FRIENDS OF FREZCHEM (Version 15)

Attached is a "beta" version of the FREZCHEM model that includes chloride, bromide, perchlorate, nitrate, sulfate, and bicarbonate-carbonate salts, strong acid chemistry, ferrous and ferric iron chemistry, aluminum and silicon chemistries, ammonia and ammonium chemistries, and gas hydrate chemistry. This version includes both temperature and pressure dependencies. This folder includes a FORTRAN program listing(which you can download directly), four input files, a list of chemical species in the model (Table 1), instructions for model input (Tables 2-5 and 8), and three examples of model outputs (Tables 6-7 and 9).

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. A user-friendly version (10.2) is available at http://frezchem.dri.edu. 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 (giles.marion@dri.edu). Indicate the FREZCHEM version you are using (e.g., FREZCHEM12.2) 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 vaterite) 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 mineral database. This is most simply done by assigning the stable mineral an arbitrary high K_{sp} through SOLIDPHASE.txt. The # of the K_{sp} for a specific mineral in the FORTRAN program 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). If you input Fe, Al, Si, or alkalinity, then you will have four options on how to deal with pH; adding NH_3-NH_4 adds a fifth option (see Table 2).

The validation of this model is discussed in 14 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; (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; (7) Marion et al. (2006) Modeling gas hydrate equilibria in electrolyte solutions. CALPHAD, 30:248-259; (8) Marion (2007) Adapting molar data (without density) for molal models. Computers & Geosciences, 33:829-834. (9) Marion and Kargel (2008) Cold Aqueous Planetary Geochemistry with FREZCHEM: From Modeling to the Search for Life at the Limits. Springer; (10) Marion et al. (2008) Modeling ferrous-ferric iron chemistry with application to Martian surface geochemistry. Geochim. Cosmochim. Acta, 72:242-266; (11) Marion et al., (2009) Br/Cl partitioning in chloride minerals in the Burns formation on Mars. Icarus, 200:436-445; (12) Marion et al. (2009). Modeling aluminum-silicon chemistries and application to Australian playa lakes as analogues for Mars. Geochim. Cosmochim. Acta. 73:3493-3511; (13) Marion et al., (2011). Modeling hot spring chemistries with applications to Martian silica formation. Icarus. 212:629-642; and (14) Marion et al. (2012). Modeling ammonia-ammonium aqueous chemistries in the Solar System's icy bodies. Icarus. 220:932-946.

Compared to earlier versions, this Version 15 of the FREZCHEM model contains new parameterizations dealing with ammonia and ammonium species. In addition, Version 15 has lowered the temperature level to 173 K (see Table 9).

A fundamental change was made in FREZCHEM 13 on how to input data into the model. Earlier versions required inputs via the computer screen. Versions 13-15 require inputs via data files; this approach simplifies and speeds up model inputting. There are four input files that must be built to run FREZCHEM. Table 2 describes the main model inputs; Table 3 presents the main Input.txt file; and Table 4 describes in more detail how to handle gases for these inputs. There are three minor input files that are lumped together in Table 5. Table 2 is just a verbal description of the material that is in the Input.txt file of Table 3. Similarly, Table 4 describes in more detail how gases need to be dealt with in Input.txt (Table 3). In the Input.txt file, note that inputs are all placed to the left of the ",". Also, do not remove the ",". That comma separates model input from descriptive words. The three minor files in Table 5 include: (A) SOLIDPHASE.txt, (B) SOLIDMASS.txt, and (C) NUANCES.txt. SOLIDPHASE.txt allows the user to remove all solid phases from equilibrium calculations or some specific minerals. That option allows for a pure solution phase calculation without any minerals precipitating. In the

molar to molal conversion example in Table 7, all solid phases had to be removed. Note the assigned exceptionally high equilibrium constants in Table 7, which is what keeps the solid phases from precipitating. In the Phoenix site calculation (Table 6), we removed magnesite ($MgCO_3$) and dolomite [$CaMg(CO_3)_2$] from model calculations (Table 5), which led to calcite ($CaCO_3$) and hydromagnesite [$3Mg(CO_3)_2 \bullet MgSO_4 \bullet 3H_2O$] precipitating (Table 6). Generally, model calculations start with aqueous/gas phases, without initial solid phases; but if you want a particular solid phase to control the solution phase chemical composition, then you can specify the solid phase and its mole mass (Table 5); the mole mass is an arbitrary amount that must not completely dissolve in 1.0 kg H_2O. For example, we assumed that Earth seawater would have been saturated with dolomite during Snowball Earth (Marion and Kargel, 2008). Changing the first line of SOLIDMASS.txt from No(0) to YES(1) and specifying dolomite would allow saturation with dolomite. The NUANCES.txt file allows for temperature, water content, or pressure changes to be adjusted during a specific run. For example, if you want to know the eutectic temperature of a salt assemblage, and you know that this will occur slightly below 259 K, you could change the ΔT term from 5 K between 298 and 263 K (as assigned by Input.txt) to 1 K between 263 and 259 K, and 0.1 K below 259 K (Table 5). This scenario would allow for a more accurate estimate of the eutectic temperature than using either a 5 K or 1 K term for the ΔT decrement. With respect to NUANCES.txt, always retain two steps for temperature, water content, and pressure changes, even if you need to duplicate two steps (e.g., 263.15 0.1, 263.15 0.1).

Table 1. A listing of chemical species in the FREZCHEM model (Version 15.1).

A. Solution and Atmospheric Species

#	Species	#	Species	#	Species	#	Species	#	Species
1	Na^+(aq)	16	Cl^-(aq)	201	CO_2(aq)	216	$Fe(OH)_2^0$(aq)	231	HF^0(aq)
2	K^+(aq)	17	SO_4^{2-}(aq)	202	$FeCO_3°$(aq)	217	$Fe(OH)_3^-$(aq)	232	Sr^{2+}(aq)
3	Ca^{2+}(aq)	18	OH^-(aq)	203	HCl(g)	218	$FeOH^{2+}$(aq)	233	NH_3^0(g)
4	Mg^{2+}(aq)	19	HCO_3^-(aq)	204	$CaCO_3°$(aq)	219	$Fe(OH)_2^+$(aq)	234	NH_3^0(aq)
5	H^+(aq)	20	CO_3^{2-}(aq)	205	$MgCO_3°$(aq)	220	$Fe(OH)_3^0$(aq)		
6	$MgOH^+$(aq)	21	HSO_4^-(aq)	206	HNO_3(g)	221	$Fe(OH)_4^-$(aq)		
7	Fe^{2+}(aq)	22	NO_3^-(aq)	207	H_2SO_4(g)	222	$Al(OH)^{2+}$(aq)		
8	$FeOH^+$(aq)	23	Br^-(aq)	208	H_2O(g)	223	$Al(OH)_2^+$(aq)		
9	Fe^{3+}(aq)	24	ClO_4^-(aq)	209	CO_2(g)	224	$Al(OH)_3^0$(aq)		
10	Al^{3+}(aq)	25	$B(OH)_4^-$(aq)	210	H_2O(l)	225	$Al(OH)_4^-$(aq)		
11	NH_4^+(aq)			211	O_2(g)	226	$Si(OH)_4^0$(aq)		
				212	O_2(aq)	227	$SiO(OH)_3^-$(aq)		
				213	H_2(g)	228	$SrCO_3^0$ (aq)		
				214	CH_4(g)	229	$B(OH)_3^0$(aq)		
				215	CH_4(aq)	230	F^-(aq)		

