A FREZCHEM Program Guide

Program listings and FORTRAN codes for various version of the FREZCHEM model (versions 5.2 to 9.2) are available from the senior author (giles.marion@dri.edu; http://frezchem.dri.edu). In this appendix, we first describe the data input; then we examine four output files that deal with (1) seawater freezing, (2) strong acids, (3) gas hydrates, and (4) a pressure application. But before discussing these examples, there are some limitations that the user needs to be aware of.

A.1 Model Input Limitations

There are a few incompatibilities among model inputs. For example, the equations used to estimate pH for an alkaline system (Eq. 3.29) and an acidic system (Eq. 3.32) are incompatible. Therefore, when defining an alkaline system ($pH > 4.5$), be certain to assign "acidity" a value of 0.0, which bypasses the acidity algorithms. Similarly, when defining an acidic system ($pH < 4.5$), be certain to assign alkalinity a value of 0.0, which by-passes the alkalinity algorithms. The pH calculations (Eqs. 3.29 and 3.32) use a charge balance equation. If the initial input charges are unbalanced, then the model forces a charge balance by adjusting the pH and the ion concentrations that are a function of pH (e.g., HCO_3^-). If the initial charge is badly out of balance, then the calculated pH is also likely to be a poor estimate. As a **general rule**, it is best to adjust initial model inputs to provide a perfect charge balance.

An alkalinity specification can also conflict with CO_2 gas hydrates. Here the problem has to do with the magnitude of P_{CO_2}. The equations governing CO_2 solubility and carbonic acid dissociation are only defined for low P_{CO_2} values (0.0 to 1 bar) (Plummer and Busenberg 1982). At 10 °C, the equilibrium P_{CO_2} for $CO_2 \cdot 6H_2O$ in pure water is ca. 45 bars. Such high values are beyond the range of validity of the alkalinity relationships. Therefore caution is necessary in interpreting alkalinity/CO_2 gas hydrate applications. A way to get around this problem is illustrated with a gas hydrate example (Table A.4), where P_{CO_2} is assigned a constant value and P_{CH4} is allowed to change with pressure, which works for $CH_4 \cdot 6H_2O$. If $CO_2 \cdot 6H_2O$ is the desired gas hydrate, then an alternative is to remove alkalinity from the input database. For example, seawater alkalinity only represents 0.37% of the total anion charge (Table A.2); removing alkalinity and an equivalent amount of Ca ($CaCO_3$ is precipitating) solves the alkalinity/CO_2 gas hydrate problem.

The FREZCHEM model was designed to characterize aqueous electrolyte solutions. To work properly, there must always be ions in solution, even if only hypothetical. To simulate pure water, pure gas hydrate, pure ice, or other nonion equilibria, you need to add minor concentrations of ions (e.g., $Na = Cl = 1 \times 10^{-6}\,m$). Such minor concentrations do not significantly affect the thermodynamic properties, but they do allow for proper model calculations.

A.2 Model Inputs

Table A.1 describes how data is input into the FREZCHEM model. This is specifically for version 9.2. Earlier versions have similar but fewer inputs. Pay particular attention to the units of gas concentrations. Versions of the model before 9.2 required gas concentrations in atm., while version 9.2 requires units of bars. Most of the program inputs are relatively self-explanatory (Table A.1). A few additional words are necessary to assure gas hydrates are handled correctly in the model.

There are two systems for inputting CH_4 and CO_2 gases into gas hydrate systems: an "open" carbon system, where the $P_{(g)}$ is fixed at a given total pressure, and a "closed" carbon system where the total carbon is fixed. The open carbon system would be appropriate for the base of a gas hydrate deposit where a large amount of free gas is present. In this open case, the gas content is present in excess and the water content is limiting. As a consequence, water may be converted entirely into hydrate ice. This is similar to what happens to water ice as the temperature decreases to the eutectic. On the other hand, the closed carbon system would be appropriate for minor amounts of CH_4 or CO_2 in, for example, an ice core. Here carbon is limiting and water is present in excess. This closed carbon case requires estimating the carbon present in the gas, aqueous, and solid phases. The existing model can input the amount of carbon in the aqueous and solid phases. The amount of carbon in the gas phase is arbitrarily estimated from the $P_{(g)}$ in 100 ml of gas, which is added to the carbon in the other phases. The total amount of carbon is such a system is small, and, as temperature or pressure changes, gas hydrates would rapidly precipitate at equilibrium. As a consequence, in the closed carbon system model, the assumption is made that all the carbon solidifies at the temperature or pressure where the system first reaches gas hydrate equilibrium. This closed carbon model is appropriate for estimating gas hydrate equilibrium temperatures and pressures but not the actual content of gas hydrates because of the arbitrary nature of estimating the carbon content of the gas phase.

To explore how pressure affects gas hydrate equilibria, you need to select the Pressure Pathway (Table A.1), plus you need to specify gas-phase mole fractions [$x_{(g)}$] for $CO_{2(g)}$ and/or $CH_{4(g)}$ (Table A.1). Then the model calculates increasing $P_{(g)}$ using the equation

$$P_{(g)} = x_{(g)} P_T \, , \tag{A.1}$$

where P_T is the specified total pressure.

If both $CH_{4(g)}$ and $CO_{2(g)}$ are present in the gas phase, there is an option to consider a mixed $(CH_4\text{-}CO_2)\cdot 6H_2O$ gas hydrate (MIX = 1, yes; MIX = 2, no). See Sect. 3.3.4 for a description of the mixture model. The option “MIX = 2, no” is a “nonsense” option that allows the program to treat the two gas systems as independent components. In reality, if both $CH_{4(g)}$ and $CO_{2(g)}$ are present, then a mixed structure I gas hydrate forms (Marion et al. 2006).

In addition of the instructions in Table A.1, there are also other, less frequently used, options that require changes in the program code. You might want to remove some solid phases from the mineral database for specific applications. For example, to simulate seawater, you might want to remove dolomite and magnesite from the mineral database because these minerals are not currently precipitating from seawater; instead, calcite is the normal seawater precipitate. Or you might want to remove all solid phases to simulate a pure solution-phase model. Instructions for removing selective minerals or all minerals are given at the end of the Parameter subroutine. If, for any reason, you want to assure that a solution is saturated with respect to a specific mineral (e.g., dolomite), then you can specify a mole amount that is sufficient to assure saturation (e.g., 0.1 moles). See comments in the middle of the main program. Also, you can refine a temperature change, evaporation, or pressure change step size as the model approaches equilibrium. See comments at the end of the main program.

A.3 Model Outputs

A.3.1 Seawater Freezing

Table A.2 is model output for seawater freezing at 253.15 K. Beneath the title, the output includes temperature, ionic strength, density of the solution (ρ), osmotic coefficient (ϕ), amount of unfrozen water, amount of ice, and pressure on the system. Beneath this line are the solution and gaseous species in the system. The seven columns include species identification, initial concentration, final (equilibrium) concentration, activity coefficient, activity, moles in the solution phase, and mass balance. The mass balance column only contains those components for which a mass balance is maintained. The number of these components minus 1 is generally the number of independent components in the system (in this case, $8 - 1 = 7$). The mass balances (col. 7) should equal the initial concentrations (col. 2). This mass balance comparison is a good check on the computational accuracy.

Solid phases that precipitate at −20 °C include ice, mirabilite, and calcite (Table A.2). In this particular case, we used the equilibrium crystallization option; as a consequence, the columns labeled "Moles" and "Accumulated moles" are identical. Had we used fractional crystallization, then the "Moles" column would have contained the moles of the solid phase that precipitated in the last temperature/evaporation/pressure step, and the "Accumulated moles" would include the total precipitation of that solid phase over all steps.

A.3.2 Strong Acid

The second output example (Table A.3) deals with strong acids. This is part of the simulation of the hypothetical acidic ocean for Europa described in Fig. 5.24.

At 263.15 K, the calculated pH is 0.02; this is just above the point where the pH dips into the negative range (Fig. 5.24). Because acidity (H^+) is specified as input (0.515 m), the system maintains a mass balance for H^+ (Table A.3); this is in contrast to the other examples (Tables A.2, A.4, and A.5) where the mass of H^+ is unconstrained. Note that a significant amount of solution "H" is present as H^+ and HSO_4^-. The number of independent components in this case (4) is again equal to the components under "Mass balance" (5) – 1.

Solids precipitating at 263.15 K include ice, mirabilite, and $MgSO_4{\cdot}12H_2O$ (Table A.3, Fig. 5.24). In this case, the bulk of the original water (1000 g) is actually present as hydrated salts (mirabilite = 132.2 g water; $MgSO_4{\cdot}12H_2O$ = 566.7 g water). In addition to using a comparison of "Initial conc." and "Mass balance" to check on the internal consistency of the model calculations (see above), solution activity products can be compared to equilibrium constants for solids that are precipitating. For example,

$$\left(a_{\mathrm{Mg}^{2+}}\right)\left(a_{\mathrm{SO}_4^{2-}}\right)(a_w)^{12} = K_{sp(\mathrm{MgSO_4\cdot 12H_2O})}\,, \tag{A.2}$$

which gives

$$(0.13813)(0.043025)(0.90762)^{12} = 0.18570 \times 10^{-2}\,, \tag{A.3}$$

$$0.18572 \times 10^{-2} \approx 0.18570 \times 10^{-2}\,, \tag{A.4}$$

which is within convergence criteria of perfect agreement.

A.3.3 Gas Hydrates

The third example of model outputs deals with gas hydrates (Table A.4), which was part of our snowball Earth simulations (Fig. 5.6). The P_{CO_2}, in this case, was set equal to 0.12 bars and was independent of total pressure; this served to prevent P_{CO_2} from becoming too high and beyond the validity of the alkalinity relationships (Sect. A.1). The P_{CH_4}, on the other hand, was allowed to increase with pressure and served as a surrogate for all potential gas hydrates.

Ferrous iron [Fe(II)] was arbitrarily set for these simulations; note that virtually all the Fe(II) precipitates as siderite ($FeCO_3$) (Table A.4), as was pointed out earlier (Table 5.2). During the snowball Earth phase, the assumption was made that seawater would be saturated with dolomite. To assure dolomite saturation, we arbitrarily set dolomite content equal to 0.1 moles at the start of the simulations [X(61) = 0.1]; this was done by incorporating a new line of code at the beginning of the program where molal concentrations are inputted (see version 9.2 comments in main program). Note the especially high Ca, Mg, and alkalinity contents under "Mass balance." This is a case where mass balance does not equal initial concentration because of the addition of solid-phase dolomite. Adding the 0.1 moles of dolomite to the initial concentrations does equal the Ca, Mg, and alkalinity contents under "Mass balance."

In Fig. 5.7, we pointed out that the stability fields of ice and $CH_4{\cdot}6H_2O$ ($x = 1.0$) overlap. Table A.4 shows equilibria at 22.0 bars of pressure, where ice is stable, and at 23.0 bars of pressure, where $CH_4{\cdot}6H_2O$ is stable. The transition from ice to $CH_4{\cdot}6H_2O$ occurs precisely at 22.4 bars of pressure (0.220 km), which is what is plotted at −3.37 °C in Fig. 5.7.

The number of components under "Mass balance" is nine, which means eight independent components for this system. Had we specified a "closed" carbon system for both CO_2 and CH_4, then the total number of independent components would have been ten instead of eight because the masses associated with CO_2 and CH_4 would then be fixed.

A.3.4 Pressure Application

Earlier, we examined the movement of salts through a Martian regolith under a freezing regime (Fig. 5.18). Initially, each layer (0.5 km) was separately equilibrated; this initial step removed virtually all the Fe(II) as siderite, most of the Ca as calcite, and a lesser percent of Mg as hydromagnesite. In a second step, we froze the system from the top down, which led to salt exclusion, increasing salt concentrations with depth, and additional precipitation of calcite and hydromagnesite (Fig. 5.18).

Table A.5 is the output file for salts in the 4.5- to 5.0-km layer, where the system pressure is 484.5 bars ($102 \text{ bars km}^{-1} \times 4.75 \text{ km}$). The temperature of 268.28 K is the freezing point depression for this particular composition and pressure; at 268.27 K, ice forms. The pH of this system is 8.02. The number of independent components is seven. This example deals with lithostatic pressures on solutions dispersed in a regolith, which is fundamentally different from the previous examples (Tables A.2–A.4) that dealt with seawaters.

Table A.1. Model Inputs (version 9.2) (hit return after every entry)

Title: Any alphanumeric character up to 50 characters.

Freeze (1) or evaporation (2) or pressure (3) pathway: Enter 1, 2, or 3 depending on whether you want to simulate a temperature change (1), an evaporation (2), or a pressure change (3). For evaluating a single point, enter 1.

Equilibrium (1) or fractional (2) crystallization: In equilibrium crystallization (1), precipitated solids are allowed to reequilibrate with the solution phase as environmental conditions change. In fractional crystallization (2), precipitated solids are removed and not allowed to reequilibrate with the solution phase as environmental conditions change.

Open (1) or closed (2) carbon system: If you want the gas partial pressure of CO_2 or CH_4 to be fixed at a given total pressure, enter 1. If you want the total carbon to be fixed, enter 2.

Sodium (m/kg): Enter sodium molality [moles/kg (water)]. Otherwise, enter 0.0.

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

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

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

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

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

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

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

Carbonate alkalinity: Enter as equivalents/kg (water). If alkalinity = 0.0, then you **must** enter 0.0. The latter will cause the model to skip all bicarbonate-carbonate, pH chemistries in the model.

Initial pH: If alkalinity > 0.0, then the model will calculate pH, given an initial pH estimate that is specified here. If this estimate is far removed from the true pH, then the model may not converge.

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. Thus 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. NB: 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.

Table A.1. (continued)

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 = $CO_2(g)$/total pressure]. For pure CO_2, enter 1.0. If 0.0, then $CO_2(g)$ is fixed and independent of total pressure.

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

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

Mole Fraction of CH_4: Enter the mole fraction of CH_4 (g) for the system (mole fraction = CH_4 (g)/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_2Gas Hydrate?: If both $CH_4(g)$ and $CO_2(g)$ are specified as inputs, then you can use these 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 = 2).

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

For temperature change pathway (1):

Final temperature (K): Enter final temperature of simulation (e.g., 273.15).

Temperature decrement (K): The temperature interval between simulations (e.g., 5). For the above temperature designations, the model would calculate equilibrium starting at 298.15 K and ending at 273.15 K at 5-K intervals. If you want to change the decrement in a run (e.g., to reduce the step size near an equilibrium), see the comments near the end of the main program.

For evaporation pathway (2):

Initial water (g): Normally enter "1000" at this point. The standard weight basis of the model is 1000 g water plus associated salts. If 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 1000 g, 950 g,. . . 100 g. If you want to change the decrement in a run (e.g., to reduce the step size near an equilibrium), see the comments near the end of the main program.

