

# Geofluids — Part IV

## Introduction to Geochemical and Reactive Transport Modeling

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# Lecturers' introduction



Dr. Svetlana Kyas, Post-Doctoral Associate in  
Geothermal Energy & Geofluids



Dr. Allan Leal, Senior Research Assistant in  
Geothermal Energy & Geofluids

# Introduction

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# Introduction

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## Course introduction

## Course goal

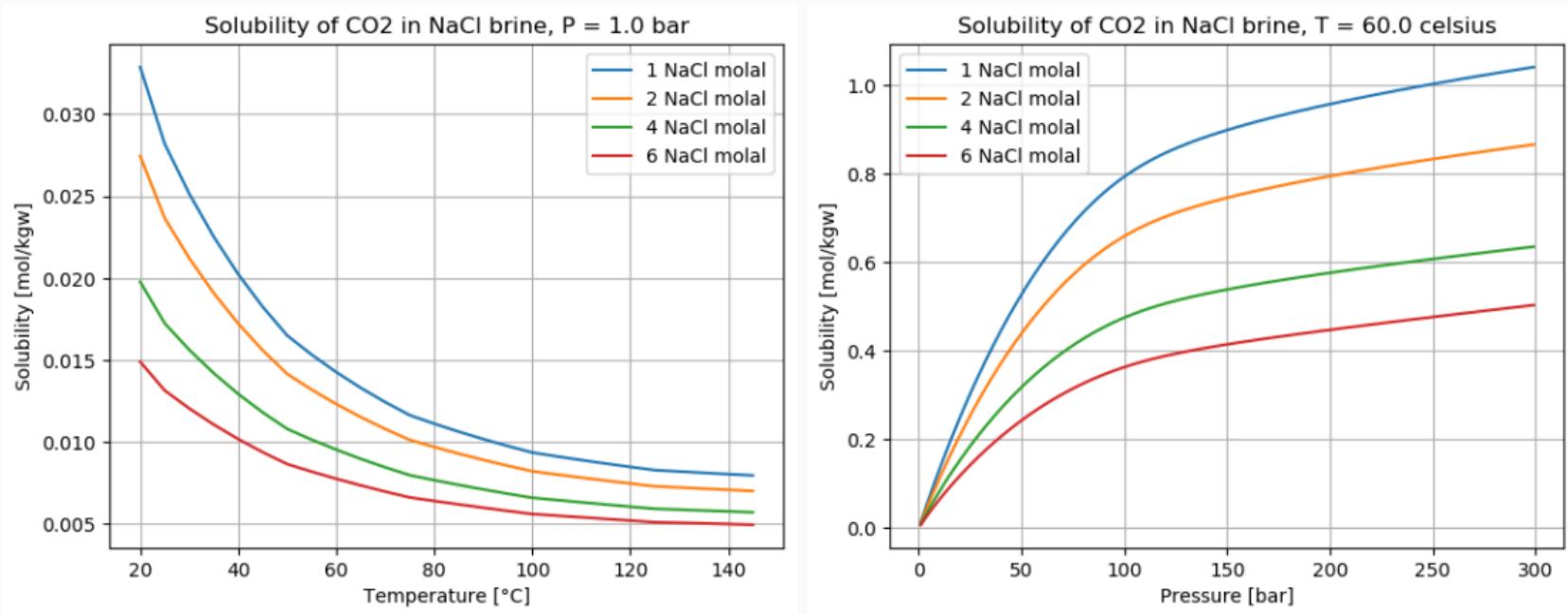
- By the end of this course, you should become familiar with the fundamentals of **geochemical and reactive transport modeling** that includes of the following concepts:
  - chemical equilibrium;
  - chemical kinetics; and
  - chemical transport.
- For **numerical simulations** of simple geochemical and reactive transport problems, we will use Python and Reaktoro ([reaktoro.org](http://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 ( $\text{HO}_2(\text{l})$ ,  $\text{HCl}(\text{aq})$ ,  $\text{Na}^+$ , etc),
    - gaseous ( $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{S}(\text{g})$ ), 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, $\text{CO}_2(\text{g})$ solubility in the NaCl-brine



**Note:** See Jupyter notebook tutorial  *$\text{CO}_2$  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 Jupyter 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](mailto:svetlana.kyas@erdw.ethz.ch).

