FRIENDS OF FREZCHEM (Version 5.2)

Attached is a "beta" version of the FREZCHEM model that includes chloride, sulfate, and bicarbonate-carbonate salts (FREZCHEM5.2). This folder includes a FORTRAN program listing(which you can download directly), a list of chemical species in the model (Table 1), instructions for model input, and an example of model output.

This model is very much a work in progress. I will be mainly adding new chemistries to the model in the next few years. I have not spend much time debugging the model or making it user-friendly. In addition, there are convergence problems, at times, with the model. My version of the model was created with Absoft's ProFortran for the Macintosh. Porting this code to another fortran compiler is always problematic. If you have problems, contact me via e-mail(gmarion@dri.edu). Indicate the FREZCHEM version you are using (e.g., FREZCHEM5.2) and your model input.

The model is an equilibrium chemical thermodynamic model, meaning it will always select the most stable minerals. There are a few minerals (e.g., aragonite and ikaite) that are always metastable with respect to other minerals (e.g., calcite). To explicitly include a metastable mineral in your calculations necessitates removing the stable mineral from the minerals database. This is most simply done by assigning the stable mineral an arbitrary high K_{sp}. See the comments at the end of the "Parameter" subroutine on how to do this. The # of the K_{sp} for a specific mineral is the same as the solid phase # in Table 1 (e.g., K_{52} is the solubility product for calcite). If you are using the model to calculate pH, then you should make sure that the initial solution is charge-balanced. Otherwise, the model will force a charge balance by changing the bicarbonate-carbonate or acid concentrations, which could lead to a serious error in calculated pH if the solution is badly charge-balanced. If necessary, force a charge-balance in the initial solution by changing a major constituent that minimizes the effect on pH (e.g., Na or Cl).

The validation of this model is discussed in three publications: (1) Spencer et al., (1990) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO_4-H_2O system. Geochim. Cosmochim. Acta, 54:575-590; (2) Marion and Farren, (1999) Mineral solubilities in the Na-K-Mg-Ca-Cl-SO_4-H_2O system: A re-evaluation of the sulfate chemistry in the Spencer-Møller-Weare model. Geochim. Cosmochim. Acta, 63:1305-1318; and (3) Marion (2001) Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system. Geochim. Cosmochim. Acta, 1883-1896.

Table 1. A listing of chemical species in the FREZCHEM model (version 5.2).

A. Solution and Atmospheric Species

#	Species	#	Species	#	Species
1	Na^{+}(aq)	11	Cl^{-}(aq)	21	CO_2(aq)
2	K^{+}(aq)	12	SO_4^{2-}(aq)	22	
3	Ca^{2+}(aq)	13	OH^{-}(aq)	23	
4	Mg^{2+}(aq)	14	HCO_3^{-}(aq)	24	$CaCO_3^{\circ}$(aq)
5	H^{+}(aq)	15	CO_3^{2-}(aq)	25	$MgCO_3^{\circ}$(aq)
6		16		26	
7		17		27	
8		18		28	H_2O(g)
9		19		29	CO_2(g)
10		20		30	H_2O(l)

B. Solid Phase Species

#	Species	#	Species	#	Species
31	H_2O(cr,I)	46	$MgSO_4 \bullet K_2SO_4 \bullet 6H_2O$(cr)	61	$CaMg(CO_3)_2$(cr)
32	$NaCl \bullet 2H_2O$(cr)	47	$Na_2SO_4 \bullet MgSO_4 \bullet 4H_2O$(cr)	62	$Na_2CO_3 \bullet 7H_2O$(cr)
33	NaCl(cr)	48	$CaSO_4 \bullet 2H_2O$(cr)	63	$KHCO_3$(cr)
34	KCl(cr)	49	$CaSO_4$(cr)	64	$CaCO_3$(cr,aragonite)
35	$CaCl_2 \bullet 6H_2O$(cr)	50	$MgSO_4 \bullet 12H_2O$(cr)	65	$CaCO_3$(cr,vaterite)
36	$MgCl_2 \bullet 6H_2O$(cr)	51	$Na_2SO_4 \bullet 3K_2SO_4$(cr)		
37	$MgCl_2 \bullet 8H_2O$(cr)	52	$CaCO_3$(cr,calcite)		
38	$MgCl_2 \bullet 12H_2O$(cr)	53	$MgCO_3$(cr)		
39	$KMgCl_3 \bullet 6H_2O$(cr)	54	$MgCO_3 \bullet 3H_2O$(cr)		
40	$CaCl_2 \bullet 2MgCl_2 \bullet 12H_2O$(cr)	55	$MgCO_3 \bullet 5H_2O$(cr)		
41	$Na_2SO_4 \bullet 10H_2O$(cr)	56	$CaCO_3 \bullet 6H_2O$(cr)		
42	Na_2SO_4(cr)	57	$NaHCO_3$(cr)		
43	$MgSO_4 \bullet 6H_2O$(cr)	58	$Na_2CO_3 \bullet 10H_2O$(cr)		
44	$MgSO_4 \bullet 7H_2O$(cr)	59	$NaHCO_3 \bullet Na_2CO_3 \bullet 2H_2O$(cr)		
45	K_2SO_4(cr)	60	$3MgCO_3 \bullet Mg(OH)_2 \bullet 3H_2O$(cr)		