Table A.1. (continued)

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

Table A.2. Seawater Freezing

```
Temp(K)      Ion. str.    RHO          Phi          H2O (g)      Ice( g)      Press.
                                                                              (bars)
253.15       5.3658       1.1821       1.1949       119.15       876.08       1.0132

Solution     Initial      Final                                               Mass
SPECIES      conc.        conc.        Act. coef.   Activity     Moles        balance
NA           0.48610      3.6350       0.60965      2.2161       0.43311      0.48610
K            0.10580E-01  0.88795E-01  0.36930      0.32792E-01  0.10580E-01  0.10580E-01
CA           0.10650E-01  0.80088E-01  0.66744      0.53454E-01  0.95426E-02  0.10650E-01
MG           0.54750E-01  0.45949      0.83287      0.38269      0.54748E-01  0.54750E-01
H            0.43135E-07  0.74937E-08  3.7860       0.28371E-07  0.89288E-09
MGOH         0.00000      0.30775E-06  0.54815      0.16870E-06  0.36669E-07
CL           0.56664      4.7556       0.85911      4.0856       0.56664      0.56664
SO4          0.29270E-01  0.23293E-01  0.15949E-01  0.37150E-03  0.27754E-02  0.29270E-01
OH           0.80342E-07  0.14894E-06  0.23857E-01  0.35532E-08  0.17746E-07
HCO3         0.23000E-02  0.67038E-03  0.35346      0.23695E-03  0.79877E-04  0.23000E-02
CO3          0.00000      0.72520E-05  0.11142E-01  0.80805E-07  0.86409E-06
CO2          0.23919E-04  0.26151E-04  2.7363       0.71559E-04  0.31160E-05
CACO3        0.00000      0.82036E-05  1.0000       0.82036E-05  0.97746E-06
MGCO3        0.00000      0.14663E-04  1.0000       0.14663E-04  0.17471E-05
CO2(BAR)     0.36447E-03  0.36447E-03  0.99108      0.36122E-03  0.00000
H2O(BAR)     0.59398E-02                            .10407E-02
H2O(L)       55.50 8                                .82311       6.6139       55.508

Solid                               Equil.          Accum.
SPECIES                 Moles       constant        moles
ICE                     48.630      0.82312         48.630
NACL.2H2O               0.00000     8.3964          0.00000
NACL                    0.00000     23.777          0.00000
KCL                     0.00000     1.6878          0.00000
CACL2.6H2O              0.00000     905.66          0.00000
MGCL2.6H2O              0.00000     50099.          0.00000
MGCL2.8H2O              0.00000     2765.6          0.00000
MGCL2.12H2O             0.00000     71.792          0.00000
KMGCL3.6H2O             0.00000     2328.8          0.00000
CACL2.2MGCL2.12H2O      0.00000     0.44358E+20     0.00000
NA2SO4.10H2O            0.26495E-01 0.26044E-03     0.26495E-01
NA2SO4                  0.00000     0.47236         0.00000
MGSO4.6H2O              0.00000     0.17365E-01     0.00000
MGSO4.7H2O              0.00000     0.30124E-02     0.00000
K2SO4                   0.00000     0.25490E-02     0.00000
MGSO4.K2SO4.6H2O        0.00000     0.14492E-05     0.00000
NA2SO4.MGSO4.4H2O       0.00000     0.29347E-02     0.00000
CASO4.2H2O              0.00000     0.14314E-04     0.00000
CASO4                   0.00000     0.94256E-04     0.00000
MGSO4.12H2O             0.00000     0.76631E-03     0.00000
NA2SO4.3K2SO4           0.00000     0.67174E-10     0.00000
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Table A.2. (continued)

```
CACO3(CALCITE)          0.11064E-02      0.43185E-08      0.11064E-02
MGCO3                   0.00000          0.59380E-07      0.00000
MGCO3.3H2O              0.00000          0.29948E-04      0.00000
MGCO3.5H2O              0.00000          0.27452E-04      0.00000
CACO3.6H2O              0.00000          0.16425E-07      0.00000
NAHCO3                  0.00000          0.12013          0.00000
NA2CO3.10H2O            0.00000          0.31966E-02      0.00000
NAHCO3.NA2CO3.2H2O      0.00000          0.30301E-01      0.00000
3MGCO3.MG(OH)2.3H2O     0.00000          0.36356E-33      0.00000
CAMG(CO3)2              0.00000          0.14022E-15      0.00000
NA2CO3.7H2O             0.00000          0.27789E-01      0.00000
KHCO3                   0.00000          0.36768          0.00000
CACO3(ARAGONITE)        0.00000          0.65648E-08      0.00000
CACO3(VATERITE)         0.00000          0.21983E-07      0.00000
HNO3.3H2O               0.00000          171.86           0.00000
KNO3                    0.00000          0.35949E-01      0.00000
NANO3                   0.00000          2.9739           0.00000
HCL.3H2O                0.00000          10605.           0.00000
H2SO4.6.5H2O            0.00000          28.096           0.00000
H2SO4.4H2O              0.00000          999.90           0.00000
HCL.6H2O                0.00000          1000.0           0.00000
NANO3.NA2SO4.2H2O       0.00000          0.84122E-01      0.00000
NA3H(SO4)2              0.00000          0.55904E-01      0.00000
NAHSO4.H2O              0.00000          42.328           0.00000
K3H(SO4)2               0.00000          0.50489E-04      0.00000
K5H3(SO4)4              0.00000          0.88999E-08      0.00000
K8H6(SO4)7.H2O          0.00000          0.44537E-12      0.00000
KHSO4                   0.00000          0.66187          0.00000
MGSO4.H2O               0.00000          47.746           0.00000
FESO4.7H2O              0.00000          0.11380E-02      0.00000
FESO4.H2O               0.00000          0.47599          0.00000
FECL2.6H2O              0.00000          8232.3           0.00000
FECL2.4H2O              0.00000          0.10000E+07      0.00000
FECO3                   0.00000          0.18333E-10      0.00000
FE(OH)3                 0.00000          0.14608E+15      0.00000
CO2.6H2O                0.00000          1.4185           0.00000
CH4.6H2O                0.00000          3.8708           0.00000

Iterations = 16
```

Table A.3. Strong acid

```
Temp(K)      Ion. str.    RHO          Phi          H2O(g)       Ice (g)      Press.
                                                                              (bars)
263.15       6.6373       1.1508       0.98802      235.25       65.800       1.0132

Solution     Initial      Final                                               Mass
SPECIES      conc.        conc.        Act. coef.   Activity     moles        Balance
NA           1.6200       0.64651      0.36435      0.23555      0.15209      1.6200
MG           2.8670       1.0436       0.13236      0.13813      0.24550      2.8670
H            0.51500      1.2939       0.74045      0.95807      0.30440      0.51500
SO4          3.9345       1.5662       0.27472E-01  0.43025E-01  0.36844      3.9345
OH           0.14587E-13  0.19128E-14  0.19846      0.37962E-15  0.45000E-15
HSO4         0.00000      0.89523      1.7337       1.5521       0.21060
H2SO4(BAR)   0.00000                                .33866E-22
H2O(BAR)     0.49589E-02                            .25954E-02
H2O(L)                                 55.508       .90762       13.058       55.508

Solid                                   Equil.          Accum.
SPECIES                 Moles           constant        moles
ICE                     3.6525          0.90762         3.6525
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            0.73395         0.90537E-03     0.73395
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              0.00000         0.18490E-04     0.00000
CASO4                   0.00000         0.94050E-04     0.00000
MGSO4.12H2O             2.6215          0.18570E-02     2.6215
NA2SO4.3K2SO4           0.00000         0.30930E-09     0.00000
CACO3(CALCITE)          0.00000         0.43033E-08     0.00000
MGCO3                   0.00000         999.90          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     0.00000         0.52738E-34     0.00000
CAMG(CO3)2              0.00000         999.90          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         2.3218          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
```

Table A.3. (continued)

```
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          0.30291E+14      0.00000
CO2.6H2O           0.00000          3.8247           0.00000
CH4.6H2O           0.00000          9.8303           0.00000

Iterations = 12
```

Table A.4. Snowball Earth (P = 22 bars)

```
Temp (K)     Ion. str.    RHO          Phi          H2O (g)      Ice (g)      Press.(bars)
269.78       1.1948       1.0462       0.90033      872.39       127.61       22.013

Solution     Initial      Final                                               Mass
SPECIES      conc.        conc.        Act. coef.   Activity     Moles        balance
NA           0.65072      0.74590      0.58667      0.43760      0.65072      0.65072
K            0.14810E-01  0.16976E-01  0.54160      0.91943E-02  0.14810E-01  0.14810E-01
CA           0.14910E-01  0.28765E-01  0.18186      0.52313E-02  0.25094E-01  0.11491
MG           0.76650E-01  0.99533E-01  0.18345      0.18259E-01  0.86832E-01  0.17665
H            0.41971E-06  0.32686E-06  0.77747      0.25413E-06  0.28515E-06
MGOH         0.00000      0.80770E-08  0.86688      0.70018E-08  0.70463E-08
FE           0.14910E-01  0.18860E-04  1.0549       0.19896E-04  0.16454E-04  0.14910E-01
FEOH         0.00000      0.26680E-08  0.86469      0.23070E-08  0.23276E-08
CL           0.79329      0.90933      0.67374      0.61265      0.79329      0.79329
SO4          0.40980E-01  0.46974E-01  0.72763E-01  0.34180E-02  0.40980E-01  0.40980E-01
OH           0.68471E-08  0.94432E-08  0.33906      0.32018E-08  0.82382E-08
HCO3         0.32200E-02  0.16215E-01  0.52963      0.85877E-02  0.14146E-01  0.40322
CO3          0.00000      0.11352E-04  0.63513E-01  0.72099E-06  0.99033E-05
CO2          0.85930E-02  0.73746E-02  1.2540       0.92476E-02  0.64336E-02
FECO3        0.00000      0.21260E-06  1.0000       0.21260E-06  0.18547E-06
CACO3        0.00000      0.44890E-05  1.0000       0.44890E-05  0.39161E-05
MGCO3        0.00000      0.75996E-05  1.0000       0.75996E-05  0.66298E-05
CH4          0.21503E-02  0.41284E-01  1.2636       0.52167E-01  0.36016E-01
CH4(BAR)     1.0132       22.013       0.94879      20.886       0.00000
CO2(BAR)     0.12000      0.12000      0.84531      0.10144      0.00000
H2O(BAR)     0.46099E-02                            .45102E-02
H2O(L)       55.508                                 .96943       48.425       55.508

Solid                                   Equil.          Accum.
SPECIES                 Moles           constant        moles
ICE                     7.0833          0.96943         7.0833
NACL.2H2O               0.00000         16.160          0.00000
NACL                    0.00000         30.659          0.00000
KCL                     0.00000         3.3876          0.00000
CACL2.6H2O              0.00000         1639.5          0.00000
MGCL2.6H2O              0.00000         56916.          0.00000
MGCL2.8H2O              0.00000         6256.8          0.00000
MGCL2.12H2O             0.00000         450.17          0.00000
KMGCL3.6H2O             0.00000         6785.2          0.00000
CACL2.2MGCL2.12H2O      0.00000         0.46835E+19     0.00000
NA2SO4.10H2O            0.00000         0.21216E-02     0.00000
NA2SO4                  0.00000         0.51235         0.00000
MGSO4.6H2O              0.00000         0.20178E-01     0.00000
MGSO4.7H2O              0.00000         0.56803E-02     0.00000
K2SO4                   0.00000         0.57253E-02     0.00000
MGSO4.K2SO4.6H2O        0.00000         0.75677E-05     0.00000
NA2SO4.MGSO4.4H2O       0.00000         0.36648E-02     0.00000
CASO4.2H2O              0.00000         0.21880E-04     0.00000
CASO4                   0.00000         0.94803E-04     0.00000
MGSO4.12H2O             0.00000         0.33979E-02     0.00000
NA2SO4.3K2SO4           0.00000         0.10059E-08     0.00000
CACO3(CALCITE)          0.00000         0.44905E-08     0.00000
MGCO3                   0.00000         0.29502E-07     0.00000
MGCO3.3H2O              0.00000         0.11135E-04     0.00000
MGCO3.5H2O              0.00000         0.72384E-05     0.00000
CACO3.6H2O              0.00000         0.52616E-07     0.00000
NAHCO3                  0.00000         0.17664         0.00000
NA2CO3.10H2O            0.00000         0.12319E-01     0.00000
NAHCO3.NA2CO3.2H2O      0.00000         0.49625E-01     0.00000
3MGCO3.MG(OH)2.3H2O     0.00000         0.20069E-34     0.00000
CAMG(CO3)2              0.89812E-01     0.49654E-16     0.89812E-01
NA2CO3.7H2O             0.00000         0.75074E-01     0.00000
KHCO3                   0.00000         0.62665         0.00000
CACO3(ARAGONITE)        0.00000         0.65686E-08     0.00000
CACO3(VATERITE)         0.00000         0.20047E-07     0.00000
```

Table A.4. (continued)

```
HNO3.3H2O            0.00000        552.06         0.00000
KNO3                 0.00000        0.13366        0.00000
NANO3                0.00000        2.3780         0.00000
HCL.3H2O             0.00000        13809.         0.00000
H2SO4.6.5H2O         0.00000        16.942         0.00000
H2SO4.4H2O           0.00000        1031.8         0.00000
HCL.6H2O             0.00000        978.59         0.00000
NANO3.NA2SO4.2H2O    0.00000        0.11297        0.00000
NA3H(SO4)2           0.00000        0.15590        0.00000
NAHSO4.H2O           0.00000        31.454         0.00000
K3H(SO4)2            0.00000        0.60930E-04    0.00000
K5H3(SO4)4           0.00000        0.27170E-07    0.00000
K8H6(SO4)7.H2O       0.00000        0.48939E-12    0.00000
KHSO4                0.00000        1.2824         0.00000
MGSO4.H2O            0.00000        5.3255         0.00000
FESO4.7H2O           0.00000        0.17336E-02    0.00000
FESO4.H2O            0.00000        0.31455        0.00000
FECL2.6H2O           0.00000        2785.5         0.00000
FECL2.4H2O           0.00000        14020.         0.00000
FECO3                0.14893E-01    0.14345E-10    0.14893E-01
FE(OH)3              0.00000        0.11382E+14    0.00000
CO2.6H2O             0.00000        7.3200         0.00000
CH4.6H2O             0.00000        18.074         0.00000

Iterations = 3
```

Table A.4. Snowball Earth (P = 23 bars)

```
Temp(K)      Ion. str.    RHO          Phi          H2O (g)      Ice (g)      Press.
                                                                              (bars)
269.78       1.1985       1.0464       0.90052      869.57       0.00000      23.013

