Geofluids — Part IV

Introduction to Geochemical and Reactive Transport Modeling

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Lecturers' introduction

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Introduction

Introduction

Course introduction

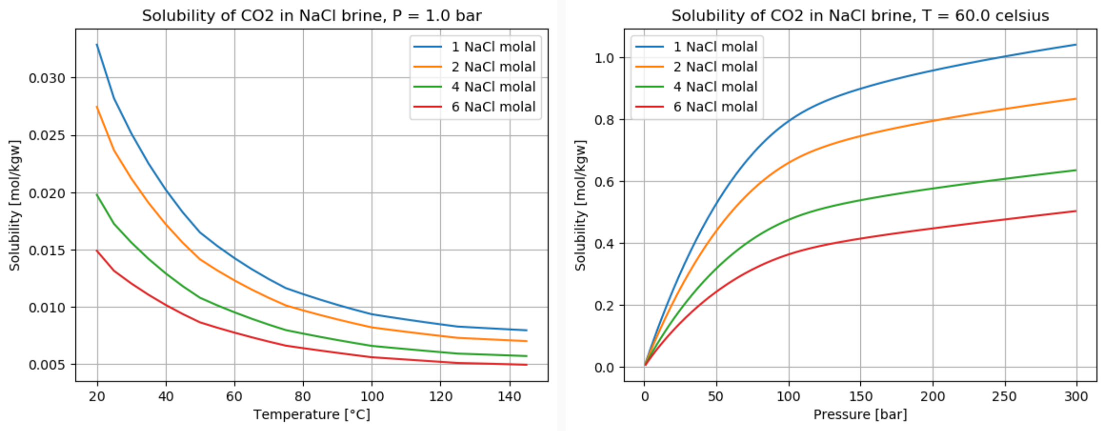
Course goal

- By the end of this course, you should become familiar with the fundamentals of **geochemical and reactive transport modeling** that includes of the following concepts:
  - chemical equilibrium;
  - chemical kinetics; and
  - chemical transport.
- For **numerical simulations** of simple geochemical and reactive transport problems, we will use Python and Reaktoro (`reaktoro.org`, computational framework that provides numerical methods for modeling chemically reactive processes governed by either chemical equilibrium, chemical kinetics, etc).

Computational exercises

- This course will include a **computational project** using Python.
  - The project **is not graded!** But helpful in preparing for the final exam.
  - It will involve chemical reaction calculations for a **chemical system** containing different phases, such as
    - aqueous (HO_2(l), HCl(aq), Na^+, etc),
    - gaseous (CO_2(g), H_2S(g)), and
    - mineral (e.g., calcite, dolomite, halite).
  - The goal of these calculations can be, for example, to determine the solubility of minerals and gases in saline waters (brine) at different salinities, temperatures, and pressures.
  - **Optional**: We can select the time (to meet online) so that you get to ask your questions, and I will be able to clarify them.
- Other computational tasks will be given throughout the lectures as **exercises, code-listings, and tutorials** (using python scripts or Jupyter Notebooks).
- Lectures will contain **interactive quizzes** helping to understand and apply the presented material.

Example of geochemical calculations, CO_2(g) solubility in the NaCl-brine



Note: See Jupyter notebook tutorial *CO_2 solubility in NaCl-brine*.

Poll on the Python background

http://etc.ch/SA8F

or

Tips for learning Python

- It is sufficient to learn the **basics of the Python 3** (e.g., working with lists or numpy arrays, calling a function, plotting):

  `https://www.programiz.com/python-programming/tutorial`

- Consider installing Python 3 using **Anaconda** using

  `https://www.anaconda.com/distribution/`

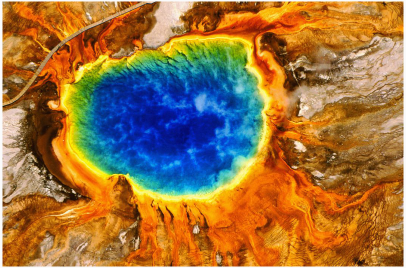
- Instruction of **installing Reaktoro** are also given using Anaconda.
  Note: Videos *Into words*, *Installation on Windows / IoS*, and *Reaktoro Jyputer Notebook Installation* with explanation on Reaktoro installation and Jupyter Notebook tutorials execution are available `here`.
- To ask any questions, you can use my email `svetlana.kyas@erdw.ethz.ch`.