B. Solid Phase Species

#	Species	#	Species	#	Species	#	Species	#	Species	#	Species
31	H_2O(cr,I)	51	$Na_2SO_4•3K_2SO_4$(cr)	71	$H_2SO_4•4H_2O$(cr)	91	$FeCl_3•2KCl•H_2O$(cr)	111	$K_2Fe(II)_5Fe(III)_4(SO_4)_{12}•18H_2O$(cr)	131	$NaClO_4•2H_2O$(cr)
32	$NaCl•2H_2O$(cr)	52	$CaCO_3$(cr,calcite)	72	$HCl•6H_2O$(cr)	92	$Fe_2(SO_4)_3$(cr)	112	$AlCl_3•6H_2O$(cr)	132	NH_4Cl(cr)
33	NaCl(cr)	53	$MgCO_3$(cr)	73	$NaNO_3•Na_2SO_4•2H_2O$(cr)	93	$Fe_2(SO_4)_3•2K_2SO_4•14H_2O$(cr)	113	$Al_2(SO_4)_3•17H_2O$(cr)	133	$(NH_4)_2SO_4$(cr)
34	KCl(cr)	54	$MgCO_3•3H_2O$(cr)	74	$Na_3H(SO_4)_2$(cr)	94	$K_2SO_4•FeSO_4•6H_2O$(cr)	114	NaBr	134	$NH_3•H_2O$(cr)
35	$CaCl_2•6H_2O$(cr)	55	$MgCO_3•5H_2O$(cr)	75	$NaHSO_4•H_2O$(cr)	95	$Na_2SO_4•FeSO_4•4H_2O$(cr)	115	$MgBr_2$	135	NH_4NO_3(cr)
36	$MgCl_2•6H_2O$(cr)	56	$CaCO_3•6H_2O$(cr)	76	$K_3H(SO_4)_2$(cr)	96	$Fe_2(SO_4)_3•9H_2O$(cr)	116	$Al(OH)_3$(cr)	136	NH_4HCO_3(cr)
37	$MgCl_2•8H_2O$(cr)	57	$NaHCO_3$(cr)	77	$K_5H_3(SO_4)_4$(cr)	97	$Fe_2(SO_4)_3•H_2SO_4•8H_2O$(cr)	117	SiO_2 (quartz)(cr)	137	NH_4ClO_4(cr)
38	$MgCl_2•12H_2O$(cr)	58	$Na_2CO_3•10H_2O$(cr)	78	$K_8H_6(SO_4)_7•H_2O$(cr)	98	$KFe_3(SO_4)_2(OH)_6$(cr)	118	SiO_2 (amorphous)	138	$NH_3•2H_2O$(cr)
39	$KMgCl_3•6H_2O$(cr)	59	$NaHCO_3•Na_2CO_3•2H_2O$(cr)	79	$KHSO_4$(cr)	99	$NaFe_3(SO_4)_2(OH)_6$(cr)	119	$KAl_3(SO_4)_2(OH)_6$(cr)		
40	$CaCl_2•2MgCl_2•12H_2O$(cr)	60	$3MgCO_3•Mg(OH)_2•3H_2O$ (cr)	80	$MgSO_4•H_2O$(cr)	100	$H_3OFe_3(SO_4)_2(OH)_6$(cr)	120	$NaAl_3(SO_4)_2(OH)_6$(cr)		
41	$Na_2SO_4•10H_2O$(cr)	61	$CaMg(CO_3)_2$(cr)	81	$FeSO_4•7H_2O$(cr)	101	α-Fe_2O_3(cr)	121	$KAl_2(SO_4)_2•12H_2O$(cr)		
42	Na_2SO_4(cr)	62	$Na_2CO_3•7H_2O$(cr)	82	$FeSO_4•H_2O$(cr)	102	α-FeO(OH)(cr)	122	$NaAl(SO_4)_2•12H_2O$(cr)		
43	$MgSO_4•6H_2O$(cr)	63	$KHCO_3$(cr)	83	$FeCl_2•6H_2O$(cr)	103	γ-FeO(OH)(cr)	123	$FeSO_4•Al_2(SO_4)_3•22H_2O$(cr)		
44	$MgSO_4•7H_2O$(cr)	64	$CaCO_3$(cr,aragonite)	84	$FeCl_2•4H_2O$(cr)	104	$FeO(OH)_{0.75}(SO_4)_{0.125}$(cr)	124	$Al_2Si_2O_5(OH)_4$(cr)		
45	K_2SO_4(cr)	65	$CaCO_3$(cr,vaterite)	85	$FeCO_3$(cr)	105	$FeSO_4•4H_2O$(cr)	125	$MgSO_4•Al_2(SO_4)_3•22H_2O$(cr)		
46	$MgSO_4•K_2SO_4•6H_2O$(cr)	66	$HNO_3•3H_2O$(cr)	86	$Fe(OH)_3$(cr)	106	$Fe_2(SO_4)_3•7H_2O$(cr)	126	$NaClO_4•H_2O$(cr)		
47	$Na_2SO_4•MgSO_4•4H_2O$(cr)	67	KNO_3(cr)	87	$CO_2•6H_2O$(cr)	107	$Fe(II)Fe(III)_4(SO_4)_6(OH)_2•20H_2O$(cr)	127	$Mg(ClO_4)_2•8H_2O$(cr)		
48	$CaSO_4•2H_2O$(cr)	68	$NaNO_3$(cr)	88	$CH_4•6H_2O$(cr)	108	$Fe_5(SO_4)_6O(OH)$ $•20H_2O$(cr)	128	$Ca(ClO_4)_2•6H_2O$(cr)		
49	$CaSO_4$(cr)	69	$HCl•3H_2O$(cr)	89	$FeCl_3•10H_2O$(cr)	109	$Fe(II)Fe(III)_2(SO_4)_4•22H_2O$(cr)	129	$KClO_4$(cr)		
50	$MgSO_4•12H_2O$(cr)	70	$H_2SO_4•6.5H_2O$(cr)	90	$FeCl_3•6H_2O$(cr)	110	$Fe(II)Fe(III)_2(SO_4)_4•14H_2O$(cr)	130	$Mg(ClO_4)_2•6H_2O$(cr)		

Table 2. Description of Model Inputs (Version 15) (Compare with Table 3).

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 CO_2 or CH_4 to be fixed at a given total pressure, enter 1. If you want the total carbon to be fixed, enter 2.

Seawater Salinity: If you want seawater salinity to govern the calculations, enter 1 for Yes, and 0 for No.

Practical Salinity: If Yes in the above line, enter S_P. If No, enter 0.0.

Calcite Supersaturation in Seawater: If you want this to be considered, enter 1 for Yes, or 0 for No.

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.

Strontium (m/kg): Enter strontium molality (moles/kg(water)). Otherwise, enter 0.0.

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

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

Aluminum (m/kg): Enter aluminum molality (moles/kg(water)). Otherwise, enter 0.0.

Silicon (m/kg): Enter silicon molality (moles/kg(water)). Otherwise, enter 0.0.

Ammonium (m/kg): Enter ammonium molality (moles/kg(water)). Otherwise, enter 0.0.

