimation of C_p and S**
4. Calculation of log K_s at different temperatures

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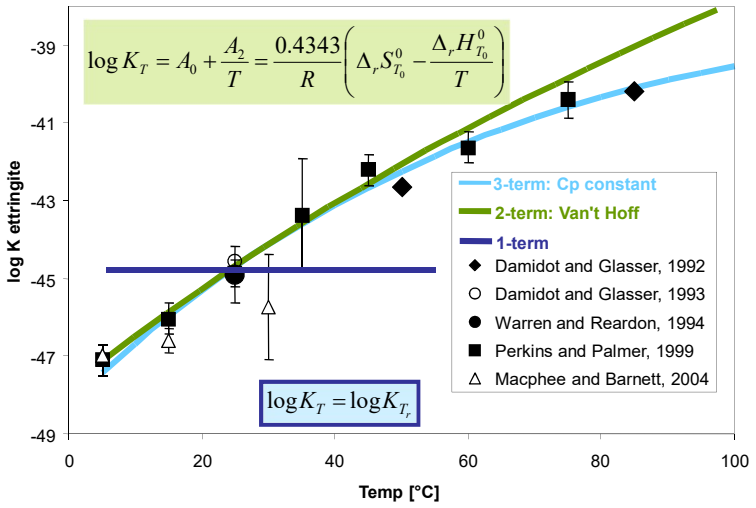
Effect of temperature

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

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



Lothenbach ea CCR 38, 2008

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Thermodynamic data:

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

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

K_{S0} ↔ Gibbs free energy

Influence of temperature $\log K_T = A_0 + \frac{A_2}{T} + A_3 \ln T$

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

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

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

34

We can estimate S and Cp (but better not ΔH_f and ΔG_f)

1) From **similar solids** (avoiding liquid water)

H.C. Helgeson, J.M. Delany, H.W. Nesbitt, D.K. Bird, Summary and critique of the thermodynamic properties of rock-forming minerals, Am J Sci, 278-A (1978) 1-229

G.M. Anderson, D.A. Crerar, Thermodynamics in Geochemistry: the Equilibrium Model, Oxford University Press, Oxford, 1993.

2) **Volume based thermodynamics (VBT)**

L. Glasser, The effective volumes of waters of crystallization & the thermodynamics of cementitious materials, Cement, 3 (2021) 100004.

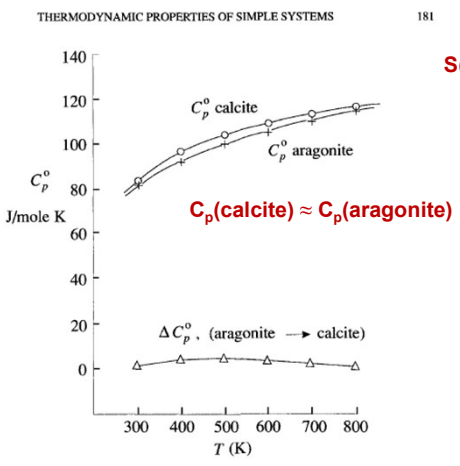
S. Ghazizadeh, T. Hanein, J.L. Provis, T. Matschei, Estimation of standard molar entropy of cement hydrates and clinker minerals, Cem Concr Res, 136 (2020) 106188.

L. Glasser, H.D.B. Jenkins, Predictive thermodynamics for ionic solids and liquids, Physical Chemistry Chemical Physics, 18 (2016) 21226-21240.

35

We can estimate S and Cp (but better not ΔH_f and ΔG_f)

1) From similar solids (avoiding liquid water)



C_p(calcite) ≈ C_p(aragonite)

FIG. 7.10. Heat capacities of calcite and aragonite, showing that ΔC_p° varies much less than either C_p°.

S(calcite) ≈ S(aragonite)

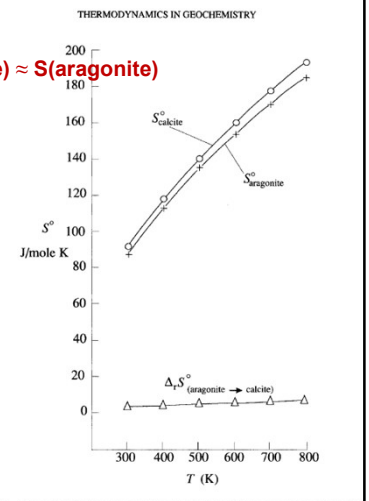


FIG. 7.11. Entropies of calcite and aragonite, showing that ΔS° varies much less than either S°.

