Geofluids — Part IV

Introduction to Geochemical and Reactive Transport Modeling

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Table of contents i

Chemical equilibrium from a thermodynamic and mathematical perspective

Chemical equilibrium from a thermodynamic and mathematical perspective

Gibbs energy minimization and its constraints

Chemical equilibrium from a thermodynamic perspective

- A system under prescribed temperature T and pressure P is in chemical equilibrium if its **Gibbs energy** G is at a minimum.
    - this results from the *second law of thermodynamic* that says that a system tends to a state of maximum entropy S.
    - the minimum Gibbs energy condition arises because $G := H - TS$, where H is enthalpy.
    - **Note**:
      Entropy S is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work.
      Enthalpy H is a property of a thermodynamic system, defined as the sum of the system's internal energy and the product of its pressure and volume.

- Analogy to the **mechanical equilibrium**: a *ball rolling down a hill*. We want to find the **final position** of the ball that results in a minimum for its **potential energy**.

- In thermodynamics, we want to find the **composition (amounts of each species)**, in every phase, that **minimizes the Gibbs energy** of the chemical system.

2

Constraints in a chemical equilibrium state

- In **mechanical equilibrium**, a ball rolling down a hill is **constrained by its surface topology**.
- In **thermodynamics**, the species in a chemical system seeking a state of chemical equilibrium is also **constrained by some conditions**:
  - **its nonnegativity** (species amounts cannot be negative),
  - **mass conservation**.

Mass conservation constraints in chemical equilibrium   i

To illustrate **mass conservation constraints** the following problem:

- mix 100 moles of H_2O and 2 moles of CO_2 and **calculate the equilibrium state of the system**.
- these two substances will react and form several species (H^+, HCO_3^- etc.).

Quiz: at chemical equilibrium, what can we tell about the amounts of H, O, C, Z?

http://etc.ch/oyhr   or

Answer: 200 mols of H, 104 mols of O, and 2 mols of C, the final charge must be equal to the initial charge.

Mass conservation constraints in chemical equilibrium ii

- Calculating chemical equilibrium requires finding a composition for the system (i.e., amount of species, usually defined by vector $n = [n_{H^+}, n_{HCO_3^-}, \ldots]$) that **minimizes its Gibbs energy** and simultaneously satisfies **mass conservation** of:
    - **chemical elements**; and
    - **electric charge**.
- **Note**: we use the term **elements** represented by vector b to denote both *chemical elements* and *electric charge*, i.e., $b = [b_H, b_O, b_C, b_Z]$.

Chemical equilibrium problem for the H_2O–CO_2 system

Given *temperature* T, *pressure* P and the *amounts of elements* H, O, C, determine the **amounts of the species at equilibrium**:

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

Questions:

- What are the amounts of each chemical species at equilibrium?

- Which phases exist at equilibrium?

- How much carbon dioxide, CO_2(g), dissolved as carbon-bearing aqueous species?

- How much solvent water, H_2O(aq), evaporated to the gas phase as vapor H_2O(g)?

- What is the concentration of H^+(aq), which is related to pH (acidity)?

Mass conservation constraints for the H_2O–CO_2 system at equilibrium

- At equilibrium, the amounts of the species:

$$n = \left(n_{H_2O(aq)},\ n_{H^+(aq)},\ n_{OH^-(aq)},\ n_{CO_3^{2-}(aq)},\ n_{HCO_3^-(aq)},\ n_{CO_2(aq)},\ n_{CO_2(g)},\ n_{H_2O(g)}\right)$$

must satisfy the **mass conservation equations** for each element:

$$2n_{H_2O(aq)} + n_{H^+(aq)} + n_{OH^-(aq)} + n_{HCO_3^-(aq)} + 2n_{H_2O(g)} = b_H \quad (1)$$

$$n_{H_2O(aq)} + n_{OH^-(aq)} + 3n_{CO_3^{2-}(aq)} + 3n_{HCO_3^-(aq)} + 2n_{CO_2(aq)} + 2n_{CO_2(g)} + n_{H_2O(g)} = b_O \quad (2)$$

$$n_{CO_3^{2-}(aq)} + n_{HCO_3^-(aq)} + n_{CO_2(aq)} + n_{CO_2(g)} = b_C \quad (3)$$

$$n_{H^+(aq)} - n_{OH^-(aq)} - 2n_{CO_3^{2-}(aq)} - n_{HCO_3^-(aq)} = b_Z \quad (4)$$

- **Exercise**: Show that, for this specific system, the conservation equation for electrical charge, Z, is *linearly dependent* on the other equations.

Mass conservation constraints written in matrix form

The mass balance equations can be written in matrix form:

Mass conservation equation in matrix form

$$An = b$$

where:

- A is the **formula matrix** of the system
- $n = (n_1, \ldots, n_N)$ is the **vector of species amounts**
- $b = (b_1, \ldots, b_E)$ is the **vector of element amounts**

Constructing the formula matrix for the H_2O–CO_2 system i

Consider the following ordering for species and elements in the system:

Index	Species	Index	Element
0	$H_2O(aq)$	0	H
1	$H^+(aq)$	1	O
2	$OH^-(aq)$	2	C
3	$CO_3^{2-}(aq)$	3	Z
4	$HCO_3^-(aq)$		
5	$CO_2(aq)$		
6	$CO_2(g)$		
7	$H_2O(g)$		

Exercise: Construct the formula matrix A for this system, where
the coefficient A_{ij} characterises the contribution of species i into the element j.