If Iron, Aluminum, Silicon, Alkalinity, or Ammonia-Ammonium are selected, then choose an acidity option:

Acidity ignored(Option 1), enter 1.

Acidity fixed by pH(Option 2), enter 2.

Acidity fixed by H^+ ion concentration(Option 3), enter 3.

Acidity fixed by alkalinity(Option 4), enter 4.

Acidity fixed by NH_3(aq) and NH_4(aq)(Option 5), enter 2.

Initial pH: Option 1, enter 0; Option 2, enter pH; Options 3 and 4, enter an approximate pH; Option 5, enter 10.

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

Bromide (m/kg): Enter bromide molality (moles/kg(water)). Otherwise, enter 0.0.

Perchlorate (m/kg): Enter perchlorate 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.

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(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 HNO_3) and leave other acid partial pressure unspecified (e.g., H_2SO_4 = 0.0).

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

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

Boron (m/kg): Enter boron molality (moles/kg(water)). Otherwise, enter 0.0.

Fluoride (m/kg): Enter fluoride molality (moles/kg(water)). Otherwise, enter 0.0.

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

Initial CO_2(bars): If alkalinity > 0.0 or CO_2 hydrates are simulated, then specify the initial concentration of CO_2(g) in bars.

Mole Fraction of CO_2: Enter the mole fraction of CO_2(g) for the system (mole fraction = P_{CO2}/total pressure). For pure CO_2, enter 1.0. If 0.0, then CO_2(g) is fixed and independent of total pressure.

O_2(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 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 CH_4(bars): If CH_4 hydrates are simulated, then specify the initial concentration of CH_4(g) in bars.

Mole Fraction of CH_4: Enter the mole fraction of CH_4(g) for the system (mole fraction = P_{CH4}/total pressure). For pure CH_4, enter 1.0. If 0.0, then CH_4(g) is fixed and independent of total pressure.

Mixed CH_4-CO_2 Gas Hydrate?: If both CH_4(g) and CO_2(g) are specified as inputs, then you can use this data to estimate the stability of a mixed CH_4-CO_2 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Initial NH_3(bars): If NH_3(g) are inputs, then specify the initial concentration of NH_3(g) in bars. Do not enter positive values (> 0) for both NH_3(bars) and NH_3(aq).

Initial NH_3(aq): If NH_3(aq) are inputs, then enter NH_3(aq) molality (moles/kg(water)). Do not enter positive values (> 0) for both NH_3(bars) and NH_3(aq).

Molar to Molal Conversion?: If you want to convert molar data into molal concentrations, then enter (YES = 1) or (NO = 0). If yes, then:

Salinity/liter: You must enter the total aqueous salinity (g salt/liter), which can be calculated from molar data [g salt/liter = $\sum$(moles/liter) x (g salt/mole)]. In the case depicted in Table 7, the SL value is 316.57 g salt/liter (5.417 x 58.44).

Initial Temperature(K): Enter the temperature in absolute degrees (K) for start of simulation (e.g., 273.15).

For Temperature Change Pathway(1):

Final Temperature(K): Enter final temperature of simulation (e.g., 263.15).

Temperature Decrement(K): The temperature interval between simulations (e.g. 1). For the above temperature designations, the model would calculate equilibrium starting at 273.15 K and ending at 263.15 K at 1 K intervals. If you want to change the decrement in a run (e.g., to reduce the step size near an equilibrium), see File "NUANCES.txt."

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 Files "NUANCES.txt."

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 File "NUANCES."

Table 3. Input.txt. This is the main input file for applications of FREZCHEM. In this particular case, the model simulates a perchlorate chemistry from 273.15 K to 263.15 K (Table 6).

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TITLE: This is a Mars Phoenix test case.
1, FREEZE(1) OR EVAPORATION(2) OR PRESSURE(3) SCENARIO ? CALLED PATH BELOW.
2, EQUILIBRIUM(1) OR FRACTIONAL(2) CRYSTALLIZATION?
1, OPEN(1) OR CLOSED(2) CARBON SYSTEM?
0, WANT SEAWATER SALINITY(Sp) TO GOVERN THE CALCULATIONS,Y=1,N=0.
0.0, IF YES ABOVE, ENTER SEAWATER PRACTICAL SALINITY(Sp) OR 0.0.
0, WANT SEAWATER CARBONATE SUPERSATURATION TO BE CONSIDERED? Y=1,N=0.
1.5E-3, SODIUM(M/KG).
0.3E-3, POTASSIUM(M/KG).
0.4E-3, CALCIUM(M/KG).
2.5E-3, MAGNESIUM(M/KG).
0.00, STRONTIUM(M/KG).
0.00, FERROUS IRON(M/KG).
0.00, FERRIC IRON (M/KG).
0.00, ALUMINUM(M/KG).
0.00, SILICA (M/KG).
0.00, AMMONIUM(M/KG).

FOR FE,AL,SI, AND ALKALINE CHEMISTRIES,DO YOU WANT ACIDITY
IGNORED(1),OR FIXED BY PH(2), OR ACIDITY(3), OR
ALKALINITY(4)? IF YES, THEN ENTER NUM. NOTE THAT OPTIONS 3
AND 4 REQUIRE A FURTHER SPECIFICATION BELOW. OPTIONS 2-4
WILL ADJUST SOLUTION-PHASE CHARGE BALANCE AS AL, FE, OR SI
REACTIONS PRODUCE ACIDITY BY ASSUMING H+ REACTS WITH ROCKS
TO RELEASE NA,K,CA,MG,OR FE(II) IONS. SOME OF THE LATTER
IONS MUST BE PRESENT AS INPUT TO SERVE AS AN ION SINK/SOURCE.
FOR NH3(AQ) + NH4(AQ) CASE, SET OPTION = 2, WITH PH = 10.0.

4, SPECIFY ABOVE ACIDITY OPTION.
7.70, SPECIFY INITIAL PH.
0.45E-3, CHLORIDE(M/KG).
0.00, BROMIDE(M/KG).
3.0E-3, PERCHLORATE(M/KG).
0.8E-3, SULFATE(M/KG).
0.00, NITRATE(M/KG).
2.55E-3, ALKALINITY(EQUIVALENTS/KG).
0.00, ACIDITY(EQUIVALENTS/KG).
0.00, IF YOU WANT TO SPECIFY HCL(BARS), ENTER VALUE HERE.
0.00, IF YOU WANT TO SPECIFY HNO3(BARS), ENTER VALUE HERE.
0.00, IF YOU WANT TO SPECIFY H2SO4(BARS), ENTER VALUE HERE.
0.00, BORON (M/KG).
0.00, FLUORIDE(M/KG).
1.01325, INITIAL TOTAL PRESSURE(BARS).
3.0E-3, INITIAL CO2(BARS).
0.0, ENTER MOLE FRACTION OF CO2, 0=FIXED CO2, 1=PURE CO2.
0.00, INITIAL O2(BARS).
0.0, INITIAL CH4(BARS).
0.0, ENTER MOLE FRACTION OF CH4, 0=FIXED CHR, 1=PURE CH4.
0, CONSIDER A MIXED CO2-CH4 GAS HYDRATE(YES=1, NO=0)?
0.00, INITIAL NH3(G)(BARS), DO NOT INCLUDE BOTH NH3 INPUTS.
0.00, INITIAL NH3(AQ)(M/KG), DO NOT INCLUDE BOTH NH3 INPUTS.
0, MOLAR TO MOLAL CONVERSION? YES=1,NO=0.
0.0, IF YES ABOVE, ENTER SALINITY(G)/LITER.
273.15, INITIAL TEMPERATURE(K).
263.15, FINAL TEMPERATURE(K), IF PATH =1, OTHERWISE, SET = 0.
1.00, TEMPERATURE DECREMENT(K), IF PATH = 1, OTHERWISE, SET = 0.
1000, INITIAL WATER(G), IF PATH = 2, OTHERWISE, SET = 1000.
0.00, FINAL WATER (G), IF PATH = 2, OTHERWISE, SET = 0.
```

