FRIENDS OF FREZCHEM (Version 17)

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, methane, ethane, and propane 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 inputs (Tables 2-5, 8, and 10), and four examples of model outputs (Tables 6-7, 9 and 11).

This model is very much a work in progress. I may be adding new chemistries to the model in the next few years. I have not spent 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. Once you have a FREZCHEM model working, verify correctness from an example from published data (see examples below). If you have additional problems, contact me via e-mail (giles.marion@dri.edu). Indicate the FREZCHEM version you are using (e.g., FREZCHEM17) 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 17 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; (14) Marion et al. (2012). Modeling ammonia-ammonium aqueous chemistries in the Solar System's icy bodies. Icarus. 220:932-946; (15) Marion et al. (2013). Sulfite-sulfide-sulfate-carbonate equilibria with applications to Mars. Icarus. 225:342-351; (16) Marion et al (2014). Modeling nitrogen-gas, -liquid, -solid chemistries at low temperatures (173-298 K) with applications to Titan. Icarus. 236:1-8; and (17) Marion et al (2015). Modeling nitrogen and methane with ethane and propane gas hydrates at low temperatures (173-290 K) with applications to Titan. Icarus. 257:355-361.

Compared to earlier versions, this Version 17 of the FREZCHEM model contains new parameterizations dealing with ethane, propane, methane, and nitrogen species. Also, Versions 15-17 lowered the temperature level to 173 K (see Tables 8-11).

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 13-17 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 a previous Phoenix site calculation (Marion et al., 2010), we removed magnesite ($MgCO_3$) and dolomite [$CaMg(CO_3)_2$] from model calculations (Table 5A), which led to calcite ($CaCO_3$) and hydromagnesite [$3Mg(CO_3)_2 \cdot MgSO_4 \cdot 3H_2O$] precipitating. 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 5B); 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 5C). 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 17.1).

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	$Fe(OH)_3^0(aq)$	235	$SO_2^0(g)$
6	$MgOH^+(aq)$	21	$HSO_4^-(aq)$	206	$HNO_3(g)$	221	$Fe(OH)_4^-(aq)$	236	$SO_2^0(aq)$
7	$Fe^{2+}(aq)$	22	$NO_3^-(aq)$	207	$H_2SO_4(g)$	222	$Al(OH)^{2+}(aq)$	237	$H_2S^0(g)$
8	$FeOH^+(aq)$	23	$Br^-(aq)$	208	$H_2O(g)$	223	$Al(OH)_2^+(aq)$	238	$H_2S^0(aq)$
9	$Fe^{3+}(aq)$	24	$ClO_4^-(aq)$	209	$CO_2(g)$	224	$Al(OH)_3^0(aq)$	239	$N_2(g)$
10	$Al^{3+}(aq)$	25	$B(OH)_4^-(aq)$	210	$H_2O(l)$	225	$Al(OH)_4^-(aq)$	240	$N_2(aq)$
11	$NH_4^+(aq)$	26	$HSO_3^-(aq)$	211	$O_2(g)$	226	$Si(OH)_4^0(aq)$	241	$C_2H_6(g)$
		27	$SO_3^{2-}(aq)$	212	$O_2(aq)$	227	$SiO(OH)_3^-(aq)$	242	$C_2H_6(aq)$
		28	$HS^-(aq)$	213	$H_2(g)$	228	$SrCO_3^0(aq)$	243	$C_3H_8(g)$
		29	$S^{2-}(aq)$	214	$CH_4(g)$	229	$B(OH)_3^0(aq)$	244	$C_3H_8(aq)$
				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	$KAl_3(SO_4)_2(OH)_6(cr)$	139	$K_2SO_3(cr)$
40	$CaCl_2•2MgCl_2•12H_2O(cr)$	60	$4MgCO_3•Mg(OH)_2•4H_2O(cr)$	80	$MgSO_4•H_2O(cr)$	100	$H_3OFe_3(SO_4)_2(OH)_6(cr)$	120	$NaAl_3(SO_4)_2(OH)_6(cr)$	140	$Na_2SO_3•7H_2O(cr)$
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	$KAl_2(SO_4)_2•12H_2O(cr)$	141	$CaSO_3•0.5H_2O(cr)$
42	$Na_2SO_4(cr)$	62	$Na_2CO_3•7H_2O(cr)$	82	$FeSO_4•H_2O(cr)$	102	α-FeO(OH)(cr)	122	$NaAl(SO_4)_2•12H_2O(cr)$	142	$MgSO_3•6H_2O(cr)$
43	$MgSO_4•6H_2O(cr)$	63	$KHCO_3(cr)$	83	$FeCl_2•6H_2O(cr)$	103	γ-FeO(OH)(cr)	123	$FeSO_4•Al_2(SO_4)_3•22H_2O(cr)$	143	$FeSO_3•5H_2O(cr)$
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	$Al_2Si_2O_5(OH)_4(cr)$	144	$(NH_4)_2SO_3•H_2O(cr)$
45	$K_2SO_4(cr)$	65	$CaCO_3(cr,vaterite)$	85	$FeCO_3(cr)$	105	$FeSO_4•4H_2O(cr)$	125	$MgSO_4•Al_2(SO_4)_3•22H_2O(cr)$	145	$FeS_2(cr)$
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	$NaClO_4•H_2O(cr)$	146	$N_2•6H_2O(cr)$
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	$Mg(ClO_4)_2•8H_2O(cr)$	147	$CaSO_4•0.5H_2O(cr)$
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	$Ca(ClO_4)_2•6H_2O(cr)$	148	$C_2H_6•6H_2O(cr)$
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	$KClO_4(cr)$	149	$C_3H_8•6H_2O(cr)$
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 17) (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.