Solution     Initial      Final                                               Mass
SPECIES      conc.        conc.        Act. coef.   Activity     Moles        balance
NA           0.65072      0.74832      0.58658      0.43895      0.65072      0.65072
K            0.14810E-01  0.17031E-01  0.54140      0.92207E-02  0.14810E-01  0.14810E-01
CA           0.14910E-01  0.28833E-01  0.18184      0.52432E-02  0.25073E-01  0.11491
MG           0.76650E-01  0.99831E-01  0.18349      0.18318E-01  0.86810E-01  0.17665
H            0.41971E-06  0.32593E-06  0.77808      0.25360E-06  0.28342E-06
MGOH         0.00000      0.81206E-08  0.86670      0.70382E-08  0.70615E-08
FE           0.14910E-01  0.18880E-04  1.0567       0.19950E-04  0.16418E-04  0.14910E-01
FEOH         0.00000      0.26812E-08  0.86450      0.23179E-08  0.23315E-08
CL           0.79329      0.91228      0.67378      0.61467      0.79329      0.79329
SO4          0.40980E-01  0.47127E-01  0.72612E-01  0.34219E-02  0.40980E-01  0.40980E-01
OH           0.68471E-08  0.94913E-08  0.33840      0.32118E-08  0.82534E-08
HCO3         0.32200E-02  0.16167E-01  0.52940      0.85588E-02  0.14058E-01  0.40322
CO3          0.00000      0.11425E-04  0.63108E-01  0.72104E-06  0.99352E-05
CO2          0.85930E-02  0.73213E-02  1.2546       0.91857E-02  0.63664E-02
FECO3        0.00000      0.21320E-06  1.0000       0.21320E-06  0.18539E-06
CACO3        0.00000      0.44964E-05  1.0000       0.44964E-05  0.39100E-05
MGCO3        0.00000      0.76219E-05  1.0000       0.76219E-05  0.66278E-05
CH4          0.21503E-02  0.42960E-01  1.2646       0.54329E-01  0.37357E-01
CH4(BAR)     1.0132       23.013       0.94652      21.782       0.00000
CO2(BAR)     0.12000      0.12000      0.83840      0.10061      0.00000
H2O(BAR)     0.46099E-02                            .45060E-02
H2O(L)       55.508                                 .96930       48.269       55.508

Solid                           Equil.          Accum.
SPECIES         Moles           constant        moles
ICE             0.00000         0.96950         0.00000
NACL.2H2O       0.00000         16.167          0.00000
NACL            0.00000         30.679          0.00000
KCL             0.00000         3.3898          0.00000
CACL2.6H2O      0.00000         1640.1          0.00000
MGCL2.6H2O      0.00000         56946.          0.00000
MGCL2.8H2O      0.00000         6258.2          0.00000
MGCL2.12H2O     0.00000         450.02          0.00000
```

Table A.4. (continued)

```
KMGCL3.6H2O             0.00000         6794.8          0.00000
CACL2.2MGCL2.12H2O      0.00000         0.46969E+19     0.00000
NA2SO4.10H2O            0.00000         0.21253E-02     0.00000
NA2SO4                  0.00000         0.51354         0.00000
MGSO4.6H2O              0.00000         0.20213E-01     0.00000
MGSO4.7H2O              0.00000         0.56891E-02     0.00000
K2SO4                   0.00000         0.57362E-02     0.00000
MGSO4.K2SO4.6H2O        0.00000         0.75930E-05     0.00000
NA2SO4.MGSO4.4H2O       0.00000         0.36796E-02     0.00000
CASO4.2H2O              0.00000         0.21929E-04     0.00000
CASO4                   0.00000         0.95046E-04     0.00000
MGSO4.12H2O             0.00000         0.34007E-02     0.00000
NA2SO4.3K2SO4           0.00000         0.10139E-08     0.00000
CACO3(CALCITE)          0.00000         0.45038E-08     0.00000
MGCO3                   0.00000         0.29581E-07     0.00000
MGCO3.3H2O              0.00000         0.11161E-04     0.00000
MGCO3.5H2O              0.00000         0.72522E-05     0.00000
CACO3.6H2O              0.00000         0.52708E-07     0.00000
NAHCO3                  0.00000         0.17682         0.00000
NA2CO3.10H2O            0.00000         0.12339E-01     0.00000
NAHCO3.NA2CO3.2H2O      0.00000         0.49783E-01     0.00000
3MGCO3.MG(OH)2.3H2O     0.00000         0.20294E-34     0.00000
CAMG(CO3)2              0.89833E-01     0.49933E-16     0.89833E-01
NA2CO3.7H2O             0.00000         0.75223E-01     0.00000
KHCO3                   0.00000         0.62717         0.00000
CACO3(ARAGONITE)        0.00000         0.65872E-08     0.00000
CACO3(VATERITE)         0.00000         0.20107E-07     0.00000
HNO3.3H2O               0.00000         551.92          0.00000
KNO3                    0.00000         0.13375         0.00000
NANO3                   0.00000         2.3797          0.00000
HCL.3H2O                0.00000         13805.          0.00000
H2SO4.6.5H2O            0.00000         16.964          0.00000
H2SO4.4H2O              0.00000         1033.3          0.00000
HCL.6H2O                0.00000         977.59          0.00000
NANO3.NA2SO4.2H2O       0.00000         0.11328         0.00000
NA3H(SO4)2              0.00000         0.15590         0.00000
NAHSO4.H2O              0.00000         31.482          0.00000
K3H(SO4)2               0.00000         0.60930E-04     0.00000
K5H3(SO4)4              0.00000         0.27170E-07     0.00000
K8H6(SO4)7.H2O          0.00000         0.48939E-12     0.00000
KHSO4                   0.00000         1.2836          0.00000
MGSO4.H2O               0.00000         5.3380          0.00000
FESO4.7H2O              0.00000         0.17363E-02     0.00000
FESO4.H2O               0.00000         0.31530         0.00000
FECL2.6H2O              0.00000         2787.5          0.00000
FECL2.4H2O              0.00000         14033.          0.00000
FECO3                   0.14893E-01     0.14385E-10     0.14893E-01
FE(OH)3                 0.00000         0.11382E+14     0.00000
CO2.6H2O                0.00000         7.3182          0.00000
CH4.6H2O                1.2066          18.066          1.2066

Iterations = 3
```

Table A.5. Mars Regolith

```
Temp(K)      Ion. str.    RHO          Phi          H2O (g)      Ice (g)      Press.
                                                                              (bars)
268.28       0.48032      1.0437       0.83074      999.08       0.00000      484.50

Solution     Initial      Final                                               Mass
SPECIES      conc.        conc.        Act. coef.   Activity     Moles        balance
NA           0.21510      0.21530      0.64014      0.13782      0.21510      0.21510
K            0.19200E-01  0.19218E-01  0.65199      0.12530E-01  0.19200E-01  0.19200E-01
CA           0.14070E-02  0.47339E-03  0.17557      0.83114E-04  0.47296E-03  0.14070E-02
MG           0.13340      0.64172E-01  0.20350      0.13059E-01  0.64113E-01  0.13340
H            0.15749E-07  0.14394E-07  0.66694      0.96001E-08  0.14381E-07
MGOH         0.00000      0.16225E-06  0.71089      0.11535E-06  0.16211E-06
CL           0.17680      0.17696      0.70657      0.12504      0.17680      0.17680
SO4          0.48000E-01  0.48044E-01  0.18075      0.86839E-02  0.48000E-01  0.48000E-01
OH           0.23143E-06  0.22936E-06  0.54025      0.12391E-06  0.22915E-06
HCO3         0.23111      0.83117E-01  0.62800      0.52197E-01  0.83041E-01  0.23111
CO3          0.00000      0.38196E-02  0.52089E-01  0.19896E-03  0.38161E-02
CO2          0.10524E-02  0.10685E-02  1.1046       0.11803E-02  0.10675E-02
CACO3        0.00000      0.20076E-04  1.0000       0.20076E-04  0.20058E-04
MGCO3        0.00000      0.14711E-02  1.0000       0.14711E-02  0.14698E-02
CO2(BAR)     0.50000E-01  0.50000E-01  0.12096      0.60482E-02  0.00000
H2O(BAR)     0.28776E-02                            .28495E-02
H2O(L)       55.508                                 .99073       55.458       55.508

Solid                                   Equil.          Accum.
SPECIES                 Moles           constant        moles
ICE                     0.00000         0.99077         0.00000
NACL.2H2O               0.00000         18.212          0.00000
NACL                    0.00000         39.472          0.00000
KCL                     0.00000         4.1861          0.00000
CACL2.6H2O              0.00000         1764.9          0.00000
MGCL2.6H2O              0.00000         70328.          0.00000
MGCL2.8H2O              0.00000         6413.0          0.00000
MGCL2.12H2O             0.00000         315.35          0.00000
KMGCL3.6H2O             0.00000         11330.          0.00000
CACL2.2MGCL2.12H2O      0.00000         0.19267E+20     0.00000
NA2SO4.10H2O            0.00000         0.37515E-02     0.00000
NA2SO4                  0.00000         1.3812          0.00000
MGSO4.6H2O              0.00000         0.42041E-01     0.00000
MGSO4.7H2O              0.00000         0.10526E-01     0.00000
K2SO4                   0.00000         0.12019E-01     0.00000
MGSO4.K2SO4.6H2O        0.00000         0.27611E-04     0.00000
NA2SO4.MGSO4.4H2O       0.00000         0.20469E-01     0.00000
CASO4.2H2O              0.00000         0.56356E-04     0.00000
CASO4                   0.00000         0.29233E-03     0.00000
MGSO4.12H2O             0.00000         0.42295E-02     0.00000
NA2SO4.3K2SO4           0.00000         0.22604E-07     0.00000
CACO3(CALCITE)          0.91398E-03     0.16536E-07     0.91398E-03
MGCO3                   0.00000         3387.4          0.00000
MGCO3.3H2O              0.00000         0.33512E-04     0.00000
MGCO3.5H2O              0.00000         0.17425E-04     0.00000
CACO3.6H2O              0.00000         0.10157E-06     0.00000
NAHCO3                  0.00000         0.25645         0.00000
NA2CO3.10H2O            0.00000         0.21644E-01     0.00000
NAHCO3.NA2CO3.2H2O      0.00000         0.18391         0.00000
3MGCO3.MG(OH)2.3H2O     0.16954E-01     0.34197E-32     0.16954E-01
CAMG(CO3)2              0.00000         13028.          0.00000
NA2CO3.7H2O             0.00000         0.16329         0.00000
KHCO3                   0.00000         0.84309         0.00000
```

Table A.5. (continued)

```
CACO3(ARAGONITE)     0.00000          0.22903E-07      0.00000
CACO3(VATERITE)      0.00000          0.75891E-07      0.00000
HNO3.3H2O            0.00000          444.85           0.00000
KNO3                 0.00000          0.16394          0.00000
NANO3                0.00000          3.2207           0.00000
HCL.3H2O             0.00000          11512.           0.00000
H2SO4.6.5H2O         0.00000          33.139           0.00000
H2SO4.4H2O           0.00000          2005.9           0.00000
HCL.6H2O             0.00000          614.08           0.00000
NANO3.NA2SO4.2H2O    0.00000          0.33811          0.00000
NA3H(SO4)2           0.00000          0.15607          0.00000
NAHSO4.H2O           0.00000          44.699           0.00000
K3H(SO4)2            0.00000          0.58754E-04      0.00000
K5H3(SO4)4           0.00000          0.24568E-07      0.00000
K8H6(SO4)7.H2O       0.00000          0.46538E-12      0.00000
KHSO4                0.00000          1.7528           0.00000
MGSO4.H2O            0.00000          17.449           0.00000
FESO4.7H2O           0.00000          0.32131E-02      0.00000
FESO4.H2O            0.00000          0.91684          0.00000
FECL2.6H2O           0.00000          4033.6           0.00000
FECL2.4H2O           0.00000          22219.           0.00000
FECO3                0.00000          0.49614E-10      0.00000
FE(OH)3              0.00000          0.14144E+14      0.00000
CO2.6H2O             0.00000          5.7776           0.00000
CH4.6H2O             0.00000          13.232           0.00000