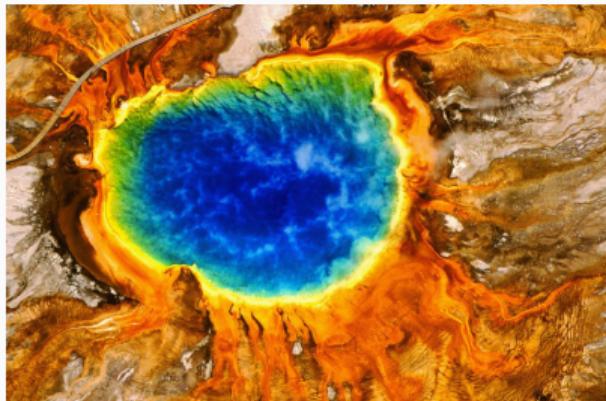
## **Introduction**

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**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.

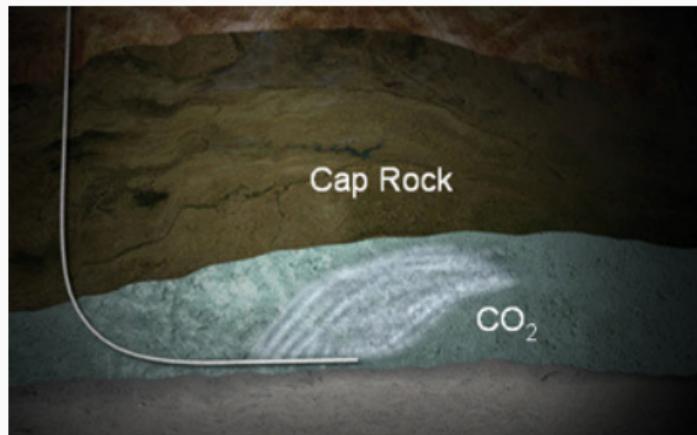
# Geochemical modeling applications, Scaling prediction in wells



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<sub>2</sub> storage in geologic formations



Once CO<sub>2</sub> 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<sub>2</sub> dissolves and how much CO<sub>2</sub> continues mobile as gas or supercritical fluid.



Brine with dissolved CO<sub>2</sub> becomes acidic. It can then more easily **react with rock minerals**. This changes rock properties, such as **porosity** and **permeability**. Geochemical calculations can tell **how much rock minerals dissolve**.

# Geochemical modeling applications, Water analysis

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 NO <sub>3</sub> /L	17
Sulphate	mg SO <sub>4</sub> /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.

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)	

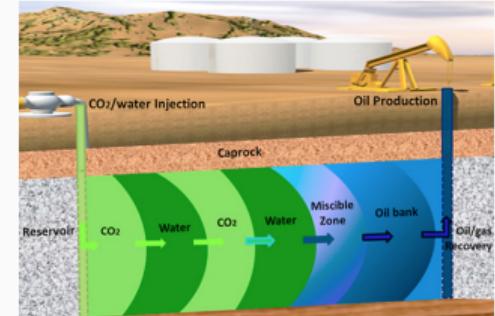
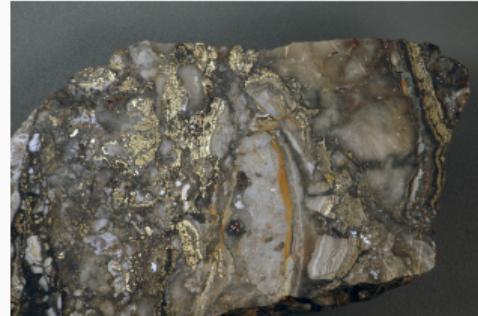
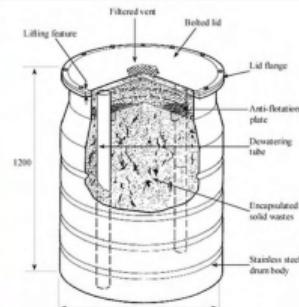
**Questions** we want to answer:

