FRIENDS OF FREZCHEM (Version 8.3)

Attached is a "beta" version of the FREZCHEM model that includes chloride, nitrate, sulfate, and bicarbonate-carbonate salts, strong acid chemistry, and ferrous iron chemistry. This version includes both temperature and pressure dependencies (FREZCHEM8.3). 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 (Table 2), and an example of model output (Table 3).

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. Indicate the FREZCHEM version you are using (e.g., FREZCHEM8.3) 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 six 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; (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, 65:1883-1896; (4) Marion (2002) A molal-based model for strong acid chemistry at low temperatures (<200 to 298 K). Geochim. Cosmochim. Acta, 66:2499-2516; (5) Marion et al. (2003) Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars. Geochim. Cosmochim. Acta, 67:4251-4266, and (6) Marion et al. (2005) Effects of pressure on aqueous chemical equilibria at subzero temperatures with applications to Europa. Geochim. Cosmochim. Acta, 69:259-274.

Table 1. A listing of chemical species in the FREZCHEM model (Version 8.3).

A. Solution and Atmospheric Species

#	Species	#	Species	#	Species	#	Species
1	$Na^+(aq)$	11	$Cl^-(aq)$	21	$CO_2(aq)$	151	$O_2(g)$
2	$K^+(aq)$	12	$SO_4^{2-}(aq)$	22	$FeCO_3°(aq)$	152	$O_2(aq)$
3	$Ca^{2+}(aq)$	13	$OH^-(aq)$	23	$HCl(g)$	153	$H_2(g)$
4	$Mg^{2+}(aq)$	14	$HCO_3^-(aq)$	24	$CaCO_3°(aq)$		
5	$H^+(aq)$	15	$CO_3^{2-}(aq)$	25	$MgCO_3°(aq)$		
6	$MgOH^+(aq)$	16	$HSO_4^-(aq)$	26	$HNO_3(g)$		
7	$Fe^{2+}(aq)$	17	$NO_3^-(aq)$	27	$H_2SO_4(g)$		
8	$FeOH^+(aq)$	18		28	$H_2O(g)$		
9		19		29	$CO_2(g)$		
10		20		30	$H_2O(l)$		

B. Solid Phase Species

#	Species	#	Species	#	Species	#	Species
31	$H_2O(cr,I)$	46	$MgSO_4•K_2SO_4•6H_2O(cr)$	61	$CaMg(CO_3)_2(cr)$	76	$K_3H(SO_4)_2(cr)$
32	$NaCl•2H_2O(cr)$	47	$Na_2SO_4•MgSO_4•4H_2O(cr)$	62	$Na_2CO_3•7H_2O(cr)$	77	$K_5H_3(SO_4)_4(cr)$
33	$NaCl(cr)$	48	$CaSO_4•2H_2O(cr)$	63	$KHCO_3(cr)$	78	$K_8H_6(SO_4)_7•H_2O(cr)$
34	$KCl(cr)$	49	$CaSO_4(cr)$	64	$CaCO_3(cr,aragonite)$	79	$KHSO_4(cr)$
35	$CaCl_2•6H_2O(cr)$	50	$MgSO_4•12H_2O(cr)$	65	$CaCO_3(cr,vaterite)$	80	$MgSO_4•H_2O(cr)$
36	$MgCl_2•6H_2O(cr)$	51	$Na_2SO_4•3K_2SO_4(cr)$	66	$HNO_3•3H_2O(cr)$	81	$FeSO_4•7H_2O(cr)$
37	$MgCl_2•8H_2O(cr)$	52	$CaCO_3(cr,calcite)$	67	$KNO_3(cr)$	82	$FeSO_4•H_2O(cr)$
38	$MgCl_2•12H_2O(cr)$	53	$MgCO_3(cr)$	68	$NaNO_3(cr)$	83	$FeCl_2•6H_2O(cr)$
39	$KMgCl_3•6H_2O(cr)$	54	$MgCO_3•3H_2O(cr)$	69	$HCl•3H_2O(cr)$	84	$FeCl_2•4H_2O(cr)$
40	$CaCl_2•2MgCl_2•12H_2O(cr)$	55	$MgCO_3•5H_2O(cr)$	70	$H_2SO_4•6.5H_2O(cr)$	85	$FeCO_3(cr)$
41	$Na_2SO_4•10H_2O(cr)$	56	$CaCO_3•6H_2O(cr)$	71	$H_2SO4•4H_2O(cr)$	86	$Fe(OH)_3(cr)$
42	$Na_2SO_4(cr)$	57	$NaHCO_3(cr)$	72	$HCl•6H_2O(cr)$		
43	$MgSO_4•6H_2O(cr)$	58	$Na_2CO_3•10H_2O(cr)$	73	$NaNO_3•Na_2SO_4•2H_2O(cr)$		
44	$MgSO_4•7H_2O(cr)$	59	$NaHCO_3•Na_2CO_3•2H_2O(cr)$	74	$Na_3H(SO_4)_2(cr)$		
45	$K_2SO_4(cr)$	60	$3MgCO_3•Mg(OH)_2•3H_2O(cr)$	75	$NaHSO_4•H_2O(cr)$		

Table 2. Model Inputs (Version 8.3) (hit return after every entry).