Iterations = 3
```

B Parameter Tables

This appendix contains a complete listing of all parameters used in the FREZCHEM model (version 9.2). Tables B.1–B.6 deal primarily with model parameterizations as a function of temperature at 1.01 bar pressure. Tables B.7–B.11 list volumetric parameters used in developing a pressure dependence for the model. Table B.12 deals with gas hydrate equilibria.

Table B.1 lists all the chemical reactions and their temperature dependence. Table B.2 lists the Debye–Hückel constants (A_ϕ and A_v) as a function of temperature and pressure. Table B.3 lists the numerical arrays used for calculating unsymmetrical interactions (Equations 2.62 and 2.66). Table B.4 lists binary Pitzer-equation parameters for cations and anions as a function of temperature. Table B.5 lists ternary Pitzer-equation parameters for cations and anions as a function of temperature. Table B.6 lists binary and ternary Pitzer-equation parameters for soluble gases as a function of temperature. Table B.7 lists equations used to estimate the molar volume of liquid water and water ice as a function of temperature at 1.01 bar pressure and their compressibilities. Table B.8 lists equations for the molar volume and the compressibilities of soluble ions and gases as a function of temperature. Table B.9 lists the molar volumes of solid phases. Table B.10 lists volumetric Pitzer-equation parameters for ion interactions as a function of temperature. Table B.11 lists pressure-dependent coefficients for volumetric Pitzer-equation parameters. Table B.12 lists parameters used to estimate gas fugacities using the Duan et al. (1992b) model.

Several of these tables are fitted to the equation

$$P(T)_i = a_{1i} + a_{2i}T + a_{3i}T^2 + a_{4i}T^3 + \frac{a_{5i}}{T} + a_{6i}\ln(T) + \frac{a_{7i}}{T^2} + a_{8i}T^4\,. \quad \text{(B.1)}$$

In Table B.1, $P(T)_i = \mathrm{Ln}(K)$, except for ice (see footnote); in Tables B.4–B.6, B.8, and B.10, $P(T)_i$ is a Pitzer-equation parameter.

Table B.1. Chemical reactions and their equation parameters used in the FREZCHEM model (version 9.2).[a] (Numbers are in computer scientific notation, where e $\pm$ xx stands for $10^{\pm xx}$)

Reaction	Equation parameters							
Solution–solid-phase equilibria	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$H_2O(cr,I)$ $\leftrightarrow$ $H_2O(l)$	1.906354e0	−1.880285e-2	6.603001e-5	−3.419967e-8				
$NaCl(cr)$ $\leftrightarrow$ $Na^+(aq) + Cl^-(aq)$	9.14839001e3	8.22348745e0	−8.1288759e-3	3.95552403e-6	−1.54040868e5	−1.83624247e3		
$NaCl{\cdot}2H_2O(cr)$ $\leftrightarrow$ $Na^+(aq) + Cl^-(aq) + 2H_2O(l)$	−1.2222551e4	−9.8806459e0	8.46685083e-3	−3.4459117e-6	2.09823965e5	2.42328528e3		
$KCl(cr)$ $\leftrightarrow$ $K^+(aq) + Cl^-(aq)$	−1.62917341e3	−1.51940390e0	1.45249679e-3	−6.9427505e-7	2.26012743e4	3.33075506e2		
$MgCl_2{\cdot}6H_2O(cr)$ $\leftrightarrow$ $Mg^{2+}(aq) + 2Cl^-(aq) + 6H_2O(l)$	7.52225099e2	1.17584653e-1			−2.43223909e4	−1.21990076e2		
$MgCl_2{\cdot}8H_2O(cr)$ $\leftrightarrow$ $Mg^{2+}(aq) + 2Cl^-(aq) + 8H_2O(l)$	2.27801976e3	6.49361616e-1			−6.23075123e4	−3.95438891e2		
$MgCl_2{\cdot}12H_2O(cr)$ $\leftrightarrow$ $Mg^{2+}(aq) + 2Cl^-(aq) + 12H_2O(l)$	2.55008896e5	2.44532240e2	−2.48807876e-1	1.22425236e-4	−4.02988342e6	−5.18668604e4		
$CaCl_2{\cdot}6H_2O(cr)$ $\leftrightarrow$ $Ca^{2+}(aq) + 2Cl^-(aq) + 6H_2O(l)$	1.42290062e5	1.61973105e2	−1.95332071e-1	1.17636119e-4	−2.04059847e6	−2.97464810e4		
$FeCl_2{\cdot}4H_2O(cr)$ $\leftrightarrow$ $Fe^{2+}(aq) + 2Cl^-(aq)$[c]	−4.594879e0	1.45731e-1	−3.461353e-4					
$FeCl_2{\cdot}6H_2O(cr)$ $\leftrightarrow$ $Fe^{2+}(aq) + 2Cl^-(aq) + 6H_2O(l)$	−3.607762e2	4.61798e0	−1.886403e-2	2.525105e-5				
$KMgCl_3{\cdot}6H_2O(cr)$ $\leftrightarrow$ $K^+(aq) + Mg^{2+}(aq) + 3Cl^-(aq) + 6H_2O(l)$	−4.45702171e1	2.32023790e-1	−7.14935692e-4	5.32658215e-7	−4.24817923e3	8.59110245e0		
$CaCl_2{\cdot}2MgCl_2{\cdot}12H_2O(cr)$ $\leftrightarrow$ $Ca^{2+}(aq) + 2Mg^{2+}(aq) + 6Cl^-(aq) + 12H_2O(l)$	8.03777918e1	−1.388069e-1						

Table B.1. (continued)

Solution–solid-phase equilibria	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$Na_2SO_4(cr)$ $\leftrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$	−1.238537e0	1.929792e-3						
$Na_2SO_4{\cdot}10H_2O(cr)$ $\leftrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$ $+ 10H_2O(l)$	−4.633773e1	1.753075e-1	−9.822103e-5					
$K_2SO_4(cr)$ $\leftrightarrow 2K^+(aq) + SO_4^{2-}(aq)$	6.500e0				−3.1573e3			
$MgSO_4{\cdot}H_2O(cr)$ $\leftrightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ $+ H_2O(l)$	1.306284e2	−8.44064e-1	1.356205e-3					
$MgSO_4{\cdot}6H_2O(cr)$ $\leftrightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ $+ 6H_2O(l)$	−5.7876e0	6.8509e-3						
$MgSO_4{\cdot}7H_2O(cr)$ $\leftrightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ $+ 7H_2O(l)$	3.956e0				−2.4710e3			
$MgSO_4{\cdot}12H_2O(cr)$ $\leftrightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ $+ 12H_2O(l)$	−2.95818e1	8.851618e-2						
$CaSO_4(cr)$ $\leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$	−7.822042e1	6.908174e-1	−2.246589e-3	2.344988e-6				
$CaSO_4{\cdot}2H_2O(cr)$ $\leftrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$ $+ 2H_2O(l)$	−9.107165e1	7.584271e-1	−2.370863e-3	2.456876e-6				
$FeSO_4{\cdot}H_2O(cr)$ $\leftrightarrow Fe^{2+}(aq) + SO_4^{2-}(aq)$ $+ H_2O(l)$	6.324332e0	−2.7915e-2						
$FeSO_4{\cdot}7H_2O(cr)$ $\leftrightarrow Fe^{2+}(aq) + SO_4^{2-}(aq)$ $+ 7H_2O(l)$	2.096187e1	−2.343349e-1	4.928070e-4					
$Na_2SO_4{\cdot}3K_2SO_4(cr)$ $\leftrightarrow 2Na^+(aq) + 6K^+(aq)$ $+ 4SO_4^{2-}(aq)$	−6.207986e1	1.527005e-1						

Table B.1. (continued)

Solution–solid-phase equilibria	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O(cr)$ $\leftrightarrow 2Na^+(aq) + Mg^{2+}(aq)$ $+ 2SO_4^{2-}(aq) + 4H_2O(l)$	−7.9121e0	8.220223e-3						
$MgSO_4 \cdot K_2SO_4 \cdot 6H_2O(cr)$ $\leftrightarrow 2K^+(aq) + Mg^{2+}(aq)$ $+ 2SO_4^{2-}(aq) + 6H_2O(l)$	−8.661262e1	4.70966e-1	−7.186864e-4					
$NaNO_3(cr)$ $\leftrightarrow Na^+(aq) + NO_3^-(aq)$	7.016265e2	−9.648812e0	5.093224e-2	−1.227837e-4				1.144431e-7
$KNO_3(cr)$ $\leftrightarrow K^+(aq) + NO_3^-(aq)$	−4.652079e1	2.575014e-1	−3.431593e-4					
$NaNO_3 \cdot Na_2SO_4 \cdot 2H_2O(cr)$ $\leftrightarrow 3Na^+(aq) + NO_3^-(aq)$ $+ SO_4^{2-}(aq) + 2H_2O(l)$	1.419947e2	−1.11958e0	2.16824e-3					
$NaHCO_3(cr)$ $\leftrightarrow Na^+(aq) + HCO_3^-(aq)$	1.391669e2	−1.556298e0	5.625521e-3	−6.6461e-6				
$Na_2CO_3 \cdot 7H_2O(cr)$ $\leftrightarrow 2Na^+(aq) + CO_3^{2-}(aq)$ $+ 7H_2O(l)$	−1.807263e1	5.723688e-2						
$Na_2CO_3 \cdot 10H_2O(cr)$ $\leftrightarrow 2Na^+(aq) + CO_3^{2-}(aq)$ $+ 10H_2O(l)$	−7.861589e0	−5.802879e-2	2.622444e-4					
$NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O(cr)$ $\leftrightarrow 3Na^+(aq) + HCO_3^-(aq)$ $+ CO_3^{2-}(aq) + 2H_2O(l)$	−9.986743e0	2.563766e-2						
$KHCO_3(cr)$ $\leftrightarrow K^+(aq) + HCO_3^-(aq)$	−6.500201e0	1.301118e-2	3.442106e-5					
$MgCO_3(cr)$ $\leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$	−2.8902e1				3.1043e3			
$MgCO_3 \cdot 3H_2O(cr)$ $\leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$ $+ 3H_2O(l)$	5.847459e1	−4.688674e-1	7.771429e-4					
$MgCO_3 \cdot 5H_2O(cr)$ $\leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$ $+ 5H_2O(l)$	9.556371e2	−1.003715e1	3.464409e-2	−3.978274e-5				

Table B.1. (continued)

Solution–solid-phase equilibria	a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
$MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O(cr) \leftrightarrow 2Mg^{2+}(aq) + CO_3^{2-}(aq) + 2OH^-(aq) + 3H_2O(l)$	−1.27801e2				1.2861e4			
$CaCO_3(cr) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$ (calcite)	−3.958293e2	−1.79586e-1			6.537774e3	7.1595e1		
$CaCO_3(cr) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$ (aragonite)	−3.959924e2	−1.79586e-1			6.685079e3	7.1595e1		
$CaCO_3(cr) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$ (vaterite)	−3.963428e2	−1.79586e-1			7.079731e3	7.1595e1		
$CaCO_3{\cdot}6H_2O(cr) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq) + 6H_2O(l)$	3.6798e-1				−4.63073e3			
$CaMg(CO_3)_2(cr) \leftrightarrow Ca^{2+}(aq) + Mg^{2+}(aq) + 2CO_3^{2-}(aq)$	−5.5261e1				4.7485e3			
$FeCO_3(cr) \leftrightarrow Fe^{2+}(aq) + CO_3^{2-}(aq)$	−2.9654e1				1.24845e3			
$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \leftrightarrow 4Fe(OH)_3(cr) + 8H^+(aq)$	−8.786e0				1.04807e4			
$HCl{\cdot}3H_2O(cr) \leftrightarrow H^+(aq) + Cl^-(aq) + 3H_2O(l)$	5.142350e0	1.630170e-2						
$HCl{\cdot}6H_2O(cr) \leftrightarrow H^+(aq) + Cl^-(aq) + 6H_2O(l)$	4.367384e0	3.637139e-3						
$HNO_3{\cdot}3H_2O(cr) \leftrightarrow H^+(aq) + NO_3^-(aq) + 3H_2O(l)$	−1.270087e1	7.050180e-2						

Table B.1. (continued)

Solution–solid-phase equilibria	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$H_2SO_4{\cdot}4H_2O(cr) \leftrightarrow 2H^+(aq) + SO_4^{2-}(aq) + 4H_2O(l)$	−7.103329e1	6.235489e-1	−1.279573e-3					
$H_2SO_4{\cdot}6.5H_2O(cr) \leftrightarrow 2H^+(aq) + SO_4^{2-}(aq) + 6.5H_2O(l)$	−8.947832e1	7.407673e-1	−1.477903e-3					
$Na_3H(SO_4)_2(cr) \leftrightarrow 3Na^+(aq) + H^+(aq) + 2SO_4^{2-}(aq)$	−2.122993e3	2.296880e1	−8.282936e-2	9.946746e-5				
$NaHSO_4{\cdot}H_2O(cr) \leftrightarrow Na^+(aq) + HSO_4^-(aq) + H_2O(l)$	6.581474e2	−6.926105e0	2.431396e-2	−2.830635e-5				
$K_3H(SO_4)_2(cr) \leftrightarrow 3K^+(aq) + H^+(aq) + 2SO_4^{2-}(aq)$	4.561655e1	−4.356452e-1	8.546984e-4					