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.

Specify Initital pH. (e.g., 7.0)

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 with pH chemistries in the model.

Sulfite Alkalinity: Enter as equivalents/kg(water). If alkalinity = 0.0, then you must enter 0.0.

Sulfide Acidity: Enter as equivalents/kg(water). If acidity = 0.0, then you must enter 0.0.

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 is 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).

Initial N_2(bars): If the atmospheric concentration of nitrogen is known, then specify here. Otherwise, enter 0.0.

Mole Fraction of N_2: Enter the mole fraction of N_2(g) for the system (mole fraction = P_{N2}/total pressure). For pure N_2, enter 1.0. If 0.0, then N_2(g) is fixed and independent of total pressure.

Mixed N_2-CH_4 Gas Hydrate?: If both N_2(g) and CH_4(g) are specified as inputs, then you can use this data to estimate the stability of a mixed N_2-CH_4 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed N_2-CO_2 Gas Hydrate?: If both N_2(g) and CO_2(g) are specified as inputs, then you can use this data to estimate the stability of a mixed N_2-CO_2 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_2H_6-C_3H_8 Gas Hydrate?: If both C_2H_6(g) and C_3H_8(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_2H_6-C_3H_8 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_2H_6-CH_4 Gas Hydrate?: If both C_2H_6(g) and CH_4(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_2H_6-CH_4 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_3H_8-CH_4 Gas Hydrate?: If both C_3H_8(g) and CH_4(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_3H_8-CH_4 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_2H_6-N_2 Gas Hydrate?: If both C_2H_6(g) and N_2(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_2H_6-N_2 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_3H_8-N_2 Gas Hydrate?: If both C_3H_8(g) and N_2(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_3H_8-N_2 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_2H_6-CO_2 Gas Hydrate?: If both C_2H_6(g) and CO_2(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_2H_6-CO_2 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

Mixed C_3H_8-CO_2 Gas Hydrate?: If both C_3H_8(g) and CO_2(g) are specified as inputs, then you can use this data to estimate the stability of a mixed C_3H_8-CO_2 gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

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

Salinity/liter: If yes above, then 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 File "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.txt."