Title: Any alphanumeric character up to 50 characters.

Freeze(1) or Evaporation(2) or Pressure (3) Pathway: Enter 1, 2, or 3 depending on whether you want to simulate a temperature change (1) an evaporation (2), or a pressure change (3). 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)). Otherwise, enter 0.0.

Potassium (m/kg): Enter potassium molality (moles/kg(water)). Otherwise, enter 0.0.

Calcium (m/kg): Enter calcium molality (moles/kg(water)). Otherwise, enter 0.0.

Magnesium (m/kg): Enter magnesium molality (moles/kg(water)). Otherwise, enter 0.0.

Iron (m/kg): Enter iron molality (moles/kg(water)). Otherwise, enter 0.0.

Chloride (m/kg): Enter chloride molality (moles/kg(water)). Otherwise, enter 0.0.

Sulfate (m/kg): Enter sulfate molality (moles/kg(water)). Otherwise, enter 0.0.

Nitrate (m/kg): Enter nitrate molality (moles/kg(water)). Otherwise, enter 0.0.

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 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.

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

Acidity: Enter as equivalents/kg(water). This is the total hydrogen concentration, if known initially. Generally this is only known for strong acid solutions. For example, for a 1 molal H_2SO_4 solution, enter 2.00. Otherwise, enter 0.0. The equations used to calculate pH for the alkalinity and acidity cases are incompatible. So, a specification of either carbonate alkalinity or acidity requires

that the other variable be assigned a value of 0.00. This will channel the calculations to the proper algorithm.

HCl(atm): If the HCl atmospheric concentration is known, then specify here. Otherwise, enter 0.0. If you specify 0.0, then the model will calculate HCl(atm). Note that if you specify HCl(atm) or the other acids below, then these properties override the total acidity specification (see above). That is, the solution is equilibrated with the atmospheric concentration. Note, you can, if desired, specify atmospheric concentrations for some acids (e.g., HCl and HNO_3) and leave other acid partial pressure unspecified (e.g., H_2SO_4 = 0.0).

HNO_3(atm): If the HNO_3 atmospheric concentration is known, then specify here. Otherwise, enter 0.0.

H_2SO_4(atm): If the H_2SO_4 atmospheric concentration is known, then specify here. Otherwise, enter 0.0.

O_2(atm): If the atmospheric concentration of oxygen is known, then specify here. Otherwise, enter 0.0. If you are interested in ferrous iron chemistry, then you may want to assign O_2 a value of 0.0. Otherwise, it is likely that the insolubility of ferric minerals in the presence of O_2 will cause all the iron to precipitate as a ferric mineral [see discussions in Marion et al., (2003a) iron paper].

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

For Temperature Change Pathway(1):

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(2):

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.

Initial Total Pressure (bars): Enter the initial total pressure of the system.

For Pressure Pathway(3):

Final Pressure(bars): Enter the final pressure of the simulation [e.g., 101.01325 bars (100 atm)].

Pressure Increment(bars): Enter the pressure increment. For example, if initial pressure is 1.01 bars, final pressure is 101.01 bars, and pressure increment is 1.0 bars, then the simulation would calculate at 1.01, 2.01, 3.01, ...101.01325 bars. If you want to change the increment in a run, see the comments near the end of the main program.

Model Output.

"Ion.Str." is the ionic strength of the equilibrium solution. "RHO" is the density of the 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 3 is an example where we specified a 1.0 m NaCl plus 0.1 m $Fe(HCO_3)_2$ solution at 263.15 K and 100 bars. The P_{CO2} was set at 3.6e-4 atm (current Earth P_{CO2}) and P_{O2} was set at 0.0 to simulate ferrous iron chemistry. Under these conditions, about 61% of the water is present as ice and virtually all (99.96%) of the Fe^{2+} has precipitated as siderite ($FeCO_3$). The calculated pH is 6.96. The solution at this temperature is considerably undersaturated with respect to hydrohalite ($NaCl•2H_2O$).

