

FRIENDS OF FREZCHEM (Version 9.2)

Attached is a "beta" version of the FREZCHEM model that includes chloride, nitrate, sulfate, and bicarbonate-carbonate salts, strong acid chemistry, ferrous iron chemistry, and gas hydrate chemistry. This version includes both temperature and pressure dependencies (FREZCHEM9.2). 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 (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., FREZCHEM9.2) 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 seven 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-SO₄-H₂O system. *Geochim. Cosmochim. Acta*, 54:575-590; (2) Marion and Farren, (1999) Mineral solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O 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-SO₄-OH-HCO₃-CO₃-CO₂-H₂O 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; (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; and (7) Marion et al. (2006) Modeling gas hydrate equilibria in electrolyte solutions. *CALPHAD*, 30:248-259.

Table 1. A listing of chemical species in the FREZCHEM model (Version 9.2).

<u>A. Solution and Atmospheric Species</u>			
#	Species	#	Species
1	Na ⁺ (aq)	11	Cl ⁻ (aq)
2	K ⁺ (aq)	12	SO ₄ ²⁻ (aq)
3	Ca ²⁺ (aq)	13	OH ⁻ (aq)
4	Mg ²⁺ (aq)	14	HCO ₃ ⁻ (aq)
5	H ⁺ (aq)	15	CO ₃ ²⁻ (aq)
6	MgOH ⁺ (aq)	16	HSO ₄ ⁻ (aq)
7	Fe ²⁺ (aq)	17	NO ₃ ⁻ (aq)
8	FeOH ⁺ (aq)	18	
9		19	
10		20	
21	CO ₂ (aq)	21	CO ₂ (aq)
22	FeCO ₃ ^o (aq)	22	FeCO ₃ ^o (aq)
23	HCl(g)	23	HCl(g)
24	CaCO ₃ ^o (aq)	24	CaCO ₃ ^o (aq)
25	MgCO ₃ ^o (aq)	25	MgCO ₃ ^o (aq)
26	HNO ₃ (g)	26	HNO ₃ (g)
27	H ₂ SO ₄ (g)	27	H ₂ SO ₄ (g)
28	H ₂ O(g)	28	H ₂ O(g)
29	CO ₂ (g)	29	CO ₂ (g)
30	H ₂ O(l)	30	H ₂ O(l)
<u>B. Solid Phase Species</u>			
#	Species	#	Species
31	H ₂ O(cr,l)	46	MgSO ₄ •K ₂ SO ₄ •6H ₂ O(cr)
32	NaCl•2H ₂ O(cr)	47	Na ₂ SO ₄ •MgSO ₄ •4H ₂ O(cr)