Model Input (hit return after every entry).

Title: Any alphanumeric character up to 50 characters.

Freeze(1) or Evaporation(2) Scenario: Enter 1 or 2 depending on whether you want to simulate a temperature change (1) or evaporation (2). For evaluating a single point, enter "1".

Equilibrium(1) or Fractional(2) Crystallization: In equilibrium crystallization (1), precipitated solids are allowed to re-equilibrate with the solution phase as environmental conditions change. In fractional crystallization (2), precipitated solids are removed and not allowed to re-equilibrate with the solution phase as environmental conditions change.

Sodium (m/kg): Enter sodium molality (moles/kg(water)).

Potassium (m/kg): Enter potassium molality (moles/kg(water)).

Calcium (m/kg): Enter calcium molality (moles/kg(water)).

Magnesium (m/kg): Enter magnesium molality (moles/kg(water)).

Initial pH: If alkalinity > 0.0, then the model will calculate pH, given an initial pH estimate that is specified here. If this estimate is far removed from the true pH, then the model may not converge.

Chloride (m/kg): Enter chloride molality (moles/kg(water)).

Sulfate (m/kg): Enter sulfate molality (moles/kg(water)).

CO_2(atm): If alkalinity > 0.0, then specify the concentration of CO_2(g) in atmospheres.

Carbonate Alkalinity: Enter as equivalents/kg(water). If alkalinity = 0.0, then you must enter 0.0. The latter will cause the model to skip all bicarbonate-carbonate, pH chemistries in the model.

Initial Temperature(K): Enter the temperature in absolute degrees (K) for start of simulation (e.g., 298.15).

For Temperature Change Pathway:

Final Temperature(K): Enter final temperature of simulation (e.g., 273.15).

Temperature Decrement(K): The temperature interval between simulations (e.g. 5). For the above temperature designations, the model would calculate equilibrium starting at 298.15 K and ending at 273.15 K at 5 K intervals. If you want to change the decrement in a run (e.g., to reduce the step size near an equilibrium), see the comments near the end of the main program.

For Evaporation Pathway:

Initial Water (g): Normally enter "1000" at this point. The standard weight basis of the model is 1000 g water plus associated salts. In you enter 100, instead of 1000, the initial ion concentrations, specified above, will be multiplied by 10.0 (1000/100) as the starting compositions for calculations. This feature of the model is useful in precisely locating where minerals start to precipitate during the evaporation process without having to calculate every small change between 1000 g and 1 g.

Final Water (g): Enter the final amount of water that you want to remain in the system (e.g., 100).

Water Decrement (g): Enter the water decrement for simulations (e.g., 50 g). Specifying initial = 1000, final = 100, and decrement = 50 would result in calculations at 1000g, 950g, ...100g. If you want to change the decrement in a run (e.g., to reduce the step size near an equilibrium), see the comments near the end of the main program.

Model Output (Table 2).

"Ion.Str." is the ionic strength of the equilibrium solution. "AH2O" is the activity of liquid water in the equilibrium solution. "Phi" is the osmotic coefficient of the equilibrium solution. "H2O(g)" is the amount of water remaining as liquid. "Ice" is the amount of water that is present as ice. The mass basis for calculation in the model is 1.0 kg of water (except for evaporation); therefore, the water in liquid water + ice + hydrated salts should always sum to 1.0 kg. The data under "Initial Conc." are the input concentrations. "Final Conc." are the equilibrium concentrations. Act. coef. (activity coefficient) and activity are self-explanatory. Moles are the # of moles in the solution or solid phase. For the major constituents, the "Mass Balance" column should agree with the input column ("Initial Conc."); this is the best check on the internal consistency of the calculations. The "Accum Moles" in the solids section are the net # of moles of that solid that have precipitated. For equilibrium crystallization, accum. moles = moles(solid). For fractional crystallization accum. moles ≥ moles (solids); in this case, moles represent the solids that have precipitated in the last interval (e.g., between 15 and 10 °C), while accum. moles represent the total precipitate (e.g., between 25 and 10 °C).

