

Extension, generation and application of the thermodynamic databases for PHREEQC using the ion activity model by Pitzer based on available thermodynamic data from literature

MHSE 36 Internship Hydro Sciences

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1 Introduction

PHREEQC is a computer program conceived to perform geochemical aqueous calculations. The PHREEQC currently incorporates different models such as two aqueous ion-association models, the aqueous Pitzer-specific ion-interaction model, and the aqueous SIT model (Specific Ion Interaction Theory) (PHREEQC Version 3 (2013)). In addition to the various aqueous models that use ion-association and Debye Hückel expressions, the Pitzer aqueous model is used in the presence of high ionic strength (high-salinity) in aqueous solution that exceeds the Debye theory range and has the most consistent aqueous data than other models. It has however only a limited number of elements. The main purpose of this paper is to extend, generate and apply the PHREEQC database through available thermodynamic data from the FREZCHEM model developed using the Pitzer approach.

2 Methods and materials

2.1 An overview of FREZCHEM Model

2.1.1 A Short Description

The FREZCHEM Model is a thermodynamic chemical equilibrium model which used the Pitzer method for the temperature range from -100 to 25 ° C and the pressure range from 1 to 1000 bar developed by (G.M. Marion, J.S. Kargel, J.K. Crowley, D.C.

Catling (2013)). A re-evaluation of Pitzer parameters and solubility products is needed in order to substitute $A\phi$ in the FREZCHEM model with current equation. Among the 9 variants of the FREZCHEM model, the final version of the Na-K-NH₄-Mg-Ca-Fe(II)-Fe(III)-Al-H-Cl-ClO₄-Br-SO₄-NO₃-OH-CO₃-CO₂-CH₄-NH₃-Si-H₂O system has been parameterised; It also includes 108 solid phases, including ice, 16 chloride minerals, 36 sulfate minerals, 16 carbonate minerals, 5 solid-phase acids, 5 iron oxide/hydroxides, four aluminium hydroxides, 2 silica minerals, 2 ammonia minerals, 2 gas hydrates, and 2 bromide sinks (G.M. Marion, J.S. Kargel, J.K. Crowley, D.C. Catling (2013)).

2.1.2 Temperature and Pressure dependencies

The challenges in the development of the model are the balance between water ice, liquid water and water vapour. So-called, the relationship of freezing point depression (fpd) is central to any model being created. Such phase relationships in a model help to figure out the properties of one phase (gas) based on the properties of the (aqueous) measured one. In addition, the lower temperature range from 219 K to 195 K was extended including strong acids in the FREZCHEM model in which fpd data did not fit together. Therefore, the re-evaluation of equation is required. The activity of the pure water is estimated from:

$$a_w = \frac{f_i}{f_w} = K_{ice} \approx \frac{P_i}{P_w}, \quad (\text{EQ 1})$$

where f_i and f_w are the fugacities of water vapour above pure ice and pure liquid water, P_i and P_w are the corresponding partial pressures and the value for K_{ice} estimated from the clegg- Brimblecombe (1995) equation (Ronald J. Spencer, Nancy Møller, and John H. Weare (1989)).

In FREZCHEM Model, the density of the pure water at $T \geq 273\text{K}$ and $P = 1.01$ bars is calculated with the Kell (1975) equation is given by,

$$1000\rho_w^0 = \left(\frac{999.83952 + 16.94518t - 7.98704 * 10^{-3}t^2}{-4.617046 * 10^{-5}t^3 + 1.05563 * 10^{-7}t^4 - 2.805425 * 10^{-10}t^5} \right) / (1.0 + 1.687985 * 10^{-2}t),$$

Where t is the temperature ($^{\circ}\text{C}$). (EQ 2)

2.2 The Pitzer Approach

2.2.1 The Osmotic Coefficient and Activity Coefficients

The Pitzer method is used as a function of temperature and pressure for anions (X), cations (M), neutral species (N) in condensed solutions to measure the osmotic coefficients (ϕ) and the solute activity coefficients (γ).