33	NaCl(cr)	48	CaSO ₄ •2H ₂ O(cr)
34	KCl(cr)	49	CaSO ₄ (cr)
35	CaCl ₂ •6H ₂ O(cr)	50	MgSO ₄ •12H ₂ O(cr)
36	MgCl ₂ •6H ₂ O(cr)	51	Na ₂ SO ₄ •3K ₂ SO ₄ (cr)
37	MgCl ₂ •8H ₂ O(cr)	52	CaCO ₃ (cr,calcite)
38	MgCl ₂ •12H ₂ O(cr)	53	MgCO ₃ (cr)
39	KMgCl ₃ •6H ₂ O(cr)	54	MgCO ₃ •3H ₂ O(cr)
40	CaCl ₂ •2MgCl ₂ •12H ₂ O(cr)	55	MgCO ₃ •5H ₂ O(cr)
41	Na ₂ SO ₄ •10H ₂ O(cr)	56	CaCO ₃ •6H ₂ O(cr)
42	Na ₂ SO ₄ (cr)	57	NaHCO ₃ (cr)
43	MgSO ₄ •6H ₂ O(cr)	58	Na ₂ CO ₃ •10H ₂ O(cr)
44	MgSO ₄ •7H ₂ O(cr)	59	NaHCO ₃ •Na ₂ CO ₃ •2H ₂ O(cr)
45	K ₂ SO ₄ (cr)	60	3MgCO ₃ •Mg(OH) ₂ •3H ₂ O(cr)
61	CaMg(CO ₃) ₂ (cr)	61	CaMg(CO ₃) ₂ (cr)
62	Na ₂ CO ₃ •7H ₂ O(cr)	62	Na ₂ CO ₃ •7H ₂ O(cr)
63	KHCO ₃ (cr)	63	KHCO ₃ (cr)
64	CaCO ₃ (cr,aragonite)	64	CaCO ₃ (cr,aragonite)
65	CaCO ₃ (cr,vaterite)	65	CaCO ₃ (cr,vaterite)
66	HNO ₃ •3H ₂ O(cr)	66	HNO ₃ •3H ₂ O(cr)
67	KNO ₃ (cr)	67	KNO ₃ (cr)
68	NaNO ₃ (cr)	68	NaNO ₃ (cr)
69	HCl•3H ₂ O(cr)	69	HCl•3H ₂ O(cr)
70	H ₂ SO ₄ •6.5H ₂ O(cr)	70	H ₂ SO ₄ •6.5H ₂ O(cr)
71	H ₂ SO ₄ •4H ₂ O(cr)	71	H ₂ SO ₄ •4H ₂ O(cr)
72	HCl•6H ₂ O(cr)	72	HCl•6H ₂ O(cr)
73	NaNO ₃ •Na ₂ SO ₄ •2H ₂ O(cr)	73	NaNO ₃ •Na ₂ SO ₄ •2H ₂ O(cr)
74	Na ₃ H(SO ₄) ₂ (cr)	74	Na ₃ H(SO ₄) ₂ (cr)
75	NaHSO ₄ •H ₂ O(cr)	75	NaHSO ₄ •H ₂ O(cr)
76	K ₃ H(SO ₄) ₂ (cr)	76	K ₃ H(SO ₄) ₂ (cr)
77	K ₅ H ₃ (SO ₄) ₄ (cr)	77	K ₅ H ₃ (SO ₄) ₄ (cr)
78	K ₈ H ₆ (SO ₄) ₇ •H ₂ O(cr)	78	K ₈ H ₆ (SO ₄) ₇ •H ₂ O(cr)
79	KHSO ₄ (cr)	79	KHSO ₄ (cr)
80	MgSO ₄ •H ₂ O(cr)	80	MgSO ₄ •H ₂ O(cr)
81	FeSO ₄ •7H ₂ O(cr)	81	FeSO ₄ •7H ₂ O(cr)
82	FeSO ₄ •H ₂ O(cr)	82	FeSO ₄ •H ₂ O(cr)
83	FeCl ₂ •6H ₂ O(cr)	83	FeCl ₂ •6H ₂ O(cr)
84	FeCl ₂ •4H ₂ O(cr)	84	FeCl ₂ •4H ₂ O(cr)
85	FeCO ₃ (cr)	85	FeCO ₃ (cr)
86	Fe(OH) ₃ (cr)	86	Fe(OH) ₃ (cr)
87	CO ₂ •6H ₂ O(cr)	87	CO ₂ •6H ₂ O(cr)
88	CH ₄ •6H ₂ O(cr)	88	CH ₄ •6H ₂ O(cr)