```
0, WATER DECREMENT(K), IF PATH = 2, OTHERWISE, SET = 0.
0, FINAL PRESSURE(BARS), IF PATH = 3, OTHERWISE, SET = 0.
0, PRESSURE INCREMENT(BARS), IF PATH = 3, OTHERWISE, SET = 0.
```

Table 4. Inputting Gases into 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	0	0	1
9. INITIAL NH3	0	USER SPECIFICATION	0

	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	0
6. INITIAL CH4	USER SPECIFICATION
7. MOLE FRACTION OF CH4	USER SPECIFICATION
8. MIXED CH4-CO2 GAS HYDRATE	1
9. INITIAL NH3	0

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 FC13.3 lines 300 and 316.

Table 5. Minor input files for FREZCHEM 13.3

(A). SOLIDPHASE.txt

```
0, WANT ALL SOLID PHASES TO BE REMOVED, YES=1, NO=0.
2, WANT SPECIFIC SOLID PHASES REMOVED, SPECIFY # OF CASES.
53, SPECIFY SAMPLE # TO BE REMOVED.
61, SPECIFY SAMPLE # TO BE REMOVED.
```

(B). SOLIDMASS.txt

```
0, WANT STARTING MINERALS TO CONTAIN MASS, YES=1, NO=0.
1, SPECIFY NUMBER OF MINERALS TO HAVE INITIAL MASS.
61 10.000, SPECIFY MINERAL NUMBER AND MASS(MOLES).
```

(C). NUANCES.txt

