

FRIENDS OF FREZCHEM (Version 13.3)

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, 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} . 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, or Si, then you will have four options on how to deal with pH (see Table 2).

The validation of this model is discussed in 13 publications: (1) Spencer et al. (1990) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system. *Geochim. Cosmochim. Acta*, 54:575-590; (2) Marion and Farren (1999) Mineral solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O system: A re-evaluation of the sulfate chemistry in the Spencer-Møller-Weare model. *Geochim. Cosmochim. Acta*, 63:1305-1318; (3) Marion (2001) Carbonate mineral solubility at low temperatures in the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system. *Geochim. Cosmochim. Acta*, 65:1883-

1896; (4) Marion (2002) A molal-based model for strong acid chemistry at low temperatures (<200 to 298 K). *Geochim. Cosmochim. Acta*, 66:2499-2516; (5) Marion et al. (2003) Modeling aqueous ferrous iron chemistry at low temperatures with application to Mars. *Geochim. Cosmochim. Acta*, 67:4251-4266; (6) Marion et al. (2005) Effects of pressure on aqueous chemical equilibria at subzero temperatures with applications to Europa. *Geochim. Cosmochim. Acta*, 69:259-274; (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; and (13) Marion et al., (in preparation). Modeling aqueous perchlorate chemistries with applications to Mars. *Icarus*.

Compared to Version 12.2, this version of the FREZCHEM model contains new parameterizations dealing with perchlorate salts and minor seawater species [Sr, B(OH)₃, F]. In addition, Version 13.3 has an option for estimating seawater properties based on salinities [S_A(absolute salinity) or S_P (practical salinity)] and seawater supersaturation with respect to calcite (or aragonite).

A fundamental change was made in FREZCHEM 13 on how to input data into the model. Earlier versions required inputs via the computer screen. Version 13 requires 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 [$\text{CaMg}(\text{CO}_3)_2$] from model calculations (Table 5), which led to calcite (CaCO_3) and hydromagnesite [$3\text{Mg}(\text{CO}_3)_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$] 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) 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 13.3).

A. Solution and Atmospheric Species									
#	Species	#	Species	#	Species	#	Species	#	Species
1	Na ⁺ (aq)	11	Cl ⁻ (aq)	21	CO ₂ (aq)	151	O ₂ (g)	166	Si(OH) ₄ ⁰ (aq)
2	K ⁺ (aq)	12	SO ₄ ²⁻ (aq)	22	FeCO ₃ ⁰ (aq)	152	O ₂ (aq)	167	Si(OH) ₃ ⁻ (aq)
3	Ca ²⁺ (aq)	13	OH ⁻ (aq)	23	HCl(g)	153	H ₂ (g)	168	
4	Mg ²⁺ (aq)	14	HCO ₃ ⁻ (aq)	24	CaCO ₃ ⁰ (aq)	154	CH ₄ (g)	169	B(OH) ₃ ⁰ (aq)
5	H ⁺ (aq)	15	CO ₃ ²⁻ (aq)	25	MgCO ₃ ⁰ (aq)	155	CH ₄ (aq)	170	F ⁻ (aq)
6	MgOH ⁺ (aq)	16	HSO ₄ ⁻ (aq)	26	HNO ₃ (g)	156	Fe(OH) ₂ ⁰ (aq)	171	HF ⁰ (aq)
7	Fe ²⁺ (aq)	17	NO ₃ ⁻ (aq)	27	H ₂ SO ₄ (g)	157	Fe(OH) ₃ ⁻ (aq)	172	Sr ²⁺ (aq)
8	FeOH ⁺ (aq)	18	Br ⁻ (aq)	28	H ₂ O(g)	158	FeOH ²⁺ (aq)		
9	Fe ³⁺ (aq)	19	ClO ₄ ⁻ (aq)	29	CO ₂ (g)	159	Fe(OH) ₂ ⁺ (aq)		
10	Al ³⁺ (aq)	20	B(OH) ₄ ⁻ (aq)	30	H ₂ O(l)	160	Fe(OH) ₃ ⁰ (aq)		
						161	Fe(OH) ₄ ⁻ (aq)		
						162	Al(OH) ₂ ⁺ (aq)		
						163	Al(OH) ₂ ⁺ (aq)		
						164	Al(OH) ₃ ⁰ (aq)		
						165	Al(OH) ₄ ⁻ (aq)		