Debye and Hückel (1923) developed an early model based on mechanical statistics. The model established is, however, only applicable for intermediate concentrations

up to ($I = 0.1 - 0.5$ m) (Giles M. Marion, Jeffrey S. Kargel (2008)). Several attempts have been made to expand such equations to higher concentration. Pitzer had developed the higher concentration ($I > 0.5$ m) model.

Pitzer assumed the excess Gibbs free energy (G_{ex}) through the following relation (Giles M. Marion, Jeffrey S. Kargel (2008)).

$$G^{ex} = w_w f(I) + \frac{1}{w_w} \sum \lambda_{ij}(I) n_i n_j + \frac{1}{w_w^2} \sum \sum \mu_{ijk} n_i n_j n_k \quad (\text{EQ 3})$$

Where n_i is species moles i. $f(I)$ is an ionic resistance mechanism for long-range electrostatic forces. The word λ_{ij} reflects the short-range powers between species i and j. The term μ_{ijk} represents interactions of short-range triple particles. Such concepts define the high concentration critical ion-ion, ion-neutral, neutral-neutral species and triple particle interactions that differentiate the Pitzer approach from the Debye-Hückel approach.

The osmotic coefficient is given by

$$(\phi - 1) = \left(\frac{2}{\sum m_i} \right) \left\{ \begin{aligned} & \frac{-A^\phi I^{1.5}}{(1 + b\sqrt{I})} + \sum \sum m_c m_a (B_{ca}^\phi + Z C_{ca}) \\ & + \sum \sum m_c m_{c'} (\phi_{cc'}^\phi + \sum m_a \psi_{cc'a}) \\ & + \sum \sum m_a m_{a'} (\phi_{aa'}^\phi + \sum m_a \psi_{aa'c}) \\ & + \sum \sum m_n m_c \lambda_{nc} + \sum \sum m_n m_a \lambda_{na} + \sum \sum \sum m_n m_c m_a \zeta_{n,c,a} \end{aligned} \right\} \quad (\text{EQ 4})$$

The activity coefficient for an anion “X” is given by

$$\ln(\gamma_X) = Z_X^2 F + \sum m_c (2B_{cX} + Z C_{cX}) + \sum m_a (2\phi_{Xa} + \sum m_c \psi_{Xac}) + \sum \sum m_c m_{c'} \psi_{cc'X} + |Z_X| \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nX} + \sum \sum m_n m_c \zeta_{ncX} \quad (\text{EQ 5})$$

Similarly the activity coefficient for a cation “M” is given by

$$\ln(\gamma_M) = Z_M^2 F + \sum m_a (2B_{Ma} + Z C_{Ma}) + \sum m_c (2\phi_{Mc} + \sum m_a \psi_{Mca}) + \sum \sum m_a m_{a'} \psi_{aa'M} + |Z_M| \sum \sum m_c m_a C_{ca} + 2 \sum m_n \lambda_{nM} + \sum \sum m_n m_a \zeta_{nMa} \quad (\text{EQ 6})$$

Finally, the activity coefficient for a neutral species “N” is given by

$$\ln(\gamma_N) = \sum m_c (2\lambda_{Nc}) + \sum m_a (2\lambda_{Na}) + \sum \sum m_c m_a \zeta_{Nca} \quad (\text{EQ 7})$$

Where A_ϕ is the Debye-Hückel parameter at 25°C $A_\phi = 0.3915$ (Giles M. Marion, Jeffrey S. Kargel (2008)), b is a constant and B , C , ϕ , ψ , ζ are the Pitzer-equation ion interaction coefficients, z_i and m_i are the charge number and molality of the i^{th} ion, F and Z are equation functions. The terms B describe cation-cation interactions, are 3 parameter functions: $B^{(0)}_{MX}$, $B^{(1)}_{MX}$, $B^{(2)}_{MX}$. C describes cation-anion interaction as

C_{ca} . The subscripts c, a, n refers to cation, anion and neutral species, plus a', c' is anion and cation. The term I is defined by the ionic strength of:

$$I = 0.5 \sum m_i z_i^2, \quad (\text{EQ 8})$$

where Z is defined by :

$$Z = \sum m_i |z_i| \quad (\text{EQ 9})$$

The osmotic coefficient (ϕ) related to the activity of water (a_w) is given by

$$a_w = \exp\left(\frac{-\phi \sum m_i}{55.50844}\right) \quad (\text{EQ 10})$$

The above mentioned equations are taken from (Giles M. Marion, Jeffrey S. Kargel (2008)).