G.M. Anderson, D.A. Crerar, Thermodynamics in Geochemistry: the Equilibrium Model, Oxford University Press, Oxford, 1993

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We can estimate Cp

Empa

1) From similar solids (avoiding liquid water)

$$C^\circ_{P_r,T_r,i} = \sum_j \nu_{j,i} C^\circ_{P_r,T_r,j} \qquad (78$$

H.C. Helgeson, J.M. Delany, H.W. Nesbitt, D.K. Bird, Am J Sci, 278-A (1978) 1-229

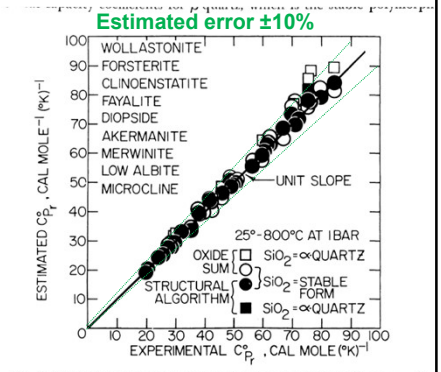


Fig. 11. Correlation of estimated and experimental standard molal heat capacities of minerals at 25°, 200°, 500°, and 800°C at 1 bar.

$C_{p,C3AH} \approx 3*C_{p,CH}+2*C_{p,Al(OH)3}$ = 3*87.51+2*93.08 **= 449 ±45 J/mol/K**

$C_{p,C3AH6} \approx C_{p,C3A}+6*C_{p,structural\ H2O}$ = 209.39+6*40.04 **= 450 ±45 J/mol/K**

$C_{p,C3AH6,\ measured} \approx$ **446** (Geiger 2012), or **459** (Ederova 1979) **J/mol/K**

Good agreement (estimation, measured values preferred)

J. Ederova, V. Satava, Heat capacities of C_3AH_6, C_4ASH_{12} and $C_6AS_3H_{32}$, Thermochim Acta, 31 (1979) 126-128.
C.A. Geiger, E. Dachs, A. Benisek, Thermodynamic behavior and properties of katoite (hydrogrossular): A calorimetric study, Am Min, 97 (2012) 1252-1255.

Summary of experimental standard molal volumes, entropies, and heat capacity power function coefficients for oxides

Empa

Mineral	Formula	$V^\circ_{P_r,T_r}$ [a]	$S^\circ_{P_r,T_r}$ [b]	$C^\circ_{P_r,T_r}$ [b,p]	Coefficients for equation (19) a [b]	$b \times 10^3$ [d]	$c \times 10^{-5}$ [e]	Temperature Range, °K
"Structural" H_2O	$H_2O_{(s)}$	13.7[m]	9.6[n]	9.57	7.11[s]	8.24[s]	0.00[s]	298-1000[s]
"Zeolitic" H_2O	$H_2O_{(z)}$	8[c]	14.1[t]	13.4	11.4[v]	0.0[v]	0.0[v]	

[a] $cm^3\ mole^{-1}$. [b] $cal\ mole^{-1}\ (°K)^{-1}$. [c] Estimated from standard molal volumes of zeolites (see text). [d] $cal\ mole^{-1}(°K)^{-2}$. [e] cal (°K) $mole^{-1}$. [f] Roble and Waldbaum (1968). [g] Stull and

cal/mol/K

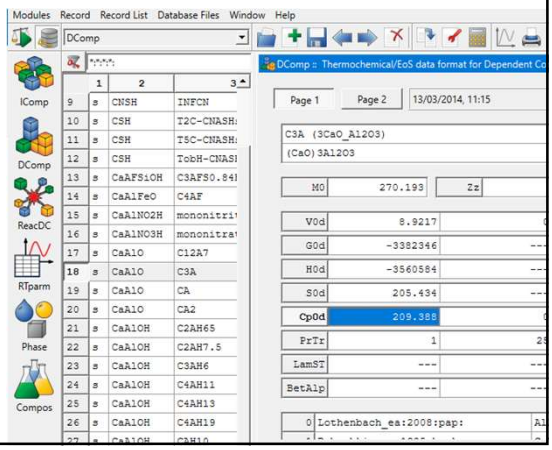
**4.184 => J/mol/K*

H.C. Helgeson, J.M. Delany, H.W. Nesbitt, D.K. Bird, Am J Sci, 278-A (1978) 1-229

Where do we get the data from ?

J/mol/K

B. Lothenbach, D. Kulik, T. Matschei, M. Balonis, L.G. Baquerizo, B.Z. Dilnesa, G.D. Miron, D. Myers, Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials, Cem Concr Res, 115 (2019) 472-506



We can estimate S

1) From similar solids (avoiding liquid water

$$S^\circ_{i,P_r,T_r} = \frac{S^\circ_{s,i,P_r,T_r}\,(V^\circ_{s,i,P_r,T_r} + V^\circ_{i,P_r,T_r})}{2V^\circ_{s,i,P_r,T_r}} \qquad (62)$$

H.C. Helgeson, J.M. Delany, H.W. Nesbitt, D.K. Bird, Am J Sci, 278-A (1978) 1-229

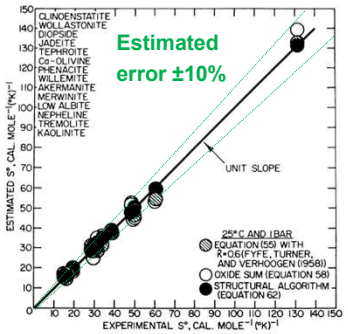


Fig. 10. Correlation of estimated and experimental standard molal entropies of minerals at 25°C and 1 bar.