B. Solid Phase Species									
#	Species	#	Species	#	Species	#	Species	#	Species
31	H ₂ O(cr,l)	51	Na ₂ SO ₄ •3K ₂ SO ₄ (cr)	71	H ₂ SO ₄ •4H ₂ O(cr)	91	FeCl ₃ •2KCl•H ₂ O(cr)	111	K ₂ Fe(II) ₅ Fe(III) ₄ (SO ₄) ₁₂ •18H ₂ O(cr)
32	NaCl•2H ₂ O(cr)	52	CaCO ₃ (cr,calcite)	72	HCl•6H ₂ O(cr)	92	Fe ₂ (SO ₄) ₃ (cr)	112	AlCl ₃ •6H ₂ O(cr)
33	NaCl(cr)	53	MgCO ₃ (cr)	73	NaNO ₃ •Na ₂ SO ₄ •2H ₂ O(cr)	93	Fe ₂ (SO ₄) ₃ •2K ₂ SO ₄ •14H ₂ O(cr)	113	Al ₂ (SO ₄) ₃ •17H ₂ O(cr)
34	KCl(cr)	54	MgCO ₃ •3H ₂ O(cr)	74	Na ₃ H(SO ₄) ₂ (cr)	94	K ₂ SO ₄ •FeSO ₄ •6H ₂ O(cr)	114	NaBr
35	CaCl ₂ •6H ₂ O(cr)	55	MgCO ₃ •5H ₂ O(cr)	75	NaHSO ₄ •H ₂ O(cr)	95	Na ₂ SO ₄ •FeSO ₄ •4H ₂ O(cr)	115	MgBr ₂
36	MgCl ₂ •6H ₂ O(cr)	56	CaCO ₃ •6H ₂ O(cr)	76	K ₃ H(SO ₄) ₂ (cr)	96	Fe ₂ (SO ₄) ₃ •9H ₂ O(cr)	116	Al(OH) ₃ (cr)
37	MgCl ₂ •8H ₂ O(cr)	57	NaHCO ₃ (cr)	77	K ₅ H ₃ (SO ₄) ₄ (cr)	97	Fe ₂ (SO ₄) ₃ •H ₂ SO ₄ •8H ₂ O(cr)	117	SiO ₂ (quartz)(cr)
38	MgCl ₂ •12H ₂ O(cr)	58	Na ₂ CO ₃ •10H ₂ O(cr)	78	K ₈ H ₆ (SO ₄) ₇ •H ₂ O(cr)	98	KFe ₃ (SO ₄) ₂ (OH) ₆ (cr)	118	SiO ₂ (amorphous)
39	KMgCl ₃ •6H ₂ O(cr)	59	NaHCO ₃ •Na ₂ CO ₃ •2H ₂ O(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 ₂ O(cr)	60	3MgCO ₃ •Mg(OH) ₂ •3H ₂ O(cr)	80	MgSO ₄ •H ₂ O(cr)	100	H ₃ OFe ₃ (SO ₄) ₂ (OH) ₆ (cr)	120	NaAl ₃ (SO ₄) ₂ (OH) ₆ (cr)
41	Na ₂ SO ₄ •10H ₂ O(cr)	61	CaMg(CO ₃) ₂ (cr)	81	FeSO ₄ •7H ₂ O(cr)	101	α-Fe ₂ O ₃ (cr)	121	KAl ₂ (SO ₄) ₂ •12H ₂ O(cr)
42	Na ₂ SO ₄ (cr)	62	Na ₂ CO ₃ •7H ₂ O(cr)	82	FeSO ₄ •H ₂ O(cr)	102	α-FeO(OH)(cr)	122	NaAl(SO ₄) ₂ •12H ₂ O(cr)
43	MgSO ₄ •6H ₂ O(cr)	63	KHCO ₃ (cr)	83	FeCl ₂ •6H ₂ O(cr)	103	γ-FeO(OH)(cr)	123	FeSO ₄ •Al ₂ (SO ₄) ₃ •22H ₂ O(cr)
44	MgSO ₄ •7H ₂ O(cr)	64	CaCO ₃ (cr,aragonite)	84	FeCl ₂ •4H ₂ O(cr)	104	FeO(OH) _{0.75} (SO ₄) _{0.125} (cr)	124	Al ₂ Si ₂ O ₅ (OH) ₄ (cr)
45	K ₂ SO ₄ (cr)	65	CaCO ₃ (cr,vaterite)	85	FeCO ₃ (cr)	105	FeSO ₄ •4H ₂ O(cr)	125	MgSO ₄ •Al ₂ (SO ₄) ₃ •22H ₂ O(cr)
46	MgSO ₄ •K ₂ SO ₄ •6H ₂ O(cr)	66	HNO ₃ •3H ₂ O(cr)	86	Fe(OH) ₃ (cr)	106	Fe ₂ (SO ₄) ₃ •7H ₂ O(cr)	126	NaClO ₄ •H ₂ O(cr)
47	Na ₂ SO ₄ •MgSO ₄ •4H ₂ O(cr)	67	KNO ₃ (cr)	87	CO ₂ •6H ₂ O(cr)	107	Fe(II)Fe(III) ₄ (SO ₄) ₆ (OH) ₂ •20H ₂ O(cr)	127	Mg(ClO ₄) ₂ •8H ₂ O(cr)
48	CaSO ₄ •2H ₂ O(cr)	68	NaNO ₃ (cr)	88	CH ₄ •6H ₂ O(cr)	108	Fe ₅ (SO ₄) ₆ O(OH)•20H ₂ O(cr)	128	Ca(ClO ₄) ₂ •6H ₂ O(cr)