Introduction

A brief overview of geochemical modeling and its applications

What is geochemical modeling?

Geochemical modeling is the use of computers to simulate **chemical reactions** occurring in geologic systems, either **near the Earth's surface** or **deep in its interior**.



Geochemical reaction calculations for thermal water analysis (Grand Prismatic, Midway Geyser Basin, Yellowstone, Wyoming, USA).

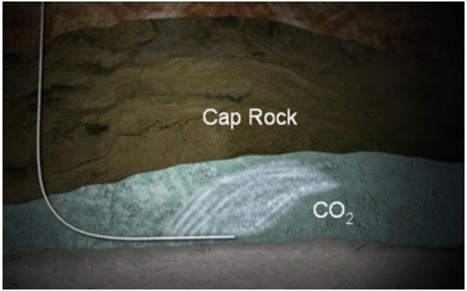
Geochemical reaction calculations for molten rocks as the magma flows from the Earth's mantle upwards.

Geochemical modeling applications, Scaling prediction in wells

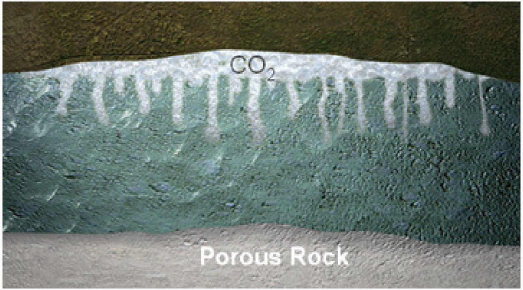
Scale formation in a well as a result of geochemical reactions leading to mineral precipitation.

- Fluids coming from a reservoir experiences **temperature/pressure changes along the wells**.
- The decrease in temperature and/or pressure can lead to chemical reactions promoting precipitation of minerals and thus **scale formation** along the well.
- Geochemical modeling can be used to **predict**, **understand**, and **assist** on the **remediation of scale formation**.

Geochemical modeling applications, CO_2 storage in geologic formations



Once CO_2 is injected in a deep saline aquifer, it starts to **dissolve into the resident brine**. Geochemical calculations can be used to calculate how much CO_2 dissolves and how much CO_2 continues mobile as gas or supercritical fluid.



Brine with dissolved CO_2 becomes acidic. It can then more easily **react with rock minerals**. This change rock properties, such as **porosity** and **permeability**. Geochemical calculations can tell **how much rock minerals dissolve**.

Given the following water analysis, with the concentration of many chemical elements and pH, **find the concentrations of all aqueous species in the water**:

PARAMETER	UNITS	RESULTS
Conductivity	uS/cm	442
PH	-	7.5
Nitrate	mg N03/L	17
Sulphate	mg S04/L	<5
Chloride	mg Cl/L	14
Sodium	mg Na/L	7
Potassium	mg K/L	0.3
Calcium	mg Ca/L	92
Iron	mg Fe/L	<0.02
Copper	mg Cu/L	<0.01
Zinc	mg Zn/L	<0.01

Water composition as a result of a water analysis.

evian

Natural Spring Water

Country	France
Source	Évian-les-Bains
Type	still
pH	7.2
Calcium (Ca)	80
Chloride (Cl^-)	6.8
Bicarbonate (HCO_3)	350
Magnesium (Mg)	26
Nitrate (NO_3)	3.7
Potassium (K)	1
Silica (SiO_2)	15
Sodium (Na)	6.5
Sulfates (SO_4)	12.6
Website	http://www.evian.com

All values in milligrams per liter (mg/l)

See Jupyter notebook tutorial *Analysis of the Evian water*.

Geochemical modeling applications: Water analysis

Selected aqueous species that could exist in that water sample:

