

A Gibbs-Pitzer standard sea ice phase diagram

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Abstract

The Gibbs-Pitzer approach (*Pitzer*, 1991) implemented in the FREZCHEM code (*Marion et al.*, 2010) provides theoretical means to calculate the equilibrium composition of partly frozen electrolyte solutions – of which sea ice is a particular example. FREZCHEM relies on a virial expansion of Gibbs free energy. The involved so-called Pitzer coefficients describe ion-solvent interactions and are compiled from experimental data. FREZCHEM is widely used to explore cold geochemical processes in the Earth's polar regions and life limits on Europa and Mars.

This small document informs on how the Gibbs-Pitzer sea ice phase diagram derived with the help of FREZCHEM 13.3 was derived in the framework of the article "Thermodynamics of sea ice phase composition revisited", published in *JGR-Oceans* (*Vancoppenolle et al.*, 2019), and on how it can be used.

1 Using the phase diagram

The Gibbs-Pitzer sea ice phase diagram is provided as a NetCDF file (`FREZCHEM_phasediagram.nc`), containing detailed diagnostics from the 41 FREZCHEM 13.3 runs made of 363 temperature levels. All included arrays are described in Table 1. The list of solutes and solid minerals are given in Table 2 and 3.

NetCDF (Network Common data form) is a standard, self-describing, machine-independent format of array-oriented data, widely used in climate sciences and compatible with standard programming languages (C, Fortran, ...) as well as with typical data processing softwares (python, R, matlab, IDL, etc...).

As an example of a possible uploading script, we provide `read_frezchem.m`, which uploads all arrays from the netcdf file into matlab.

Table 1: Arrays provided into the netcdf file. $N_T = 363$, $N_S = 41$, $N_{solute} = 21$, $N_{solid} = 101$. $P=1.0132$ bar.

Netcdf Name	Units	Long name	Dimensions
T	°C	ITS-90 Celsius Temperature	N_T
SA	g/kg	Absolute Salinity	N_S
I	mol / (kg brine)	Ionic Strength	N_S, N_T
rho	kg/m ³	Brine Density	N_S, N_T
Osm_coeff	-	Osmotic coefficient	N_S, N_T
pH	\log_{10} (mol / kg brine)	pH	N_S, N_T
Nit	.	Iterations to reach convergence	N_S, N_T
M_tot	g	Total mass of the system	N_S
M_ice	g	Mass of ice	N_S, N_T
M_H2O_liq	g	Mass of liquid H ₂ O	N_S, N_T
M_H2O_min	g	Mass of H ₂ O in minerals	N_S, N_T
M_salt_liq	g	Mass of dissolved salt	N_S, N_T
M_salt_min	g	Mass of salt in minerals	N_S, N_T
S_br	g/kg	Liquid phase salinity	N_S, N_T
S_sm	g/kg	Salinity due to minerals	N_S, N_T
f_sm	g/g	Fraction of total salt in minerals	N_S, N_T
phi_ice	kg/kg	Mass fraction of Ice <i>lh</i>	N_S, N_T
phi_H2O_liq	kg/kg	Mass fraction of Liquid H ₂ O	N_S, N_T
phi_H2O_min	kg/kg	Mass fraction of H ₂ O in minerals	N_S, N_T
phi_salt_liq	kg/kg	Mass fraction of dissolved salts	N_S, N_T
phi_salt_min	kg/kg	Mass fraction of salt in minerals	N_S, N_T
phi_liq	kg/kg	Mass fraction of all components of liquid phase	N_S, N_T
phi_solid	kg/kg	Mass fraction of all components of solid phase	N_S, N_T
phi_H2O	kg/kg	Mass fraction of H ₂ O	N_S, N_T
phi_salt	kg/kg	Mass fraction of salt	N_S, N_T
phi_tot	kg/kg	Sum of all mass fractions (conservation check)	N_S, N_T
C_error_abs	g	Conservation error (absolute)	N_S, N_T
C_error_rel	%	Conservation error (relative)	N_S, N_T
conc_solute	mol/(kg brine)	Molar concentration of solutes in liquid phase	N_{solute}, N_S, N_T
conc_solid	mol/kg	Molar concentration of solid minerals	N_{solid}, N_S, N_T
mf_solute	g/(kg brine)	Mass fraction of solutes in liquid phase	N_{solute}, N_S, N_T
mf_solid	g/kg	Mass fraction of salt in solid minerals	N_{solid}, N_S, N_T

Table 2: Indices of solutes into conc_solute and mf_solute arrays.

Index	Solute
1	Na
2	K
3	Ca
4	Mg
5	H
6	MgOH
7	Cl
8	SO ₄
9	OH
10	HCO ₃
11	CO ₃
12	HSO ₄
13	Br
14	CO ₂
15	CaCO ₃
16	MgCO ₃
17	Sr
18	B(OH) ₄
19	B(OH) ₃
20	F
21	HF

Table 3: Indices of precipitating minerals stored into conc_solid and mf_solid arrays.

Index	Mineral name	Formula
2	Hydrohalite	NaCl · 2 H ₂ O
4	Sylvite	KCl
10	Mirabilite	Na ₂ SO ₄ · 10 H ₂ O
18	Gypsum	CaSO ₄ · 2 H ₂ O
26	Ikaite	CaCO ₃ · 6 H ₂ O
20	Meridianite	MgSO ₄ · 11 H ₂ O
84	Sodium Bromide	NaBr

2 Understanding the phase diagram

The Gibbs-Pitzer diagram given in the netCDF was derived from 41 FREZCHEM 13.3 runs, each corresponding to a given absolute salinity ($S = 0.3, 1, 2, \dots, 40$ g/kg). Each run simulates the cooling and progressive freezing of an isolated standard seawater sample from $T = 0^\circ\text{C}$ down to -36.2°C over -0.1°C steps. Seawater samples are made of $M = 1000 + M_s$ grams of standard seawater, composed of 1000 g of H_2O and $M_s = 1000 \cdot S / (1000 - S)$ grams of salt, adequately distributed among the 15 species of standard seawater (Millero *et al.*, 2008, Table 3). Following the composition of standard seawater, we also imposed 385 ppm of CO_2 and $\text{pH} = 8.1$.