49 $\text{CaSO}_4(\text{cr})$
50 $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}(\text{cr})$

69 $\text{HCl} \cdot 3\text{H}_2\text{O}(\text{cr})$
70 $\text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O}(\text{cr})$

89 $\text{FeCl}_3 \cdot 10\text{H}_2\text{O}(\text{cr})$
90 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})$

109 $\text{Fe(II)Fe(III)}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}(\text{cr})$
110 $\text{Fe(II)Fe(III)}_2(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}(\text{cr})$

129 $\text{KClO}_4(\text{cr})$
130 $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}(\text{cr})$
131 $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}(\text{cr})$

Table 2. Description of Model Inputs (Version 13.3) (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 CO₂ or CH₄ 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.

If Iron, Aluminum, or Silicon are selected, then choose an acidity option:

Acidity ignored, enter 1.

Acidity fixed by pH, enter 2.

Acidity fixed by H⁺ ion concentration, enter 3.

Acidity fixed by alkalinity, enter 4.

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

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 H₂SO₄ solution, enter 2.00. Otherwise, enter 0.0. The equations used to calculate pH for the alkalinity and acidity cases are incompatible. So, a specification of either carbonate alkalinity or acidity requires that the other variable be assigned a value of 0.00. This will channel the calculations to the proper algorithm.

HCl(bars): If the HCl atmospheric concentration is known, then specify here. Otherwise, enter 0.0. If you specify 0.0, then the model will calculate HCl(bars). Note that if you specify HCl(bars) or the other acids below, then these properties override the total acidity specification (see above). That is, the solution is equilibrated with the atmospheric concentration. Note, you can, if desired, specify atmospheric concentrations for some acids (e.g., HCl and HNO₃) and leave other acid partial pressure unspecified (e.g., H₂SO₄ = 0.0).

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

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

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

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

O₂(bars): If the atmospheric concentration of oxygen is known, then specify here. Otherwise, enter 0.0. If you are interested in ferrous iron chemistry, then you may want to assign O₂

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

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

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

Mixed CH₄-CO₂ Gas Hydrate?: If both CH₄(g) and CO₂(g) are specified as inputs, then you can use this data to estimate the stability of a mixed CH₄-CO₂ gas hydrate (YES = 1) or treat the two gases as independent gas hydrates (NO = 0).

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 = Σ(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) .

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.

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, 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
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		

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 ΔH_2O , WHERE CHANGE SHOULD BE MADE.
10 0.1, WATER CONTENT AND ΔH_2O , 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 (55.425×18.0153). 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 \geq 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, meridianite, 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 [= 5.417×58.44 (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 an Earth seawater simulation from 273 K to 268 K. This type of simulation is only valid for Earth seawater. The 5th line selects seawater salinity ($S_p =$ practical salinity) as a driver; the next line requests that we want the simulation at $S_p = 40.0$; the following line requests that seawater carbonate supersaturation be considered. Selecting YES for this case will remove several carbonate minerals and ultimately will result in the precipitation of either calcite/aragonite or ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$). See Marion et al. (2008, Ocean Sci. Discuss. 5:1-19) for a discussion of this approach. The following seawater ionic concentrations in Table 8 were all taken from Millero et al. (2008, Deep Sea Research, 55:50-72) and represent the standard concentrations for S_A (absolute salinity) = 35.165 g/kg ($S_p = 35.00$). Because we specified that we wanted to simulate a seawater $S_p = 40.0$, the S_A 35.165 g/kg data in this table will be multiplied by $(40/35) \times 35.165$ to generate the S_A data for the simulation.