2.2.2 Temperature and Pressure dependencies

The temperature dependencies of Pitzer parameters and equilibrium constants were determined from isothermal datasets and conform to the following equation (Giles M. Marion, Jeffrey S. Kargel (2008)).

$$P(T)_i = a_{1i} + a_{2i}T + a_{3i}T^2 + a_{4i}T^3 + \frac{a_{5i}}{T} + a_{6i} \ln(T) + \frac{a_{7i}}{T^2} + a_{8i}T^4, \quad (\text{EQ 11})$$

where $P(T)_i$ is the i^{th} Pitzer parameter or $\ln(K)$ except for ice and T is the absolute temperature (K).

The volumetric properties of the solution are correlated with the effect of pressure on the chemical equilibria or the excess Gibbs energy .

In Pitzer approach, the expression for excess volume of mixing is given by,

$$V_{mix}^{ex} = A_v \left(\frac{1}{b} \right) \ln(1 + bI^{0.5}) + 2RT * \sum \sum m_c m_a [B_{c,a}^v + (\sum m_c z_c) C_{c,a}^v] \quad (\text{EQ 12})$$

Where A_v is the volumetric Pitzer-Debye - Hückel parameter, I is the ionic strength, b is a constant, and $B_{c,a}^v$ and $C_{c,a}^v$ are the functions of $B(0)^v_{ca}$, $B(1)^v_{ca}$, $B(2)^v_{ca}$ and $C(1)^v_{ca}$.

The density (ρ) of an aqueous solution can be determined with the following equation,

$$\rho = \frac{1000 + \sum m_i M_i}{\frac{1000}{\rho^0} + \sum m_i \bar{V}_i^0 + V_{mix}^{ex}} \quad (\text{EQ 13})$$

Where m_i is the molal concentration, M_i is the molar mass, ρ^0 is the density of pure water at a given temperature and pressure, \bar{V}_i^0 is the partial molar volume at infinite dilution of solution species, and V_{mix}^{ex} is the excess volume of mixing which is described in EQ .

2.3 Incorporation of FREZCHEM Model to PHREEQC

The main objective is to incorporate FREZCHEM Model on PHREEQC with the available database on the literatures. Nevertheless, FREZCHEM is an independent model that was only created and compiled on FORTRAN. In order to include the FREZCHEM parameters and solubility products into the PHREEQC system, the temperature dependencies equations for both model must be fitted.

The temperature dependencies of Pitzer parameters (P) and solubility product (K) at a temperature (T) are expressed in FREZCHEM on the EQ 11 above.

In PHREEQC on the other hand, the specific equation for Pitzer parameter (P) temperature dependence is defined as (Jonathan D. Tonar, Ronald S. Sletten (2013))

$$P(T) = a_1 + a_2 \left(\frac{1}{T} - \frac{1}{T_R} \right) + a_3 \ln \left(\frac{T}{T_R} \right) + a_4 (T - T_R) + a_5 (T^2 - T_R^2) + a_6 \left(\frac{1}{T^2} - \frac{1}{T_R^2} \right), \quad (\text{EQ 14})$$

and also the separate equation for the temperature dependence of solubility products is given by,

$$\log K(T) = a_1 + a_2 T + \frac{a_3}{T} + a_4 \ln T + \frac{a_5}{T^2} + a_6 T^2, \quad (\text{EQ 15})$$

where T_R is the reference temperature 298.15 K, T is the given temperature range from -70 to 25 °C (Jonathan D. Tonar, Ronald S. Sletten (2013)).