```
0, WANT TO REDUCE TEMPERATURE DECREMENT AT LOWER T? YES=1, NO=0.
263.15 1.0, TEMPERATURE AND ΔT, WHERE CHANGE SHOULD BE MADE.
259.15 0.1, TEMPERATURE AND ΔT, WHERE CHANGE SHOULD BE MADE.
0, WANT TO REDUCE WATER DECREMENT AT LOWER WATER? YES=1,NO=0.
100 1, WATER CONTENT AND ΔH2O, WHERE CHANGE SHOULD BE MADE.
10 0.1, WATER CONTENT AND ΔH2O, WHERE CHANGE SHOULD BE MADE.
0, WANT TO INCREASE(OR DECREASE) PRESSURE INCREMENT AT HIGHER P? YES = 1, N=0.
17 1, PRESSURE AND ΔP, WHERE CHANGE SHOULD BE MADE.
50 10, PRESSURE AND ΔP, WHERE CHANGE SHOULD BE MADE.
```

Model Outputs.

"Ion.Str." is the ionic strength of the equilibrium solution (see Table 6). "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 formed ice between 264.15 K and 263.15 K. The total ice that formed between 273 and 263 is 998.50 g (55.425 x 18.0153). 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 at 273 K. "Final Conc." are the equilibrium concentrations at 263 K. Act. coef. (activity coefficient) and activity are self-explanatory. Moles are the # of moles in the solution phase. For the major constituents, the "Mass Balance" column should generally 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 264 K and 263 K), while accum. moles represent the total precipitate (e.g., between 273 K and 263 K).

Table 6 is a case where we examined a predominantly sodium/magnesium, perchlorate/alkaline system for the Mars Phoenix site (see the Input.txt file in Table 3). During the freezing process from 273 K to 263 K, 99.85 % of the original water at 273 K precipitated as ice, largely because the initial solution at 273 K was dilute. For example, the ionic strength changed from 0.0113 m at 273 K to 4.43 m at 263 K (Table 6). The pH of the system that began at 7.58 at 273 K did not change at 263 K. During this 10 K drop in temperature, ice, gypsum, calcite, hydromagnesite, meridianiite, and $KClO_4$ precipitated (Table 6). In this simulation, 99.3 % of K precipitated as $KClO_4$ and 91.4 % of Ca precipitated as calcite due to the relative insolubility of these salts.

Table 7 is a case where we converted molar into molal concentrations. In the upper table there are three columns labeled rho, SA, and CF that represent model calculated estimates of density (kg(soln.)/liter or g/cm^3), absolute salinity [g salt/kg(soln.)], and the conversion factor [liters/kg(H_2O)]. The iterations quickly converted molar concentrations (5.4170 moles/liter under Initial Conc.) into molal concentrations [6.1458 moles/kg(H_2O) under Final Conc.]. In addition to inputs of molar concentrations, this algorithm also requires salinity on a liter basis(SL)(see Table 3). In this case, the SL value is 316.57 g/liter [= 5.417 x 58.44 (molecular weight of NaCl)]. So even with no prior knowledge about solution density (the model arbitrarily

assigns initial density = 1.00 g/cm^3), we were able to quickly calculate density and convert molar to molal concentrations. In turn, molal concentrations could be directly imported into FREZCHEM to explore geochemical processes. Note that all the potential solid phases were assigned high solubility products to prevent their precipitation (Table 7). FORTRAN model inputs to accomplish this negation of solid phases are in the SOLIDPHASE.txt file in Table 5 and must be implemented by the user. See the previously cited Marion (2007) paper for a fuller discussion of the techniques used in this algorithm.

Table 8 is an input file for a Titan simulation from 273 K to 173 K that is dominated with NH_3(aq), NH_3(g), and NH_4(aq). Table 9 is the output of this simulation after the initial temperature at 273 K dropped to 173 K. At 173 K, ice had formed and methane hydrate, NH_4Cl, and $(NH_4)_2SO_4$ had precipitated (Table 9). NH_3(aq), which started at 10.0 molal, has risen to 36.27 molal that is approaching the eutectic where $NH_3 \bullet 2H_2O$ would precipitate. In this case, the pH started at 10.0 (Table 8) and rose to 18.03 (Table 9). The latter may not be accurate.

Table 6. TITLE: This is a Mars Phoenix test case.

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
263.15	4.4341	1.190748	1.1547	1.4335	0.15936	1.0132

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Moles	Mass Balance
NA	0.15000E-02	1.0464	0.36262	0.37944	0.15000E-02	0.15000E-02
K	0.30000E-03	0.14507E-02	0.14468	0.20988E-03	0.20795E-05	0.30000E-03
CA	0.39960E-03	0.19102E-01	0.13255	0.25320E-02	0.27383E-04	0.40000E-03
MG	0.24983E-02	0.97242	0.62766	0.61035	0.13940E-02	0.25000E-02
H	0.22216E-07	0.30313E-07	0.85842	0.26022E-07	0.43455E-10	
MGOH	0.13644E-07	0.37543E-05	0.27618	0.10369E-05	0.53819E-08	
CL	0.45000E-03	0.31392	0.89489	0.28092	0.45000E-03	0.45000E-03
SO4	0.80000E-03	0.41156	0.21534E-01	0.88625E-02	0.58997E-03	0.80000E-03
OH	0.64370E-07	0.82155E-07	0.17013	0.13977E-07	0.11777E-09	
HCO3	0.25417E-02	0.85965E-02	0.26401	0.22696E-02	0.12323E-04	0.25500E-02
CO3	0.20718E-05	0.15711E-03	0.87551E-02	0.13755E-05	0.22522E-06	
HSO4	0.00000	0.13489E-07	0.64365	0.86819E-08	0.19336E-10	
CLO4	0.30000E-02	1.8849	2.3245	4.3815	0.27021E-02	0.30000E-02
CO2	0.22865E-03	0.37351E-03	0.94650	0.35353E-03	0.53543E-06	
CACO3	0.39907E-06	0.46792E-05	1.0000	0.46792E-05	0.67076E-08	
MGCO3	0.16568E-05	0.44646E-03	1.0000	0.44646E-03	0.64000E-06	
CO2(BAR)	0.30000E-02	0.30000E-02	0.99212	0.29764E-02	0.00000	
H2O(BAR)	0.61153E-02			.25954E-02		
H2O(L)	55.508			.90762	0.79572E-01	55.508

Solid SPECIES	Moles	Equil. Constant	Accum. Moles
ICE	0.88460E-02	0.90762	55.426
NACL.2H2O	0.00000	12.571	0.00000
NACL	0.00000	27.853	0.00000
KCL	0.00000	2.5902	0.00000
CACL2.6H2O	0.00000	1252.1	0.00000
MGCL2.6H2O	0.00000	55413.	0.00000
MGCL2.8H2O	0.00000	4682.9	0.00000
MGCL2.12H2O	0.00000	199.88	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	0.82765E-06	0.18490E-04	0.68720E-05
CASO4	0.00000	0.94050E-04	0.00000
MGSO4.11H2O	0.20316E-03	0.18624E-02	0.20316E-03
NA2SO4.3K2SO4	0.00000	0.30930E-09	0.00000
CACO3(CALCITE)	0.00000	0.43033E-08	0.36574E-03
MGCO3	0.00000	0.10000E+21	0.00000
MGCO3.3H2O	0.00000	0.15229E-04	0.00000
MGCO3.5H2O	0.00000	0.96139E-05	0.00000
CACO3.6H2O	0.00000	0.32915E-07	0.00000
NAHCO3	0.00000	0.14567	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	0.31881E-06	0.52738E-34	0.22556E-03
CAMG(CO3)2	0.00000	0.10000E+21	0.00000
NA2CO3.7H2O	0.00000	0.49255E-01	0.00000
KHCO3	0.00000	0.50021	0.00000
CACO3(ARAGONITE)	0.00000	0.63986E-08	0.00000
CACO3(VATERITE)	0.00000	0.20194E-07	0.00000
HNO3.3H2O	0.00000	347.82	0.00000
KNO3	0.00000	0.80269E-01	0.00000

NANO3	0.00000	2.3217	0.00000
HCL.3H2O	0.00000	12483.	0.00000
H2SO4.6.5H2O	0.00000	22.486	0.00000
H2SO4.4H2O	0.00000	999.90	0.00000
HCL.6H2O	0.00000	1000.0	0.00000
NANO3.NA2SO4.2H2O	0.00000	0.84024E-01	0.00000
NA3H(SO4)2	0.00000	0.14086	0.00000
NAHSO4.H2O	0.00000	30.543	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	0.97421	0.00000
MGSO4.H2O	0.00000	11.329	0.00000
FESO4.7H2O	0.00000	0.13913E-02	0.00000
FESO4.H2O	0.00000	0.36005	0.00000
FECL2.6H2O	0.00000	3983.3	0.00000
FECL2.4H2O	0.00000	17767.	0.00000
FECO3	0.00000	0.15200E-10	0.00000
FE(OH)3	0.00000	0.19277E+06	0.00000
CO2.6H2O	0.00000	3.8247	0.00000
CH4.6H2O	0.00000	9.8303	0.00000
FECL3.10H20	0.00000	0.67445E-02	0.00000
FECL3.6H2O	0.00000	0.81059E-01	0.00000
FECL3.2KCL.H20	0.00000	0.34624	0.00000
FE2(SO4)3	0.00000	17467.	0.00000
FE2(SO4)3.2K2SO4.14H	0.00000	0.14132E-13	0.00000
K2SO4.FESO4.6H2O	0.00000	0.26655E-05	0.00000
NA2SO4.FESO4.4H2O	0.00000	0.12041E-02	0.00000
FE2(SO4)3.9H2O	0.00000	1.2562	0.00000
FE2(SO4)3.H2SO4.8H2O	0.00000	1131.0	0.00000
KFE3(SO4)2(OH)6	0.00000	0.62069E-09	0.00000
NAFE3(SO4)2(OH)6	0.00000	0.16520E-02	0.00000
H3OFE3(SO4)2(OH)6	0.00000	0.17877	0.00000
a-FE2O3	0.00000	1273.6	0.00000
a-FEO(OH)	0.00000	43.380	0.00000
g-FEO(OH)	0.00000	3733.4	0.00000
FEO(OH)3/4(SO4)1/8	0.00000	735.55	0.00000
FESO4.4H2O	0.00000	0.20472E-01	0.00000
FE2(SO4)3.7H2O	0.00000	9.9758	0.00000
FE(II)FE(III)4(SO4)6	0.00000	0.26300E-18	0.00000
FE(III)5(SO4)6O(OH).	0.00000	0.36340E-18	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.21803E-16	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.34754E-09	0.00000
K2FE(II)5FE(III)4(SO	0.00000	0.31007E-30	0.00000
ALCL3.6H2O	0.00000	12997.	0.00000
AL2(SO4)3.17H2O	0.00000	0.10094E-05	0.00000
NABR	0.00000	0.00000	0.00000
MGBR2	0.00000	0.00000	0.00000
AL(OH)3	0.00000	0.24780E+11	0.00000
SIO2(QUARTZ)	0.00000	0.27438E-04	0.00000
SIO2(AMORPHOUS)	0.00000	0.90848E-03	0.00000
KAL3(SO4)2(OH)6	0.00000	0.53774E+06	0.00000
NAAL3(SO4)2(OH)6	0.00000	0.13264E+10	0.00000
KAL(SO4)2.12H2O	0.00000	0.41766E-07	0.00000
NAAL(SO4)2.12H2O	0.00000	0.22929E-04	0.00000
FESO4.AL2(SO4)3.22H2	0.00000	0.27653E-08	0.00000
AL2SI2O5(OH)4	0.00000	0.46066E+10	0.00000
MGSO4.AL2(SO4).22H2O	0.00000	0.96704E-08	0.00000
NACLO4.H2O	0.00000	62.358	0.00000
MG(CLO4)2.8H2O	0.00000	0.24261E+06	0.00000
CA(CLO4)2.6H2O	0.00000	0.84561E+06	0.00000
KCLO4	0.43075E-06	0.91970E-03	0.29792E-03
MG(CLO4)2.6H2O	0.00000	0.12054E+07	0.00000
NACLO4.2H2O	0.00000	35.934	0.00000

PRACTICAL SALINITY = 0.000000 ABSOLUTE SALINITY = 0.000000
pH= 7.58466 pHF= 7.51836 pHT= 7.35851 pH(SWS)= 7.35851