Constructing the formula matrix for the H_2O-CO_2 system ii

Answer:

$$A = \begin{array}{c} \\ \text{H} \\ \text{O} \\ \text{C} \\ \text{Z} \end{array} \begin{array}{cccccccc} H_2O(aq) & H^+(aq) & OH^-(aq) & CO_3^{2-}(aq) & HCO_3^-(aq) & CO_2(aq) & CO_2(g) & H_2O(g) \\ 2 & 1 & 1 & 0 & 1 & 0 & 0 & 2 \\ 1 & 0 & 1 & 3 & 3 & 2 & 2 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 \\ 0 & 1 & -1 & -2 & -1 & 0 & 0 & 0 \end{array}$$

Quiz: Which of the following linearly dependency relation is true for the rows of A:

(1) $\text{row(Z)} = \text{row(H)} - 2\,\text{row(O)}$

(2) $\text{row(Z)} = \text{row(H)} - 2\,\text{row(O)} + 2\,\text{row(C)}$

(3) $\text{row(Z)} = \text{row(H)} - 2\,\text{row(O)} + 4\,\text{row(C)}$

(4) $\text{row(Z)} = \text{row(H)} - 2\,\text{row(O)} + 6\,\text{row(C)}$

Answer: (3)

http://etc.ch/oyhr   or

10

Calculating the amounts of elements from species amounts

Exercise: Given

$$
n = \begin{bmatrix} n_{H_2O(aq)} \\ n_{H^+(aq)} \\ n_{OH^-(aq)} \\ n_{CO_3^{2-}(aq)} \\ n_{HCO_3^-(aq)} \\ n_{CO_2(aq)} \\ n_{CO_2(g)} \\ n_{H_2O(g)} \end{bmatrix} = \begin{bmatrix} n_0 \\ n_1 \\ n_2 \\ n_3 \\ n_4 \\ n_5 \\ n_6 \\ n_7 \end{bmatrix} = \begin{bmatrix} 55.4551 \\ 1.23485 \cdot 10^{-4} \\ 8.39739 \cdot 10^{-11} \\ 4.93648 \cdot 10^{-11} \\ 1.23484 \cdot 10^{-4} \\ 0.032861 \\ 1.96702 \\ 0.0531732 \end{bmatrix},
\qquad \text{calculate} \qquad
b = \begin{bmatrix} b_H \\ b_O \\ b_C \\ b_Z \end{bmatrix} = A\,n.
$$

Instead of doing such calculation manually (tedious and error prone), let's use **Python**:

- for Python shell, you can use an online tool `repl.it/languages/python`
- Python source code can be downloaded from *mass-balance-with-blanks.py*.

```
1 # Import the Python package Numpy so we can perform linear algebra
     calculations
2 import numpy
3
4 # Create a list of species name
5 species = ['H2O(aq)', 'H+', 'OH-', 'CO3--', 'HCO3-', 'CO2(aq)', 'CO2(g)', 'H2O
     (g)']
6
7 # Create a list of rows of the formula matrix A
8 A = [[],
9      [],
10      [],
11      []]
12
13 # Create a list with the amounts of species (in moles)
14 n = []
15
```

Calculating the amounts of elements using Python – Source ii

```python
16  # Transform Python lists A and n into Numpy arrays
17  A = numpy.array(A)
18  n = numpy.array(n)
19
20  # Multiply matrix A and vector n to calculate the amounts of elements, b
21  b = A.dot(n)
22
23  # Create a list with the names of the elements
24  elements = ['H', 'O', 'C', 'Z']
25
26  # Create a list with the molar masses of H, O, C, Z
27  molar_masses_elements = []
28
29  # Loop over all elements, their amounts, and their molar masses
30  for element, amount, molarmass in zip(elements, b, molar_masses_elements):
31      print('Element %s has %f moles and %f grams' % (element, amount, amount*
        molarmass))
```

```python
32
33 print("") # Just to skip one line in the output
34
35 # Alternative way of looping over all species using an index i
36 for i in range(len(species)):
37     # Calculate the molar mass of current species
38     molar_mass = A[:, i].dot(molar_masses_elements)
39     # Calculate the mass of current species
40     mass =
41     print('Species {} has {} moles and {} grams.'.format(species[i], n[i],
    mass))
```

Listing 1: Calculating the amounts of elements using Python

Calculating the amounts of elements using Python – Output

The Python code has to have the following output:

```
1  Element H has 111.0168 moles and 111.8938 grams
2  Element O has 59.5084 moles and 952.0988 grams
3  Element C has 2.0000 moles and 24.0215 grams
4  Element Z has 0.0000 moles and 0.0000 grams
5
6  Species H2O(aq) has 5.5455e+01 moles and 9.9903e+02 grams
7  Species H+ has 1.2349e-04 moles and 1.2446e-04 grams
8  Species OH- has 8.3974e-11 moles and 1.4282e-09 grams
9  Species CO3-- has 4.9365e-11 moles and 2.9623e-09 grams
10 Species HCO3- has 1.2348e-04 moles and 7.5346e-03 grams
11 Species CO2(aq) has 3.2861e-02 moles and 1.4462e+00 grams
12 Species CO2(g) has 1.9670e+00 moles and 8.6568e+01 grams
13 Species H2O(g) has 5.3173e-02 moles and 9.5793e-01 grams
```

Listing 2: Calculating the amounts of elements using Python – Output

Answer: To check the correctness of the gaps in the code, use the *source code*.