Cl-(aq)	CuO(aq)	H2(aq)	HNO2(aq)	KSO4-(aq)	OH-(aq)	SO3--(aq)
ClO-(aq)	CuO2--(aq)	H2N2O2(aq)	HNO3(aq)	N2(aq)	S2--(aq)	SO4--(aq)
ClO2-(aq)	CuOH+(aq)	H2O(aq)	HO2-(aq)	N2H5+(aq)	S2O3--(aq)	Zn++(aq)
ClO3-(aq)	Fe++(aq)	H2O2(aq)	HS-(aq)	N2H6++(aq)	S2O4--(aq)	ZnCl+(aq)
ClO4-(aq)	Fe+++(aq)	H2S(aq)	HS2O3-(aq)	N2O2--(aq)	S2O5--(aq)	ZnCl2(aq)
Cu+(aq)	FeCl+(aq)	H2S2O3(aq)	HS2O4-(aq)	NH3(aq)	S2O6--(aq)	ZnCl3-(aq)
Cu++(aq)	FeCl++(aq)	H2S2O4(aq)	HSO3-(aq)	NH4+(aq)	S2O8--(aq)	ZnO(aq)
CuCl(aq)	FeCl2(aq)	HCl(aq)	HSO4-(aq)	NO2-(aq)	S3--(aq)	ZnO2--(aq)
CuCl+(aq)	FeO(aq)	HClO(aq)	HSO5-(aq)	NO3-(aq)	S3O6--(aq)	ZnOH+(aq)
CuCl2(aq)	FeO+(aq)	HClO2(aq)	HZnO2-(aq)	Na+(aq)	S4--(aq)	
CuCl2-(aq)	FeO2-(aq)	HCuO2-(aq)	K+(aq)	NaCl(aq)	S4O6--(aq)	
CuCl3-(aq)	FeOH+(aq)	HFeO2(aq)	KCl(aq)	NaOH(aq)	S5--(aq)	
CuCl3--(aq)	FeOH++(aq)	HFeO2-(aq)	KHSO4(aq)	NaSO4-(aq)	S5O6--(aq)	
CuCl4--(aq)	H+(aq)	HN2O2-(aq)	KOH(aq)	O2(aq)	SO2(aq)	

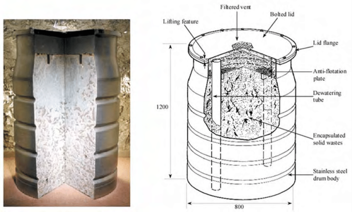
Questions we want to answer:

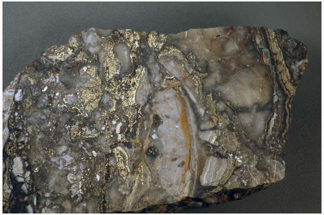
- What are the **amounts of these species**?
- How **saturated** is the water **with respect to several minerals**?

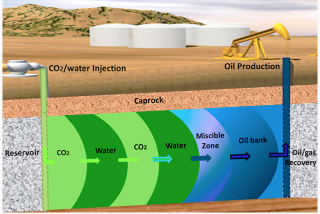
  Note: *saturation* is the tendency of the solution to dissolve/precipitate a mineral.

Other applications for geochemical modeling

- Geochemical reaction calculations can be used for a wide range of **industrial and environmental applications**:
  - nuclear waste management to ensure radionuclides remain properly stored for thousands/millions of years;
  - ore-forming processes;
  - geochemical reactions in geothermal and hydrothermal systems;
  - enhanced oil and gas recovery (prediction of gas and mineral solubility at the wide range of temperatures and pressures);
  - transport of reactive solution in porous and fractured media.







Introduction

Chemical equilibrium and chemical kinetics for modeling geochemical systems

Chemical reaction behavior, Initial intuition

- Consider 1 kg of H_2O mixed with 1 mg of NaCl (halite).
- Chemical reactions that occur among the species in the solution and the halite are as follows:

$$\mathrm{NaCl(halite, s)} \rightleftharpoons \mathrm{Na^+ + Cl^-}$$
$$\mathrm{Na^+ + Cl^-} \rightleftharpoons \mathrm{NaCl(aq)}$$
$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+ + OH^-}$$

- Detailed steps:
  - **pure water** solution contains species: H_2O, H^+, OH^-, O_2(aq), H_2(aq)
  - **scale of the species** in water solution: 55.508 mol of H_2O, 1e-7 mol of H^+, 1e-7 mol of OH^- (to make sure the charge balance), 1e-31 mol of O_2(aq), 1e-31 mol of H_2(aq)
  - after **mixing** NaCl(s) we have in addition: Na^+, Cl^-, NaCl(aq), HCl(aq), NaOH(aq)
  - **new ions** H^+ and Cl^- produce $\mathrm{H^+ + Cl^-} \rightleftharpoons \mathrm{HCl(aq)}$
- What can we say about the **behavior and time-scale** of the these species after 1 ms, 1 s, 1 min?