Table 2. Model Inputs (Version 9.2) (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.

Open(1) or Closed(2) Carbon System: If you want the gas partial pressure of CO₂ or CH₄ to be fixed at a given total pressure, enter 1. If you want the total carbon to be fixed, enter 2.

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 ferrous 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.

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 H₂SO₄ 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(bars): 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(bars). Note that if you specify HCl(bars) 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 HNO₃) and leave other acid partial pressure unspecified (e.g., H₂SO₄ = 0.0).

HNO₃(bars): If the HNO₃ atmospheric concentration is known, then specify here. Otherwise, enter 0.0.

H₂SO₄(bars): If the H₂SO₄ atmospheric concentration is known, then specify here. Otherwise, enter 0.0.

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

Initial CO₂(bars): If alkalinity > 0.0 or CO₂ hydrates are simulated, then specify the initial concentration of CO₂(g) in bars.

Mole Fraction of CO₂: Enter the mole fraction of CO₂(g) for the system (mole fraction = CO₂(g)/total pressure). For pure CO₂, enter 1.0. If 0.0, then CO₂(g) is fixed and independent of total pressure.

O₂(bars): 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 O₂ a value of 0.0. Otherwise, it is likely that the insolubility of ferric minerals in the presence of O₂ will cause all the iron to precipitate as a ferric mineral [see discussions in Marion et al., (2003a) iron paper].

Initial CH₄(bars): If CH₄ hydrates are simulated, then specify the initial concentration of CH₄(g) in bars.

Mole Fraction of CH₄: Enter the mole fraction of CH₄(g) for the system (mole fraction = CH₄(g)/total pressure). For pure CH₄, enter 1.0. If 0.0, then CH₄(g) is fixed and independent of total pressure.

Mixed CH₄-CO₂ Gas Hydrate?: If both CH₄(g) and CO₂(g) are specified as inputs, then you can use this data to estimate the stability of a mixed CH₄-CO₂ gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 2).

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.

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.

Inputting Gases To The Model

SYSTEM INPUTS	NO GASES	FIXED GAS CONCS.	VARIABLE GAS CONCS.
1. OPEN CARBON SYSTEM	1	1	1
2. INITIAL TOTAL PRESSURE	USER SPECIFICATION	USER SPECIFICATION	USER SPECIFICATION
3. INITIAL CO2	0	USER SPECIFICATION	USER SPECIFICATION
4. MOLE FRACTION OF CO2	0	0	USER SPECIFICATION
5. INITIAL O2	0	USER SPECIFICATION	0
6. INITIAL CH4	0	USER SPECIFICATION	USER SPECIFICATION
7. MOLE FRACTION OF CH4	0	0	USER SPECIFICATION
8. MIXED CH4-CO2 GAS HYDRATE	----	2	1
CLOSED CARBON			
1. OPEN CARBON SYSTEM	2		
2. INITIAL TOTAL PRESSURE	USER SPECIFICATION		
3. INITIAL CO2	USER SPECIFICATION		
4. MOLE FRACTION OF CO2	USER SPECIFICATION		
5. INITIAL O2			
6. INITIAL CH4	USER SPECIFICATION		
7. MOLE FRACTION OF CH4	USER SPECIFICATION		
8. MIXED CH4-CO2 GAS HYDRATE	1		

NO GASES means that you do not want any gases considered in these chemical equilibrium calculations.

FIXED GAS CONCS. means that you want the user specified gas concentrations to remain fixed as T, P, and H2O content change. For example, atm. CO2 is equal to 3.80e-4 bars.

VARIABLE GAS CONCS. were specifically designed for CO2 and CH4 gas hydrate equilibrium which allows gas pressures to increase as total pressure increases.

CLOSED CARBON was specifically designed for CO2 and CH4 gas hydrate equilibrium in small volumes (e.g., ice pockets).

The aqueous component contains 1.0 kg of water. The air component contains 0.1 liter.

To change the aqueous/air ratio, change the 0.1 liter multiplier in FC9.2 lines 211, 229, 2639, and 2647.

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 \geq 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 solution plus equal mole fractions of CO₂(g) and CH₄(g) at 263.15 K and 30 bars. Under these conditions, a mixed gas hydrate formed. Note that equal gas phase partial pressures (15 bars) does not lead to equal solid phase compositions (CO₂•6H₂O = 5.16 moles, CH₄•6H₂O = 2.42 moles). This occurs because of the greater solubility of CO₂, relative to CH₄, in aqueous solutions. Also this case is very close to saturation with hydrohalite (NaCl•2H₂O), which occurs at 262.95 K, which is the eutectic temperature below which only solid phases can exist.

Table 3. The equilibrium composition of a salt/gas hydrate solution at subzero temperatures.