Table 3. Ferrous iron at subzero temperature and 100 bars

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
263.15	2.5754	1.1087	0.95996	388.34	611.66	100.00

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Moles	Mass Balance
NA	1.0000	2.5750	0.61916	1.5944	1.0000	1.0000
H	0.12898E-07	0.70740E-07	1.5537	0.10991E-06	0.27471E-07	0.27471E-07
FE	0.10000	0.10601E-03	13.051	0.13836E-02	0.41169E-04	0.10000
FEOH	0.00000	0.19993E-06	0.94112	0.18816E-06	0.77642E-07	
CL	1.0000	2.5750	0.61934	1.5948	1.0000	1.0000
OH	0.16050E-06	0.37631E-07	0.10047	0.37808E-08	0.14614E-07	
HCO3	0.20000	0.21148E-03	0.42254	0.89357E-04	0.82125E-04	0.20000
CO3	0.00000	0.35672E-06	0.41313E-01	0.14737E-07	0.13853E-06	
CO2	0.36773E-04	0.24557E-04	2.0540	0.50440E-04	0.95365E-05	
FECO3	0.00000	0.26604E-06	1.0000	0.26604E-06	0.10331E-06	
CO2(ATM)				.36000E-03		
H2O(ATM)				.25801E-02		
H2O(L)	55.508			.91425	21.556	55.508

Solid SPECIES	Moles	Equil. Constant	Accum. Moles
ICE	33.952	0.91424	33.952
NACL.2H2O	0.00000	13.199	0.00000
NACL	0.00000	29.921	0.00000
KCL	0.00000	2.7778	0.00000
CACL2.6H2O	0.00000	1307.6	0.00000
MGCL2.6H2O	0.00000	58898.	0.00000
MGCL2.8H2O	0.00000	4833.5	0.00000
MGCL2.12H2O	0.00000	194.54	0.00000
KMGCL3.6H2O	0.00000	5289.5	0.00000
CACL2.2MGCL2.12H2O	0.00000	0.15132E+20	0.00000
NA2SO4.10H2O	0.00000	0.10939E-02	0.00000
NA2SO4	0.00000	0.61858	0.00000
MGSO4.6H2O	0.00000	0.22375E-01	0.00000
MGSO4.7H2O	0.00000	0.51610E-02	0.00000
K2SO4	0.00000	0.50363E-02	0.00000
MGSO4.K2SO4.6H2O	0.00000	0.56606E-05	0.00000
NA2SO4.MGSO4.4H2O	0.00000	0.49257E-02	0.00000
CASO4.2H2O	0.00000	0.23451E-04	0.00000
CASO4	0.00000	0.12326E-03	0.00000
MGSO4.12H2O	0.00000	0.20403E-02	0.00000
NA2SO4.3K2SO4	0.00000	0.72743E-09	0.00000
CACO3(CALCITE)	0.00000	0.58781E-08	0.00000
MGCO3	0.00000	0.49432E-07	0.00000
MGCO3.3H2O	0.00000	0.19553E-04	0.00000
MGCO3.5H2O	0.00000	0.11798E-04	0.00000
CACO3.6H2O	0.00000	0.39722E-07	0.00000
NAHCO3	0.00000	0.16232	0.00000
NA2CO3.10H2O	0.00000	0.82623E-02	0.00000
NAHCO3.NA2CO3.2H2O	0.00000	0.55277E-01	0.00000
3MGCO3.MG(OH)2.3H2O	0.00000	0.17193E-33	0.00000
CAMG(CO3)2	0.00000	0.12423E-15	0.00000
NA2CO3.7H2O	0.00000	0.61170E-01	0.00000
KHCO3	0.00000	0.54829	0.00000
CACO3(ARAGONITE)	0.00000	0.86310E-08	0.00000
CACO3(VATERITE)	0.00000	0.27683E-07	0.00000
HNO3.3H2O	0.00000	340.89	0.00000
KNO3	0.00000	0.87069E-01	0.00000
NANO3	0.00000	2.5235	0.00000
HCL.3H2O	0.00000	12093.	0.00000
H2SO4.6.5H2O	0.00000	25.893	0.00000
H2SO4.4H2O	0.00000	1173.1	0.00000
HCL.6H2O	0.00000	903.33	0.00000
NANO3.NA2SO4.2H2O	0.00000	0.11346	0.00000
NA3H(SO4)2	0.00000	0.14086	0.00000
NAHSO4.H2O	0.00000	33.647	0.00000
K3H(SO4)2	0.00000	0.53417E-04	0.00000
K5H3(SO4)4	0.00000	0.17412E-07	0.00000
K8H6(SO4)7.H2O	0.00000	0.41716E-12	0.00000

KHSO4	0.00000	1.0738	0.00000
MGSO4.H2O	0.00000	14.523	0.00000
FESO4.7H2O	0.00000	0.16432E-02	0.00000
FESO4.H2O	0.00000	0.46284	0.00000
FECL2.6H2O	0.00000	4312.7	0.00000
FECL2.4H2O	0.00000	19708.	0.00000
FECO3	0.99959E-01	0.20391E-10	0.99959E-01
FE(OH)3	0.00000	0.30291E+14	0.00000

Iterations = 5