As per (Jonathan D. Tonar, Ronald S. Sletten (2013)), the EQ 11 FREZCHEM parameters and solubility products are mounted in the temperature range of -70 to 25 °C to PHREEQC EQ 14 and EQ 15 . It is also important to remember the Debye Hückel constant ($A\phi$), which is integral in Pitzer but handled differently in PHREEQC and FREZCHEM, when integrating parameters from one model to another.

In FREZCHEM, the virial coefficients a_i define the constant ($A\phi$). To keep the PHREEQC compatible with the FREZCHEM, the source code of the PHREEQC has been modified to use the FREZCHEM equation for ($A\phi$).

Jonathan D. Tonar, Ronald S. Sletten (2013) has created a small FREZCHEM database for Na-K-Mg-Ca-H-Cl-CO₃-SO₄-HCO₃-H₂O-CO₂ system which includes 35 solid phases, including ice for PHREEQC. The purpose of this work is to expand the thermodynamic databases available for the FREZCHEM. Using the available massive Pitzer parameters and the solubility products in the FREZCHEM version series, five solid phases were carefully selected and fitted to the PHREEQC parameters without altering the present original values from the literature database series (see Table 1) (Ronald J. Spencer, Nancy Møller, and John H. Weare (1989)).

Table 1: List of Solid phases and its equation parameters

Solid Phase	Equation parameters						Reference
	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆	
MgSO ₄ :12H ₂ O	-12.8472	0.038442	0.00	0.00	0.00	0.00	G.M. Marion, Ronald E. Farren (1999)
HCl:3H ₂ O	2.233293	0.00	0.00708	0.00	0.00	0.00	G.M. Marion (2000)
HCl:6H ₂ O	1.896729	0.00	0.00158	0.00	0.00	0.00	G.M. Marion (2002)

Table 2 : Molar Volume

Solid Phase	Molar Volume (cm ³ /mole)	Reference
MgSO ₄ :12H ₂ O	220.5	G.M. Marion, David C. Catling, and Jeffrey S. Kargel (2006)
HCl:3H ₂ O	62.51	G.M. Marion, David C. Catling, and Jeffrey S. Kargel (2006)
HCl:6H ₂ O	101.06	G.M. Marion, David C. Catling, and Jeffrey S. Kargel (2006)

The Pitzer syntax for integrating FREZCHEM parameters in PHREEQC is given below (PHREEQC Version 3 (2013)),

Line 1 : B0

Line 2 : cation anion (Coefficients for the temperature dependence - A₀, A₁, A₂, A₃, A₄, A₅)

Line 3 : B1

Line 4 : B2

Line 5 : C0

Line 6 : THETA

Line 7 : cation anion or anion anion (Coefficients for the temperature dependence - A₀, A₁, A₂, A₃, A₄, A₅)

Line 8 : LAMBDA

Line 9 : neutral anion or cation (Coefficients for the temperature dependence - A₀, A₁, A₂, A₃, A₄, A₅)

Line 10 : PSI

Line 11 : anion anion cation or cation anion anion (Coefficients for the temperature dependence - A₀, A₁, A₂, A₃, A₄, A₅)

Line 12 : ZETA

Line 13 : neutral cation anion (Coefficients for the temperature dependence - A_0 , A_1 , A_2 , A_3 , A_4 , A_5)

Line 14 : MU

Line 15 : neutral neutral neutral (Coefficients for the temperature dependence - A_0 , A_1 , A_2 , A_3 , A_4 , A_5)

Line 16 : ETA

Line 17 : neutral cation cation or neutral anion anion (Coefficients for the temperature dependence - A_0 , A_1 , A_2 , A_3 , A_4 , A_5)

Line 18 : alphas

Line 19 : cation anion α_1 and α_2

3 Results

3.1 The solid phase: $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$

In FREZCHEM Model, the solid phase $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ achieved a maximum concentration of around 3.1 moles (Marion) from -1 to 8°C by precipitating $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$, later (>8°C) by removing from the model the following solid phases such as Kieserite, hexa-hydrate and epsomite . At the same time ice formation starts from -1.5 °C onwards. In comparison, when modeling in the PHREEQC FREZCHEM database, the maximum concentration of $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ starts to increase once it reaches >0°C. The following Figure 1 shows that both models obtained the maximum concentration of $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ at different temperature.