Chemical equilibrium formulated as Gibbs energy minimization problem

Gibbs energy minimization (GEM) problem

Given temperature T, pressure P, and amounts of elements $b = (b_1, \ldots, b_E)$, find the amounts of species $n = (n_1, \ldots, n_N)$ that solve the **constrained minimization problem**:

$$\min_n G(n; T, P) \quad \text{subject to} \quad An = b \quad \text{and} \quad n \geq 0.$$

where:

- G is the Gibbs energy of the system, a function of $n = (n_1, \ldots, n_N)$ as well as temperature T and pressure P;
- $An = b$ are the mass conservation constraints for each element;
- $n \geq 0$ are the non-negative constraints for the amounts of each species.

Gibbs energy function

- **The Gibbs energy function**, G, is defined as:

$$G = \sum_{i=1}^{N} n_i \mu_i,$$

where μ_i is the **chemical potential** of the ith species.

- G has units of J, and μ_i units of J/mol.

Chemical equilibrium from a thermodynamic and mathematical perspective

Chemical potential of chemical species

Chemical potential and its interpretation

- The **chemical potential of a substance** μ_i is a measure of its tendency to transform into other substances.
- In the following reaction:

$$A \rightleftharpoons B,$$

  - $\mu_A > \mu_B$: substance A will tend to transform to B
  - $\mu_A = \mu_B$: substances A and B are in equilibrium, no transformation is happening
  - $\mu_A < \mu_B$: substance B will tend to transform to A

- The higher the value of μ_A, the higher the tendency for A to transform to B.

18

Chemical potential and its interpretation, Example

- Consider the following reaction:

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

- We have the following three cases:

Case I	Case II	Case III
$\mu_{CO_2(g)} = -390.347 \,\text{kJ/mol}$	$\mu_{CO_2(g)} = -390.347 \,\text{kJ/mol}$	$\mu_{CO_2(g)} = -389.185 \,\text{kJ/mol}$
$\mu_{CO_2(aq)} = -390.347 \,\text{kJ/mol}$	$\mu_{CO_2(aq)} = -517.800 \,\text{kJ/mol}$	$\mu_{CO_2(aq)} = -383.861 \,\text{kJ/mol}$

- **Quiz**: what is the tendency for $CO_2(g)$ in each of cases?
- **Answer**:
    - **Case I**: Since $\mu_{CO_2(g)} = \mu_{CO_2(aq)}$, the reaction is in **equilibrium**.
    - **Case II**: Since $\mu_{CO_2(g)} > \mu_{CO_2(aq)}$, $CO_2(g)$ tends to **dissolve**.
    - **Case III**: Since $\mu_{CO_2(g)} < \mu_{CO_2(aq)}$, $CO_2(g)$ tends to form, **exsolve**.

Chemical potentials and direction of reactions

- The chemical potentials of substances μ_i can be used to indicate which direction a reaction should proceed:

$$A + B \rightleftharpoons C + 2\,D$$

- $\mu_A + \mu_B > \mu_C + 2\,\mu_D$: substances A and B will tend to transform to C and D
- $\mu_A + \mu_B = \mu_C + 2\,\mu_D$: substances A, B, C, and D are in equilibrium
- $\mu_A + \mu_B < \mu_C + 2\,\mu_D$: substances C and D will tend to transform to A and B
- **Warning:** Note the coefficients in the reactions are used when checking the direction of the reaction!

$$\underline{1}\,A + \underline{1}\,B \rightleftharpoons \underline{1}\,C + \underline{2}\,D$$

Consider the following reaction and the subsequent three cases:

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

Case I

$\mu_{H_2O(aq)} = -239.614\,\text{kJ/mol}$

$\mu_{CO_2(g)} = -390.347\,\text{kJ/mol}$

$\mu_{HCO_3^-(aq)} = -610.019\,\text{kJ/mol}$

$\mu_{H^+(aq)} = -19.942\,\text{kJ/mol}$

Case II

$\mu_{H_2O(aq)} = -239.614\,\text{kJ/mol}$

$\mu_{CO_2(g)} = -390.347\,\text{kJ/mol}$

$\mu_{HCO_3^-(aq)} = -717.639\,\text{kJ/mol}$

$\mu_{H^+(aq)} = -41.454\,\text{kJ/mol}$

Case III

$\mu_{H_2O(aq)} = -239.614\,\text{kJ/mol}$

$\mu_{CO_2(g)} = -389.185\,\text{kJ/mol}$

$\mu_{HCO_3^-(aq)} = -606.776\,\text{kJ/mol}$

$\mu_{H^+(aq)} = -16.699\,\text{kJ/mol}$

Quiz:

- What is the direction of the reaction in each case?
- In each case, is $CO_2(g)$ tending to dissolve or exsolve?