$S_{C3AH6} \approx (3*S_{CH}+2*S_{AH1.5})*(3*V_{CH}+2*V_{AH1.5}+V_{C3AH6})/2/(3*V_{CH}+2*V_{AH1.5})$ =
(3*83.4+2*70.08)*(3*33.1+2*32.0 +149.7)/2/(3*33.1+2*32.0) = 390.4*0.96 **= 374 ±37 J/mol/K**

$S_{C3AH6} \approx (S_{C3A}+6*S_{stH2O})*(V_{C3A}+6*V_{stH2O}+V_{C3AH6}/2/(V_{C3A}+6*V_{H2O})$ =
(205.4+6*40.2)* (89.2+6*13.8+149.7) /2/(89.2+6*13.8) = 446.4*0.94 = **418 ±42** J/mol/K

$S_{C3AH6,\ measured} \approx$ **422** (Geiger 2012) **J/mol/K**

Adequate agreement (estimation, measured values preferred)

C.A. Geiger, E. Dachs, A. Benisek, Thermodynamic behavior and properties of katoite (hydrogrossular): A calorimetric study, Am Min, 97 (2012) 1252-1255.

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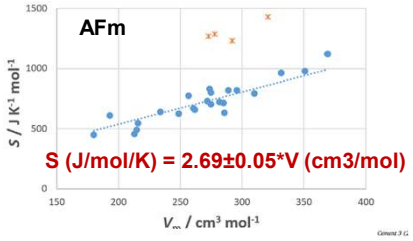
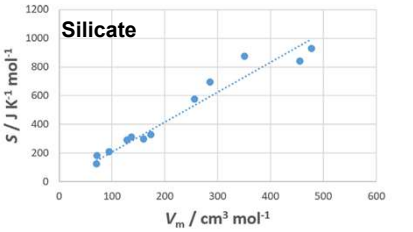
We can estimate S and Cp (but better not ΔH_f and ΔG_f)

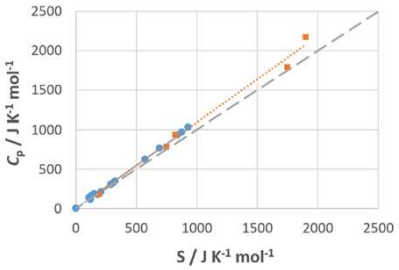
2) Volume based thermodynamics (VBT)



S (J/mol/K) = 2.69±0.05*V (cm3/mol)



S (J/mol/K) = 2.08±0.08*V (cm3/mol)



Cp (J/mol/K) = 1.1*S (J/mol/K)

L. Glasser, The effective volumes of waters of crystallization & the thermodynamics of cementitious materials, Cement, 3 (2021) 100004.

40

We can estimate S

2) Volume based thermodynamics (VBT); V_{C3AH6} = 149 cm3/mol	J/mol/K
S (J/mol/K) = 2.69±0.05*V (cm3/mol) for AFm, Glasser 2021)	**403±7**
*S (J/mol/K) = 2.08±0.08*V (cm3/mol) for crystalline CSH, Glasser 2021)*	*311±12*
*S (J/mol/K) = 2.26±0.09*V (cm3/mol) + 15±6 anhydrous solid, Glasser 2016)*	*353±42*
S (J/mol/K) = 2.62±0.05*V (cm3/mol) + 6±6 hydrous solid, (Glasser ea 2016, Gahzizadeh ea 2020)	**399±29**
S (J/mol/K) = from similar solids	374 ±37 418 ±42

$S_{C3AH6,\ measured}$ ≈ **422** (Geiger 2012) **J/mol/K**

Adequate agreement (estimation!)

measured values preferred > similar solids > VBT

L. Glasser, The effective volumes of waters of crystallization & the thermodynamics of cementitious materials, Cement, 3 (2021) 100004.
S. Ghazizadeh, T. Hanein, J.L. Provis, T. Matschei, Estimation of standard molar entropy of cement hydrates and clinker minerals, Cem Concr Res, 136 (2020) 106188.
L. Glasser, H.D.B. Jenkins, Predictive thermodynamics for ionic solids and liquids, Physical Chemistry Chemical Physics, 18 (2016) 21226-21240 L.