$K_5H_3(SO_4)_4(cr) \leftrightarrow 5K^+(aq) + 3H^+(aq) + 4SO_4^{2-}(aq)$	−3.552640e1	6.711111e-2						
$K_8H_6(SO_4)_7{\cdot}H_2O(cr) \leftrightarrow 8K^+(aq) + 6H^+(aq) + 7SO_4^{2-}(aq) + H_2O(l)$	9.591803e1	−9.575202e-1	1.841905e-3					
$KHSO_4(cr) \leftrightarrow K^+(aq) + HSO_4^-(aq)$	−1.019832e1	3.865551e-2						
$CO_2{\cdot}6H_2O(cr) \leftrightarrow CO_2(g) + 6H_2O(l)$	−2.676925e1	1.147623e-1	−3.016638e-5					
$CH_4{\cdot}6H_2O(cr) \leftrightarrow CH_4(g) + 6H_2O(l)$ $T \geq 285K$	1.649717e2	−1.214645e0	2.284327e-3					
$CH_4{\cdot}6H_2O(cr) \leftrightarrow CH_4(g) + 6H_2O(l)$ $T < 285K$	−2.224001e1	9.319961e-2						

Table B.1. (continued)

Gas–solution-phase equilibria	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$H_2O(g) \leftrightarrow H_2O(l)^d$	9.053594e1	−7.215505e-1	2.112659e-3	−2.254724e-6				
$CO_2(g) \leftrightarrow CO_2(aq)^d$	2.495691e2	4.570806e-2			−1.593281e4	−4.045154e1	1.541270e6	
$O_2(g) \leftrightarrow O_2(aq)^d$	2.98399e-1				−5.59617e3		1.049668e6	
$CH_4(g) \leftrightarrow CH_4(aq)^e$								
$HCl(g) \leftrightarrow HCl(aq)^d$	7.812179e1	−3.696246e-1	6.735943e-4	−5.00638e-7				
$HNO_3(g) \leftrightarrow HNO_3(aq)^d$	3.94005278e2	1.31442311e-1	−4.20928363e-5		−3.0203522e3	−7.1001998e1		
$H_2SO_4(g) \leftrightarrow H_2SO_4(aq)^d$	1.71812e2	−6.503309e-1	6.909049e-4					
$Mg^{2+}(aq) + H_2O(l) \leftrightarrow MgOH^+(aq) + H^+(aq)$	−1.1668e0				−7.7593e3			
$Fe^{2+}(aq) + H_2O(l) \leftrightarrow FeOH^+(aq) + H^+(aq)$	3.93e-1				−6.6392e3			
$CaCO_3^0(aq) \leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$	2.829430e3	6.89486e-1			−8.177113e4	−4.85818e2		
$MgCO_3^0(aq) \leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$	7.4201e1				−2.517845e3	−1.272433e1		
$FeCO_3^0(aq) \leftrightarrow Fe^{2+}(aq) + CO_3^{2-}(aq)$	−1.46641e1				1.36517e3			
$H_2O(l) \leftrightarrow H^+(aq) + OH^-(aq)$	−1.4816780e2	8.933802e-1	−2.332199e-3	2.146860e-6				
$CO_2(aq) + H_2O(l) \leftrightarrow H^+(aq) + HCO_3^-(aq)$	−8.204327e2	−1.4027266e-1			5.027549e4	1.268339e2	−3.879660e6	

Table B.1. (continued)

Gas–solution-phase equilibria	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
HCO_3^-(aq) $\leftrightarrow H^+$(aq) + CO_3^{2-}(aq)	−2.484192e2	−7.489962e-2			1.186243e4	3.892561e1	−1.297999e6	
HSO_4^{-1}(aq) $\leftrightarrow H^+$(aq) + SO_4^{2-}(aq)	1.2956527e3	5.704742e-1	−2.57206e-4		−3.056394e4	−2.360504e2		
$2H_2O$(l) $\leftrightarrow 2H_2$(g) + O_2(g)[d]	3.92869e1				−6.87562e4			

[a] See Tables 3.2 and 3.3 for the primary source of these parameters.

[b] Parameters are for the equation $\ln(K) = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6\mathrm{Ln}(T) + a_7/T^2 + a_8T^4$, where T is temperature (K), except for ice [H_2O(cr,I)], which is given as $K = a_1 + a_2T \ldots$.

[c] This equation does not extrapolate well to temperatures below ≈ 263 K. Removed from model mineral database below 263 K.

[d] The gas equations in Table B.1 are written in units of "atm." These are converted to bars within the FREZCHEM model.

[e] $\ln(K) = -4.30210345\text{e}1 + 6.83277221\text{e-}2T + 5.68718730\text{e}3/T - 3.56636281\text{e-}5T^2 + 5.79133791\text{e}1/(680 - T) - 6.11616662\text{e-}3P + 7.85528103\text{e-}4P\mathrm{Ln}(T) + 9.42540759\text{e-}2P/T - 1.92132040\text{e-}2P/(680 - T) + 9.17186899\text{e-}6P^2/T$, where T is temperature (K) and P is pressure (bars).

Table B.2. The Debye–Hückel constants used in the FREZCHEM model. T is temperature (K), and P is pressure (bars). (Numbers are in computer scientific notation, where e$\pm xx$ stands for $10^{\pm xx}$)

Equation	Reference
$A_\phi = 8.66836498\text{e}1 + 8.48795942\text{e-}2T - 8.88785150\text{e-}5T^2$ $+4.88096393\text{e-}8T^3 - 1.32731477\text{e}3/T$ $-1.76460172\text{e}1\text{Ln}(T)$	Spencer et al. 1990
$A_v = 3.73387 - 2.89662\text{e-}2T + 1.29461\text{e-}3P - 5.62291\text{e-}6TP$ $+7.62143\text{e-}5T^2 + 4.09944\text{e-}8P^2$	Marion et al. 2005

Table B.3. Numerical arrays for calculating $J(x)$ and $J'(x)$ (Eqs. 2.62 and 2.66) (Pitzer, 1991)

k	a_k^I	a_k^{II}
0	1.925154014814667	0.628023320520852
1	−0.060076477753119	0.462762985338493
2	−0.029779077456514	0.150044637187895
3	−0.007299499690937	−0.028796057604906
4	0.000388260636404	−0.036552745910311
5	0.000636874599598	−0.001668087945272
6	0.000036583601823	0.006519840398744
7	−0.000045036975204	0.001130378079086
8	−0.000004537895710	−0.000887171310131
9	0.000002937706971	−0.000242107641309
10	0.000000396566462	0.000087294451594
11	−0.000000202099617	0.000034682122751
12	−0.000000025267769	−0.000004583768938
13	0.000000013522610	−0.000003548684306
14	0.000000001229405	−0.000000250453880
15	−0.000000000821969	0.000000216991779
16	−0.000000000050847	0.000000080779570
17	0.000000000046333	0.000000004558555
18	0.000000000001943	−0.000000006944757
19	−0.000000000002563	−0.000000002849257
20	−0.000000000010991	0.000000000237816

Table B.4. Binary Pitzer-equation parameters for cations and anions used in the FREZCHEM model.[a] (Numbers are in computer scientific notation, where e$\pm xx$ stands for $10^{\pm xx}$)

Pitzer	Equation parameter[b]							
Parameter	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$C^{\phi}_{\mathrm{Na,Cl}}$	1.70761824e0	2.32970177e-3	−2.46665619e-6	1.21543380e-9.	−1.35583596e0	−3.87767714e-1		
$B^{(0)}_{\mathrm{Na,Cl}}$	7.87239712e0	−8.3864096e-3	1.44137774e-5	−8.780301e-9.	−4.96920671e2	−8.20972560e-1		
$B^{(1)}_{\mathrm{Na,Cl}}$	8.66915291e2	6.06166931e-1	−4.8048921e-4	1.88503857e-7	−1.70460145e4	−1.67171296e2		
$C^{\phi}_{\mathrm{K,Cl}}$	−3.27571680e0	−1.27222054e-3	4.71374283e-7	1.1162507e-11	9.07747666e1	5.80513562e-1		
$B^{(0)}_{\mathrm{K,Cl}}$	2.65718766e1	9.92715099e-3	−3.62323330e-6	−6.28427180e-11	−7.55707220e2	−4.67300770e0		
$B^{(1)}_{\mathrm{K,Cl}}$	1.69742977e3	1.22270943e0	−9.99044490e-4	4.04786721e-7	−3.28684422e4	−3.28813848e2		
$C^{\phi}_{\mathrm{Mg,Cl}}$	5.9532e-2	−2.49949e-4	2.41831e-7					
$B^{(0)}_{\mathrm{Mg,Cl}}$	3.13852913e2	2.61769099e-1	−2.46268460e-4	1.15764787e-7	−5.53133381e3	−6.21616862e1		
$B^{(1)}_{\mathrm{MgCl}}$	−3.18432525e4	−2.86710358e1	2.78892838e-2	−1.3279705e-5	5.24032958e5	6.40770396e3		
$C^{\phi}_{\mathrm{Ca,Cl}}$	2.64231655e1	2.46922993e-2	−2.48298510e-5	1.22421864e-8	−4.18098427e2	−5.35350322e0		
$B^{(0)}_{\mathrm{Ca,Cl}}$	−5.62764702e1	−3.00771997e-2	1.05630400e-5	3.3331626e-9.	1.11730349e3	1.06664743e1		
$B^{(1)}_{\mathrm{Ca,Cl}}$	3.4787e0	−1.5417e-2	3.1791e-5					
$C^{\phi}_{\mathrm{Fe,Cl}}$	−8.61e-3							
$B^{(0)}_{\mathrm{Fe,Cl}}$	3.359e-1							
$B^{(1)}_{\mathrm{Fe,Cl}}$	3.83836e1	−1.236e-1						
$C^{\phi}_{\mathrm{Na,SO_4}}$	1.470571e1	−2.293478e-1	1.350491e-3	−3.537708e-6				3.466102e-9.
$B^{(0)}_{\mathrm{Na,SO_4}}$	−3.447035e1	5.312162e-1	−3.119749e-3	8.181394e-6				−8.022815e-9.
$B^{(1)}_{\mathrm{Na,SO_4}}$	5.161188e1	−8.245243e-1	4.902233e-3	−1.280795e-5				1.252258e-8
$C^{\phi}_{\mathrm{K,SO_4}}$	7.0e-4	4.8e-5	9.0e-9.	3.26e-10	−7.68e0	2.835e-3		
$B^{(0)}_{\mathrm{K,SO_4}}$	−7.568e-1	2.529e-3	3.65e-8	5.31e-10	−1.08e0	−1.25e-3		
$B^{(1)}_{\mathrm{K,SO_4}}$	1.953e0	−3.996e-3	3.55e-7	1.669e-8	2.67e1	−4.785e-2		
$C^{\phi}_{\mathrm{Mg,SO_4}}$	2.230e-1	−6.101e-4	−1.0e-9.	−1.096e-9.	4.265e1	−1.792e-2		
$B^{(0)}_{\mathrm{Mg,SO_4}}$	1.678e0	−5.514e-3	5.97e-7	1.5651e-8	−2.2392e2	6.594e-2		
$B^{(1)}_{\mathrm{Mg,SO_4}}$	1.484e0	6.274e-3	5.41e-6	8.84e-8	−1.3210e3	3.0605e-1		
$B^{(2)}_{\mathrm{Mg,SO_4}}$	1.8829e2	−1.03999e0	1.2242e-3	3.4974e-6	8.975e4	−6.79235e1		
$C^{\phi}_{\mathrm{Ca,SO_4}}$	3.3e-2	−1.529e-4	8.97e-7	1.569e-9.	1.1e0	−1.2755e-2		

Table B.4. (continued)

Pitzer	Equation parameter[b]							
Parameter	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$B^{(0)}_{\mathrm{Ca,SO_4}}$	7.95e-2	−1.22e-4	5.001e-6	6.704e-9.	−1.5228e2	−6.885e-3		
$B^{(1)}_{\mathrm{Ca,SO_4}}$	2.8945e0	7.434e-3	5.287e-6	−1.01513e-7	−2.08505e3	1.345e0		
$B^{(2)}_{\mathrm{Ca,SO_4}}$	−5.704e1	−1.028e-2	−2.235e-4	3.526e-7	5.788e3	−1.8378e0		
$C^{\phi}_{\mathrm{Fe,SO_4}}$	2.09e-2							
$B^{(0)}_{\mathrm{Fe,SO_4}}$	1.29506e1	−3.86e-2	3.91e-5		−1.38964e3			
$B^{(1)}_{\mathrm{Fe,SO_4}}$	8.758343e1	−6.383194e-1	1.190408e-3					
$B^{(2)}_{\mathrm{Fe,SO_4}}$	−4.20e1							
$C^{\phi}_{\mathrm{Na,NO_3}}$	0.00							
$B^{(0)}_{\mathrm{Na,NO_3}}$	7.088889e-1	−5.599812e-3	1.085e-5					
$B^{(1)}_{\mathrm{Na,NO_3}}$	8.312979e1	−6.161264e-1	1.1334e-3					
$C^{\phi}_{\mathrm{K,NO_3}}$	6.669e-2	−2.0505e-4						
$B^{(0)}_{\mathrm{K,NO_3}}$	−2.948e-1	7.326e-4						
$B^{(1)}_{\mathrm{K,NO_3}}$	−6.2735e0	2.1149e-2						
$C^{\phi}_{\mathrm{Mg,NO_3}}$	−2.062e-2							
$B^{(0)}_{\mathrm{Mg,NO_3}}$	5.207e-1	−5.1525e-4						
$B^{(1)}_{\mathrm{MgNO_3}}$	2.9242e0	−4.4925e-3						
$C^{\phi}_{\mathrm{Ca,NO_3}}$	−2.014e-2							
$B^{(0)}_{\mathrm{Ca,NO_3}}$	3.687e-1	−5.295e-4						
$B^{(1)}_{\mathrm{Ca,NO_3}}$	4.1485e0	−9.1875e-3						
$C^{\phi}_{\mathrm{Fe,NO_3}}$[c]	−2.062e-2							
$B^{(0)}_{\mathrm{Fe,NO_3}}$[c]	5.207e-1	−5.1525e-4						
$B^{(1)}_{\mathrm{Fe,NO_3}}$[c]	2.9242e0	−4.4925e-3						
$C^{\phi}_{\mathrm{Na,HCO_3}}$	0.00							
$B^{(0)}_{\mathrm{Na,HCO_3}}$	−3.72624193e1	−1.445932e-2			6.82885977e2	6.8995857e0		

Table B.4. (continued)

Pitzer Parameter	a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
$B^{(1)}_{\mathrm{Na,HCO_3}}$	−6.14635193e1	−2.446734e-2			1.129389146e3	1.14108589e1		
$C^{\phi}_{\mathrm{Na,CO_3}}$	5.2e-3							
$B^{(0)}_{\mathrm{Na,CO_3}}$	−6.05387702e1	−2.3301655e-2			1.1083760518e3	1.119855531e1		
$B^{(1)}_{\mathrm{Na,CO_3}}$	−2.375156616e2	−9.989121e-2			4.412511973e3	4.45820703e1		