- 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

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Chemical equilibrium and chemical kinetics for modeling geochemical systems

## Chemical reaction behavior, Initial intuition

- Consider 1 kg of H<sub>2</sub>O mixed with 1 mg of NaCl (halite).
- Chemical reactions that occur among the species in the solution and the halite are as follows:

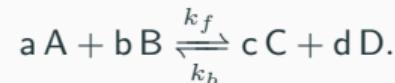


- Detailed steps:
  - **pure water** solution contains species: H<sub>2</sub>O, H<sup>+</sup>, OH<sup>-</sup>, O<sub>2</sub>(aq), H<sub>2</sub>(aq)
  - **scale of the species** in water solution: 55.508 mol of H<sub>2</sub>O, 1e-7 mol of H<sup>+</sup>, 1e-7 mol of OH<sup>-</sup> (to make sure the charge balance), 1e-31 mol of O<sub>2</sub>(aq), 1e-31 mol of H<sub>2</sub>(aq)
  - after **mixing** NaCl(s) we have in addition: Na<sup>+</sup>, Cl<sup>-</sup>, NaCl(aq), HCl(aq), NaOH(aq)
  - **new ions** H<sup>+</sup> and Cl<sup>-</sup> produce  $\text{H}^+ + \text{Cl}^- \rightleftharpoons \text{HCl(aq)}$
- 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):



- **Homogeneous or heterogeneous:**

- A **homogeneous** reaction involves a single phase, e.g.,



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



# Chemical kinetics vs. Chemical equilibrium

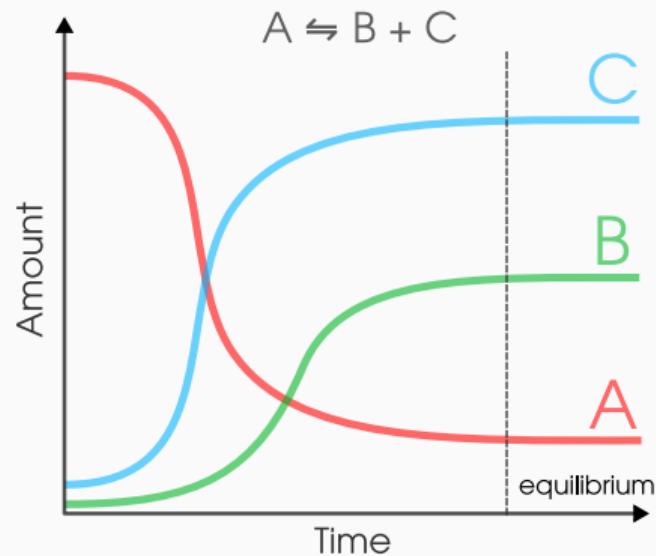
## Chemical Kinetics

- 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



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

# Examples of chemical equilibrium reactions

- **Bottle with soda drink**

- $\text{CO}_2(\text{g})$  dissolved in the liquid
- $\text{CO}_2(\text{g})$  is in the space between the liquid and the cap
- $\text{CO}_2$  is constantly moving from the liquid to the gas phase, and back

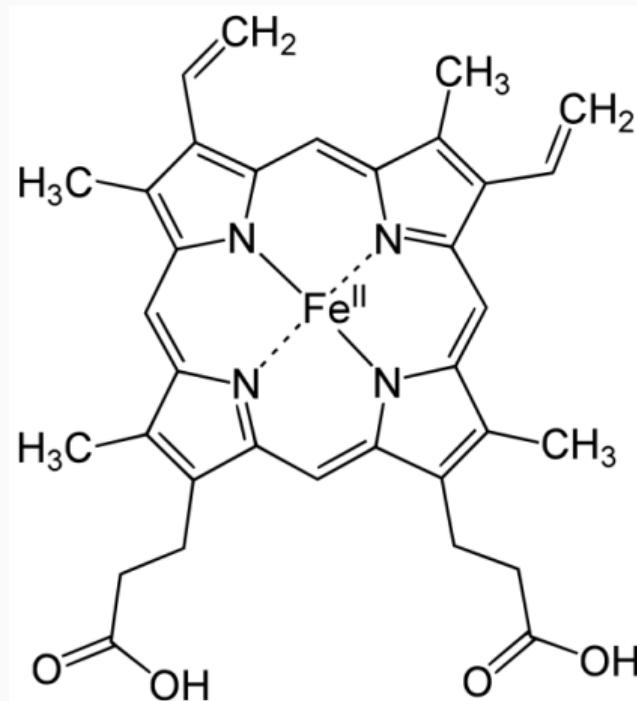


- **(Oxy)haemoglobin reactions in blood**

- haemoglobin takes up oxygen and releases it



- 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**

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**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