Table 3. Input.txt. This is the main input for applications of FREZCHEM.
In this particular case, the model simulates C2H6-C3H8 chemistry at 273.15 K.
See Table 6 for this account.

```
TITLE:  Ethane-Propane model parameters
1, FREEZE(1) OR EVAPORATION(2) OR PRESSURE(3) SCENARIO ? CALLED PATH BELOW.
2, EQUILIBRIUM(1) OR FRACTIONAL(2) CRYSTALLIZATION?
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.
1.00, 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).
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.

1, SPECIFY ABOVE ACIDITY OPTION
0.0, SPECIFY INITIAL PH.
1.00, CHLORIDE(M/KG).
0.00, BROMIDE(M/KG).
0.00, PERCHLORATE(M/KG).
0.00, SULFATE(M/KG).
0.00, NITRATE(M/KG).
0.00, CARBON ALKALINITY(EQUIVALENTS/KG).
0.00, SULFITE ALKALINITY(EQUIVALENTS/KG).
0.00, SULFIDE ACIDITY(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).
10.00, INITIAL TOTAL PRESSURE(BARS).
0.00, INITIAL CO2(BARS).
0.00, ENTER MOLE FRACTION OF CO2, 0=FIXED CO2, 1=PURE CO2.
0.00, INITIAL O2(BARS).
0.00, INITIAL CH4(BARS).
0.00, ENTER MOLE FRACTION OF CH4, 0=FIXED CH4, 1=PURE CH4.
0.00, CONSIDER A MIXED CO2-CH4 GAS HYDRATE,MIX(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.
0.00, INITIAL N2(BARS)
0.00, ENTER MOLE FRACTION OF N2, 0=FIXED N2, 1=PURE N2.
0.00, CONSIDER A MIXED N2-CH4 GAS HYDRATE,MIX2(YES=1, NO=0)?
0.00, CONSIDER A MIXED N2-C02 GAS HYDRATE,MIX3(YES=1, NO=0)?
6.00, INITIAL C2H6(BARS)
0.00, ENTER MOLE FRACTION OF C2H6, 0=FIXED C2H6, 1=PURE C2H6.
4.00, INITIAL C3H8(BARS)
0.00, ENTER MOLE FRACTION OF C3H8, 0=FIXED C3H8, 1=PURE C3H8.
1, CONSIDER A MIXED C2H6-C3H8 GAS HYDRATE,MIX4 (YES=1, NO=0)?
0, CONSIDER A MIXED C2H6-CH4 GAS HYDRATE,MIX5(YES=1, NO=0)?
0, CONSIDER A MIXED C3H8-CH4 GAS HYDRATE,MIX6(YES=1, NO=0)?
0, CONSIDER A MIXED C2H6-N2 GAS HYDRATE,MIX7(YES=1, NO=0)?
0, CONSIDER A MIXED C3H8-N2 GAS HYDRATE,MIX8(YES=1, NO=0)?
0, CONSIDER A MIXED C2H6-CO2 GAS HYDRATE,MIX9(YES=1, NO=0)?
```

0, CONSIDER A MIXED C3H8-CO2 GAS HYDRATE,MIX10(YES=1, NO=0)?
0, MOLAR TO MOLAL CONVERSION? YES=1,NO=0.
0.00, IF YES ABOVE, ENTER SALINITY(G)/LITER.
273.15, INITIAL TEMPERATURE(K).
273.15, FINAL TEMPERATURE(K), IF PATH =1, OTHERWISE, SET = 0.
0.00, 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.
0.00, WATER DECREMENT(K), IF PATH = 2, OTHERWISE, SET = 0.
10.00, FINAL PRESSURE(BARS), IF PATH = 3, OTHERWISE, SET = 0.
0.00, 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 17.1

(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 273.15 K. 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 (Table 3). "Final Conc." are the equilibrium concentrations at 273 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.

Table 6 is a case where we examined sodium/chloride/ethane/propane (Marion et al., 2015) (see the Input.txt file in Table 3). The high concentrations of ethane and propane cases causes a solid phase of these gases forming together on a mixed gas hydrate. See the bottom of Table 6 with both ethane and propane forming together.

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), NH_4(aq), and CH_4(g). 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 $NH_3 \cdot 2H_2O$ 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 10 is an input file for a Titan simulation from 273 to 173 K that is dominated with NH_3(aq), NH_3(g), NH_4(aq), N_2(bars), and CH_4(bars). Table 11 is the output of this simulation after the initial temperature at 273 K dropped to 173 K. At 173 K, ice had formed, NH_4Cl and $(NH_4)_2SO_4$ had precipitated, and $N_2 \cdot 6H_2O$-$CH_4 \cdot 6H_2O$ had formed. NH_3(aq), which started at 10.0 molal, has risen to 30.34 molal. In this case, the pH started at 10.0 (Table 10) and rose to 17.89. These Tables 10-11 are very similar to Tables 8-9, except that a mixed gas hydrate formed in this case and methane hydrate formed in the previous case.

TABLE 6. TITLE. This is a C2H6-C3H8 model test case (Version 17).