41

We can estimate Cp

2) Volume based thermodynamics (VBT); V_{C3AH6} = 149 cm3/mol	J/mol/K
Cp (J/mol/K) = 1.1*S for AFm, Glasser 2021)	**443±8**
*Cp (J/mol/K) = 1.1*S for crystalline CSH, Glasser 2021)*	*343±13*
Cp (J/mol/K) = 2.2*V (cm3/mol) -0.8 solids, *Glasser 2016)*	**328±80**
Cp (J/mol/K) = from similar solids	449 ±45 450 ±45

$C_{p,C3AH6,\ measured}$ ≈ **446** (Geiger 2012), or **459** (Ederova 1979) **J/mol/K**

Adequate agreement (estimation!)

measured values preferred > similar solids > VBT

L. Glasser, The effective volumes of waters of crystallization & the thermodynamics of cementitious materials, Cement, 3 (2021) 100004.
L. Glasser, H.D.B. Jenkins, Predictive thermodynamics for ionic solids and liquids, Physical Chemistry Chemical Physics, 18 (2016) 21226-21240 L.

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Solubility products

1. General considerations
2. Measured concentrations ⇔ log K_s
3. Estimation of C_p and S

4. **Calculation of log K_s at different temperatures**

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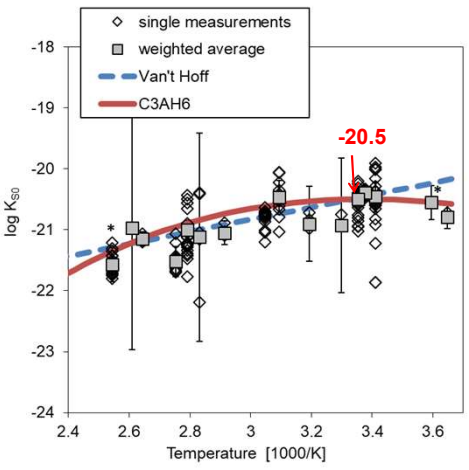
Solubility of C_3AH_6



Van't Hoff equation
2-term extrapolation
(for isoelectric reactions only)

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

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

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

Van't Hoff not adequate for non-isolelectric reaction

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

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

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

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

44

Temperature extraplotion

C3AH6

Ca3Al2O6(H2O)6

	SC	DC				REsDC
0	2	d	a	Al	AlO2-	bn_
1	3	d	a	Ca	Ca+2	an_
2	4	d	a	wX	OH-	bn_
3	4	d	a	w_	H2O@	an_
4	0	n	s	CaAlOH	C3AH6	cem_
5	-1	n	s	CaAlOH	C3AH6	cem_

V0r	-13.264	14.97007	14.97
logKr	3.162278e-21	-20.5	---
G0r	117014.9	-5008155	-5008155
H0r	-6634.562	-5537274	---
S0r	-414.7222	421.7	421.7
Cp0r	-880.3617	445.6	445.6

All information needed can be entered in ReacDC in GEMS

Use RTParm for calculations

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

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

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

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

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Step 1 make a new ReacDC fo

ReacDC: Please, set a new record key 1)

s:CaAlOH:C3AH6:*:

s — Phase state code of new Depender

CaAlOH — ID of a group to which this new De

C3AH6 — Name of this new reaction-defined

cem — Thermodynamic data subset (TDS)

Ok | Reset | From List

GEM-Selektor ReacDC Setup: s:CaAlOH:C3AH6:cem:

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):

O 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 f reaction and the new DC it defines.

Select here method codes for T,P correction of standard molar properties of the reaction and DC

General method code for temperature corrections: 2)

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

< Back | Next>

Step 2 - Selection of ReacDC/DComp involved in the reaction

To (re)select different species to be involved into reaction, activate the 'Full-list selection' checkbox; toggle it back to see only the selected records again. In the full list, first the ReacDC 'r' and then the DComp 'd' record keys appear; use the filtering settings below to show only relevant records.

Full-list selection

Tick here to see full list

Select all | Clear selection

	Source	Aggr.State	Group	Name	Comment
1	d	a	Al	AlO2-	bn_
2	d	a	Ca	Ca+2	an_
3	d	a	wX	OH-	bn_
4	d	a	w_	H2O@	an_

3)

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Step 1: make a new ReacDC for C3AH6

reacDC

DComp

$\Delta H_{f,C3AH6} \approx$ -6.6 kJ/mol

$\Delta H_{f,C3AH6} \approx$ 5537 kJ/mol

Adapt r

Log K

Final values as aide memoire

DComp :: Thermochemical/EoS data format for Dependent Components

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C3AH6

Ca3Al2O6(H2O)6

M0	378.2853	Zz	0
V0d	14.9702		0
G0d	-5008155		2800
H0d	-5537245		2840.346
S0d	421.7		1.6
Cp0d	445.598		0
PrTr	1		25
LamST	---		---
BetAlp	---		---

0	Lothenbach_ea:2012:pap:	all log K
1	Taylor:1997:book:	V0 (dens

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C3AH6

Ca3Al2O6(H2O)6

	SC	DC				REsDC
0	2	d	a	Al	AlO2-	bn_
1	3	d	a	Ca	Ca+2	an_
2	4	d	a	wX	OH-	bn_
3	4	d	a	w_	H2O	an_
4	0	n	s	CaAlOH	C3AH6	cem_
5	-1	n	s	CaAlOH	C3AH6	cem_