$C^{\phi}_{\mathrm{K,HCO_3}}$	0.00							
$B^{(0)}_{\mathrm{K,HCO_3}}$	−3.088232e-1	1.00e-3			−6.9869e-4	−4.701488e-6		
$B^{(1)}_{\mathrm{K,HCO_3}}$	−2.802e-1	1.09999e-3			9.36932e-4	6.15660566e-6		
$C^{\phi}_{\mathrm{K,CO_3}}$	5.0e-4							
$B^{(0)}_{\mathrm{K,CO_3}}$	−1.991649e-1	1.10e-3			1.8063362e-5			
$B^{(1)}_{\mathrm{K,CO_3}}$	1.330579e-1	4.36e-3			1.1899e-3			
$C^{\phi}_{\mathrm{Mg,HCO_3}}$	0.00							
$B^{(0)}_{\mathrm{Mg,HCO_3}}$	1.369710e4	8.250840e0	−4.34e-3		−2.734061716e5	−2.607115202e3		
$B^{(1)}_{\mathrm{Mg,HCO_3}}$	−1.578398351e5	−9.27779354e1	4.77642e-2		3.2032096948e6	2.9927151503e4		
$C^{\phi}_{\mathrm{Ca,HCO_3}}$	0.00							
$B^{(0)}_{\mathrm{Ca,HCO_3}}$	2.957653405e4	1.8447305e1	−9.989e-3		−5.765205185e5	−5.6611237e3		
$B^{(1)}_{\mathrm{Ca,HCO_3}}$	−1.0288510522e3	−3.725876718e-1	8.9691e-5		2.6492240303e4	1.8313155672e2		
$C^{\phi}_{\mathrm{Fe,HCO_3}}{}^{c}$	0.00							
$B^{(0)}_{\mathrm{Fe,HCO_3}}{}^{c}$	1.369710e4	8.250840e0	−4.34e-3		−2.734061716e5	−2.607115202e3		
$B^{(1)}_{\mathrm{Fe,HCO_3}}x^{c}$	−1.578398351e5	−9.27779354e1	4.77642e-2		3.2032096948e6	2.9927151503e4		
$C^{\phi}_{\mathrm{Na,OH}}$	−2.011610e-1	2.492005e-3	−9.411507e-6	1.127798e-8				
$B^{(0)}_{\mathrm{Na,OH}}$	−1.290052e1	1.108975e-1	−3.208817e-4	3.124540e-7				
$B^{(1)}_{\mathrm{Na,OH}}$	−7.698673e0	7.152585e-2	−2.187257e-4	2.290117e-7				
$C^{\phi}_{\mathrm{K,OH}}$	4.1e-3							
$B^{(0)}_{\mathrm{K,OH}}$	1.298e-1							
$B^{(1)}_{\mathrm{K,OH}}$	3.20e-1							
$C^{\phi}_{\mathrm{Ca,OH}}$	0.00							

Table B.4. (continued)

Pitzer Parameter	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$B^{(0)}_{\mathrm{Ca,OH}}$	−1.747e-1							
$B^{(1)}_{\mathrm{Ca,OH}}$	−2.303e-1							
$B^{(2)}_{\mathrm{Ca,OH}}$	−5.72e0							
$C^{\phi}_{\mathrm{MgOH,Cl}}$	0.00							
$B^{(0)}_{\mathrm{MgOH,Cl}}$	−1.0e-1							
$B^{(1)}_{\mathrm{MgOH,Cl}}$	1.658e0							
$C^{\phi}_{\mathrm{FeOH,Cl}}$ [c]	0.00							
$B^{(0)}_{\mathrm{FeOH,Cl}}$ [c]	−1.0e-1							
$B^{(1)}_{\mathrm{FeOH,Cl}}$ [c]	1.658e0							
$C^{\phi}_{\mathrm{H,Cl}}$	−2.78619e-3	1.735035e-5	−5.937631e-8					
$B^{(0)}_{\mathrm{H,Cl}}$	3.56122e-1	−5.305245e-4						
$B^{(1)}_{\mathrm{H,Cl}}$	−7.420199e0	1.158740e-1	−6.666408e-4	1.685445e-6				−1.564321e-9
$C^{\phi}_{\mathrm{H,NO_3}}$	1.264791e-1	−8.808517e-4	1.469263e-6					
$B^{(0)}_{\mathrm{H,NO_3}}$	−1.019608e0	8.052811e-3	−1.414706e-5					
$B^{(1)}_{\mathrm{H,NO_3}}$	−6.829838e0	7.588276e-2	−2.843828e-4	3.695995e-7				
$C^{(0)}_{\mathrm{H,SO_4}}$	−5.315201e-1	8.619821e-3	−5.14571e-5	1.350347e-7				−1.314709e-10
$C^{(1)}_{\mathrm{H,SO_4}}$	−7.766817e2	1.164255e1	−6.537128e-2	1.626702e-4				−1.513403e-7
$B^{(0)}_{\mathrm{H,SO_4}}$	1.388618e1	−2.200263e-1	1.314763e-3	−3.475869e-6				3.420786e-9
$B^{(1)}_{\mathrm{H,SO_4}}$	−1.679737e2	2.609701e0	−1.526685e-2	3.984122e-5				−3.908818e-8
$C^{(0)}_{\mathrm{H,HSO_4}}$	9.773929e-2	−1.148641e-3	4.422169e-6	−5.765707e-9				
$C^{(1)}_{\mathrm{H,HSO_4}}$	1.099940e2	−1.969903e0	1.289248e-2	−3.672285e-5				3.850406e-8
$B^{(0)}_{\mathrm{H,HSO_4}}$	−6.888679e-1	1.195453e-2	−4.667571e-5	5.878913e-8				
$B^{(1)}_{\mathrm{H,HSO_4}}$	−3.815780e2	6.261241e0	−3.789588e-2	1.006085e-4				−9.906089e-8
$C^{\phi}_{\mathrm{Na,HSO_4}}$	0.00							

Table B.4. (continued)

Pitzer Parameter	a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
$B^{(0)}_{\mathrm{Na,HSO_4}}$	4.54e-2							
$B^{(1)}_{\mathrm{Na,HSO_4}}$	−6.7010e0	2.5352e-2						
$C^{\phi}_{\mathrm{K,HSO_4}}$	0.00							
$B^{(0)}_{\mathrm{K,HSO_4}}$	−3.0e-4							
$B^{(1)}_{\mathrm{K,HSO_4}}$ [d]	1.004759e2	−7.127881e-1	1.262349e-3					
$C^{\phi}_{\mathrm{Mg,HSO_4}}$ [d]	3.075223e0	−2.094837e-2	3.566667e-5					
$B^{(0)}_{\mathrm{Mg,HSO_4}}$ [d]	1.175741e0	−2.374627e-3						
$B^{(1)}_{\mathrm{Mg,HSO_4}}$ [d]	−4.091076e2	2.838782e0	−4.902359e-3					
$C^{\phi}_{\mathrm{Ca,HSO_4}}$	0.00							
$B^{(0)}_{\mathrm{Ca,HSO_4}}$	6.19e-2							
$B^{(1)}_{\mathrm{Ca,HSO_4}}$	2.602e0							
$C^{\phi}_{\mathrm{Fe,HSO_4}}$	0.00							
$B^{(0)}_{\mathrm{Fe,HSO_4}}$	6.758464e1	−7.649696e-1	2.894494e-3	−3.636364e-6				
$B^{(1)}_{\mathrm{Fe,HSO_4}}$	3.48e0							

[a] See Tables 3.2 and 3.3 for the primary source of these parameters.

[b] Parameters are for the equation: Pitzer parameter $= a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6\mathrm{Ln}(T) + a_7/T^2 + a_8T^4$, where T is temperature (K).

[c] Assumed the same as the Mg analogs.

[d] These equations are only valid between 0 and 25°C. At subzero temperatures, use $B^{(1)}_{\mathrm{K,HSO_4}} = -0.0371$, $\Psi_{\mathrm{K,H,SO_4}} = -0.0064$, $C^{\phi}_{\mathrm{Mg,HSO_4}} = 0.0143$, $B^{(0)}_{\mathrm{Mg,HSO_4}} = 0.5315$, $B^{(1)}_{\mathrm{Mg,HSO_4}} = 0.5361$, $\Psi_{\mathrm{Mg,H,HSO_4}} = -0.0234$, and $\Psi_{\mathrm{SO_4,HSO_4,Mg}} = -0.0884$.

Table B.5. Ternary Pitzer-equation parameters for cations and anions used in the FREZCHEM model.[a] (Numbers are in computer scientific notation, where e$\pm xx$ stands for $10^{\pm xx}$)

Pitzer	Equation parameter[b]							
parameter	a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
$\Theta_{Na,K}$	−1.82266741e1	−3.6903847e-3			6.12415011e2	3.02994981e0		
$\Psi_{Na,K,Cl}$	6.48108127e0	1.46803468e-3			−2.04354019e2	−1.09448043e0		
Ψ_{Na,K,SO_4}	−5.63e-2	1.4146e-3	2.3e-8	−2.1088e-8	−2.5661e2	1.8538e-1		
$\Psi_{Na,K,NO3}$	−0.0012							
$\Psi_{Na,K,HCO3}$	−0.0079							
$\Psi_{Na,K,CO3}$	0.003							
$\Theta_{Na,Mg}$	0.070							
$\Psi_{Na,Mg,Cl}$	−3.109870e-2	5.4464780e-5			1.99404210e0			
Ψ_{Na,Mg,SO_4}	−1.207e-1	5.235e-4	−5.39e-7	−4.39e-10	−1.723e1	1.2645e-2		
Ψ_{Na,Mg,NO_3}	−0.0099							
$\Theta_{Na,Ca}$	3.0e-2	−1.9e-5		9.5e-10	−2.50e0	1.3e-3		
$\Psi_{Na,Ca,Cl}$	−7.63980e0	−1.2990e-2	1.1060e-5			1.8475e0		
Ψ_{Na,Ca,SO_4}	−8.08e-2	4.6565e-3	5.546e-6	−1.4107e-7	−1.0915e3	9.6985e-1		
Ψ_{Na,Ca,NO_3}	−3.481452e-2	1.285714e-4						
$\Theta_{Na,Fe}$	0.080							
$\Psi_{Na,Fe,Cl}$	−0.014							
Ψ^{c}_{Na,Fe,SO_4}	−1.207e-1	5.235e-4	−5.39e-7	−4.39e-10	−1.723e1	1.2645e-2		
$\Theta_{Na,H}$	0.036							
$\Psi_{Na,H,Cl}$	−0.0037							
Ψ_{Na,H,NO_3}	−7.707985e-2	2.482609e-4						
Ψ_{Na,H,HSO_4}	−0.0129							
$\Theta_{K,Mg}$	0.1167							
$\Psi_{K,Mg,Cl}$	5.0362230e-2	−8.750820e-6			−2.899090e1			
Ψ_{K,Mg,SO_4}	−1.18e-1	−4.78e-5	−3.27e-7	−9.37e-10	3.344e1	−8.84e-3		
Ψ_{K,Mg,NO_3}	−6.494e-1	2.00e-3						
$\Theta_{K,Ca}$	2.365710e0	−4.540e-3			−2.84940e2			
$\Psi_{K,Ca,Cl}$	−5.930e-2	2.54280e-4			−1.34390e1			
Ψ_{K,Ca,NO_3}	−9.011042e-1	2.944255e-3						
$\Theta^{c}_{K,Fe}$	0.1167							
$\Psi^{c}_{K,Fe,Cl}$	5.0362230e-2	−8.750820e-6			−2.899090e1			
Ψ^{c}_{K,Fe,SO_4}	−1.18e-1	−4.78e-5	−3.27e-7	−9.37e-10	3.344e1	−8.84e-3		
$\Theta_{K,H}$	0.005							
$\Psi_{K,H,Cl}$	−0.0114							

Table B.5. (continued)

Pitzer parameter	Equation parameter[b] a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
$\Psi_{\mathrm{K,H,NO_3}}$	−2.089075e0	1.399737e-2	−2.360221e-5					
$\Psi_{\mathrm{K,H,SO_4}}$	−1.4967e0	5.456e-3						
$\Psi_{\mathrm{K,H,HSO_4}}$	−0.0303							
$\Theta_{\mathrm{Mg,Ca}}$	5.31274136e0	−6.3424248e-3			−9.83113847e2			
$\Psi_{\mathrm{Mg,Ca,Cl}}$	4.15790220e1	1.30377312e-2			−9.81658526e2	−7.4061986e0		
$\Psi_{\mathrm{Mg,Ca,SO_4}}$	0.024							
$\Theta_{\mathrm{Mg,Fe}}$	0.0							
$\Psi_{\mathrm{Mg,Fe,Cl}}$	0.0							
$\Psi_{\mathrm{Mg,Fe,SO_4}}$	0.0							
$\Theta_{\mathrm{Mg,H}}$	0.10							
$\Psi_{\mathrm{Mg,H,Cl}}$	−0.0077							
$\Psi_{\mathrm{Mg,H,HSO_4}}$	−4.525314e-2	7.995736e-5						
$\Psi_{\mathrm{Mg,MgOH,Cl}}$	0.028							
$\Theta^{\mathrm{c}}_{\mathrm{Ca,Fe}}$	5.31274136e0	−6.3424248e-3			−9.83113847e2			
$\Psi^{\mathrm{c}}_{\mathrm{Ca,Fe,Cl}}$	4.15790220e1	1.30377312e-2			−9.81658526e2	−7.4061986e0		
$\Psi^{\mathrm{c}}_{\mathrm{Ca,Fe,SO_4}}$	0.024							
$\Theta_{\mathrm{Ca,H}}$	0.092							
$\Psi_{\mathrm{Ca,H,Cl}}$	−0.0142							
$\Theta_{\mathrm{Fe,H}}$	0.0							
$\Psi_{\mathrm{Fe,H,Cl}}$	−1.4157e-1	5.15e-4						
$\Psi^{\mathrm{c}}_{\mathrm{Fe,H,SO_4}}$	0.0							
$\Psi_{\mathrm{Fe,H,HSO_4}}$	5.75716e1	−5.7767e-1	1.924796e-3	−2.129138e-6				
$\Psi^{\mathrm{c}}_{\mathrm{Fe,FeOH,Cl}}$	0.028							
$\Theta_{\mathrm{Cl,SO_4}}$	7.0e-2			−7.8e-10	−1.00e0			
$\Psi_{\mathrm{Cl,SO_4,Na}}$	2.554e-2	−6.138e-5	−9.0e-9	3.04e-10	−8.9e-1	−2.275e-3		
$\Psi_{\mathrm{Cl,SO_4,K}}$	6.08e-2	−1.824e-4	−2.15e-8	−3.28e-10	5.22e0	−3.01e-3		
$\Psi_{\mathrm{Cl,SO_4,Mg}}$	5.869e-2	−8.97e-5	4.7e-8	6.5e-11	−2.413e1	4.345e-3		
$\Psi_{\mathrm{Cl,SO_4,Ca}}$	−2.63e-2	−9.46e-5	−3.125e-7	−1.28e-9	2.944e1	−6.49e-3		
$\Psi^{\mathrm{c}}_{\mathrm{Cl,SO_4,Fe}}$	5.869e-2	−8.97e-5	4.7e-8	6.5e-11	−2.413e1	4.345e-3		
$\Psi_{\mathrm{Cl,SO_4,H}}$	0.0							
$\Theta_{\mathrm{Cl,NO_3}}$	0.016							
$\Psi_{\mathrm{Cl,NO_3,Na}}$	−5.773862e-1	3.94084e-3	−6.80e-6					
$\Psi_{\mathrm{Cl,NO_3,K}}$	−1.065548e0	6.957931e-3	−1.142531e-5					
$\Psi_{\mathrm{Cl,NO_3,Mg}}$	0.0046							

Table B.5. (continued)

Pitzer parameter	Equation parameter[b] a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
$\Psi_{\mathrm{Cl,NO_3,Ca}}$	−0.0409							
$\Psi_{\mathrm{Cl,NO_3,H}}$	0.0							
$\Theta_{\mathrm{Cl,HCO_3}}$	0.03							
$\Psi_{\mathrm{Cl,HCO_3,Na}}$	−3.9e-3	−3.25e-5	−6.6e-8	−2.74e-10	5.83e0	−9.85e-4		
$\Psi_{\mathrm{Cl,HCO_3,Mg}}$	−0.096							
$\Psi^{\mathrm{c}}_{\mathrm{Cl,HCO_3,Fe}}$	−0.096							
$\Theta_{\mathrm{Cl,CO_3}}$	−0.02							
$\Psi_{\mathrm{Cl,CO_3,Na}}$	9.6e-3	4.7e-6	−3.75e-8	−2.23e-10	2.94e0	−5.2e-4		
$\Psi_{\mathrm{Cl,CO_3,K}}$	0.004							
$\Theta_{\mathrm{Cl,HSO_4}}$	−0.006							
