

CHEMSIMUL 2008 : exemple 4 dissolution $\text{Ca}(\text{OH})_2$



\$ IDENTIFICATION

Dissolution of $\text{Ca}(\text{OH})_2$ in stirred pure water (25°C)
general formulas for the temperature
Date: Novembre 2008

\$ CHEMICAL SYSTEM

* Water equilibrium $\text{H}_2\text{O}/\text{OH}^-$ pKe = 13.9951

RE67: $\text{H}_2\text{O} + \text{H}_2\text{O} = \text{OH}^- + \text{H}_3\text{O}^+$; A=<k67

RE68: $\text{OH}^- + \text{H}_3\text{O}^+ = \text{H}_2\text{O} + \text{H}_2\text{O}$; A=<k68

* $\text{Ca}^{++}/\text{CaOH}^+$ equilibrium pKa = 12.8335

RE173: $\text{Ca}^{++} + \text{OH}^- = \text{CaOH}^+$; A=<k173

RE174: $\text{CaOH}^+ = \text{Ca}^{++} + \text{OH}^-$; A=<k174

* $\text{CaOH}^+/\text{Ca}(\text{OH})_2[0]$ equilibrium pKa = 12.9071

RE175: $\text{CaOH}^+ + \text{OH}^- = \text{Ca}(\text{OH})_2[0]$; A=<k175

RE176: $\text{Ca}(\text{OH})_2[0] = \text{CaOH}^+ + \text{OH}^-$; A=<k176

\$ SYMBOLIC CONSTANTS

S=1 ! powder area (m2)

k1d=2.2E-4 ! dissolution constant (mol.dm-3.
s-1.m-2)

* Molar Masses (kg/mol)

MMOH^- =17.00734E-3

MMH_3O^+ =19.02322E-3

MMCa^{++} =40.078E-3

MMCaOH^+ =57.08534E-3

$\text{MMCa}(\text{OH})_2[0]$ =74.09268E-3

* Ionic product of water (coefficients)

a1=-4.098

a2=-3245.2

a3=2.2362E5

a4=-3.984E7

a5=13.957

a6=-1262.3

a7=8.5641E5

* Density of water (coefficients)

b1=1.99274064

b2=1.09965342

b3=-0.510839303

b4=-1.75493479

b5=-45.5170352

b6=-6.74694450E5

\$ REFRESHABLE PARAMETERS

* Density of water at any TEMP (kg/m3)

< TAU=1-(TEMP/647.096)

<

RHOW=322*(1+b1*TAU^(1/3)+b2*TAU^(2/3)+b3*TAU^(5/3)+b4*TAU^(16/3)+b5*TAU^(43/3)+b6*TAU^(110/3))

* Density of the solution at any TEMP (kg/m3)

< B=5.623989E-3*EXP(636.343926/TEMP)*(TEMP^1.762599)

< RHOLIq=RHOW+B*SIGMAMiCi/(SIGMAMiCi+18.01528E-3*H2O)

* Mass of water in the solution (kg/dm3)

< CUC=1E-3*RHOLIq-SIGMAMiCi

* Ionic strength with concentrations in mol/kg

< IS=ION/CUC

* Activity coefficients (Davies' formula)

< g1=10^(-0.5092*(SQRT(IS)/(1+SQRT(IS))-0.3*IS))

< g2=10^(-2.0368*(SQRT(IS)/(1+SQRT(IS))-0.3*IS))

* Water equilibrium at any TEMP

<

Kw=(10^(a1+a2/TEMP+a3/TEMP^2+a4/TEMP^3))*(RHOW/1E3)^(a5+a6/TEMP+a7/TEMP^2)

< k68=2.55842E12-2.94443E10*TEMP+(1.19514E8*TEMP^2)-(2.00153E5*TEMP^3)+(1.28E2*TEMP^4)

< k67=k68*Kw*CUC^2/(g1*g1*(H2O+SIGMACi)^2)

**exemple
sans
irradiation**

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```
* Solubility product of Ca(OH)2 at any TEMP (mol/kg)^3
< Kport=7.14866E242*EXP(-24245.4/TEMP)/(TEMP^85.9872)
```

```
* 1st Ca complexation Ca[+]/CaOH[+]
< KCal=1.8674E-75*EXP(5562.7264/TEMP)*(TEMP^27.3952)
< k173=1E9 ! estimation
< k174=k173/(KCal*g2)
```

```
* 2nd Ca complexation CaOH[+]/Ca(OH)2[0]
< KCa2=3.0464E106*EXP(-4430.59/TEMP)/(TEMP^39.9934)
< k175=1E7 ! estimation
< k176=k175/(KCa2*g1^2)
```

```
< pH=-LOG10(g1*H3O[+])
```

\$ EXCHANGE EQUATIONS

```
* Dissolution of Ca(OH)2 powder
d(Ca(OH)2)/dt= S*k1d*((Ca[+]*g2*(OH[-]*g1)^2/
(Kport*CUC^3))-1)
d(Ca[+])/dt= -S*k1d*((Ca[+]*g2*(OH[-]*g1)^2/
(Kport*CUC^3))-1)
d(OH[-])/dt=-2*S*k1d*((Ca[+]*g2*(OH[-]*g1)^2/
(Kport*CUC^3))-1)
```

\$ CONCENTRATIONS ! (mol/dm3)

```
* Pure water
CON(H2O)=55.34465932228825
CON(H3O[+])=1.0030629166912707E-7
CON(OH[-])=1.0030629166912707E-7
CON(Ca(OH)2)=0.1 ! Solide Ca(OH)2
```

\$ MISCELLANEOUS

```
IONIC
TEMP=298.15
```

\$ INTEGRATION

```
TEND=600
```

\$ GRAPHICS

```
PE1:Ca[+]
PE2:CaOH[+]
PE3:Ca(OH)2[0]
PE4:Ca[+]+CaOH[+]+Ca(OH)2[0]
PE5:Ca(OH)2 ! residual solid (mol/dm3)
PE10:IS ! ionic strength (mol/kg)
PE11:g1 ! activity coefficient 1
PE12:g2 ! activity coefficient 2
PE13:pH
* relative undersaturation for Ca(OH)2
PE14:(Ca[+]*g2*(OH[-]*g1)^2/(Kport*CUC^3))-1
```

```
PLOT(PE1,PE2,PE3,PE4)
PLOT(PE5)
PLOT(PE10)
PLOT(PE11,PE12)
PLOT(PE13)
PLOT(PE14)
```

\$ OUTPUT CONTROL

```
DIG=6
PRINTS=240
```

\$ END DATA

*exemple
sans
irradiation*