V0r	-13.264	14.97007	14
logKr	3.162278e-21	-20.5	
G0r	117014.9	-5008155	-5008
H0r	-6634.562	-5537274	
S0r	-414.7222	421.7	42
Cp0r	-880.3617	445.6	44
NisoX	---	---	

Step 2: Temperature dependence_RTParm

RTParm 1)

Please, select a source record from:

DComp | ReacDC | Cancel

ReacDC: Select one key of a source ReacDC record

Please, select one record key. Filter: *

s CaAlOH C3AH6 cem_

2)

s:CaAlOH:C3AH6:cem_:r:*:

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

CaAlOH — Group to which source Dependent Component belongs

Tick here to see full list

C3AH6 — Name of source Dependent Component

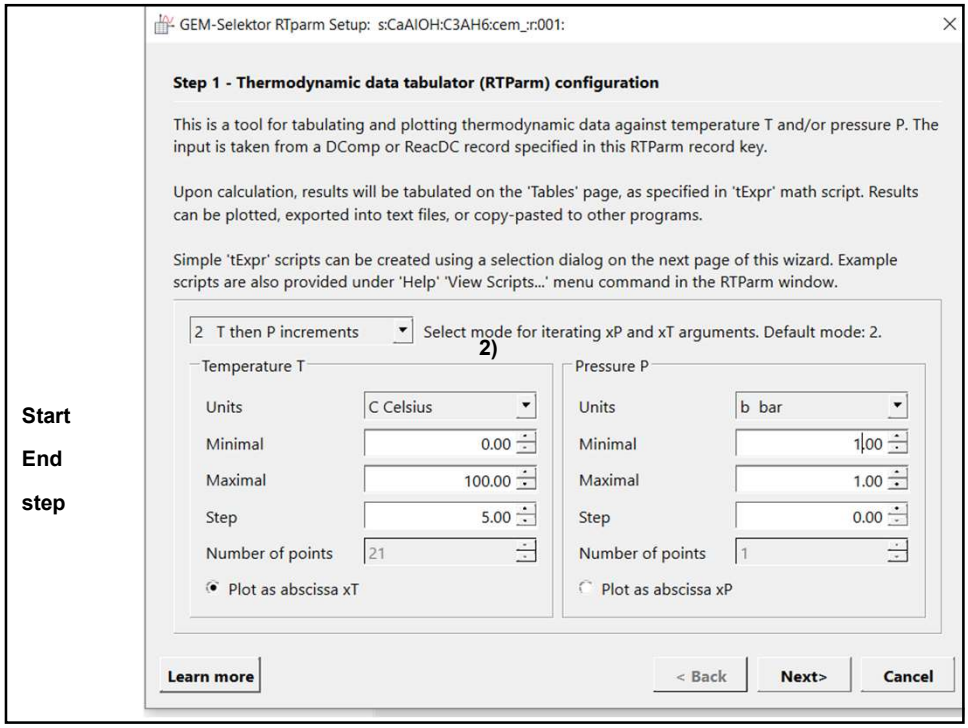
cem_ — Code of source thermodynamic data set