Table 9 is the output of this simulation after the initial temperature at 273 K dropped to 268 K. At 268 K, ice has formed and ikaite has started to precipitate (Table 9). Now if you wanted to run this simulation at a different S_p value (e.g., 30), all that needs to be done in Table 8 is to replace the value of 40 with 30 in line 6.

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.Coeff.	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 . 10H2O	0.00000	0.67445E-02	0.00000
FECL3 . 6H2O	0.00000	0.81059E-01	0.00000
FECL3 . 2KCL . H2O	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.Coeff.	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
FECL3.10H2O	0.00000	0.10000E+31	0.00000
FECL3.6H2O	0.00000	0.10000E+31	0.00000
FECL3.2KCL.H2O	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. Seawater Test Case

TITLE: This is an Earth seawater test case.
1, FREEZE(1) OR EVAPORATION(2) OR PRESSURE(3) SCENARIO ? CALLED PATH BELOW.
1, EQUILIBRIUM(1) OR FRACTIONAL(2) CRYSTALLIZATION?
1, OPEN(1) OR CLOSED(2) CARBON SYSTEM?
1, WANT SEAWATER SALINITY(Sp) TO GOVERN THE CALCULATIONS,Y=1,N=0.
40.0, IF YES ABOVE, ENTER SEAWATER PRACTICAL SALINITY(Sp) OR 0.0.
1, WANT SEAWATER CARBONATE SUPERSATURATION TO BE CONSIDERED? Y=1,N=0.
0.48606, SODIUM(M/KG) .
0.01058, POTASSIUM(M/KG) .
0.01066, CALCIUM(M/KG) .
0.05474, MAGNESIUM(M/KG)
0.00009, 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) .

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.

4, SPECIFY ABOVE ACIDITY OPTION.
8.00, SPECIFY INITIAL PH.
0.56576, CHLORIDE(M/KG) .
0.00087, BROMIDE(M/KG) .
0.00, PERCHLORATE(M/KG) .
0.02926, SULFATE(M/KG) .
0.00, NITRATE(M/KG) .
0.00240, 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.
0.00043, BORON (M/KG) .
0.00007, FLUORIDE(M/KG) .
1.01325, INITIAL TOTAL PRESSURE(BARS) .
3.85E-4, 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 CH4, 1=PURE CH4 .
0, CONSIDER A MIXED CO2-CH4 GAS HYDRATE(YES=1, NO=0)?
0, MOLAR TO MOLAL CONVERSION? YES=1,NO=0 .
0.0, 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, 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. An Earth seawater simulation.

TITLE: This is an Earth seawater test case.