Reaction classification

- **Irreversible** or **reversible**:
  - An **irreversible** reaction is one that occurs in only one direction and continues in this direction until at least one of the reactants is depleted.
  - A **reversible** reaction can occur in both directions (with forward and backward reaction reaction coefficients k_f and k_b, respectively):

$$\mathrm{a\,A + b\,B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{c\,C + d\,D}.$$

- **Homogeneous** or **heterogeneous**:
  - A **homogeneous** reaction involves a single phase, e.g.,

$$\text{Formation of ammonia}: \mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$$

$$\text{Oxidation of sulfur dioxide}: \mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

  - A **heterogeneous** reaction involves more than one phase, e.g.,

$$\text{Carbonation}: \mathrm{Ca(OH)_2(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + H_2O(l)}$$

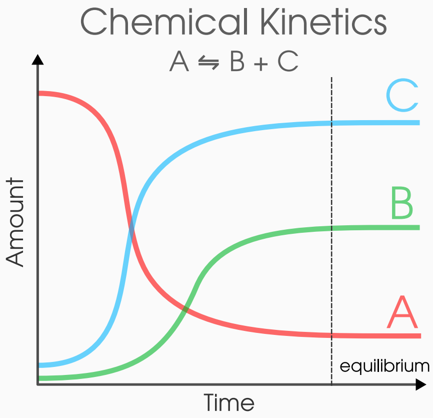
Chemical kinetics vs. Chemical equilibrium

Chemical Kinetics

- Focuses on **pathways of reactions** and **its rate**.
- Used to compute the amounts of the reacting species **over time**.

Chemical Equilibrium

- Focuses on the reactions with **net rates are zero**.
- Used to directly compute the final composition of the species when the reactions are **in equilibrium**.



Chemical kinetics evolution of species A, B, and C over time.

Examples of chemical equilibrium reactions

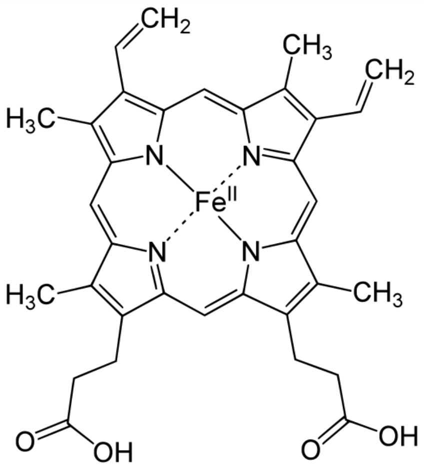
- **Bottle with soda drink**
  - $CO_2(g)$ dissolved in the liquid
  - $CO_2(g)$ is in the space between the liquid and the cap
  - CO_2 is constantly moving from the liquid to the gas phase, and back

$$CO_2(g) + H2O(l) \rightleftharpoons H_2CO_3(aq)$$

- **(Oxy)haemoglobin reactions in blood**
  - haemoglobin takes up oxygen and releases it

$$\text{haemoglobin}(aq) + 4O_2(g) \rightleftharpoons \text{haemoglobin}(O_2)_4(aq)$$

  - oxyhaemoglobin goes through the blood stream to cells



Hemoglobin structure.

Examples of chemical kinetics reactions

- **Corrosion**, a natural process that converts a refined metal into a more chemically stable form such as oxide, hydroxide, or sulfide.
  - galvanic corrosion
  - electrolytic corrosion
  - microbial corrosion
  - high temperature corrosion
- **Fluid catalytic cracking (FCC)**, a conversion process of petroleum crude oils into gasoline, olefinic gases, and other products. Used in petroleum refineries.

Introduction

Chemical equilibrium, Practical observations

Chemical equilibrium, Practical observations

- Chemical reactions **alter the amounts of species over time**, where species can be distributed among one or more phases (minerals, gaseous, mineral).
- Each of these reactions have **forward and backward rates**.
- Consider the reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + 2\mathrm{D},$$

- Rate of the reaction is measured in mol/s.
- Assume at some time t this reaction has a **forward rate** of **2 mol/s** and a **backward rate** of **1 mol/s**.
- **Net rate of the reaction** = **forward rate - backward rate**.

Production and consumption rates

Consider the reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + 2\mathrm{D}.$$

Question: What is **rate of production/consumption** of A, B, C and D (in mol/s)?

http://etc.ch/SA8F or

Answer: production rates are 1 mol/s for C, 2 mol/s for D; consumption rates are -1 mol/s for A, -1 mol/s for B.