r — Source of input data for DC { r d }

001 — Variant number of this RTParm calculation task <integer>

Ok | Reset | From List | Help | Cancel

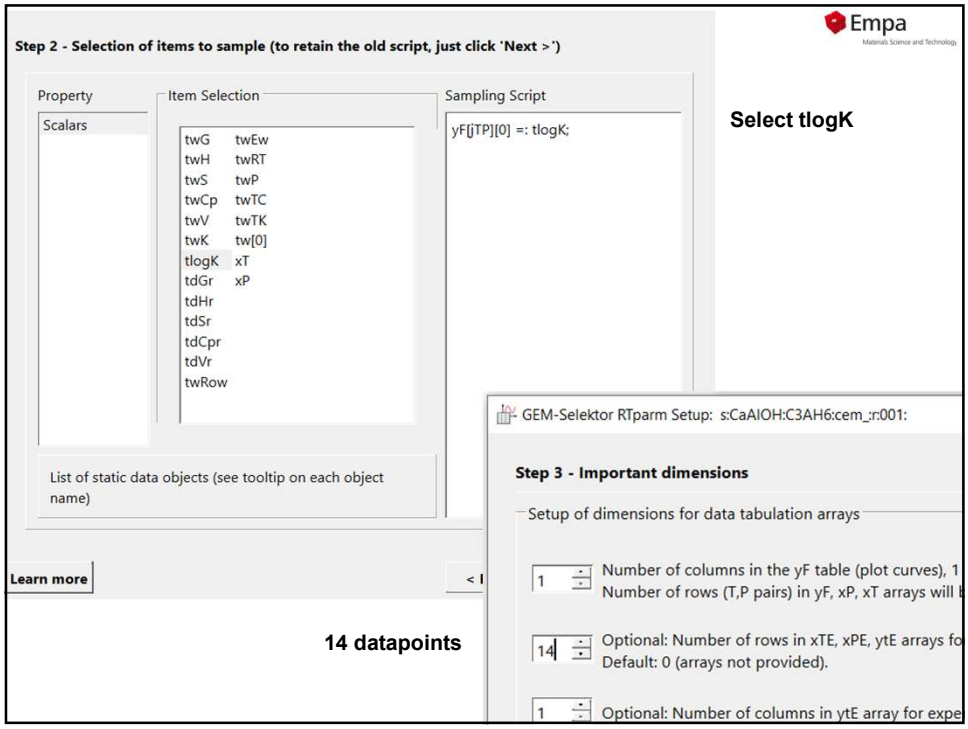
3) Any number



Start

End

step

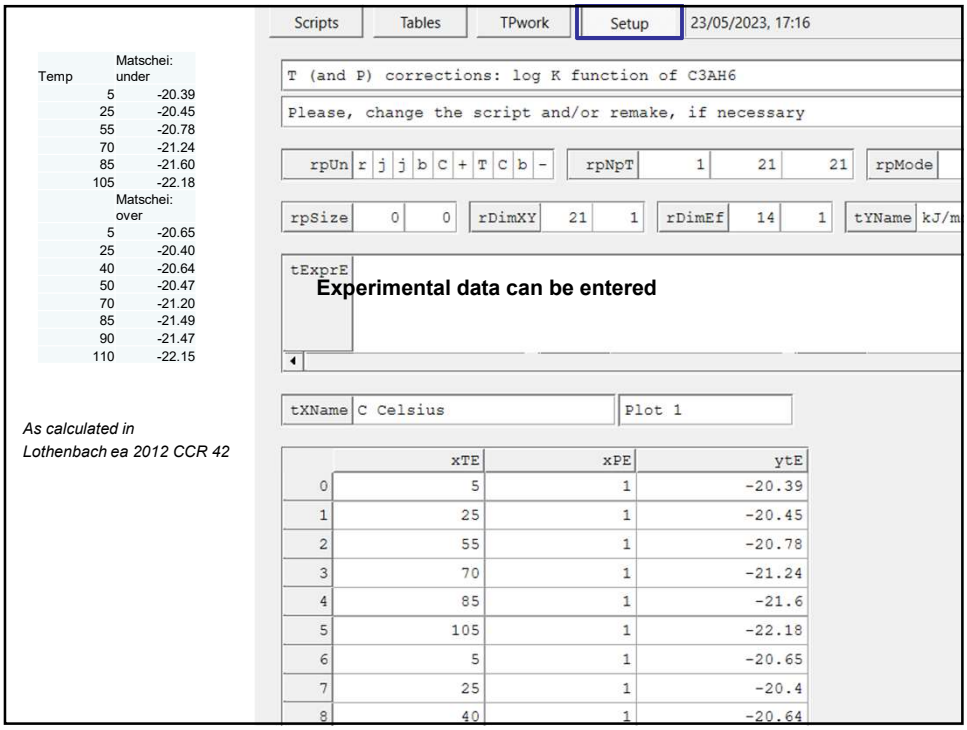


Select tlogK

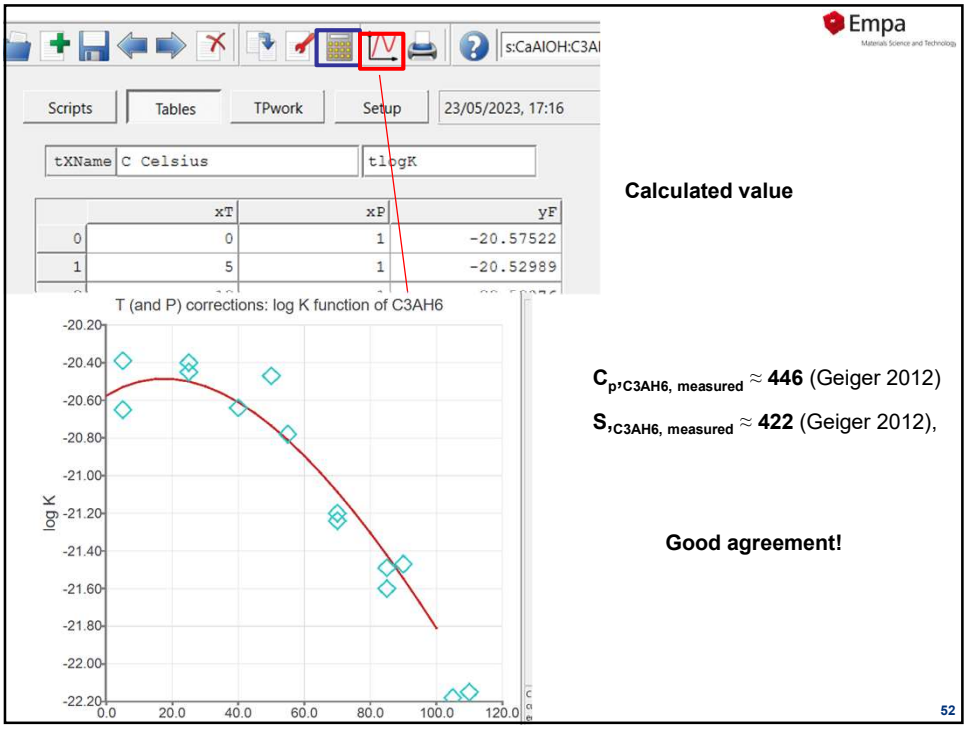
14 datapoints

Temp	Matschei: under
5	-20.39
25	-20.45
55	-20.78
70	-21.24
85	-21.60
105	-22.18
	Matschei: over
5	-20.65
25	-20.40
40	-20.64
50	-20.47
70	-21.20
85	-21.49
90	-21.47
110	-22.15

As calculated in Lothenbach ea 2012 CCR 42



	xTE	xPE	ytE
0	5	1	-20.39
1	25	1	-20.45
2	55	1	-20.78
3	70	1	-21.24
4	85	1	-21.6
5	105	1	-22.18
6	5	1	-20.65
7	25	1	-20.4
8	40	1	-20.64



	xT	xP	yF
0	0	1	-20.57522
1	5	1	-20.52989

Step 3: make an additional ReacDC for C3AH6

«C3AH6.cem2»

$C_{p,C3AH6} \approx$ **328** (Glasser 2016)

$S_{,C3AH6} \approx$ **399** (Glasser 2016)

Page 1 | Page 2 | 23/05/2023, 17:27

C3AH6

Ca3Al2O6(H2O)6

	SC	DC				REsDC