Temp (K)	Ion.Str.	RHO	Phi	H2O (g)	Ice (g)	Press. (bars)
268.15	1.8172	1.068097	0.91881	454.12	545.88	1.0132
Solution SPECIES	Initial Conc.	Final Conc.	Act.Coeff.	Activity	Moles	Mass Balance
NA	0.55550	1.2232	0.56962	0.69679	0.55550	0.55550
K	0.12091E-01	0.26626E-01	0.50655	0.13487E-01	0.12091E-01	0.12091E-01
CA	0.12179E-01	0.26664E-01	0.18823	0.50189E-02	0.12109E-01	0.12183E-01
MG	0.62545E-01	0.13757	0.19658	0.27044E-01	0.62475E-01	0.62560E-01
H	0.13480E-07	0.38413E-08	0.91360	0.35094E-08	0.17444E-08	
MGOH	0.19374E-06	0.74316E-06	0.83392	0.61973E-06	0.33748E-06	
CL	0.64658	1.4238	0.66408	0.94553	0.64658	0.64658
SO4	0.33440E-01	0.73637E-01	0.48602E-01	0.35789E-02	0.33440E-01	0.33440E-01
OH	0.26911E-06	0.78690E-06	0.23820	0.18744E-06	0.35734E-06	0.35734E-06
HCO3	0.26717E-02	0.45881E-02	0.47839	0.21949E-02	0.20835E-02	0.27429E-02
CO3	0.16269E-04	0.25790E-03	0.47186E-01	0.12169E-04	0.11712E-03	
HSO4	0.00000	0.88387E-09	0.59609	0.52686E-09	0.40138E-09	
BR	0.99429E-03	0.21895E-02	0.79177	0.17336E-02	0.99429E-03	0.99429E-03
CO2	0.24797E-04	0.26933E-04	1.3442	0.36203E-04	0.12231E-04	
CACO3	0.42729E-05	0.74304E-04	1.0000	0.74304E-04	0.33743E-04	
MGCO3	0.15028E-04	0.18604E-03	1.0000	0.18604E-03	0.84485E-04	
SR	0.10286E-03	0.22650E-03	0.18823	0.41711E-04	0.10286E-03	
B (OH) 4	0.49143E-03	0.23581E-03	0.26645	0.62832E-04	0.10708E-03	0.49143E-03
B (OH) 3	0.00000	0.84635E-03	1.0214	0.86449E-03	0.38434E-03	
F	0.80000E-04	0.17617E-03	0.66408	0.11699E-03	0.80000E-04	0.80000E-04
HF	0.00000	0.33714E-09	1.0000	0.33714E-09	0.15310E-09	
CO2 (BAR)	0.38500E-03	0.38500E-03	0.99258	0.38214E-03	0.00000	
H2O (BAR)	0.59873E-02			.39932E-02		
H2O (L)	55.508			.95281	25.207	55.508
Solid SPECIES	Moles	Equil. Constant	Accum. Moles			
ICE	30.301	0.95281	30.301			
NACL.2H2O	0.00000	15.126	0.00000			
NACL	0.00000	29.671	0.00000			
KCL	0.00000	3.1457	0.00000			
CACL2.6H2O	0.00000	1516.9	0.00000			
MGCL2.6H2O	0.00000	56264.	0.00000			
MGCL2.8H2O	0.00000	5828.1	0.00000			
MGCL2.12H2O	0.00000	364.70	0.00000			
KMGCL3.6H2O	0.00000	6034.2	0.00000			
CACL2.2MGCL2.12H2O	0.00000	0.55300E+19	0.00000			
NA2SO4.10H2O	0.00000	0.16757E-02	0.00000			
NA2SO4	0.00000	0.48623	0.00000			
MGSO4.6H2O	0.00000	0.19244E-01	0.00000			
MGSO4.7H2O	0.00000	0.52005E-02	0.00000			
K2SO4	0.00000	0.51211E-02	0.00000			
MGSO4.K2SO4.6H2O	0.00000	0.61454E-05	0.00000			
NA2SO4.MGSO4.4H2O	0.00000	0.33198E-02	0.00000			
CASO4.2H2O	0.00000	0.20328E-04	0.00000			
CASO4	0.00000	0.91123E-04	0.00000			
MGSO4.11H2O	0.00000	0.28909E-02	0.00000			
NA2SO4.3K2SO4	0.00000	0.66368E-09	0.00000			
CACO3 (CALCITE)	0.00000	0.98263E-07	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	0.40438E-04	0.45699E-07	0.40438E-04			
NAHCO3	0.00000	0.16544	0.00000			
NA2CO3.10H2O	0.00000	0.10405E-01	0.00000			
NAHCO3.NA2CO3.2H2O	0.00000	0.44512E-01	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	0.65575E-01	0.00000			
KHCO3	0.00000	0.58495	0.00000			
CACO3 (ARAGONITE)	0.00000	0.10000E+31	0.00000			
CACO3 (VATERITE)	0.00000	0.10000E+31	0.00000			
HNO3.3H2O	0.00000	494.82	0.00000			
KNO3	0.00000	0.11690	0.00000			
NANO3	0.00000	2.3077	0.00000			
HCL.3H2O	0.00000	13543.	0.00000			
H2SO4.6.5H2O	0.00000	18.005	0.00000			
H2SO4.4H2O	0.00000	999.90	0.00000			
HCL.6H2O	0.00000	1000.0	0.00000			
NANO3.NA2SO4.2H2O	0.00000	0.98803E-01	0.00000			
NA3H(SO4)2	0.00000	0.15600	0.00000			