TITLE: Ethane-Propane model parameters

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
273.15	4.9973	1.179424	1.1596	200.11	0.00000	10.000

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Mass Moles	Balance
NA	1.0000	4.9973	0.79687	3.9822	1.0000	1.0000
CL	1.0000	4.9973	0.79687	3.9822	1.0000	1.0000
C2H6	0.00000	0.43766E-03	1.0000	0.43766E-03	0.87579E-04	
C2H6(BAR)	6.0000	6.0000	0.91179	5.4707	0.00000	
C3H8	0.00000	0.24686E-03	1.0000	0.24686E-03	0.49398E-04	
C3H8(BAR)	4.0000	4.0000	0.83553	3.3421	0.00000	
H2O(BAR)	0.00000			0.49637E-02		
H2O(L)	55.508			0.81156	11.108	55.508

Solid SPECIES	Equil. Moles	Constant	Accum. Moles
ICE	0.00000	1.0006	0.00000
NACL.2H2O	0.00000	18.024	0.00000
NACL	0.00000	31.511	0.00000
KCL	0.00000	3.7939	0.00000
CACL2.6H2O	0.00000	1864.4	0.00000
MGCL2.6H2O	0.00000	56203.	0.00000
MGCL2.8H2O	0.00000	7092.6	0.00000
MGCL2.12H2O	0.00000	703.86	0.00000
KMGCL3.6H2O	0.00000	7913.7	0.00000
CACL2.2MGCL2.12H2O	0.00000	0.28307E+19	0.00000
NA2SO4.10H2O	0.00000	0.31319E-02	0.00000
NA2SO4	0.00000	0.50094	0.00000
MGSO4.6H2O	0.00000	0.20213E-01	0.00000
MGSO4.7H2O	0.00000	0.62385E-02	0.00000
K2SO4	0.00000	0.64584E-02	0.00000
MGSO4.K2SO4.6H2O	0.00000	0.95278E-05	0.00000
NA2SO4.MGSO4.4H2O	0.00000	0.35823E-02	0.00000
CASO4.2H2O	0.00000	0.22341E-04	0.00000
CASO4	0.00000	0.88664E-04	0.00000
MGSO4.11H2O	0.00000	0.47867E-02	0.00000
NA2SO4.3K2SO4	0.00000	0.15245E-08	0.00000
CACO3(CALCITE)	0.00000	0.42634E-08	0.00000
MGCO3	0.00000	0.24765E-07	0.00000
MGCO3.3H2O	0.00000	0.92331E-05	0.00000
MGCO3.5H2O	0.00000	0.65397E-05	0.00000
CACO3.6H2O	0.00000	0.63633E-07	0.00000
NAHCO3	0.00000	0.19214	0.00000
NA2CO3.10H2O	0.00000	0.16045E-01	0.00000
NAHCO3.NA2CO3.2H2O	0.00000	0.51998E-01	0.00000
3MGCO3.MG(OH)2.3H2O	0.00000	0.97044E-35	0.00000
CAMG(CO3)2	0.00000	0.10502E+21	0.00000
NA2CO3.7H2O	0.00000	0.88807E-01	0.00000
KHCO3	0.00000	0.69006	0.00000
CACO3(ARAGONITE)	0.00000	0.62039E-08	0.00000
CACO3(VATERITE)	0.00000	0.18560E-07	0.00000
HNO3.3H2O	0.00000	702.14	0.00000
KNO3	0.00000	0.16835	0.00000
NANO3	0.00000	2.4921	0.00000
HCL.3H2O	0.00000	14648.	0.00000
H2SO4.6.5H2O	0.00000	13.542	0.00000
H2SO4.4H2O	0.00000	1012.9	0.00000
HCL.6H2O	0.00000	990.78	0.00000
NANO3.NA2SO4.2H2O	0.00000	0.13255	0.00000
NA3H(SO4)2	0.00000	0.15009	0.00000
NAHSO4.H2O	0.00000	32.905	0.00000
K3H(SO4)2	0.00000	0.67048E-04	0.00000
K5H3(SO4)4	0.00000	0.34065E-07	0.00000
K8H6(SO4)7.H2O	0.00000	0.56476E-12	0.00000
KHSO4	0.00000	1.4448	0.00000
MGSO4.H2O	0.00000	3.5982	0.00000