Chemical equilibrium of species

Questions: What happens when this **net rate** is **zero**?

Answer: The amounts of each species in the system **no longer experience any change**, and they are in **chemical equilibrium**.

Example: mixing 1 kg of H_2O with NaCl (halite):

$$
\begin{aligned}
\mathrm{NaCl(halite, s)} &\rightleftharpoons \mathrm{Na^+ + Cl^-} \\
\mathrm{Na^+ + Cl^-} &\rightleftharpoons \mathrm{NaCl(aq)} \\
\mathrm{H_2O} &\rightleftharpoons \mathrm{H^+ + OH^-}
\end{aligned}
$$

- If we take **1 mg of NaCl**, eventually, all salt fully dissolves, so the net rate of production of Na^+ and C^- becomes zero.
- If we take **100 mg of NaCl**: eventually, water solution will be saturated with the salt, so Na^+ and C^- is precipitating NaCl with the similar rate as it is dissolving.

Note: See Jupyter notebook tutorial *On mixing table salt with water* and tutorial video `here`.

Example of aqueous-gaseous reactions in equilibrium

- Consider the following **CO_2 dissolution/exsolution reaction**:

$$H_2O(aq) + CO_2(g) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

- This reaction is in equilibrium when CO_2(g) is **dissolving** (*from gas to solution*) and **exsolving** (*from solution to gas*) at the same rate.
- Alternatively, we can have the following **aqueous-gaseous reaction**:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

- **Good to know:** The **solubility of CO_2** (i.e., the maximum amount of CO_2 that the solution can dissolve at given temperature, pressure, and fluid composition conditions) can be calculated considering this reaction (and all others) in equilibrium.

Note: See Jupyter notebook tutorial on *Opening bottle of soda* and tutorial video `here`.

Example of aqueous-mineral reaction in equilibrium

- Consider the following calcite dissolution/precipitation **heterogeneous** reaction:

$$\mathrm{CaCO_3(s, calcite)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + \mathrm{CO_3^{2-}(aq)}$$

- This reaction is in equilibrium when calcite is **dissolving** (*from solid to solution*) and **precipitating** (*from solution to solid*) at the same rate.
- **Good to know:** The **solubility of calcite** (i.e., the maximum amount of calcite that the solution can dissolve at given temperature, pressure, and fluid composition conditions) can be calculated considering this reaction (and others) in equilibrium.

Introduction

Defining the chemical system in the geochemical modeling problem

Defining the chemical system for the modeling problem

- A chemical system is a collection of phases (one or more). Examples:
  - a chemical system with only an aqueous phase;
  - a chemical system with aqueous and gaseous phase (CO_2(g));
  - a chemical system with aqueous, gaseous, and mineral phases.
- Each phase has one or more chemical species:
  - aqueous: H_2O(aq), H^+(aq), OH^-(aq), HCO_3^-(aq), CO_3^{2-}(aq), CO_2(aq), Ca^{2+}(aq)
  - gaseous: H_2O(g), CO_2(g), O_2(g), H_2S(g)
  - calcite: $CaCO_3$(s)
  - solids: combination of several minerals, e.g., Granite: 30% of Calcite, 33% of Albite, 32% of K-Feldspar, 5% of Muscovite.
  - oil
  - biomass (to simulate life of bacterias)
- In geochemical modeling, suitable phases and their species need to be considered. They must be added either:
  - manually (naming each species separately, e.g., ['H2O(l)', 'H+', 'OH-', 'Na+', ...]) or
  - automatically from databases (load all the species containing elements ['H', 'O', 'C']).

Demonstration of chemical system definition i

```python
# Import reaktoro package
from reaktoro import *

# Initialize the database
db = Database("supcrt98")

# Access all the aqueous species
for species in db.aqueousSpecies():
  print(species.name())

# Access all the mineral species
for species in db.mineralSpecies():
  print(species.name())

# Define chemical editor to set up the phases of the system
editor = ChemicalEditor(db) # ChemicalEditor recieves the db instance
# Define phases
```

Demonstration of chemical system definition ii

```python
editor.addAqueousPhaseWithElements("H O Na Cl C Ca Fe")
editor.addGaseousPhase("H2O(g) CO2(g) O2(g)")
editor.addMineralPhase("Calcite")
editor.addMineralPhase("Halite")

# Create chemical system object, we pass object of ChemicalEditor
system = ChemicalSystem(editor)
print(system)

```

Listing 1: System definition

See also Jupyter notebook tutorials *Database class*, *Chemical editor class*, and *Chemical system class* with corresponding *explanation videos*.