NAHSO4.H2O	0.00000	30.390	0.00000
K3H(SO4)2	0.00000	0.58580E-04	0.00000
K5H3(SO4)4	0.00000	0.24354E-07	0.00000
K8H6(SO4)7.H2O	0.00000	0.46354E-12	0.00000
KHSO4	0.00000	1.1819	0.00000
MGSO4.H2O	0.00000	6.1091	0.00000
FESO4.7H2O	0.00000	0.15964E-02	0.00000
FESO4.H2O	0.00000	0.31315	0.00000
FECL2.6H2O	0.00000	2974.2	0.00000
FECL2.4H2O	0.00000	14680.	0.00000
FECO3	0.00000	0.13913E-10	0.00000
FE(OH)3	0.00000	97320.	0.00000
CO2.6H2O	0.00000	6.2662	0.00000
CH4.6H2O	0.00000	15.666	0.00000
FECL3.10H2O	0.00000	0.23977E-01	0.00000
FECL3.6H2O	0.00000	0.21598	0.00000
FECL3.2KCL.H2O	0.00000	1.9922	0.00000
FE2(SO4)3	0.00000	2211.5	0.00000
FE2(SO4)3.2K2SO4.14H	0.00000	0.14132E-13	0.00000
K2SO4.FESO4.6H2O	0.00000	0.41742E-05	0.00000
NA2SO4.FESO4.4H2O	0.00000	0.12041E-02	0.00000
FE2(SO4)3.9H2O	0.00000	0.50815	0.00000
FE2(SO4)3.H2SO4.8H2O	0.00000	291.72	0.00000
KFE3(SO4)2(OH)6	0.00000	0.25237E-09	0.00000
NAFE3(SO4)2(OH)6	0.00000	0.50101E-03	0.00000
H3OFE3(SO4)2(OH)6	0.00000	0.25765E-01	0.00000
a-FE2O3	0.00000	417.03	0.00000
a-FEO(OH)	0.00000	25.575	0.00000
g-FEO(OH)	0.00000	2019.5	0.00000
FEO(OH)3/4(SO4)1/8	0.00000	394.13	0.00000
FESO4.4H2O	0.00000	0.21487E-01	0.00000
FE2(SO4)3.7H2O	0.00000	3.1277	0.00000
FE(II)FE(III)4(SO4)6	0.00000	0.43888E-19	0.00000
FE(III)5(SO4)6O(OH).	0.00000	0.53003E-19	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.22810E-16	0.00000
FE(II)FE(III)2(SO4)4	0.00000	0.14910E-09	0.00000
K2FE(II)5FE(III)4(SO	0.00000	0.15012E-31	0.00000
ALCL3.6H2O	0.00000	38430.	0.00000
AL2(SO4)3.17H2O	0.00000	0.10448E-05	0.00000
NABR	0.00000	0.00000	0.00000
MGBR2	0.00000	0.00000	0.00000
AL(OH)3	0.00000	0.10104E+11	0.00000
SiO2(QUARTZ)	0.00000	0.33982E-04	0.00000
SiO2(AMORPHOUS)	0.00000	0.10236E-02	0.00000
KAL3(SO4)2(OH)6	0.00000	75158.	0.00000
NAAL3(SO4)2(OH)6	0.00000	0.14851E+09	0.00000
KAL(SO4)2.12H2O	0.00000	0.64506E-07	0.00000
NAAL(SO4)2.12H2O	0.00000	0.26106E-04	0.00000
FESO4.AL2(SO4)3.22H2	0.00000	0.27653E-08	0.00000
AL2Si2O5(OH)4	0.00000	0.11426E+10	0.00000
MGSO4.AL2(SO4).22H2O	0.00000	0.96704E-08	0.00000
NACLO4.H2O	0.00000	74.164	0.00000
MG(CLO4)2.8H2O	0.00000	0.20398E+06	0.00000
CA(CLO4)2.6H2O	0.00000	0.89849E+06	0.00000
KCLO4	0.00000	0.12614E-02	0.00000
MG(CLO4)2.6H2O	0.00000	0.10487E+07	0.00000
NACLO4.2H2O	0.00000	46.027	0.00000

PRACTICAL SALINITY = 40.0000 ABSOLUTE SALINITY = 40.1886
pH= 8.45477 pHF= 8.41553 pHT= 8.32559 pH(SWS)= 8.29565

CONVERGENCE CRITERION = 0.100000 %
Iterations = 5