FESO4.7H2O	0.00000	0.19022E-02	0.00000
FESO4.H2O	0.00000	0.27804	0.00000
FECL2.6H2O	0.00000	2401.9	0.00000
FECL2.4H2O	0.00000	12018.	0.00000
FECO3	0.00000	0.13091E-10	0.00000
FE(OH)3	0.00000	50377.	0.00000
CO2.6H2O	0.00000	10.226	0.00000
CH4.6H2O	0.00000	24.869	0.00000
FECL3.10H20	0.00000	0.85305E-01	0.00000
FECL3.6H2O	0.00000	0.64647	0.00000
FECL3.2KCL.H20	0.00000	11.728	0.00000
FE2(SO4)3	0.00000	322.76	0.00000
FE2(SO4)3.2K2SO4.14H	0.00000	0.14972E-13	0.00000
K2SO4.FESO4.6H2O	0.00000	0.67073E-05	0.00000
NA2SO4.FESO4.4H2O	0.00000	0.12531E-02	0.00000
FE2(SO4)3.9H2O	0.00000	0.22497	0.00000
FE2(SO4)3.H2SO4.8H2O	0.00000	84.947	0.00000
KFE3(SO4)2(OH)6	0.00000	0.11157E-09	0.00000
NAFE3(SO4)2(OH)6	0.00000	0.16736E-03	0.00000
H3OFE3(SO4)2(OH)6	0.00000	0.42025E-02	0.00000
a-FE2O3	0.00000	144.71	0.00000
a-FEO(OH)	0.00000	15.483	0.00000
g-FEO(OH)	0.00000	1126.0	0.00000
FEO(OH)3/4(SO4)1/8	0.00000	218.27	0.00000
FESO4.4H2O	0.00000	0.22913E-01	0.00000
FE2(SO4)3.7H2O	0.00000	1.0818	0.00000
FE(II)FE(III)4(SO4)6	0.00000	0.88019E-20	0.00000
FE(III)5(SO4)6O(OH).	0.00000	0.93760E-20	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.25408E-16	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.70672E-10	0.00000
K2FE(II)5FE(III)4(SO	0.00000	0.10121E-32	0.00000
ALCL3.6H2O	0.00000	0.11007E+06	0.00000
AL2(SO4)3.17H2O	0.00000	0.11073E-05	0.00000
NABR	0.00000	0.00000	0.00000
MGBR2	0.00000	0.00000	0.00000
AL(OH)3	0.00000	0.42924E+10	0.00000
SIO2(QUARTZ)	0.00000	0.42476E-04	0.00000
SIO2(AMORPHOUS)	0.00000	0.11483E-02	0.00000
KAL3(SO4)2(OH)6	0.00000	11935.	0.00000
NAAL3(SO4)2(OH)6	0.00000	0.19078E+08	0.00000
KAL(SO4)2.12H2O	0.00000	0.10237E-06	0.00000
NAAL(SO4)2.12H2O	0.00000	0.30616E-04	0.00000
FESO4.AL2(SO4)3.22H2	0.00000	0.29402E-08	0.00000
AL2SI2O5(OH)4	0.00000	0.31418E+09	0.00000
MGSO4.AL2(SO4).22H2O	0.00000	0.10233E-07	0.00000
NACLO4.H2O	0.00000	87.291	0.00000
MG(CLO4)2.8H2O	0.00000	0.17010E+06	0.00000
CA(CLO4)2.6H2O	0.00000	0.92828E+06	0.00000
KCLO4	0.00000	0.17529E-02	0.00000
MG(CLO4)2.6H2O	0.00000	0.99735E+30	0.00000
NACLO4.2H2O	0.00000	59.148	0.00000
NH4CL	0.00000	7.8963	0.00000
NH42SO4	0.00000	0.61275	0.00000
NH3.H2O	0.00000	0.16559E+11	0.00000
NH4NO3	0.00000	4.0489	0.00000
NH4HCO3	0.00000	0.45449	0.00000
NH4CLO4	0.00000	0.21185	0.00000
NH3.2H2O	0.00000	527.73	0.00000
K2SO3	0.00000	29.900	0.00000
NA2SO3.7H2O	0.00000	0.40208E-01	0.00000
CASO3.0.5H2O	0.00000	0.32567E-06	0.00000
MGSO3.6H2O	0.00000	0.80796E-04	0.00000
FESO3.5H2O	0.00000	0.15700E-05	0.00000
(NH4)2SO3.H2O	0.00000	0.48449	0.00000
FES2	0.00000	0.40018E-16	0.00000
N2.6H2O	0.00000	163.28	0.00000
CASO4.0.5H2O	0.00000	0.39621E-03	0.00000
C2H6.6H2O	2.5716	1.5630	2.5716
C3H8.6H2O	4.8286	0.95486	4.8286