21

Case I:

$$\mu_{H_2O(aq)} = -239.614 \, \text{kJ/mol}$$
$$\mu_{CO_2(g)} = -390.347 \, \text{kJ/mol}$$
$$\mu_{HCO_3^-(aq)} = -610.019 \, \text{kJ/mol}$$
$$\mu_{H^+(aq)} = -19.942 \, \text{kJ/mol}$$

$$\mu_{H_2O(aq)} + \mu_{CO_2(g)} = -629.961$$
$$\mu_{HCO_3^-(aq)} + \mu_{H^+(aq)} = -629.961$$

$$\boxed{\mu_{H_2O(aq)} + \mu_{CO_2(g)} = \mu_{HCO_3^-(aq)} + \mu_{H^+(aq)}}$$

The reaction is in **equilibrium**.

Chemical potentials and direction of reactions, Exercise   iii

Case II:

$$\mu_{H_2O(aq)} = -239.614 \, \text{kJ/mol}$$
$$\mu_{CO_2(g)} = -390.347 \, \text{kJ/mol}$$
$$\mu_{HCO_3^-(aq)} = -717.639 \, \text{kJ/mol}$$
$$\mu_{H^+(aq)} = -41.454 \, \text{kJ/mol}$$

$$\mu_{H_2O(aq)} + \mu_{CO_2(g)} = -629.961$$
$$\mu_{HCO_3^-(aq)} + \mu_{H^+(aq)} = -759.093$$

$$\boxed{\mu_{H_2O(aq)} + \mu_{CO_2(g)} > \mu_{HCO_3^-(aq)} + \mu_{H^+(aq)}}$$

The reaction is proceeding to the right, and CO_2 is tending to **dissolve**.

Chemical potentials and direction of reactions , Exercise   iv

Case III:

$$\mu_{H_2O(aq)} = -239.614 \, kJ/mol$$
$$\mu_{CO_2(g)} = -390.347 \, kJ/mol$$
$$\mu_{HCO_3^-(aq)} = -717.639 \, kJ/mol$$
$$\mu_{H^+(aq)} = -41.454 \, kJ/mol$$

$$\mu_{H_2O(aq)} + \mu_{CO_2(g)} = -628.799$$
$$\mu_{HCO_3^-(aq)} + \mu_{H^+(aq)} = -623.475$$

$$\boxed{\mu_{H_2O(aq)} + \mu_{CO_2(g)} < \mu_{HCO_3^-(aq)} + \mu_{H^+(aq)}}$$

The reaction is proceeding to the left, and CO_2 is tending to **exsolve**.

Chemical potentials and direction of reactions using Python

```
1  mu_case1 = [-239.614, -390.347, -610.019, -19.942]
2  mu_case2 = [-239.614, -390.347, -717.639, -41.454]
3  mu_case3 = [-239.614, -389.185, -606.776, -16.699]
4
5  def reaction_direction(mu):
6      diff = (mu[0] + mu[1]) - (mu[2] + mu[3])
7      if diff == 0.0:
8          return 'equilibrium'
9      elif diff > 0.0:
10         return 'right'
11     else:
12         return 'left'
13
14 print( 'Case I:  ', reaction_direction(mu_case1) )
15 print( 'Case II: ', reaction_direction(mu_case2) )
16 print( 'Case III:', reaction_direction(mu_case3) )
```

Listing 3: Chemical potentials and direction of reactions using Python

Source code: *chemical-potential.py*.

Chemical potential μ_i and Gibbs energy

- The **chemical potential of a species** μ_i is equivalent to

$$\mu_i \equiv \left[\frac{\partial G}{\partial n_i}\right]_{T,P}.$$

- Thus, the infinitesimal change in Gibbs energy $\mathrm{d}G$ following an infinitesimal change in the ith species amount i

$$\mathrm{d}G = \mu_i \mathrm{d}n_i$$

at constant temperature T and pressure P.

- The **equilibrium criterion** for a multi-component system with constant T and P is

$$\sum_{i=1}^{N} \mu_i \, \mathrm{d}n_i = 0.$$

At the equilibrium point, the **Gibbs free energy at its minimum**.

Chemical potential μ_i and its definition

- The **chemical potential** μ_i of a species i is defined as

$$\mu_i = \mu_i^o + RT \ln a_i.$$

- μ_i^o is the **standard chemical potential** of the species at (T, P);
- R is the **universal gas constant**, $R = 8.314 \, \mathsf{J}/(\mathsf{mol} \cdot \mathsf{K})$;
- T and P are given temperature and pressure;
- a_i is the **activity** of the species at (T, P, n_Φ), where n_Φ is the vector of amounts of species in the phase where species i lives.
    - **Note**: the activity of an aqueous species only depends on the amounts of the aqueous species, and not on the amounts of gases, minerals, etc.!

Standard chemical potential μ_i^o

- The **standard chemical potential** μ_i^o of a species is its chemical potential at a **standard reference state**, in which $a_i = 1$ is assumed.
- For a gas:
  - μ_i^o is the chemical potential of the gas at a hypothetical ideal state with $P^o = 1\,\mathrm{bar}$;
  - $\mu_i^o = \mu_i^o(T)$ (i.e., **no pressure dependence**).
- For aqueous and mineral species, $\mu_i^o = \mu_i^o(T, P)$.
- Values for μ_i^o are calculated using equations of state, which can be computationally expensive.
- Their values are then saved in tables that can be used for interpolation.