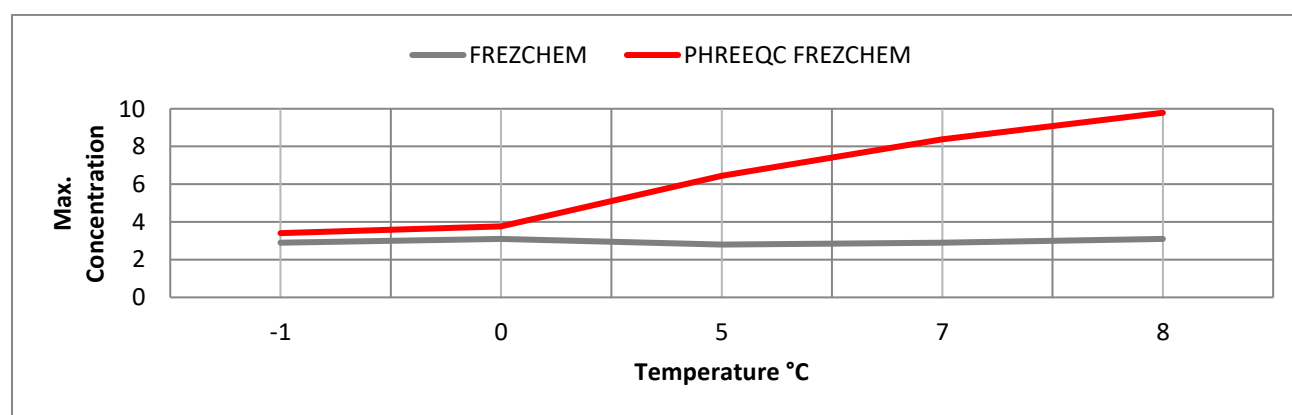


Figure 1: Comparison of FREZCHEM and PHREEQC FREZCHEM data

3.2 The solid phases: $\text{HCL} \cdot 3\text{H}_2\text{O}$ and $\text{HCL} \cdot 6\text{H}_2\text{O}$

The behaviour of added $\text{HCL} \cdot 3\text{H}_2\text{O}$ and $\text{HCL} \cdot 6\text{H}_2\text{O}$ in the PHREEQC-FREZCHEM database is represented in the following Figure 2 [Marion and Farren 1999].

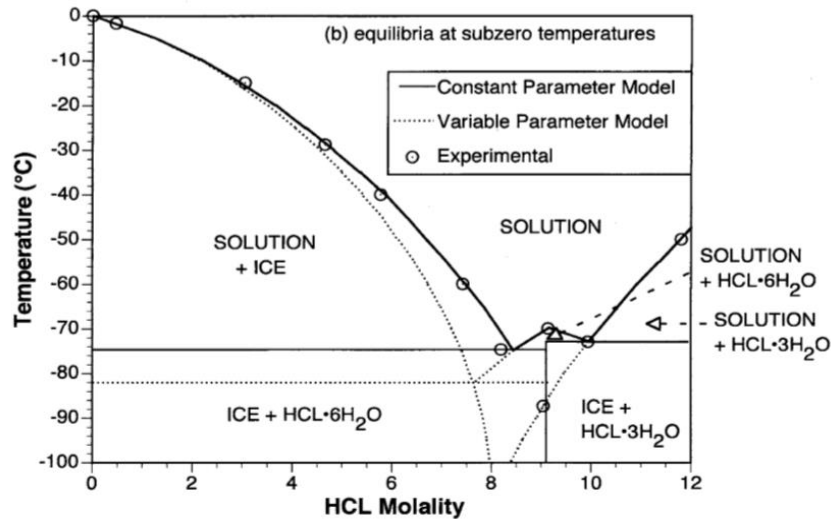


Figure 2: HCL Molality vs Temperature (G.M. Marion (2002))

The following temperature and the concentration of the solution was chosen to make sense when comparing the values from both models. While Modeling HCL:3H₂O in the FREZCHEM version 17 at 5 moles from 0°C to -82 °C , the presence of ice occurred in the solution and also from -83°C, it starts the precipitates Ice and HCL.6H₂O which means it becomes Eutectic. In the PHREEQC FREZCHEM database, the ice precipitation starts at 7.9 moles from 0°C to -85°C (See Fig). Later the full pack of Ice and HCL:6H₂O from -86°C begins precipitating. The activity of HCL:3H₂O and HCL:6H₂O in the above 0°C solution is achieved total equilibrium status.