$\Psi_{\mathrm{Cl,HSO_4,Na}}$	−0.006							
$\Psi_{\mathrm{Cl,HSO_4,H}}$	0.013							
$\Theta_{\mathrm{NO_3,SO_4}}$	2.559033e0	−1.679067e-2	2.892045e-5					
$\Psi_{\mathrm{NO_3,SO_4,Na}}$	−2.222887e-1	1.0313e-3	−1.0e-6					
$\Psi_{\mathrm{NO_3,SO_4,K}}$	−4.715997e0	3.156712e-2	−5.304224e-5					
$\Psi_{\mathrm{NO_3,SO_4,Mg}}$	−2.9392e-1	9.60e-4						
$\Psi_{\mathrm{NO_3,SO_4,Ca}}$	−0.2281							
$\Psi_{\mathrm{NO_3,SO_4,H}}$	−3.75677e-1	3.241125e-3	−8.920938e-6	7.36791e-9				
$\Psi_{\mathrm{NO_3,HCO_3,Na}}$	0.0061							
$\Psi_{\mathrm{NO_3,CO_3,Na}}$	0.0132							
$\Psi_{\mathrm{NO_3,CO_3,K}}$	0.0075							
$\Theta_{\mathrm{HCO_3,SO_4}}$	0.01							
$\Psi_{\mathrm{HCO_3,SO_4,Na}}$	−0.005							
$\Psi_{\mathrm{HCO_3,SO_4,Mg}}$	−0.161							
$\Psi^{\mathrm{c}}_{\mathrm{HCO_3,SO_4,Fe}}$	−0.161							
$\Theta_{\mathrm{HCO_3,CO_3}}$	−0.04							
$\Psi_{\mathrm{HCO_3,CO_3,Na}}$	0.002							
$\Psi_{\mathrm{HCO_3,CO_3,K}}$	0.012							
$\Theta_{\mathrm{CO_3,SO_4}}$	0.02							
$\Psi_{\mathrm{CO_3,SO_4,Na}}$	3.9e-3	3.73e-5	1.64e-7	6.16e-10	−1.822e1	3.455e-3		
$\Psi_{\mathrm{CO_3,SO_4,K}}$	−0.009							
$\Theta_{\mathrm{NO_3,HSO_4}}$	4.151797e0	−4.445727e-2	1.57303e-4	−1.876457e-7				
$\Psi_{\mathrm{NO_3,HSO_4,H}}$	−6.187135e0	9.307292e-2	−5.252546e-4	1.316116e-6				
$\Psi_{\mathrm{SO4,HSO_4,Na}}$	−0.0094							

Table B.5. (continued)

Pitzer	Equation parameter[b]							
parameter	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$\Psi_{\mathrm{SO4,HSO_4,K}}$	−0.0677							
$\Psi_{\mathrm{SO4,HSO_4,Mg}}$	−7.656214e-1	2.4871e-3						
$\Psi_{\mathrm{SO4,HSO_4,Fe}}$	0.0							
$\Theta_{\mathrm{OH,Cl}}$	−0.050							
$\Psi_{\mathrm{OH,Cl,Na}}$	−0.006							
$\Psi_{\mathrm{OH,Cl,K}}$	−0.006							
$\Psi_{\mathrm{OH,Cl,Ca}}$	−0.025							
$\Theta_{\mathrm{OH,SO_4}}$	−0.013							
$\Psi_{\mathrm{OH,SO_4,Na}}$	−0.009							
$\Psi_{\mathrm{OH,SO_4,K}}$	−0.050							
$\Theta_{\mathrm{OH,CO_3}}$	0.10							
$\Psi_{\mathrm{OH,CO_3,Na}}$	−0.017							
$\Psi_{\mathrm{OH,CO_3,K}}$	−0.01							

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[a] See Tables 3.2 and 3.3 for the primary source of these parameters.

[b] Parameters are for the equation: Pitzer parameter $= a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6\mathrm{Ln}(T) + a_7/T^2 + a_8T^4$, where T is temperature (K).

[c] Assumed the same as the Mg analogs.

Table B.6. Binary and ternary soluble gas Pitzer-equation parameters used in the FREZCHEM model.[a] (Numbers are in computer scientific notation where e±*xx* stands for $10^{\pm xx}$)

Pitzer	Equation parameter[b]							
parameter	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$\lambda_{CO_2,H}$	0.0							
$\lambda_{CO_2,Na}$	−5.49638465e3	−3.326566e0	1.7532e-3		1.09399341e5	1.047021567e3		
$\lambda_{CO_2,K}$	2.856528099e3	1.7670079e0	−9.487e-4		−5.59541929e4	−5.46074467e2		
$\lambda_{CO_2,Mg}$	−4.79362533e2	−5.41843e-1	3.8812e-4		3.589474052e3	1.043452732e2		
$\lambda_{CO_2,Ca}$	−1.27746472e4	−8.101555e0	4.42472e-3		2.455415435e5	2.452509720e3		
$\lambda^{c}_{CO_2,Fe}$	−4.79362533e2	−5.41843e-1	3.8812e-4		3.589474052e3	1.043452732e2		
$\lambda_{CO_2,Cl}$	1.659944942e3	9.964326e-1	−5.2122e-4		−3.31596177e4	−3.15827883e2		
λ_{CO_2,SO_4}	2.274656591e3	1.8270948e0	−1.14272e-3		−3.39277625e4	−4.57015738e2		
$\zeta_{CO_2,H,Cl}$	−8.04121738e2	−4.70474e-1	2.40526e-4		1.633438917e4	1.523838752e2		
$\zeta_{CO_2,Na,Cl}$	−3.79459185e2	−2.58005e-1	1.47823e-4		6.879030871e3	7.374511574e1		
$\zeta_{CO_2,K,Cl}$	−3.79686097e2	−2.57891e-1	1.47333e-4		6.853264129e3	7.379977116e1		
$\zeta_{CO_2,Mg,Cl}$	−1.34260256e3	−7.72286e-1	3.91603e-4		2.772680974e4	2.5362319406e2		
$\zeta_{CO_2,Ca,Cl}$	−1.66065290e2	−1.8002e-2	−2.47349e-5		5.256844332e3	2.7377452415e1		
$\zeta^{c}_{CO_2,Fe,Cl}$	−1.34260256e3	−7.72286e-1	3.91603e-4		2.772680974e4	2.5362319406e2		
ζ_{CO_2,H,SO_4}	0.0							
ζ_{CO_2,Na,SO_4}	6.703002482e4	3.7930519e1	−1.894730e-2		−1.39908237e6	−1.263027457e4		
ζ_{CO_2,K,SO_4}	−2.90703326e3	−2.860763e0	1.951086e-3		3.075686749e4	6.1137560512e2		
ζ_{CO_2,Mg,SO_4}	−7.37424392e3	−4.608331e0	2.489207e-3		1.431626076e5	1.412302898e3		
ζ_{CO_2,Ca,SO_4}	0.0							
$\zeta^{c}_{CO_2,Fe,SO_4}$	−7.37424392e3	−4.608331e0	2.489207e-3		1.431626076e5	1.412302898e3		
$\lambda_{O_2,H}$	−2.379e-1				8.1450e1			
$\lambda_{O_2,Na}$	−3.9548e-1		9.19882e-7		1.41307e2			
$\lambda_{O_2,K}$	−5.1698e-1				1.99431e2			
$\lambda_{O_2,Mg}$	−7.9489e-1				3.05513e2			
$\lambda_{O_2,Ca}$	2.497e-1							
$\lambda^{c}_{O_2,Fe}$	−7.9489e-1				3.05513e2			
$\lambda_{O_2,Cl}$	0.0							
λ_{O_2,SO_4}	1.00706e0				−2.74085e2			
$\lambda_{O_2,OH}$	9.3318e-1				−4.30552e2		4.98608e4	
λ_{O_2,NO_3}	−3.77e-2							

Table B.6. (continued)

Pitzer parameter	Equation parameter[b] a$_1$	a$_2$	a$_3$	a$_4$	a$_5$	a$_6$	a$_7$	a$_8$
λ_{O_2,HCO_3}	8.54e-2							
λ_{O_2,CO_3}	1.0258e0				−2.77074e2			
$\zeta_{O_2,H,Cl}$	−7.7e-3							
$\zeta_{O_2,Na,Cl}$					−2.739e0			
$\zeta_{O_2,K,Cl}$	−2.11e-2							
$\zeta_{O_2,Mg,Cl}$	−5.65e-3							
$\zeta_{O_2,Ca,Cl}$	−1.69e-2							
$\zeta^{c}_{O_2,Fe,Cl}$	−5.65e-3							
ζ_{O_2,Na,SO_4}	−4.60e-2							
ζ_{O_2,K,SO_4}	0.0							
ζ_{O_2,Mg,SO_4}	0.0							
$\zeta^{c}_{O_2,Fe,SO_4}$	0.0							
ζ_{O_2,Na,NO_3}	−1.20e-2							
ζ_{O_2,K,NO_3}	−2.81e-2							
ζ_{O_2,Ca,NO_3}	0.0							
$\zeta_{O_2,Na,OH}$	−1.25e-2							
$\zeta_{O_2,K,OH}$	2.342e-3						−8.3615e2	
ζ_{O_2,Na,HCO_3}	0.0							
ζ_{O_2,Na,CO_3}	−1.81e-2							
$\lambda^{d}_{CH4,Na}$	9.92230792e-2	2.57906811e-5						
$\lambda_{CH4,K}$	0.13909							
$\lambda_{CH4,Mg}$	0.24678							
$\lambda^{e}_{CH4,Ca}$	−5.64278808e0	8.51392725e-3			1.00057752e3			
$\lambda^{c}_{CH4,Fe}$	0.24678							
$\lambda_{CH4,Cl}$	0.00							
λ_{CH4,SO_4}	0.03041							
λ_{CH4,HCO_3}	0.00669							
λ_{CH4,CO_3}	0.16596							

Table B.6. (continued)

Pitzer parameter	Equation parameter[b] a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
$\zeta_{\mathrm{CH4,Na,Cl}}$	−0.00624							
$\zeta_{\mathrm{CH4,K,Cl}}$	−0.00382							
$\zeta_{\mathrm{CH4,Mg,Cl}}$	−0.01323							
$\zeta_{\mathrm{CH4,Ca,Cl}}$	−0.00468							
$\zeta^{c}_{\mathrm{CH4,Fe,Cl}}$	−0.01323							

[a] See Tables 3.2 and 3.3 for the primary source of these parameters.

[b] Parameters are for the equation: Pitzer parameter = $a_1 + a_2T + a_3T^2 + a_4T^3 + a_5/T + a_6\mathrm{Ln}(T) + a_7/T^2 + a_8T^4$, where T is temperature (K).

[c] Assumed the same as the Mg analogs.

[d] This equation also contains the terms $+1.83451402\text{e-}2 \times xP/T - 8.07196716\text{e-}6 \times P^2/T$, where P is pressure (bars) and T is temperature (K).

[e] This equation also contains the term $+5.27816886\text{e-}5 \times P$, where P is pressure (bars).

Table B.7. Equations for the molar volumes (cm^3/mole) of liquid water and water ice at 1.01 bar pressure and their compressibilities [cm^3/(mol·bar)] (Marion et al. 2005), where T is temperature (K) and P is pressure (bars)

$$\begin{aligned}1000\rho_w^0 = {} & (999.83952 + 16.94518 \cdot t - 7.98704 \times 10^{-3} \cdot t^2 \\ & - 4.617046 \times 10^{-5} \cdot t^3 + 1.05563 \times 10^{-7} \cdot t^4 \qquad (t = {}^\circ\mathrm{C}) \\ & - 2.805425 \times 10^{-10} \cdot t^5)/(1.0 + 1.687985 \times 10^{-2} \cdot t)\end{aligned}$$

$$\overline{V}_l^0 = \frac{18.01528}{\rho_w^0} \qquad T \geq 273.15\ \mathrm{K}$$

$$\overline{V}_l^0 = 18.0182 - 1.407964 \times 10^{-3}(T - 273.15) + 1.461418 \times 10^{-4}(T - 273.15)^2 \quad T < 273.15\ \mathrm{K}$$

$$\begin{aligned}\overline{K}_l^0 = {} & 8.62420 \times 10^{-3} - 5.06616 \times 10^{-5}T - 3.78615 \times 10^{-6}P + 2.27679 \times 10^{-8}PT \\ & + 1.18481 \times 10^{-10}P^2 + 8.20762 \times 10^{-8}T^2 \\ & - 3.63261 \times 10^{-11}PT^2 - 2.87099 \times 10^{-13}TP^2\end{aligned}$$

$$\overline{V}_{\mathrm{I,cr}}^0 = 19.30447 - 7.988471 \times 10^{-4}T + 7.563261 \times 10^{-6}T^2$$

$$\overline{K}_{\mathrm{I,cr}}^0 = 2.790102 \times 10^{-2} - 2.235440 \times 10^{-4} \cdot T + 4.497731 \times 10^{-7} \cdot T^2$$

Table B.8. Equations for the molar volumes (cm^3/mole) and the isothermal compressibilities [cm^3/(mole.bar)] of soluble ions and gases at infinite dilution. Derived from the database of Millero (1983) over a temperature range of 273 to 298 K. (Numbers are in computer scientific notation, where e±xx stands for $10^{\pm xx}$). Reprinted from Marion et al. (2005) with permission

	Equation parameter[a]		
Molar volume	a_1	a_2	a_3
H^+	0.0	0.0	0.0
Na^+	−9.0589e1	5.2876e-1	−7.68e-4
K^+	−7.2019e1	4.9128e-1	−7.36e-4
Mg^{2+}	−1.65407e2	9.6088e-1	−1.600e-3
Fe^{2+}[b]	−1.65407e2	9.6088e-1	−1.600e-3
Ca^{2+}	−1.42301e2	7.9195e-1	−1.256e-3
Cl^-	−1.02412e2	7.8012e-1	−1.264e-3
OH^-	−3.34884e2	2.16412e0	−3.536e-3
HSO_4^-	−1.85898e2	1.41308e0	−2.248e-3
NO_3^-	−1.74089e2	1.27266e0	−1.984e-3
HCO_3^-	−1.97188e2	1.41308e0	−2.248e-3
CO_3^{2-}	−3.93904e2	2.52016e0	−4.064e-3
SO_4^{2-}	−3.52433e2	2.36431e0	−3.808e-3
CO_2	33.6		
O_2	32.0		
CH_4	37.4		
Isothermal compressibility			
H^+	0.0	0.0	0.0
Na^+	−3.0891e-2	1.36923e-4	−1.56e-7
K^+	−1.0616e-2	7.613e-6	5.6e-8
Mg^{2+}	6.2899e-2	−4.8948e-4	8.44e-7
Fe^{2+}[b]	6.2899e-2	−4.8948e-4	8.44e-7
Ca^{2+}	6.3299e-2	−4.8948e-4	8.44e-7
Cl^-	−1.5576e-1	1.0101e-3	−1.644e-6
OH^-	−1.2874e-1	7.6471e-4	−1.160e-6
HSO_4^-	−1.2737e-1	7.6471e-4	−1.160e-6
NO_3^-	−7.1475e-2	4.2295e-4	−6.08e-7
HCO_3^-	−1.2763e-1	7.6471e-4	−1.160e-6
CO_3^{2-}	−3.0024e-1	1.8935e-3	−3.056e-6
SO_4^{2-}	−2.9963e-1	1.8935e-3	−3.056e-6

[a] $Y = a_1 + a_2T + a_3T^2$, where T is temperature (K).