Table 2 is an example where we specified a 1.0 m NaCl plus 0.1 m $CaCO_3$ solution at 263.15 K. Under these conditions, about 64% of the water is present as ice and virtually all of the $CaCO_3$ has precipitated as calcite. The calculated pH is 8.34. The solution at this temperature is considerably undersaturated with respect to hydrohalite ($NaCl \cdot 2H_2O$), which would be the last solid to precipitate at the eutectic below 251.15 K.

Table 2. Freezing of a NaCl-CaCO3 solution

Temp(K)	Ion.Str.	AH2O	Phi	H2O(g)	Ice(g)
263.15	2.7807	0.90743	0.97081	360.50	639.50

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Moles	Mass Balance
NA	1.0000	2.7739	0.61217	1.6981	1.0000	1.0000
CA	0.10000	0.22175E-02	0.35498	0.78717E-03	0.79940E-03	0.10000
H	0.11799E-07	0.26337E-08	1.7346	0.45684E-08	0.94943E-09	
CL	1.0000	2.7739	0.61398	1.7031	1.0000	1.0000
OH	0.35764E-06	0.90343E-06	0.88093E-01	0.79587E-07	0.32569E-06	
HCO3	0.20000	0.41204E-02	0.38438	0.15838E-02	0.14854E-02	0.20000
CO3	0.00000	0.15684E-03	0.34855E-01	0.54668E-05	0.56541E-04	
CO2	0.21410E-04	0.20118E-04	2.1537	0.43327E-04	0.72524E-05	
CACO3	0.00000	0.57705E-05	1.0000	0.57705E-05	0.20803E-05	
CO2(ATM)				.36000E-03		
H2O(L)	55.508			.90743	20.011	55.508

Solid SPECIES	Moles	Equil. Constant	Accum. Moles
ICE	35.498	0.90743	35.498
NACL.2H2O	0.00000	12.566	0.00000
NACL	0.00000	27.861	0.00000
KCL	0.00000	2.5900	0.00000
CACL2.6H2O	0.00000	1258.4	0.00000
MGCL2.6H2O	0.00000	55414.	0.00000
MGCL2.8H2O	0.00000	4683.2	0.00000
MGCL2.12H2O	0.00000	201.60	0.00000
KMGCL3.6H2O	0.00000	4526.6	0.00000
CACL2.2MGCL2.12H2O	0.00000	0.11070E+20	0.00000
NA2SO4.10H2O	0.00000	0.90537E-03	0.00000
NA2SO4	0.00000	0.48157	0.00000
MGSO4.6H2O	0.00000	0.18596E-01	0.00000
MGSO4.7H2O	0.00000	0.43652E-02	0.00000
K2SO4	0.00000	0.40945E-02	0.00000
MGSO4.K2SO4.6H2O	0.00000	0.39356E-05	0.00000
NA2SO4.MGSO4.4H2O	0.00000	0.31861E-02	0.00000
CASO4.2H2O	0.00000	0.18491E-04	0.00000
CASO4	0.00000	0.94050E-04	0.00000
MGSO4.12H2O	0.00000	0.18570E-02	0.00000
NA2SO4.3K2SO4	0.00000	0.30930E-09	0.00000
CACO3(CALCITE)	0.99199E-01	0.43033E-08	0.99199E-01
MGCO3	0.00000	0.37261E-07	0.00000
MGCO3.3H2O	0.00000	0.15229E-04	0.00000
MGCO3.5H2O	0.00000	0.96132E-05	0.00000
CACO3.6H2O	0.00000	0.32916E-07	0.00000
NAHCO3	0.00000	0.14566	0.00000
NA2CO3.10H2O	0.00000	0.69294E-02	0.00000
NAHCO3.NA2CO3.2H2O	0.00000	0.39156E-01	0.00000
3MGCO3.MG(OH)2.3H2O	0.00000	0.52738E-34	0.00000
CAMG(CO3)2	0.00000	0.68743E-16	0.00000
NA2CO3.7H2O	0.00000	0.49255E-01	0.00000
KHCO3	0.00000	0.50021	0.00000
CACO3(ARAGONITE)	0.00000	0.63985E-08	0.00000
CACO3(VATERITE)	0.00000	0.20194E-07	0.00000

Iterations = 4