pH= INF pHF= INF pHT= INF pH(SWS)= INF
pHMacinnis = INF Temp. = 273.150

CONVERGENCE CRITERION = 0.100000 %
Iterations = 2

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	Mass Moles	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	Equil. Moles	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) (Version 15).

```
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	Mass Moles	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	Equil. Moles	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

Table 10. A Titan simulation. This is the main input for applications of FREZCHEM. In this particular case, the model simulations a N2-CH4 chemistry from 273.15 to 173.15 K (Table 11)(Icarus, 2014, 226:1-8)(Version 16).

```
TITLE: SO2-H2S model parameters
1, FREEZE(1) OR EVAPORATION(2) OR PRESSURE(3) SCENARIO ? CALLED PATH BELOW.
2, EQUILIBRIUM(1) OR FRACTIONAL(2) CRYSTALLIZATION?
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.

2, SPECIFY ABOVE ACIDITY OPTION.
10.0, 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, CARBON ALKALINITY(EQUIVALENTS/KG).
0.00, SULFITE ALKALINITY(EQUIVALENTS/KG).
0.00, SULFIDE ACIDITY(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).
1.467, INITIAL TOTAL PRESSURE(BARS).
0.00, INITIAL CO2(BARS).
0.00, ENTER MOLE FRACTION OF CO2, 0=FIXED CO2, 1=PURE CO2.
0.00, INITIAL O2(BARS).
0.073, INITIAL CH4(BARS).
0.00, ENTER MOLES OF CH4, 0=FIXED CH4, 1=PURE CH4.
0.00, 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.
1.394, INITIAL N2(BARS)
0.00, ENTER MOLE FRACTION OF N2, 0=FIXED N2, 1=PURE N2.
1, CONSIDER A MIXED N2-CH4 GAS HYDRATE(YES=1, NO=0)?
0, CONSIDER A MIXED N2-C03 GAS HYDRATE(YES=1, NO=0)?
0, MOLAR TO MOLAL CONVERSION? YES=1,NO=0.
0.00, 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.
0.00, WATER DECREMENT(K), IF PATH = 2, OTHERWISE, SET = 0.
1.467, FINAL PRESSURE(BARS), IF PATH = 3, OTHERWISE, SET = 0.
0.00, PRESSURE INCREMENT(BARS), IF PATH = 3, OTHERWISE, SET = 0.

Title 11. A Titan simulation (Icarus, 2014. 236:1-8)

TITLE: SO2-H2S model parameters.

Temp(K)	Ion.Str.	RHO	Phi	H2O(g)	Ice(g)	Press.(bars)
173.15	1.3866	0.9598179	1.4682	329.63	0.00000	1.4670

Solution SPECIES	Initial Conc.	Final Conc.	Act.Coef.	Activity	Mass Moles	Balance
H	0.00000	0.31547E-17	1.2133	0.38276E-17	0.10399E-17	
NH4	3.0000	1.3862	0.40642	0.56338	0.45693	2.9292
CL	1.0000	1.3854	0.40651	0.56318	0.45668	0.99727
SO4	1.0000	0.38447E-03	94.720	0.36417E-01	0.12673E-03	0.96596
OH	0.00000	0.37478E-05	0.31837E-06	0.11932E-11	0.12354E-05	
HSO4	0.00000	0.28224E-09	0.56879	0.16054E-09	0.93037E-10	
NH3	10.000	30.337	2.9001	87.979	10.000	10.000
NH3(BAR)	0.00000	0.36472E-02	1.0000	0.36472E-02	0.00000	
CH4	0.00000	0.14507	1.0000	0.14507	0.47820E-01	
CH4(BAR)	0.73000E-01	0.73000E-01	0.98875	0.72179E-01	0.00000	
N2	0.00000	0.28157E-01	1.0000	0.28157E-01	0.92813E-02	
N2(BAR)	1.3940	1.3940	0.82061	1.1439	0.00000	
H2O(BAR)	0.00000			0.13762E-07		
H2O(L)	55.508			0.41465	18.297	55.508