[b] Assumed to be the same as Mg^{2+}.

Table B.9. Molar volumes (cm^3/mole) of solids at 298 K. These molar volumes were derived from (atomic weight/density), except for footnoted entries (Marion et al. 2005)

Solid phase	Molar volume	Solid phase	Molar volume
$NaCl$(cr) (halite)	27.02	$NaHCO_3$(cr) (nahcolite)	38.91
$NaCl{\cdot}2H_2O$(cr) (hydrohalite)	57.96	$Na_2CO_3{\cdot}7H_2O$(cr)	153.71
KCl(cr) (sylvite)	37.52	$Na_2CO_3{\cdot}10H_2O$(cr) (natron)	198.71
$MgCl_2{\cdot}6H_2O$(cr) (bischofite)	129.57	$NaHCO_3{\cdot}Na_2CO_3{\cdot}2H_2O$ (trona)	107.02
$MgCl_2{\cdot}8H_2O$(cr)[a]	159.08	$KHCO_3$(cr) (kalicinite)	46.14
$MgCl_2{\cdot}12H_2O$(cr)[a]	218.10	$MgCO_3$(cr) (magnesite)	28.02
$FeCl_2{\cdot}4H_2O$(cr)	103.01	$MgCO_3{\cdot}3H_2O$(cr) (nesquehonite)	74.79
$FeCl_2{\cdot}6H_2O$(cr)[a]	133.65	$MgCO_3{\cdot}5H_2O$(cr) (lansfordite)	100.80
$CaCl_2{\cdot}6H_2O$(cr) (antarcticite)	128.12	$3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$(cr) (hydromagnesite)	169.13
$KMgCl_3{\cdot}6H_2O$(cr) (carnallite)	172.58	$FeCO_3$(cr) (siderite)	30.49
$CaCl_2 2MgCl_2{\cdot}12H_2O$(cr) (tachyhydrite)	311.81	$CaCO_3$(cr) (calcite)	36.93
Na_2SO_4(cr) (thenardite)	53.33	$CaCO_3$(cr) (aragonite)	34.15
$Na_2SO_4{\cdot}10H_2O$(cr) (mirabilite)	219.80	$CaCO_3$(cr) (vaterite)	37.72
K_2SO_4(cr) (arcanite)	65.50	$CaCO_3{\cdot}6H_2O$(cr) (ikaite)	117.54
$MgSO_4{\cdot}H_2O$(cr) (kieserite)	56.60	$CaMg(CO_3)_2$(cr) (dolomite)	64.34
$MgSO_4{\cdot}6H_2O$(cr) (hexahydrite)	132.58	$HCl{\cdot}3H_2O$(cr)[a]	62.51
$MgSO_4{\cdot}7H_2O$(cr) (epsomite)	146.71	$HCl{\cdot}6H_2O$(cr)[a]	101.06
$MgSO_4{\cdot}12H_2O$(cr)[a]	220.50	$HNO_3{\cdot}3H_2O$(cr)[b]	73.09
$FeSO_4{\cdot}H_2O$(cr) (szomolnokite)	57.21	$H_2SO_4{\cdot}4H_2O$(cr)[a]	113.98
$FeSO_4{\cdot}7H_2O$(cr) (melanterite)	146.48	$H_2SO_4{\cdot}6.5H_2O$(cr)[a]	154.86
$CaSO_4$(cr) (anhydrite)	45.94	$NaHSO_4{\cdot}H_2O$(cr)	65.65
$CaSO_4{\cdot}2H_2O$(cr) (gypsum)	74.69	$KHSO_4$(cr) (mercallite)	58.64
$Na_2SO_4 3K_2SO_4$(cr) (aphthitalite)	246.24	$Fe(OH)_3$(cr) (ferrihydrite)	28.12
$Na_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$(cr) (bloedite)	149.98	$CH_4{\cdot}6H_2O$(cr)	135.75
$MgSO_4{\cdot}K_2SO_4{\cdot}6H_2O$(cr) (picromerite)	191.78	$CO_2{\cdot}6H_2O$(cr)	135.75
$NaNO_3$(cr) (nitratine)	37.60		
KNO_3(cr) (niter)	48.04		
$NaNO_3{\cdot}Na_2SO_4{\cdot}2H_2O$(cr) (darapskite)	119.57		

[a] Calculated from linear fits to degree of hydration.

[b] $HNO_3{\cdot}3H_2O = HCl{\cdot}3H_2O + NaNO_3 - NaCl$.

Table B.10. Volumetric Pitzer-equation parameters for ion interactions (Marion et al. 2005). (Numbers are in computer scientific notation, where e±*xx* stands for $10^{\pm xx}$). Reprinted from Marion et al. (2005) with permission

	Equation parameter[a]			
Pitzer parameter	a_1	a_2	a_3	Temperature range (K)
$B^{(0)V}_{\mathrm{Na,Cl}}$	1.088468e-4	−3.2412e-7		
$B^{(1)V}_{\mathrm{Na,Cl}}$	6.193806e-3	−4.135834e-5	6.911453e-8	252.6–298.15
$C^{V}_{\mathrm{Na,Cl}}$	−5.174534e-6	1.514940e-8		
$B^{(0)V}_{\mathrm{K,Cl}}$	6.593033e-5	−1.782e-7		
$B^{(1)V}_{\mathrm{K,Cl}}$	4.987530e-3	−3.224932e-5	5.215803e-8	273.15–298.15
$C^{V}_{\mathrm{K,Cl}}$	−7.112e-7			
$B^{(0)V}_{\mathrm{Mg,Cl}}$	6.446574e-4	−4.168596e-6	6.920e-9	
$B^{(1)V}_{\mathrm{Mg,Cl}}$	1.624497e-3	−5.618320e-6		273.15–298.15
$C^{V}_{\mathrm{Mg,Cl}}$	−5.567e-7			
$B^{(0)V}_{\mathrm{Ca,Cl}}$	1.409126e-4	−4.293e-7		
$B^{(1)V\mathrm{b}}_{\mathrm{Ca,Cl}}$	7.702445e-2	−7.785779e-4	2.612103e-6	236.9–298.15
$C^{V}_{\mathrm{Ca,Cl}}$	−6.723184e-6	2.216e-8		
$B^{(0)V}_{\mathrm{Fe,Cl}}$	1.19712e-4	−2.42e-7		
$B^{(1)V}_{\mathrm{Fe,Cl}}$	−2.40397e-3	1.80e-6		288.15–298.15
$C^{V}_{\mathrm{Fe,Cl}}$	0.00			
$B^{(0)V}_{\mathrm{Na,SO_4}}$	5.589854e-4	−1.698e-6		
$B^{(1)V}_{\mathrm{Na,SO_4}}$	3.323357e-2	−2.218483e-4	3.717169e-7	273.15–298.15
$C^{V}_{\mathrm{Na,SO_4}}$	−6.561572e-5	2.106e-7		
$B^{(0)V}_{\mathrm{K,SO_4}}$	−3.303430e-3	1.1125e-5		
$B^{(1)V}_{\mathrm{K,SO_4}}$	1.122179e-2	−3.6788e-5		273.15–298.15
$C^{V}_{\mathrm{K,SO_4}}$	1.741518e-3	−5.791e-6		
$B^{(0)V}_{\mathrm{Mg,SO_4}}$	1.789039e-4	−4.330e-7		
$B^{(1)V}_{\mathrm{Mg,SO_4}}$	3.157137e-2	−2.055400e-4	3.358883e-7	273.15–298.15
$B^{(2)V}_{\mathrm{Mg,SO_4}}$	9.096288e-2	−2.570e-4		
$C^{V}_{\mathrm{Mg,SO_4}}$	8.232980e-6	−2.629e-8		
$B^{(0)V}_{\mathrm{Fe,SO_4}}$	5.246895e-4	−1.196667e-6		
$B^{(1)V}_{\mathrm{Fe,SO_4}}$	−3.368357e-3	5.846667e-6		288.15–291.15
$B^{(2)V}_{\mathrm{Fe,SO_4}}$	0.00			
$C^{V}_{\mathrm{Fe,SO_4}}$	0.00			
$B^{(0)V}_{\mathrm{Na,HCO_3}}$	2.630581e-2	−1.820515e-4	3.141869e-7	
$B^{(1)V}_{\mathrm{Na,HCO_3}}$	−9.485264e-2	6.639475e-4	−1.157075e-6	273.15–298.15
$C^{V}_{\mathrm{Na,HCO_3}}$	1.374e-5			
$B^{(0)V}_{\mathrm{Na,CO_3}}$	2.567300e-4	−6.597813e-7		
$B^{(1)V}_{\mathrm{Na,CO_3}}$	1.488352e-2	−9.170975e-5	1.410818e-7	273.15–298.15
$C^{V}_{\mathrm{Na,CO_3}}$	−6.326112e-6	1.030e-8		

Table B.10. (continued)

	Equation parameter^a			
Pitzer parameter	a_1	a_2	a_3	Temperature range (K)
$B^{(0)V}_{\mathrm{K,HCO_3}}$	−7.241e-5			
$B^{(1)V}_{\mathrm{K,HCO_3}}$	7.527977e-2	−5.051817e-4	8.503591e-7	273.15–298.15
$C^{V}_{\mathrm{K,HCO_3}}$	3.9791e-5			
$B^{(0)V}_{\mathrm{K,CO_3}}$	1.061377e-4	−2.348475e-7		
$B^{(1)V}_{\mathrm{K,CO_3}}$	2.307677e-2	−1.421728e-4	2.179648e-7	273.15–298.15
$C^{V}_{\mathrm{K,CO_3}}$	−8.468e-7			
$B^{(0)V}_{\mathrm{Na,NO_3}}$	6.772663e-4	−4.469461e-6	7.432663e-9	
$B^{(1)V}_{\mathrm{Na,NO_3}}$	6.112177e-3	−3.714953e-5	5.670603e-8	273.15–298.15
$C^{V}_{\mathrm{Na,NO_3}}$	0.00			
$B^{(0)V}_{\mathrm{K,NO_3}}$	4.017245e-3	−2.727479e-5	4.639794e-8	
$B^{(1)V}_{\mathrm{K,NO_3}}$	−9.970759e-3	7.222127e-5	−1.295960e-7	273.15–298.15
$C^{V}_{\mathrm{K,NO_3}}$	0.00			
$B^{(0)V}_{\mathrm{Mg,NO_3}}$	1.921787e-3	−1.276510e-5	2.135779e-8	
$B^{(1)V}_{\mathrm{Mg,NO_3}}$	2.306674e-3	−8.051390e-6		273.15–298.15
$C^{V}_{\mathrm{Mg,NO_3}}$	0.00			
$B^{(0)V}_{\mathrm{Ca,NO_3}}$	2.034795e-4	−6.169134e-7		
$B^{(1)V}_{\mathrm{Ca,NO_3}}$	2.100958e-3	−7.119747e-6		279.15–298.15
$C^{V}_{\mathrm{Ca,NO_3}}$	0.00			
$B^{(0)V}_{\mathrm{Fe,NO_3}}$	1.05448e-3			
$B^{(1)V}_{\mathrm{Fe,NO_3}}$	−5.97153e-3			293.15
$C^{V}_{\mathrm{Fe,NO_3}}$	0.0			
$B^{(0)V}_{\mathrm{H,Cl}}$	1.710768e-4	−1.080235e-6	1.693469e-9	
$B^{(1)V}_{\mathrm{H,Cl}}$	0.00			268.15–298.15
$C^{V}_{\mathrm{H,Cl}}$	−5.584006e-6	3.505464e-8	−5.380952e-11	
$B^{(0)V}_{\mathrm{H,NO_3}}$	2.908819e-4	−1.909668e-6	3.163571e-9	
$B^{(1)V}_{\mathrm{H,NO_3}}$	2.191849e-3	−1.421625e-5	2.255071e-8	273.15–298.15
$C^{V}_{\mathrm{H,NO_3}}$	0.00			
$B^{(0)V}_{\mathrm{H,HSO_4}}$	9.447669e-4	−6.127516e-6	9.939028e-9	
$B^{(1)V}_{\mathrm{H,HSO_4}}$	−2.229583e-2	1.474382e-4	−2.418969e-7	
$C^{V}_{\mathrm{H,HSO_4}}$	0.00			273.15–298.15
$B^{(0)V}_{\mathrm{H,SO_4}}$	5.374354e-4	−3.519066e-6	5.951988e-9	
$B^{(1)V}_{\mathrm{H,SO_4}}$	1.326979e-2	−7.288212e-5	1.010339e-7	
$C^{V}_{\mathrm{H,SO_4}}$	0.00			

Table B.10. (continued)

Pitzer parameter	Equation parameter[a]			Temperature range (K)
	a$_1$	a$_2$	a$_3$	
$B^{(0)V}_{\mathrm{Na,HSO_4}}$	7.848698e-3	−5.199439e-5	8.721005e-8	273.15–298.15
$B^{(1)V}_{\mathrm{Na,HSO_4}}$	−3.960782e-2	2.627059e-4		
$C^{V}_{\mathrm{Na,HSO_4}}$	0.00			
$B^{(0)V}_{\mathrm{K,HSO_4}}$	1.199133e-2	−7.845685e-5	1.287364e-7	273.15–298.15
$B^{(1)V}_{\mathrm{K,HSO_4}}$	−4.699762e-2	3.063952e-4	−5.001161e-7	
$C^{V}_{\mathrm{K,HSO_4}}$	0.00			

[a] Fitted to $Y = a_1 + a_2T + a_3T^2$, where Y = Pitzer-equation volumetric parameter and T = temperature (K).

[b] This equation contains a fourth term: $-2.909328\text{e-}9T^3$.

Table B.11. Pressure-dependent parameters for Eqs. 3.23 and 3.24

			Model parameters		
Chemistry	T range (K)	P range (bars)	$K_0^{B(1)v}$	K_0^{Cv}	References
NaCl[a]	273.15 to 298.15	1 to 1002	= 1.644134e-6 − 5.245763e-9 T	= −5.658952e-8 + 1.896576e-10 T	Chen et al. (1980); Rogers and Pitzer (1982); Gates and Wood (1985)
KCl	298.15	1 to 406	= 8.78e-8	= −1.969e-9	Chen et al. (1980); Gates and Wood (1985)
$MgCl_2$	298.15	1 to 406	= 1.568e-7	= 1.062e-9	Chen et al. (1980); Gates and Wood (1985)
$CaCl_2$	298.15	1 to 407	= 1.447e-7	= 5.18e-10	Gates and Wood (1985)
Na_2SO_4	273.15 to 298.15	1 to 1002	= 5.585892e-6 − 1.7572e-8 T	= −5.890e-7 + 1.78424e-9 T	Chen et al. (1980)
$MgSO_4$	273.15 to 303.15	1 to 1014	= 3.315e-7	= 6.57e-9	Chen et al. (1980); Hogenboom et al. (1995); Hogenboom 2005 (pers. comm.)

[a] If Na $\geq$ 3.4 m, then $K_0^{B(1)\nu} = 8.11\text{e-}8$, $K_0^{C\nu} = 2.41\text{e-}10$.

Table B.12. Parameters for Duan et al. (1992b) gas fugacity model (Eqs. 3.37–3.48). (Numbers are in computer scientific notation where e$\pm xx$ stands for $10^{\pm xx}$)

	Gases		
Parameter	$CO_2(g)$	$CH_4(g)$	$H_2O(g)$[a]
T_c	304.20	190.60	647.25
P_c	73.825	46.41	221.19
a_1	8.99288497e-2	8.72553928e-2	8.64449220e-2
a_2	−4.94783127e-1	−7.52599476e-1	−3.96918955e-1
a_3	4.77922245e-2	3.75419887e-1	−5.73334886e-2
a_4	1.03808883e-2	1.07291342e-2	−2.93893e-4
a_5	−2.82516861e-2	5.49626360e-3	−4.15775512e-3
a_6	9.49887563e-2	−1.84772802e-2	1.99496791e-2
a_7	5.20600880e-4	3.18993183e-4	1.18901426e-4
a_8	−2.93540971e-4	2.11079375e-4	1.55212063e-4
a_9	−1.77265112e-3	2.01682801e-5	−1.06855859e-4
a_{10}	−2.51101973e-5	−1.65606189e-5	−4.93197687e-6
a_{11}	8.93353441e-5	1.19614546e-4	−2.73739155e-6
a_{12}	7.88998563e-5	−1.08087289e-4	2.65571238e-6
α	−1.66727022e-2	4.48262295e-2	8.96079018e-3
B	1.398e0	7.5397e-1	4.02e0
γ	2.96e-2	7.7167e-2	2.57e-2

[a] These parameters for $H_2O(g)$ are not currently being used in the FREZCHEM model.

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