Standard chemical potential tables i

μ_i^o [kJ/mol]	T [°C]	P [bar]		
		1	50	100
H$_2$O(aq)	25	-237.182	-237.093	-237.003
	50	-239.007	-238.917	-238.827
	75	-240.978	-240.887	-240.795
	100	—	-242.992	-242.899
H$^+$(aq)	25	0	0	0
	50	0	0	0
	75	0	0	0
	100	—	0	0

Standard chemical potential tables ii

μ_i^o [kJ/mol]	T [°C]	P [bar]		
		1	50	100
$CO_2(g)$	25	-394.359	-394.359	-394.359
	50	-399.741	-399.741	-399.741
	75	-405.198	-405.198	-405.198
	100	-410.727	-410.727	-410.727
$CaCO_3(s,calcite)$	25	-1129.178	-1128.997	-1128.812
	50	-1131.580	-1131.399	-1131.214
	75	-1134.150	-1133.969	-1133.784
	100	-1136.883	-1136.702	-1136.517

Chemical equilibrium from a thermodynamic and mathematical perspective

Mass action equation and equilibrium constant of the reaction

Mass action equation and equilibrium constant of the reaction

- Consider the following reaction
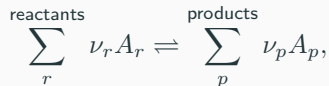
$$A + 2B \rightleftharpoons C + 3D.$$

- At equilibrium, the following **mass action equation** must be satisfied:

$$K = \frac{a_C a_D^3}{a_A a_B^2},$$

  where $K = K(T, P)$ is the **equilibrium constant** of the reaction.

- We assume $n_A, n_B, n_C, n_D > 0$ (i.e., these species are *stable at equilibrium*).

- For a **general reaction**

$$\overset{\text{reactants}}{\underset{r}{\sum}} \nu_r A_r \rightleftharpoons \overset{\text{products}}{\underset{p}{\sum}} \nu_p A_p,$$

where

  – A_r, A_p are reactant and product species
  – ν_r, ν_p are the stoichiometric coefficients,

the **general mass action equation** is

$$\boxed{K = \frac{\prod_p a_p^{\nu_p}}{\prod_r a_r^{\nu_r}}.}$$
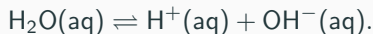
- Mass action equation is **strongly non-linear**.

Equilibrium constant of reactions from standard chemical potentials

- The **equilibrium constant of a reaction** K is defined as

$$\ln K = -\frac{1}{RT}\left[\sum_p \nu_p \mu_p^o - \sum_r \nu_r \mu_r^o\right],$$

where $R = 8.314 \, \text{J}/(\text{mol} \cdot \text{K})$ is the universal gas constant, and T is temperature (in K).

- **Quiz:** At 100 °C and 50 bar, $\mu_{\text{H}_2\text{O(aq)}}^o = -242.992 \, \text{kJ/mol}$, $\mu_{\text{H}^+\text{(aq)}}^o = 0.0 \, \text{kJ/mol}$, and $\mu_{\text{OH}^-\text{(aq)}}^o = -155.559 \, \text{kJ/mol}$. Calculate $\ln K$ and $\log K$ for the reaction:

$$\text{H}_2\text{O(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{OH}^-\text{(aq)}.$$

Hint: $\log_{10} K = \ln K \cdot \log_{10} e$.

- **Answer**: $\ln K = -28.18$ and $\log K = -12.18$.

Equilibrium constant of reactions from standard chemical potentials, Exercise

```python
from math import *

R = 8.314
T = 100 + 273.15
mu_H2O = -242.992 * 1e3
mu_OH = -155.559 * 1e3

lnK = -1/R/T *(mu_OH - mu_H2O)

print("lnK = ", lnK)
print("log10K = ", lnK * log10(e))
```

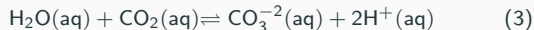**Listing 4:** Calculating equilibrium constant of reactions using Python

Consider the following *species*, *elements*, and *reactions*:

Index	Species
1	$CO_2(aq)$
2	$CO_3^{-2}(aq)$
3	$Cl^-(aq)$
4	$H^+(aq)$
5	$H_2O(l)$
6	$HCO_3^-(aq)$
7	$Na^+(aq)$
8	$OH^-(aq)$
9	$CO_2(g)$
10	$NaCl(s)$

Index	Element
1	C
2	Cl
3	H
4	Na
5	Ol

$$H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{1}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons CO_2(aq) + H_2O(aq) \tag{2}$$

$$H_2O(aq) + CO_2(aq) \rightleftharpoons CO_3^{-2}(aq) + 2H^+(aq) \tag{3}$$

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{4}$$

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq) \tag{5}$$

Exercise, Mass action and mass conservation equations ii

Tasks:

- Write the **mass action equation** for each reaction.
- Write the **mass conservation equation** for each element (start from formula matrix).

Help materials:

- Jupyter notebook tutorial *Mass balance and mass action equation* and corresponding *video* with comments on this tutorial.