Solid SPECIES	Equil. Moles	Constant	Accum. Moles
ICE	0.00000	0.45274	34.184
NACL.2H2O	0.00000	79.233	0.00000
NACL	0.00000	0.81395E-02	0.00000
KCL	0.00000	0.63477E-02	0.00000
CACL2.6H2O	0.00000	0.21027E-05	0.00000
MGCL2.6H2O	0.00000	28.814	0.00000
MGCL2.8H2O	0.00000	0.52980E-03	0.00000
MGCL2.12H2O	0.00000	0.10419E-33	0.00000
KMGCL3.6H2O	0.00000	0.36320E-01	0.00000
CACL2.2MGCL2.12H2O	0.00000	0.29714E+25	0.00000
NA2SO4.10H2O	0.00000	0.60449E-08	0.00000
NA2SO4	0.00000	0.40677	0.00000
MGSO4.6H2O	0.00000	0.10076E-01	0.00000
MGSO4.7H2O	0.00000	0.33256E-04	0.00000
K2SO4	0.00000	0.80483E-05	0.00000
MGSO4.K2SO4.6H2O	0.00000	0.27934E-11	0.00000
NA2SO4.MGSO4.4H2O	0.00000	0.15338E-02	0.00000
CASO4.2H2O	0.00000	0.14168E-07	0.00000
CASO4	0.00000	0.10338E-05	0.00000
MGSO4.11H2O	0.00000	0.41319E-06	0.00000
NA2SO4.3K2SO4	0.00000	0.33860E-15	0.00000
CACO3(CALCITE)	0.00000	0.17744E-08	0.00000
MGCO3	0.00000	0.17232E-04	0.00000
MGCO3.3H2O	0.00000	1.8115	0.00000
MGCO3.5H2O	0.00000	0.44639E+22	0.00000
CACO3.6H2O	0.00000	0.35212E-11	0.00000
NAHCO3	0.00000	47.160	0.00000
NA2CO3.10H2O	0.00000	0.43490E-04	0.00000
NAHCO3.NA2CO3.2H2O	0.00000	0.39256E-02	0.00000
3MGCO3.MG(OH)2.3H2O	0.00000	0.58049E-23	0.00000
CAMG(CO3)2	0.00000	0.82208E-12	0.00000
NA2CO3.7H2O	0.00000	0.28653E-03	0.00000
KHCO3	0.00000	0.40237E-01	0.00000
CACO3(ARAGONITE)	0.00000	0.35291E-08	0.00000
CACO3(VATERITE)	0.00000	0.24288E-07	0.00000