```
CONVERGENCE CRITERION =  0.100000 %
 Iterations =  6
```

Table 7. Conversion of a molar NaCl solution into a molal concentration.

rho	SA	CF
1.17800	268.735	1.16086
1.20181	263.411	1.12964
1.19726	264.411	1.13547
1.19812	264.223	1.13437
1.19796	264.259	1.13458
1.19799	264.252	1.13454
1.19798	264.253	1.13455
1.19798	264.253	1.13454
1.19798	264.253	1.13455

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
298.15	6.1458	1.19798	1.2846	1000.0	0.00000	1.0132

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Moles	Mass Balance
NA	5.4170	6.1458	1.0109	6.2128	6.1458	6.1458
CL	5.4170	6.1458	1.0109	6.2128	6.1458	6.1458
H2O(BAR)	0.24948E-01			.23840E-01		
H2O(L)	55.508			.75242	55.508	55.508

Solid SPECIES	Moles	Equil. Constant	Accum. Moles
ICE	0.00000	0.10000E+31	0.00000
NACL.2H2O	0.00000	0.10000E+31	0.00000
NACL	0.00000	0.10000E+31	0.00000
KCL	0.00000	0.10000E+31	0.00000
CACL2.6H2O	0.00000	0.10000E+31	0.00000
MGCL2.6H2O	0.00000	0.10000E+31	0.00000
MGCL2.8H2O	0.00000	0.10000E+31	0.00000
MGCL2.12H2O	0.00000	0.10000E+31	0.00000
KMGCL3.6H2O	0.00000	0.10000E+31	0.00000
CACL2.2MGCL2.12H2O	0.00000	0.10000E+31	0.00000
NA2SO4.10H2O	0.00000	0.10000E+31	0.00000
NA2SO4	0.00000	0.10000E+31	0.00000
MGSO4.6H2O	0.00000	0.10000E+31	0.00000
MGSO4.7H2O	0.00000	0.10000E+31	0.00000
K2SO4	0.00000	0.10000E+31	0.00000
MGSO4.K2SO4.6H2O	0.00000	0.10000E+31	0.00000
NA2SO4.MGSO4.4H2O	0.00000	0.10000E+31	0.00000
CASO4.2H2O	0.00000	0.10000E+31	0.00000
CASO4	0.00000	0.10000E+31	0.00000
MGSO4.11H2O	0.00000	0.10000E+31	0.00000
NA2SO4.3K2SO4	0.00000	0.10000E+31	0.00000
CACO3(CALCITE)	0.00000	0.10000E+31	0.00000
MGCO3	0.00000	0.10000E+31	0.00000
MGCO3.3H2O	0.00000	0.10000E+31	0.00000
MGCO3.5H2O	0.00000	0.10000E+31	0.00000
CACO3.6H2O	0.00000	0.10000E+31	0.00000
NAHCO3	0.00000	0.10000E+31	0.00000
NA2CO3.10H2O	0.00000	0.10000E+31	0.00000
NAHCO3.NA2CO3.2H2O	0.00000	0.10000E+31	0.00000
3MGCO3.MG(OH)2.3H2O	0.00000	0.10000E+31	0.00000
CAMG(CO3)2	0.00000	0.10000E+31	0.00000
NA2CO3.7H2O	0.00000	0.10000E+31	0.00000
KHCO3	0.00000	0.10000E+31	0.00000
CACO3(ARAGONITE)	0.00000	0.10000E+31	0.00000
CACO3(VATERITE)	0.00000	0.10000E+31	0.00000
HNO3.3H2O	0.00000	0.10000E+31	0.00000
KNO3	0.00000	0.10000E+31	0.00000
NANO3	0.00000	0.10000E+31	0.00000
HCL.3H2O	0.00000	0.10000E+31	0.00000
H2SO4.6.5H2O	0.00000	0.10000E+31	0.00000
H2SO4.4H2O	0.00000	0.10000E+31	0.00000

HCL.6H2O	0.00000	0.10000E+31	0.00000
NANO3.NA2SO4.2H2O	0.00000	0.10000E+31	0.00000
NA3H(SO4)2	0.00000	0.10000E+31	0.00000
NAHSO4.H2O	0.00000	0.10000E+31	0.00000
K3H(SO4)2	0.00000	0.10000E+31	0.00000
K5H3(SO4)4	0.00000	0.10000E+31	0.00000
K8H6(SO4)7.H2O	0.00000	0.10000E+31	0.00000
KHSO4	0.00000	0.10000E+31	0.00000
MGSO4.H2O	0.00000	0.10000E+31	0.00000
FESO4.7H2O	0.00000	0.10000E+31	0.00000
FESO4.H2O	0.00000	0.10000E+31	0.00000
FECL2.6H2O	0.00000	0.10000E+31	0.00000
FECL2.4H2O	0.00000	0.10000E+31	0.00000
FECO3	0.00000	0.10000E+31	0.00000
FE(OH)3	0.00000	0.10000E+31	0.00000
CO2.6H2O	0.00000	0.10000E+31	0.00000
CH4.6H2O	0.00000	0.10000E+31	0.00000
FECL3.10H20	0.00000	0.10000E+31	0.00000
FECL3.6H2O	0.00000	0.10000E+31	0.00000
FECL3.2KCL.H20	0.00000	0.10000E+31	0.00000
FE2(SO4)3	0.00000	0.10000E+31	0.00000
FE2(SO4)3.2K2SO4.14H	0.00000	0.10000E+31	0.00000
K2SO4.FESO4.6H2O	0.00000	0.10000E+31	0.00000
NA2SO4.FESO4.4H2O	0.00000	0.10000E+31	0.00000
FE2(SO4)3.9H2O	0.00000	0.10000E+31	0.00000
FE2(SO4)3.H2SO4.8H2O	0.00000	0.10000E+31	0.00000
KFE3(SO4)2(OH)6	0.00000	0.10000E+31	0.00000
NAFE3(SO4)2(OH)6	0.00000	0.10000E+31	0.00000
H3OFE3(SO4)2(OH)6	0.00000	0.10000E+31	0.00000
a-FE2O3	0.00000	0.10000E+31	0.00000
a-FEO(OH)	0.00000	0.10000E+31	0.00000
g-FEO(OH)	0.00000	0.10000E+31	0.00000
FEO(OH)3/4(SO4)1/8	0.00000	0.10000E+31	0.00000
FESO4.4H2O	0.00000	0.10000E+31	0.00000
FE2(SO4)3.7H2O	0.00000	0.10000E+31	0.00000
FE(II)FE(III)4(SO4)6	0.00000	0.10000E+31	0.00000
FE(III)5(SO4)6O(OH).	0.00000	0.10000E+31	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.10000E+31	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.10000E+31	0.00000
K2FE(II)5FE(III)4(SO	0.00000	0.10000E+31	0.00000
ALCL3.6H2O	0.00000	0.10000E+31	0.00000
AL2(SO4)3.17H2O	0.00000	0.10000E+31	0.00000
NABR	0.00000	0.10000E+31	0.00000
MGBR2	0.00000	0.10000E+31	0.00000
AL(OH)3	0.00000	0.10000E+31	0.00000
SIO2(QUARTZ)	0.00000	0.10000E+31	0.00000
SIO2(AMORPHOUS)	0.00000	0.10000E+31	0.00000
KAL3(SO4)2(OH)6	0.00000	0.10000E+31	0.00000
NAAL3(SO4)2(OH)6	0.00000	0.10000E+31	0.00000
KAL(SO4)2.12H2O	0.00000	0.10000E+31	0.00000
NAAL(SO4)2.12H2O	0.00000	0.10000E+31	0.00000
FESO4.AL2(SO4)3.22H2	0.00000	0.10000E+31	0.00000
AL2SI2O5(OH)4	0.00000	0.10000E+31	0.00000
MGSO4.AL2(SO4).22H2O	0.00000	0.10000E+31	0.00000

Iterations = 9

Table 8. A Titan simulation. This is the main input file for applications of FREZCHEM. In this particular case, the model simulates a NH3-NH4 chemistry from 273.15 K to 173.15 K (Table 9)(Icarus, 2012, 220:932-946).