0	2	d	a	Al	AlO2-	bn_
1	3	d	a	Ca	Ca+2	an_
2	4	d	a	wX	OH-	bn_
3	4	d	a	w_	H2O@	an_
4	0	n	s	CaAlOH	C3AH6	cem2
5	-1	n	s	CaAlOH	C3AH6	cem2

Final values as aide memoire

		Log K	
V0r	-13.264	14.97007	14.97
logKr	3.162278e-21	-20.5	---
G0r	117014.9	-5008155	-5008155
H0r	282.5218	-5544192	---
S0r	-391.5222	398.5	398.5
Cp0r	-762.5617	327.8	327.8
NisoX	---	---	---

$\Delta H_{r,C3AH6} \approx$ **0.3 kJ/mol**

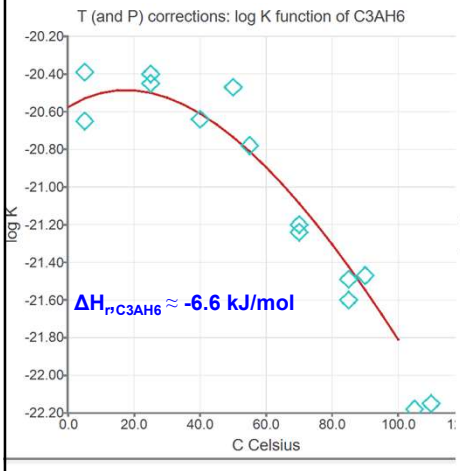
Adapt Sr, Cpr

Clone the entry in RTParm

And link it to the new ReacDC

$C_{p,C3AH6,\ measured} \approx$ **446** (Geiger 2012)

$S_{,C3AH6,\ measured} \approx$ **422** (Geiger 2012),

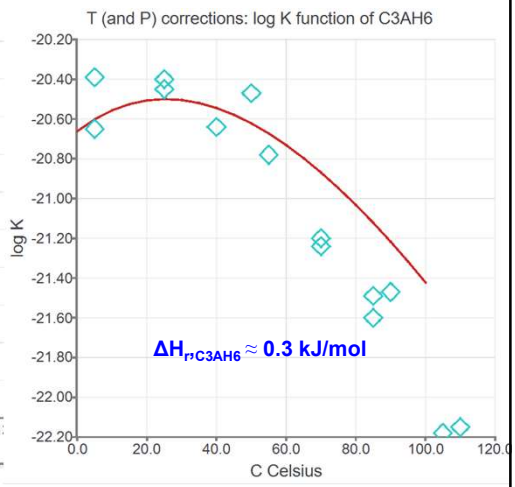


Cp determines curvature, not sensitive

Hr determines steepness

$C_{p,C3AH6} \approx$ **328** (Glasser 2016)

$S_{,C3AH6} \approx$ **399** (Glasser 2016)



Less good agreement

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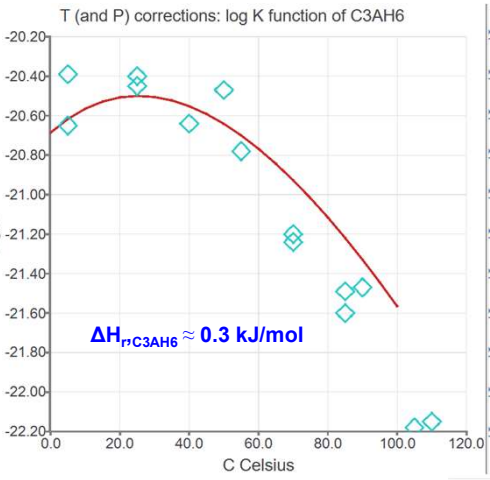
Empa