Summary on the calculation of Gibbs energy

- The **Gibbs energy** is defined as

$$G(n) = \sum_{i=1}^{\mathsf{N}} n_i \mu_i,$$

  where $n = (n_1, \ldots, n_{\mathsf{N}})$ is the vector of molar amounts of the species.

- The **chemical potential** of the ith species is defined as

$$\mu_i = \mu_i^o + RT \ln a_i(n, T, P).$$

- The **standard chemical potentials** of the species μ_i^o depend on temperature T and pressure P and can be interpolated from a table of values over several temperature and pressure points.

- The **activities** of the species a_i depend on temperature T, pressure P, and the concentrations of the species in the same phase n_Φ.
  Note: Activities are very important as they account for the non-ideal behavior of the species.

Chemical equilibrium from a thermodynamic and mathematical perspective

Other important chemical properties

Solubility of aqueous species, gases, and minerals

The **solubility** is the maximum amount of a substance that can be dissolved in a solution.

- Depends on
  - the physical and chemical properties of the solute and solvent
  - temperature,
  - pressure, and
  - presence of other chemicals (including changes to the pH) of the solution
- May be stated in various **units of concentration**: molarity, molality, mole fraction, mole ratio, mass (solute) per volume (solvent), etc.
- The **solubility of most solids** in liquid generally increases with **increasing temperature**.
- The **solubility of most gases** decreases with **increasing temperature**.
- Solubility ranges:
  - **infinitely soluble** (miscible), e.g., ethanol in water,
  - **insoluble/poorly soluble**, e.g., silver chloride in water.

Solubility product

- The **solubility product constant** K_{sp} is an equilibrium constant for a substances dissolving in an aqueous solution.

- It represents the **level/limit at which a solute dissolves in aqueous solution**.

- **More soluble** a substance is, the **higher the** K_{sp} value it has.

- Consider the general dissolution reaction below (in aqueous solutions)

$$a\,A(s) \rightleftharpoons c\,C(aq) + d\,D(aq).$$

- Let [C] and [D] denote the molarities (mol/Lw) or concentrations (mol/kgw) of the products (C and D), then K_{sp} is defined as

$$K_{sp} = [\text{C}]^c \cdot [\text{D}]^d,$$

Note: the reactant A is not included in the K_{sp} equation, because its concentrations do not change the expression. Water H_2O would be excluded as well.

Calculation of solubility of calcite, Example

- The balanced chemical equation of calcite dissolving in water is

$$CaCO_3(s) + H_2O(l) \rightleftharpoons Ca^{2+} + HCO_3^- + OH^-.$$

- A limit of how much calcite can be dissolved in a given volume of water is given by the **solubility product**

$$K_{sp} = [Ca^{2+}]^1 \cdot [HCO_3^-]^1 \cdot [OH^-]^1 \approx 10^{-12},$$

where $[\cdot]$ denotes morality of the species (mol/L).

- Since the molar ratio of products is $1:1:1$, and we assume that morality of each species increased by equal amount

$$[Ca^{2+}] \approx (10^{-12})^{1/3} \text{mol/L} = 10^{-4} \text{mol/L}.$$

- The **amount of Ca^{2+}** is equal **solubility of calcite**, so since molar amount of calcite is $1:1$ with all the products, we have

$$[CaCO_3(aq)] = [Ca^{2+}] = 10^{-4} \text{mol/L}$$

or, using molar mass of calcite 100.09 g/mol,

$$[CaCO_3(aq)] \approx 10^{-4} \text{mol/L} \cdot 100 \text{g/mol} \approx 10^{-2} \text{g/L} = 10 \text{mg/L},$$

which is relatively small in comparison to other minerals.

Dependence of calcite solubility on different factors

- Solubility of $CaCO_3$ **increases** as the pressure of the water **increases**.
- Demonstration of these properties can be found in Jupyter notebook tutorial *Calcite solubility in water and CO_2-saturated rainwater*.
- Calcite has a **very low solubility** in **pure water** (we saw an analytic estimation is 10 mg/L).
- **In rainwater** saturated with carbon dioxide (which decreases pH, making it more acidic), its **solubility increases**.
- Solubility of calcite **decreases** in the CO2-saturated water as the temperature **increases** (**unusual!**).
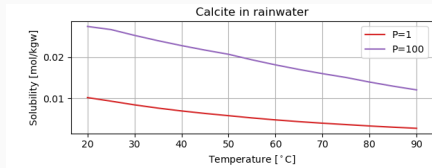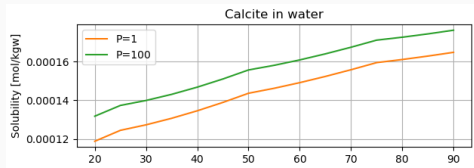
Calcite solubility in water and rain water w.r.t. temperature.

Calcite solubility example, Stalagmites and stalactites

$$CaCO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons Ca(HCO_3)_2(aq)$$
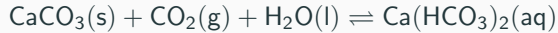
$\rightarrow$ Rainwater meets with limestone to form a solution of calcium bicarbonate.