HNO3.3H2O 0.00000 0.61102 0.00000
KNO3 0.00000 0.49287E-05 0.00000
NANO3 0.00000 0.14625E+11 0.00000
HCL.3H2O 0.00000 2879.2 0.00000
H2SO4.6.5H2O 0.00000 0.40031E-02 0.00000
H2SO4.4H2O 0.00000 0.24035 0.00000
HCL.6H2O 0.00000 147.94 0.00000
NANO3.NA2SO4.2H2O 0.00000 0.51509E+06 0.00000
NA3H(SO4)2 0.00000 0.93785E-49 0.00000
NAHSO4.H2O 0.00000 0.58236E+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 0.30115E-01 0.00000
MGSO4.H2O 0.00000 0.83112E+11 0.00000
FESO4.7H2O 0.00000 0.79480E-02 0.00000
FESO4.H2O 0.00000 4.4608 0.00000
FECL2.6H2O 0.00000 77.594 0.00000
FECL2.4H2O 0.00000 0.10026E+07 0.00000
FECO3 0.00000 0.17986E-09 0.00000
FE(OH)3 0.00000 0.36265E+14 0.00000
CO2.6H2O 0.00000 0.40848E-03 0.00000
CH4.6H2O 0.48650E-01 0.36688E-03 0.83384E-01
FECL3.10H20 0.00000 0.42606E-12 0.00000
FECL3.6H2O 0.00000 0.16131 0.00000
FECL3.2KCL.H20 0.00000 0.72905E-14 0.00000
FE2(SO4)3 0.00000 0.18464E+30 0.00000
FE2(SO4)3.2K2SO4.14H 0.00000 0.14357E-13 0.00000
K2SO4.FESO4.6H2O 0.00000 0.83703E-09 0.00000
NA2SO4.FESO4.4H2O 0.00000 0.12152E-02 0.00000
FE2(SO4)3.9H2O 0.00000 0.11488E+12 0.00000
FE2(SO4)3.H2SO4.8H2O 0.00000 0.29078E+20 0.00000
KFE3(SO4)2(OH)6 0.00000 49.109 0.00000
NAFE3(SO4)2(OH)6 0.00000 0.46291E+12 0.00000
H3OFE3(SO4)2(OH)6 0.00000 0.50881E+23 0.00000
a-FE2O3 0.00000 0.41772E+17 0.00000
a-FEO(OH) 0.00000 0.10815E+09 0.00000
g-FEO(OH) 0.00000 0.10255E+12 0.00000
FEO(OH)3/4(SO4)1/8 0.00000 0.26329E+11 0.00000
FESO4.4H2O 0.00000 0.86002E-02 0.00000
FE2(SO4)3.7H2O 0.00000 0.11091E+16 0.00000
FE(II)FE(III)4(SO4)6 0.00000 1274.6 0.00000
FE(III)5(SO4)6O(OH). 0.00000 75097. 0.00000
FE(II)FE(III)2(SO4)4 0.00000 0.62687E-17 0.00000
FE(II)FE(III)2(SO4)4 0.00000 6.1920 0.00000
K2FE(II)5FE(III)4(SO 0.00000 0.14736E+07 0.00000
ALCL3.6H2O 0.00000 0.27362E-07 0.00000
AL2(SO4)3.17H2O 0.00000 0.56149E-08 0.00000
NABR 0.00000 0.00000 0.00000
MGBR2 0.00000 0.00000 0.00000
AL(OH)3 0.00000 0.17975E+22 0.00000
SIO2(QUARTZ) 0.00000 0.70843E-07 0.00000
SIO2(AMORPHOUS) 0.00000 0.32652E-04 0.00000
KAL3(SO4)2(OH)6 0.00000 0.36156E+30 0.00000
NAAL3(SO4)2(OH)6 0.00000 0.43250E+36 0.00000
KAL(SO4)2.12H2O 0.00000 0.16824E-10 0.00000
NAAL(SO4)2.12H2O 0.00000 0.22345E-05 0.00000
FESO4.AL2(SO4)3.22H2 0.00000 0.28067E-08 0.00000
AL2SI2O5(OH)4 0.00000 0.35225E+27 0.00000
MGSO4.AL2(SO4).22H2O 0.00000 0.98113E-08 0.00000
NACLO4.H2O 0.00000 0.22234 0.00000
MG(CLO4)2.8H2O 0.00000 0.55057E+07 0.00000
CA(CLO4)2.6H2O 0.00000 9175.8 0.00000
KCLO4 0.00000 0.23020E-04 0.00000
MG(CLO4)2.6H2O 0.00000 0.10003E+31 0.00000
NACLO4.2H2O 0.00000 0.41764 0.00000
NH4CL 0.89823E-01 0.31728 0.54059
NH42SO4 0.22109E-03 0.11558E-01 0.96584
NH3.H2O 0.00000 40.337 0.00000
NH4NO3 0.00000 0.29481E-01 0.00000

NH4HCO3	0.00000	0.33196E-03	0.00000
NH4CLO4	0.00000	0.49606E-04	0.00000
NH3.2H2O	0.00000	15.162	0.00000
K2SO3	0.00000	465.91	0.00000
NA2SO3.7H2O	0.00000	0.43191E-03	0.00000
CASO3.0.5H2O	0.00000	0.11518E-05	0.00000
MGSO3.6H2O	0.00000	0.17424E-05	0.00000
FESO3.5H2O	0.00000	0.15407E-05	0.00000
(NH4)2SO3.H2O	0.00000	0.50045E-01	0.00000
FES2	0.00000	0.39899E-16	0.00000
N2.6H2O	0.24785	0.58146E-02	0.42116
CASO4.0.5H2O	0.00000	0.12851E-01	0.00000

pH= 17.8857 pHF= 17.5010 pHT= 9.54937 pH(SWS)= 9.54937 pHMacinnis = 17.6238.
Temp. =173.15. CONVERGENCE CRITERION = 0.100000. Iterations = 5