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
263.15	5.5307	1.1996	1.2105	180.81	0.00000	30.000
Solution SPECIES	Initial Conc.	Final Conc.	Act.Coeff.	Activity	Moles	Mass Balance
NA	1.0000	5.5307	0.85304	4.7179	1.0000	1.0000
CL	1.0000	5.5307	0.78857	4.3613	1.0000	1.0000
CO2	1.0632	0.38831	3.7044	1.4385	0.70210E-01	
CH4	0.33980E-01	0.15350E-01	2.7308	0.41917E-01	0.27754E-02	
CH4(BAR)	15.000	15.000	0.92495	13.874	0.00000	
CO2(BAR)	15.000	15.000	0.77221	11.583	0.00000	
H2O(BAR)	0.27023E-02			.21744E-02		
H2O(L)	55.508			.77878	10.036	55.508
Solid SPECIES	Moles	Equil. Constant	Accum. Moles			
ICE	0.00000	0.90952	0.00000			
NACL.2H2O	0.00000	12.756	0.00000			
NACL	0.00000	28.456	0.00000			
KCL	0.00000	2.6448	0.00000			
CACL2.6H2O	0.00000	1268.6	0.00000			
MGCL2.6H2O	0.00000	56436.	0.00000			
MGCL2.8H2O	0.00000	4728.1	0.00000			
MGCL2.12H2O	0.00000	198.33	0.00000			
KMGCL3.6H2O	0.00000	4741.8	0.00000			
CACL2.2MGCL2.12H2O	0.00000	0.12150E+20	0.00000			
NA2SO4.10H2O	0.00000	0.95760E-03	0.00000			
NA2SO4	0.00000	0.51879	0.00000			
MGSO4.6H2O	0.00000	0.19645E-01	0.00000			
MGSO4.7H2O	0.00000	0.45875E-02	0.00000			
K2SO4	0.00000	0.43550E-02	0.00000			
MGSO4.K2SO4.6H2O	0.00000	0.43851E-05	0.00000			
NA2SO4.MGSO4.4H2O	0.00000	0.36265E-02	0.00000			
CASO4.2H2O	0.00000	0.19840E-04	0.00000			
CASO4	0.00000	0.10190E-03	0.00000			
MGSO4.12H2O	0.00000	0.19097E-02	0.00000			
NA2SO4.3K2SO4	0.00000	0.39901E-09	0.00000			
CACO3(CALCITE)	0.00000	0.47193E-08	0.00000			
MGCO3	0.00000	0.40516E-07	0.00000			
MGCO3.3H2O	0.00000	0.16399E-04	0.00000			
MGCO3.5H2O	0.00000	0.10216E-04	0.00000			
CACO3.6H2O	0.00000	0.34802E-07	0.00000			
NAHCO3	0.00000	0.15044	0.00000			
NA2CO3.10H2O	0.00000	0.73009E-02	0.00000			
NAHCO3.NA2CO3.2H2O	0.00000	0.43388E-01	0.00000			
3MGCO3.MG(OH)2.3H2O	0.00000	0.74833E-34	0.00000			
CAMG(CO3)2	0.00000	0.81907E-16	0.00000			
NA2CO3.7H2O	0.00000	0.52525E-01	0.00000			
KHCO3	0.00000	0.51411	0.00000			
CACO3(ARAGONITE)	0.00000	0.69914E-08	0.00000			
CACO3(VATERITE)	0.00000	0.22170E-07	0.00000			
HNO3.3H2O	0.00000	345.77	0.00000			
KNO3	0.00000	0.82230E-01	0.00000			
NANO3	0.00000	2.3800	0.00000			
HCL.3H2O	0.00000	12368.	0.00000			
H2SO4.6.5H2O	0.00000	23.442	0.00000			
H2SO4.4H2O	0.00000	1048.2	0.00000			
HCL.6H2O	0.00000	970.58	0.00000			
NANO3.NA2SO4.2H2O	0.00000	0.91879E-01	0.00000			
NA3H(SO4)2	0.00000	0.14086	0.00000			
NAHSO4.H2O	0.00000	31.437	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	1.0029	0.00000			
MGSO4.H2O	0.00000	12.194	0.00000			
FESO4.7H2O	0.00000	0.14617E-02	0.00000			
FESO4.H2O	0.00000	0.38788	0.00000			

FECL2.6H2O	0.00000	4078.8	0.00000
FECL2.4H2O	0.00000	18324.	0.00000
FECO3	0.00000	0.16582E-10	0.00000
FE(OH)3	0.00000	0.30291E+14	0.00000
CO2.6H2O	5.1612	2.5839	5.1612
CH4.6H2O	2.4174	3.0950	2.4174

Iterations = 5