Example of the chemical system when H_2O and CO_2 are involved

- Assume water (H_2O) and carbon dioxide (CO_2), are mixed at given T and P.
- To model the equilibrium state resulting from this process, the first step is to think about:
  - the possible phases of matter that could exist; and
  - the species in each phase.
- **Questions we are interested in**:
  - Is CO_2 fully dissolved, or is it still present as a gas (water is already fully saturated with it)?
  - What are the amounts of each species in the chemical state after equilibration?

- A simple (but reasonable) chemical system for this problem is:

Aqueous Phase	Gaseous Phase
$H_2O(aq)$	$H_2O(g)$
$H^+(aq)$	$CO_2(g)$
$OH^-(aq)$	
$HCO_3^-(aq)$	
$CO_3^{2-}(aq)$	
$CO_2(aq)$	

Example of the chemical system when H_2O and $CaCO_3$ are involved

- Assume water (H_2O) and calcite ($CaCO_3$) are mixed at some given temperature T and pressure P.
- A simple (but reasonable) chemical system for this problem is:

Aqueous Phase	**Calcite Phase**
$H_2O(aq)$	$CaCO_3(s, calcite)$
$H^+(aq)$	
$OH^-(aq)$	
$HCO_3^-(aq)$	
$CO_3^{2-}(aq)$	
$CO_2(aq)$	
$Ca^{2+}(aq)$	

Example of the chemical system when H_2O, NaCl, and CO_2 are involved

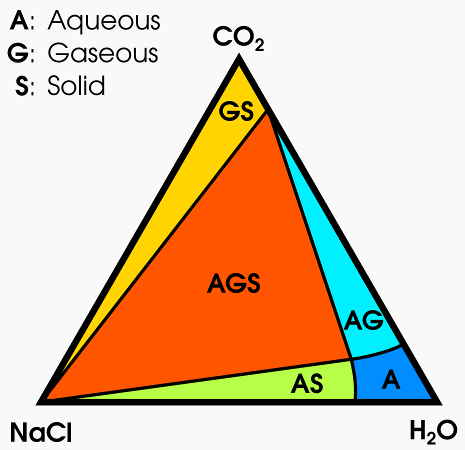
- Assume water (H_2O), carbon dioxide (CO_2), and sodium chloride (NaCl), are mixed at some given temperature T and pressure P.
- A simple (but reasonable) chemical system for this problem is:

Aqueous Phase		Gaseous Phase	Halite Phase
$H_2O(aq)$	$CO_2(aq)$	$CO_2(g)$	NaCl(s, halite)
$H^+(aq)$	$HCO_3^-(aq)$	$H_2O(g)$	
$OH^-(aq)$	$CO_3^{2-}(aq)$		
$Na^+(aq)$	NaCl(aq)		
$Cl^-(aq)$			

- **We wan to know**:
  - How does the salinity of the brine impact the solubility of the water?
  - What happens if we put too much of the table salt?
  - The phase of halite is significant to provide realistic estimation! because it has a point of solubility in water.

How many phases and species to consider for our chemical system?

- In general, the **number of phases and species** should be **as large as possible** when *defining a chemical system*.
- However, the calculations get more expensive with increasing number of species and phases.
- **Important:** Not all phases considered in the calculation will actually exist in positive amounts. Their existence depends on the input conditions.
- The ternary phase diagram on the right shows conditions in which not all phases are **stable at equilibrium**.



Ternary phase diagram.

Final considerations about defining the chemical system

- In most computer codes for modeling geochemical reactions, no manual selection of phases and species are needed.
- These can be determined **automatically** by searching in **thermodynamic databases** all possible species and phases that could exist for a given model input.
- Depending on the available database, you can model different things:
  - supcrt98.xml
  - supcrt98-organics.xml (includes organic species)
  - thermofun.json (T = 200 ^{o}C, critical temperatures and pressures of gases used in Peng-Robinson's EOS)
  - ColdChem.dat (a low-temperature aqueous thermodynamic model)

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