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THE SYSTEM IS RUNNING OUT OF WATER          (<0.1g).  THIS MEANS THAT THE MODEL IS AT THE          EUTECTIC,
BEYOND THE EUTECTIC, EVAPORATED TO DRYNESS,  OR THE MODEL IS HAVING CONVERGENCE PROBLEMS
AT T = 190.150 K AND P =  1.013 BARS
THE SOLIDS THAT ARE PRECIPITATING ARE  31  72
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Figure 3: Results from version 17 of the FREZCHEM Model

The above Figure 3 shows the results obtained from version 17 of the FREZCHEM Model. The numbers 31 and 72 reflects the solid species ICE and HCL:6H₂O, and also in the Figure 4, the results acquired from the PHREEQC FREZCHEM databases.

-----Saturation indices-----

Phase	SI**	log IAP	log K(188 K, 1 atm)	
HCL:3H ₂ O	-0.78	2.78	3.57	HCL:3H ₂ O
HCL:6H ₂ O	0.01	2.20	2.19	HCL:6H ₂ O
Ice(s)	0.13	-0.19	-0.32	H ₂ O

**For a gas, SI = log10(fugacity). Fugacity = pressure * phi / 1 atm.
For ideal gases, phi = 1.

Figure 4: Results from PHREEQC FREZCHEM Model

4 Discussion

The presence of solid phase $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$ in the PHREEQC FREZCHEM gives precise results when calculating $< 0^\circ\text{C}$. The graph indicates the concentration change as the phase concentration increases. But, the FREZCHEM model results deliver accurate results at varying temperature.

In the above mentioned results, the variation of $\text{HCL} \cdot 3\text{H}_2\text{O}$ and $\text{HCL} \cdot 6\text{H}_2\text{O}$ activity in both models is not really greater. The precipitation begins early in the FREZCHEM Model and in the PHREEQC the concentration and temperature need to increase more to get the respective effects.

The main aim is to extend, generate and apply PHREEQC databases by using the Pitzer approach to incorporate the presence of available parameters in the FREZCHEM Model. The current working FREZCHEM Model was packed with a number of solution and solid phases. However, one of the major shortcomings in integrating is the lack of key parameters and repetitive fitting in PHREEQC to the Pitzer equation parameterization.

However, FREZCHEM is the only model that calculates solution and solid phases under sub - zero temperature. But, the lack of other similar models to make them comparable, find ways to prevent errors and to expand the PHREEQC databases. The FREZCHEM model is particularly used for geochemical processes occurring in interplanetary research (MARS and Europa), where the minerals and phases are present in extreme conditions (cold environment and sub-zero temperatures) .

Also the FREZCHEM model has many imperfections including logical constraints, problems of convergence, and weak coding. The simplicity of the FREZCHEM model built in FORTRAN allows more calculation difficulties without the existence of graphical user interface and probability of obtaining results variance in different operating systems.

5 Conclusion

The main conclusion of this study were,

Comprehensive analysis of Pitzer model use and function and its implementations, comparing other available models and including 3 solid phases such as $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, $\text{HCL} \cdot 3\text{H}_2\text{O}$ and $\text{HCL} \cdot 6\text{H}_2\text{O}$ in the PHREEQC FREZCHEM database.

The further development of PHREEQC FREZCHEM databases requires the respective elements to have a complete set of key parameters and temperature dependencies. The further expansion of Pitzer model database is possible if the existing thermodynamic data sets are extended and readily available to all.

6 References

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