FREZCHEM 13.3 was downloaded from the FREZCHEM official webpage. The code was compiled on mac-osx 13.3.6 using gfortran 4.3.0.

2.1 "Sample" preparation

Our virtual samples (i.e. FREZCHEM Input.txt files) were prepared using the following procedure.

- Absolute salinity S was imposed. For each of the 15 standard seawater ionic compounds, we convert the ratio to chlorinity r_i (Millero *et al.*, 2008, Table 3, first column) into molar concentration in seawater, g/(kg sol):

$$c_i = \frac{r_i S}{A_i \sum_i r_i} \quad \text{mol/(kg sol)}, \quad (1)$$

where A_i is molecular weight (Millero *et al.*, 2008, Table 3, second column). FREZCHEM needs molalities in g/(kg H_2O), which are, for each of the 15 ions, given by:

$$m_i = \frac{c_i}{1 - S/1000}. \quad (2)$$

generate_concentrations.pro is the IDL 8.1 script file that generates the FREZCHEM input files (INPUT.txt) for a given absolute salinity.

- The operation was repeated for each of the 41 applied salinities. master.scr is the UNIX script mastering the preparation and running of the 41 FREZCHEM runs. This leads to 41 output text files (FrOut), giving the detailed composition of the output files.

2.2 Post-processing

read_frezchem.pro is an IDL script used to process the FREZCHEM output files and to derive the relevant components of the sea ice mass budget.

The following diagnostics were read and retained for post-processing: the mass of ice Ih (g), the mass of liquid H_2O (g), the molality of the 21 considered solutes (mol/kg liquid H_2O), and the moles of each of the considered 101 minerals (mol/kg), of which only 8 were found in detectable amounts. All of these were stored over the 363×41 T - S grid for further processing.

Mass conservation at temperature T and salinity S , split over the different phases and integrated over the different chemical species considered by FREZCHEM is given by:

$$1 = \phi_{br}^{\text{H}_2\text{O}} + \phi_{br}^{\text{salt}} + \phi_{ice}^{\text{H}_2\text{O}} + \phi_{sm}^{\text{H}_2\text{O}} + \phi_{sm}^{\text{salt}}. \quad (3)$$

The different terms refer to mass fractions (ϕ 's) of liquid H₂O, dissolved salts, pure ice (solid H₂O) and solid minerals split into H₂O and salt contributions, all being expressed per unit mass of sea ice. The mass fractions in equation 3 are obtained by dividing the mass of each of the compounds by the total mass of the system M_{tot} . The mass of ice and of liquid H₂O are direct FREZCHEM diagnostics. The other components of the mass budget are derived as follows:

- **Dissolved salt.** The output molalities m_i in mol / (kg H₂O) are converted, for each of the 21 output solutes, into molar concentrations c_i in mol / (kg sol), using Eq. 2 from *Butler et al.* (2016):

$$c_i = m_i \left(\frac{1000}{1000 + \sum A_i m_i} \right). \quad (4)$$

By multiplying c_i by A_i , we get mass fractions for the 21 output solutes. Summing over solutes, we get brine salinity:

$$S_{br} = \sum_i c_i A_i. \quad (5)$$

The mass of dissolved salt in the system is finally:

$$M_{br}^{\text{salt}} = \frac{S_{br} \cdot M_{br}^{\text{H}_2\text{O}}}{1000 - S_{br}} \quad (6)$$

- **Salt and water stored into minerals.** The mass fractions of salt contained into each of the solid minerals were obtained by multiplying the output concentrations (in mol/kg) by the molecular mass of all species but H₂O incorporated, in the the mineral of interest. The mass fraction of solid H₂O contained into each of the minerals is obtained by multiplying the output concentrations by the number of hydrated water molecules and by the molecular mass of water. Summing over minerals, we get, on the one hand, the mass of salt incorporated into minerals (M_{sm}^{salt}), and of water in minerals ($M_{sm}^{\text{H}_2\text{O}}$) on the other hand.
- The **total mass** of the sample M_{tot} is obtained by summing the mass of liquid H₂O and the mass of salt ($S \cdot 1000 / (1000 - S)$) at 0°C.
- The **mass fraction of total salt complexed into minerals**, f_{sm} , is diagnosed as $\phi_{sm}^{\text{salt}} / S$.

For some reason (precision of outputs, convergence of FREZCHEM, processing inconsistency, or bug), mass is not exactly conserved, with typical errors within 0.03% of 0.3 g. To warrant mass fractions summing to 1, we divided all mass fractions by

their sum. Anyone finding the reason of the non-conservation is welcome to contact us, we would update the note and the phase diagram.

Note on small processing errors. Minor processing errors in the specification of the composition of the virtual seawater samples, and in the calculation of total mass of the system were found and fixed after acceptance of the paper. The phase diagram used for the paper is `FREZCHEM_phasediagram.nc` and should be used to test exact reproductibility of the results. The revised phase diagram is `FREZCHEM_phasediagram_v2.nc` and should be used for all other purposes. The errors are well labelled in the corresponding processing scripts. Tabulated statistics (in particular Table 4 and 5 of the paper) are virtually not unaffected by the changes. Yet, the conservation error dropped by about an order of magnitude following the error fixes.

References

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