$\leftarrow$ The bicarbonate-rich water drips from the ceiling of the cave and partially evaporates, leaving behind a calcium carbonate deposit.
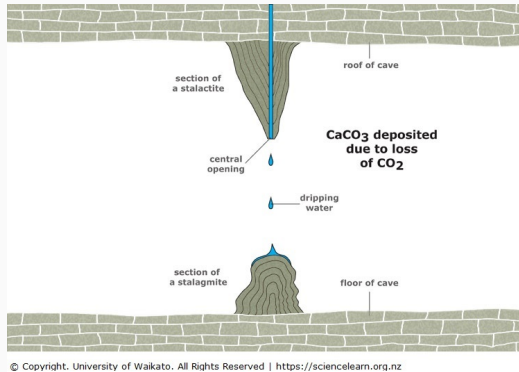
Figure 1: Diagram of cave showing formation of stalagmites and stalactites.

Figure 2: Limestone fizzes when dilute acid is placed on its surface.

Solubility of chlorargyrite, Example

- Consider dissolution reaction of chlorargyrite

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
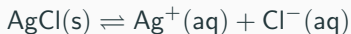
- **Quiz**: What is solubility of AgCl(s) in 1 liter of water, where $K_{sp} = 1.8 \cdot 10^{-10}$?

http://etc.ch/oyhr   or

- **Answer**: 1 liter of water can dissolve $1.34 \cdot 10^{-5}$ mol/L of AgCl(s) at room temperature.
  Note: Compared with other types of salts, AgCl is also poorly soluble in water.
  In contrast, table salt NaCl has a higher K_{sp} and is, therefore, more soluble.

Saturation index

The **saturation index** indicates the saturation state of a solution with respect to a mineral phase, which is given by

$$\boxed{SI = \log_{10} \frac{Q}{K_{sp}}},$$

where

- Q is the *ion activation product (IAP) / reaction quotient* of activities of the dissolved species (characteristic of non-equilibrium solution), and
- K_{sp} is the *solubility product / equilibrium constant*.

$$SI \begin{cases} < 0 & \text{solution is \textbf{undersaturated}} \Rightarrow \text{the mineral may be dissolved} \\ = 0 & \text{solution is \textbf{saturated}} \qquad \Rightarrow \text{the mineral in equilibrium with solution} \\ > 0 & \text{solution is \textbf{supersaturated}} \Rightarrow \text{the mineral may be precipitated} \end{cases}$$

Saturation index, Exercise

- Consider dissolution reaction of barium sulfate

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq).$$
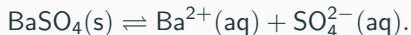
- Solubility product of barium sulfate is 1.08e-10 at 25 $^{\circ}$C.

- **Quiz**: What can be said about the water w.r.t. to barium sulfate if $[Ba^{2+}] = 2.9 \cdot$ 1e-4 molal $[SO_4^{2-}] = 1.8 \cdot$ 1e-4 molal?

http://etc.ch/oyhr   or

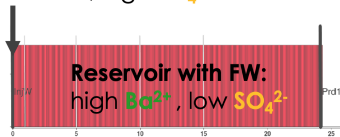- **Answer**: Water will be supersaturated with $BaSO_4(s)$.

Saturation index, Demonstration

- Demonstration of gypsum/anhydrite solubility: Jupyter notebook tutorial *Gypsum/anhydrite solubility in water*.

- Investigation on how saturated the Evian water with carbonates can be found in Jupyter notebook tutorial *Analysis of the Evian water*.

- Barite precipitation in the water flooding reactive transport example: Jupyter notebook tutorial *One-dimensional reactive transport modeling of scaling (without oil)*.
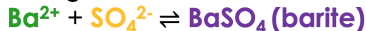

Anhydrite solubility in water
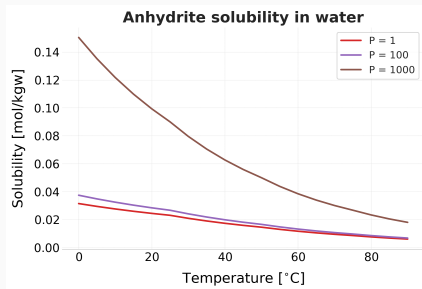
Injection well with SW:
low Ba^{2+} , high SO_4^{2-}

Reservoir with FW:
high Ba^{2+} , low SO_4^{2-}

Mixing:
$Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4$ (barite)

Electroneutrality principle

- **Electroneutrality principle** (Pauling, 1948) states that the ionic species in the electrolyte solution have equilibrium of charges on a macroscopic scale.
- It can be expressed by the charge equilibrium between the species in solution
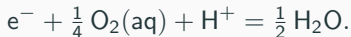
$$\sum_i Z_i m_i = 0,$$

  where Z_i are the ionic charges and m_i are the molalities of species.
- **Example**: When mixing 0.1 molal of NaCl, it dissolves to 0.1 molal Na^+ and 0.1 molal Cl^-.

Reduction/oxidation potential, pE

- **Oxidation / reduction** are the reactions, where species either esquire or lose electors, e.g.,

$$e^- + \tfrac{1}{4} O_2(aq) + H^+ = \tfrac{1}{2} H_2O.$$

- **Oxidation / reduction potential** is a **measure of the tendency** of a species to acquire/lose electrons from/to an electrode and thereby **be reduced or oxidised**.
- The **reduction/oxidation potential** pE is defined as

$$\boxed{pE = -\log_{10}(a_{e^-}) = -\tfrac{1}{n_e} \log \frac{Q_e^-}{K_e^-}}$$

where
  - $K_e^- \approx 25.5$ (at 25 °C),
  - n_e is the number of consumed/generated electrons, and
  - Q_e^- is the product of the activities of the reaction.
- A solution with a **higher pE** / **lower pE** will have a tendency to **gain electrons from** / **lose electrons to** the new species.