```
TITLE: This is a Titan NH3-NH4 case.
1, FREEZE(1) OR EVAPORATION(2) OR PRESSURE(3) SCENARIO ? CALLED PATH BELOW.
2, EQUILIBRIUM(1) OR FRACTIONAL(2) CRYSTALLIZATION?
1, OPEN(1) OR CLOSED(2) CARBON SYSTEM?
0, WANT SEAWATER SALINITY(Sp) TO GOVERN THE CALCULATIONS,Y=1,N=0.
0.0, IF YES ABOVE, ENTER SEAWATER PRACTICAL SALINITY(Sp) OR 0.0.
0, WANT SEAWATER CARBONATE SUPERSATURATION TO BE CONSIDERED? Y=1,N=0.
0.00, SODIUM(M/KG).
0.00, POTASSIUM(M/KG).
0.00, CALCIUM(M/KG).
0.00, MAGNESIUM(M/KG).
0.00, STRONTIUM(M/KG).
0.00, FERROUS IRON(M/KG).
0.00, FERRIC IRON (M/KG).
0.00, ALUMINUM(M/KG).
0.00, SILICA (M/KG).
3.00, AMMONIUM(M/KG).

FOR FE,AL,SI, AND ALKALINE CHEMISTRIES,DO YOU WANT ACIDITY
IGNORED(1),OR FIXED BY PH(2), OR ACIDITY(3), OR
ALKALINITY(4)? IF YES, THEN ENTER NUM. NOTE THAT OPTIONS 3
AND 4 REQUIRE A FURTHER SPECIFICATION BELOW. OPTIONS 2-4
WILL ADJUST SOLUTION-PHASE CHARGE BALANCE AS AL, FE, OR SI
REACTIONS PRODUCE ACIDITY BY ASSUMING H+ REACTS WITH ROCKS
TO RELEASE NA,K,CA,MG,OR FE(II) IONS. SOME OF THE LATTER
IONS MUST BE PRESENT AS INPUT TO SERVE AS AN ION SINK/SOURCE.
FOR NH3(AQ) + NH4(AQ) CASE, SET OPTION = 2, WITH PH = 10.0.

2, SPECIFY ABOVE ACIDITY OPTION.
10.00, SPECIFY INITIAL PH.
1.00, CHLORIDE(M/KG).
0.00, BROMIDE(M/KG).
0.00, PERCHLORATE(M/KG).
1.00, SULFATE(M/KG).
0.00, NITRATE(M/KG).
0.00, ALKALINITY(EQUIVALENTS/KG).
0.00, ACIDITY(EQUIVALENTS/KG).
0.00, IF YOU WANT TO SPECIFY HCL(BARS), ENTER VALUE HERE.
0.00, IF YOU WANT TO SPECIFY HNO3(BARS), ENTER VALUE HERE.
0.00, IF YOU WANT TO SPECIFY H2SO4(BARS), ENTER VALUE HERE.
0.00, BORON (M/KG).
0.00, FLUORIDE(M/KG).
10.0, INITIAL TOTAL PRESSURE(BARS).
0.00, INITIAL CO2(BARS).
0.0, ENTER MOLE FRACTION OF CO2, 0=FIXED CO2, 1=PURE CO2.
0.00, INITIAL O2(BARS).
5.00, INITIAL CH4(BARS).
0.0, ENTER MOLE FRACTION OF CH4, 0=FIXED CHR, 1=PURE CH4.
0, CONSIDER A MIXED CO2-CH4 GAS HYDRATE(YES=1, NO=0)?
0.00, INITIAL NH3(G)(BARS), DO NOT INCLUDE BOTH NH3 INPUTS.
10.00, INITIAL NH3(AQ)(M/KG), DO NOT INCLUDE BOTH NH3 INPUTS.
0, MOLAR TO MOLAL CONVERSION? YES=1,NO=0.
0.0, IF YES ABOVE, ENTER SALINITY(G)/LITER.
273.15, INITIAL TEMPERATURE(K).
173.15, FINAL TEMPERATURE(K), IF PATH =1, OTHERWISE, SET = 0.
5.00, TEMPERATURE DECREMENT(K), IF PATH = 1, OTHERWISE, SET = 0.
1000, INITIAL WATER(G), IF PATH = 2, OTHERWISE, SET = 1000.
```