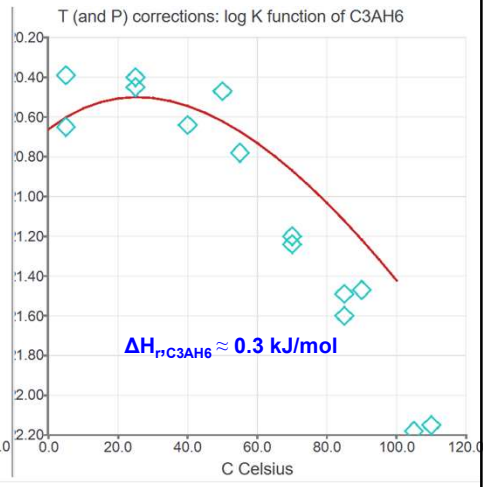
$C_{p,C3AH6,\ measured} \approx$ **446** (Geiger 2012)

$S_{,C3AH6,\ measured} \approx$ **399** (Glasser 2016)

$C_{p,C3AH6} \approx$ **328** (Glasser 2016)

$S_{,C3AH6} \approx$ **399** (Glasser 2016)





Cp determines curvature, not sensitive, cannot be fitted

Hr determines steepness

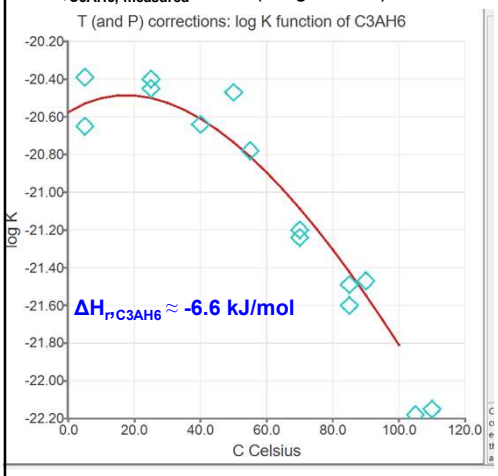
Less good agreement

55

Empa

$C_{p,C3AH6,\ measured} \approx$ **446** (Geiger 2012)

$S_{,C3AH6,\ measured} \approx$ **422** (Geiger 2012),



3-term extrapolation

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

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

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

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

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

Cp determines curvature, not sensitive

Hr determines steepness (G = H –TS) => fit of S (or H) possible)

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Measured enthalpy values for C3AH6

Measured ΔH

- -5562±5 kJ/mol, Berman 1961
- -5548 kJ/mol, Abramov 1981
- -5552±16 kJ/mol, Schoenitz 1999

↓ Calculated ΔG log K

- -5552 kJ/mol, Geiger 2012 => -5021 kJ/mol => -22

Calculated ΔH Calculated ΔG log K

- -5537 kJ/mol, Lothenbach 2012 <= -5008 kJ/mol <= -20.5

Corrected G° for Al^{3+} *Calculated ΔG* *log K*

- *-5546 kJ/mol, in progress* *<= -5017 kJ/mol* *<= -20.5*

Measured enthalpy values associated with considerable error
±16 kJ/mol (of ΔG) => correspond to 3 log units in Kso !
log K prefereable (as G depends on other data)

Berman, H. A., Newman, E. S., Heat of formation of calcium aluminate monocarbonate at 25 °C, J Res Nat Bur St-A. Phys Chem 65A, (1961), 197-207
Abramov, V. Y., Alekseev, A. I., Values of thermodynamic properties of calcium hydrogarnets of the composition $3CaO{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}(6-2x)H_2O$, J Appl Chem USSR 54, (1981), 812-815
Schoenitz, M., Navrotsky, A., Enthalpy of formation of katoite $Ca_3Al_2[(OH)_4]_3$: Energetics of the hydrogarnet substitution, Am Min 84, (1999), 389-391
Geiger, A. C., Dachs, E., Benisek, A., Thermodynamic behavior and properties of katoite (hydroglossular): a calorimetric study, Am Min 97, (2012), 1252-1255.
Lothenbach, B., Pelletier-Chaignat, L., Winnefeld, F., Stability in the system $CaO-Al_2O_3-H_2O$ CCR 42, (2012), 1621-1634.

57

Conclusions solubility products

Do under- and oversaturation experiments

Measure at different temperatures

⇒Use GEMS to calculate log K and ΔG

Compare to existing literature !
(if possible recalculate based on measured concentrations)

⇒If available, use measured S and Cp for temperature extropolation

⇒Else estimate from similar solids (if possible)

⇒ if not, use VBT

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