Hydrogen potential, pH

- The pH of a solution is an indication of the **tendency** of the solution **to donate hydrogen ions** or measure of the **relative amount of free hydrogen ions** in the solution.
- The **hydrogen potential** pH is defined as

$$\text{pH} = -\log_{10}(a_{\text{H}^+}) = -\log_{10}([H^+]).$$

- pH is a measure of how **acidic/basic** solution is in the scale from 0 till 14:
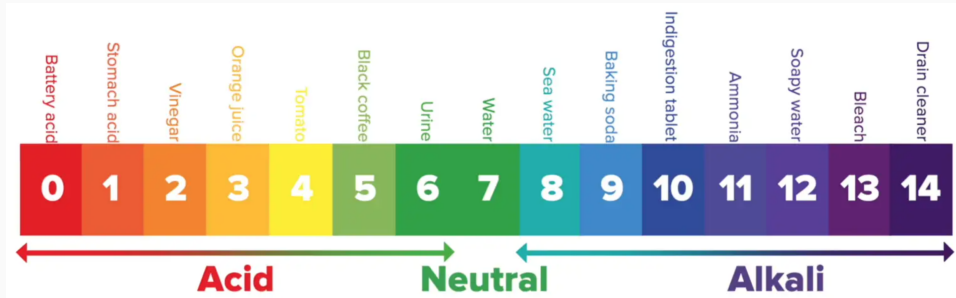
pH, Exercise

- We have completely dissolved HCl in the 300 ml of water $HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$ and it produced the solution with $pH = 1$.
- **Hint 1**: let the concentration $[H^+]$ (measured in mol/L) and a_{H^+} be the same (i.e., activity is considered as effective concentration).
- **Hint 2**: $m_{HCl} = M_{HCl} \cdot n_{HCl}$, where m is the mass of species (in kg), M is the molar mass (in kg / mol), and n is the molar amount (in mol).
- **Hint 3**: molar amount of $M_{HCl} = 36.458$ g/mol .
- **Quiz**: What was the mass of dissolved HCl?

http://etc.ch/oyhr   or

- **Answer**: 1.09374 g.

- Too high or too low pH effect aquatic / fish life.
- Large **algae blooms** can affect the pH as they photosynthesise:
  - during the day that **drives the pH down** and
 - at night when they respire, it **drives the pH up**.

  The results: **huge pH fluctuations** in water, which can affect fish quite negatively.

Figure 3: The worst algae bloom that Lake Erie has experienced in decades resulting from the record torrential spring rains washed fertilizer into the lake, promoting the growth of microcystin-producing cyanobacteria blooms.

- CO_2 added to the seawater influences the pH according to the reaction
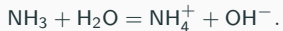
$$CO_2(g) + H_2O(l) = H^+ + HCO_3^-.$$
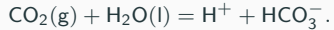
See tutorial *Dependence of the pH on the* $CO_2(g)$ *amount in seawater*.

- Adding HCl into water increases free H^+ ions and decreases pH according to the reaction

$$HCl(aq) + H_2O(l) = H_3O^+ + Cl^-,$$

whereas adding ammonia **removes** H^+ from water and increases it to produce ammonium and hydroxide, i.e.,

$$NH_3 + H_2O = NH_4^+ + OH^-.$$

See tutorial *Dependence of the pH on added contaminant in water*.

Dependence of pH on the CO_2 amount in seawater

Dependence of pH on HCl amount

Dependence of pH on NH_3 amount
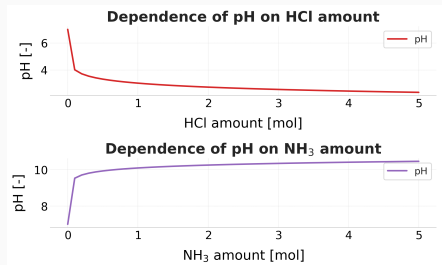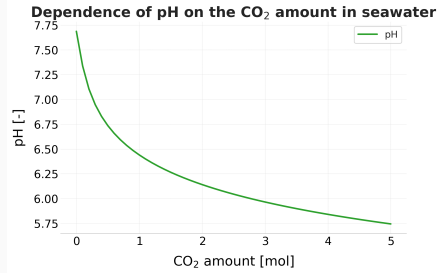
References

Peng, D.-Y. & Robinson, D. B. (1976). A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1), 59–64.

Redlich, O. & Kwong, J. N. S. (1949). On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions. *Chemical Reviews*, 44(1), 233–244.

Smith, J. M., Ness, H. C. V., & Abbott, M. M. (2005). *Introduction to chemical engineering thermodynamics*. McGraw-Hill.

Soave, G. (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, 27(6), 1197–1203.

van der Waals, J. D. (1873). *On the Continuity of the Gaseous and Liquid States*. PhD thesis, Universiteit Leiden.