```
0.00, FINAL WATER (G), IF PATH = 2, OTHERWISE, SET = 0.
0, WATER DECREMENT(K), IF PATH = 2, OTHERWISE, SET = 0.
0, FINAL PRESSURE(BARS), IF PATH = 3, OTHERWISE, SET = 0.
0, PRESSURE INCREMENT(BARS), IF PATH = 3, OTHERWISE, SET = 0.
```

Table 9. A Titan simulation (Icarus, 2012. 220:932-946).

TITLE: This is a Titan NH3-NH4 case.

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
173.15	1.3862	0.8759973	1.4671	275.69	0.00000	10.000

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Moles	Mass Balance
H	0.00000	0.77718E-18	1.1999	0.93250E-18	0.21426E-18	
NH4	3.0000	1.3861	0.40767	0.56509	0.38215	3.0000
CL	1.0000	1.3861	0.40768	0.56507	0.38213	1.0000
SO4	1.0000	0.41533E-04	909.86	0.37789E-01	0.11450E-04	1.0000
OH	0.00000	0.72284E-08	884.69	0.63948E-05	0.19928E-08	
HSO4	0.00000	0.38913E-16	0.56845	0.22120E-16	0.10728E-16	
NH3	10.000	36.272	3.5713	129.54	10.000	10.000
NH3(BAR)	0.00000	0.11087E-03	1.0000	0.11087E-03	0.00000	
CH4	0.00000	9.1645	1.0000	9.1645	0.00000	
CH4(BAR)	0.00000	5.0000	0.92416	4.6208	0.00000	
H2O(BAR)	0.00000			.92816E-08		
H2O(L)	55.508			.27966	15.303	55.509

Solid SPECIES	Moles	Equil. Constant	Accum. Moles
ICE	0.00000	0.45268	18.629
NACL.2H2O	0.00000	81.415	0.00000
NACL	0.00000	0.84048E-02	0.00000
KCL	0.00000	0.65448E-02	0.00000
CACL2.6H2O	0.00000	0.21833E-05	0.00000
MGCL2.6H2O	0.00000	30.019	0.00000
MGCL2.8H2O	0.00000	0.54878E-03	0.00000
MGCL2.12H2O	0.00000	0.10669E-33	0.00000
KMGCL3.6H2O	0.00000	0.39141E-01	0.00000
CACL2.2MGCL2.12H2O	0.00000	0.34336E+25	0.00000
NA2SO4.10H2O	0.00000	0.65083E-08	0.00000
NA2SO4	0.00000	0.44571	0.00000
MGSO4.6H2O	0.00000	0.10811E-01	0.00000
MGSO4.7H2O	0.00000	0.35567E-04	0.00000
K2SO4	0.00000	0.87467E-05	0.00000
MGSO4.K2SO4.6H2O	0.00000	0.32453E-11	0.00000
NA2SO4.MGSO4.4H2O	0.00000	0.18068E-02	0.00000
CASO4.2H2O	0.00000	0.15351E-07	0.00000
CASO4	0.00000	0.11270E-05	0.00000
MGSO4.11H2O	0.00000	0.43729E-06	0.00000
NA2SO4.3K2SO4	0.00000	0.47521E-15	0.00000
CACO3(CALCITE)	0.00000	0.19496E-08	0.00000
MGCO3	0.00000	0.18880E-04	0.00000
MGCO3.3H2O	0.00000	1.9706	0.00000
MGCO3.5H2O	0.00000	0.48181E+22	0.00000
CACO3.6H2O	0.00000	0.37849E-11	0.00000
NAHCO3	0.00000	49.470	0.00000
NA2CO3.10H2O	0.00000	0.46854E-04	0.00000
NAHCO3.NA2CO3.2H2O	0.00000	0.45061E-02	0.00000
3MGCO3.MG(OH)2.3H2O	0.00000	0.86235E-23	0.00000
CAMG(CO3)2	0.00000	0.98928E-12	0.00000
NA2CO3.7H2O	0.00000	0.31124E-03	0.00000
KHCO3	0.00000	0.42063E-01	0.00000
CACO3(ARAGONITE)	0.00000	0.38711E-08	0.00000
CACO3(VATERITE)	0.00000	0.26699E-07	0.00000
HNO3.3H2O	0.00000	0.62103	0.00000
KNO3	0.00000	0.51379E-05	0.00000
NANO3	0.00000	0.15269E+11	0.00000
HCL.3H2O	0.00000	2894.2	0.00000
H2SO4.6.5H2O	0.00000	0.42082E-02	0.00000
H2SO4.4H2O	0.00000	0.25389	0.00000
HCL.6H2O	0.00000	146.93	0.00000
NANO3.NA2SO4.2H2O	0.00000	0.58559E+06	0.00000

NA3H(SO4)2	0.00000	0.93785E-49	0.00000
NAHSO4.H2O	0.00000	0.60938E+18	0.00000
K3H(SO4)2	0.00000	0.15135E-01	0.00000
K5H3(SO4)4	0.00000	0.41467E-10	0.00000
K8H6(SO4)7.H2O	0.00000	0.43211E-06	0.00000
KHSO4	0.00000	0.31505E-01	0.00000
MGSO4.H2O	0.00000	0.90352E+11	0.00000
FESO4.7H2O	0.00000	0.84993E-02	0.00000
FESO4.H2O	0.00000	4.8511	0.00000
FECL2.6H2O	0.00000	81.034	0.00000
FECL2.4H2O	0.00000	0.10524E+07	0.00000
FECO3	0.00000	0.19735E-09	0.00000
FE(OH)3	0.00000	0.36265E+14	0.00000
CO2.6H2O	0.00000	0.40474E-03	0.00000
CH4.6H2O	0.48527E-01	0.22105E-02	3.5960
FECL3.10H20	0.00000	0.43891E-12	0.00000
FECL3.6H2O	0.00000	0.16793	0.00000
FECL3.2KCL.H20	0.00000	0.81402E-14	0.00000
FE2(SO4)3	0.00000	0.22676E+30	0.00000
FE2(SO4)3.2K2SO4.14H	0.00000	0.19306E-13	0.00000
K2SO4.FESO4.6H2O	0.00000	0.96795E-09	0.00000
NA2SO4.FESO4.4H2O	0.00000	0.14419E-02	0.00000
FE2(SO4)3.9H2O	0.00000	0.13795E+12	0.00000
FE2(SO4)3.H2SO4.8H2O	0.00000	0.37146E+20	0.00000
KFE3(SO4)2(OH)6	0.00000	56.527	0.00000
NAFE3(SO4)2(OH)6	0.00000	0.53531E+12	0.00000
H3OFE3(SO4)2(OH)6	0.00000	0.58130E+23	0.00000
a-FE2O3	0.00000	0.42230E+17	0.00000
a-FEO(OH)	0.00000	0.10846E+09	0.00000
g-FEO(OH)	0.00000	0.10294E+12	0.00000
FEO(OH)3/4(SO4)1/8	0.00000	0.26660E+11	0.00000
FESO4.4H2O	0.00000	0.92593E-02	0.00000
FE2(SO4)3.7H2O	0.00000	0.13315E+16	0.00000
FE(II)FE(III)4(SO4)6	0.00000	1869.1	0.00000
FE(III)5(SO4)6O(OH).	0.00000	0.10855E+06	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.79320E-17	0.00000
FE(II)FE(III)2(SO4)4	0.00000	7.9464	0.00000
K2FE(II)5FE(III)4(SO	0.00000	0.34573E+07	0.00000
ALCL3.6H2O	0.00000	0.29269E-07	0.00000
AL2(SO4)3.17H2O	0.00000	0.69490E-08	0.00000
NABR	0.00000	0.00000	0.00000
MGBR2	0.00000	0.00000	0.00000
AL(OH)3	0.00000	0.18472E+22	0.00000
SIO2(QUARTZ)	0.00000	0.75777E-07	0.00000
SIO2(AMORPHOUS)	0.00000	0.32652E-04	0.00000
KAL3(SO4)2(OH)6	0.00000	0.45047E+30	0.00000
NAAL3(SO4)2(OH)6	0.00000	0.54098E+36	0.00000
KAL(SO4)2.12H2O	0.00000	0.19265E-10	0.00000
NAAL(SO4)2.12H2O	0.00000	0.25714E-05	0.00000
FESO4.AL2(SO4)3.22H2	0.00000	0.37090E-08	0.00000
AL2SI2O5(OH)4	0.00000	0.42725E+27	0.00000
MGSO4.AL2(SO4).22H2O	0.00000	0.12873E-07	0.00000
NACLO4.H2O	0.00000	0.22603	0.00000
MG(CLO4)2.8H2O	0.00000	0.54775E+07	0.00000
CA(CLO4)2.6H2O	0.00000	9140.1	0.00000
KCLO4	0.00000	0.23292E-04	0.00000
MG(CLO4)2.6H2O	0.00000	0.10053E+31	0.00000
NACLO4.2H2O	0.00000	0.42354	0.00000
NH4CL	0.42506E-01	0.31928	0.61787
NH42SO4	0.10009E-04	0.12067E-01	0.99999
NH3.H2O	0.00000	40.353	0.00000
NH4NO3	0.00000	0.30043E-01	0.00000
NH4HCO3	0.00000	0.33153E-03	0.00000
NH4CLO4	0.00000	0.49215E-04	0.00000
NH3.2H2O	0.00000	15.150	0.00000

pH= 18.0303 pHF= 18.1095 pHT= 16.4013 pH(SWS)= 16.4013

```
pHMacinnis =  18.2358 Temp. =  173.150


CONVERGENCE CRITERION =  0.100000 %
 Iterations =  263
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