- 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



**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<sub>2</sub>O with NaCl (halite):



- If we take **1 mg of NaCl**, eventually, all salt fully dissolves, so the net rate of production of Na<sup>+</sup> and Cl<sup>-</sup> becomes zero.
- If we take **100 mg of NaCl**: eventually, water solution will be saturated with the salt, so Na<sup>+</sup> and Cl<sup>-</sup> 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<sub>2</sub> dissolution/exsolution reaction**:



- This reaction is in equilibrium when CO<sub>2</sub>(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**:

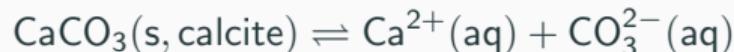


- Good to know:** The **solubility of CO<sub>2</sub>** (i.e., the maximum amount of CO<sub>2</sub> that the solution can dissolve at given temperature, pressure, and fluid composition conditions) can be calculated considering this reaction (and all others) in equilibrium.

**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:



- 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**

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**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 ( $\text{CO}_2(\text{g})$ );
  - a chemical system with aqueous, gaseous, and mineral phases.
- Each phase has one or more chemical species:
  - aqueous:  $\text{H}_2\text{O}(\text{aq})$ ,  $\text{H}^+(\text{aq})$ ,  $\text{OH}^-(\text{aq})$ ,  $\text{HCO}_3^-(\text{aq})$ ,  $\text{CO}_3^{2-}(\text{aq})$ ,  $\text{CO}_2(\text{aq})$ ,  $\text{Ca}^{2+}(\text{aq})$
  - gaseous:  $\text{H}_2\text{O}(\text{g})$ ,  $\text{CO}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ ,  $\text{H}_2\text{S}(\text{g})$
  - calcite:  $\text{CaCO}_3(\text{s})$
  - 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 bacteria)
- In geochemical modeling, suitable phases and their species need to be considered. They must be added either:
  - manually (naming each species separately, e.g.,  $[\text{'H}_2\text{O(l)'}, \text{'H}'^+, \text{'OH}'^-, \text{'Na}'^+, \dots]$ ) or
  - automatically from databases (load all the species containing elements  $[\text{'H}', \text{'O'}, \text{'C'}]$ ).

## Demonstration of chemical system definition i

```
1 # Import reaktoro package
2 from reaktoro import *
3
4 # Initialize the database
5 db = Database("supcrt98")
6
7 # Access all the aqueous species
8 for species in db.aqueousSpecies():
9     print(species.name())
10
11 # Access all the mineral species
12 for species in db.mineralSpecies():
13     print(species.name())
14
15 # Define chemical editor to set up the phases of the system
16 editor = ChemicalEditor(db) # ChemicalEditor receives the db instance
17 # Define phases
```

## Demonstration of chemical system definition ii

```
18 editor.addAqueousPhaseWithElements("H O Na Cl C Ca Fe")
19 editor.addGaseousPhase("H2O(g) CO2(g) O2(g)")
20 editor.addMineralPhase("Calcite")
21 editor.addMineralPhase("Halite")
22
23 # Create chemical system object, we pass object of ChemicalEditor
24 system = ChemicalSystem(editor)
25 print(system)
26
```

**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<sub>2</sub>O and CO<sub>2</sub> are involved

- Assume water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>), 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<sub>2</sub> 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 <sub>2</sub> O(aq)	H <sub>2</sub> O(g)
H <sup>+</sup> (aq)	CO <sub>2</sub> (g)
OH <sup>-</sup> (aq)	
HCO <sub>3</sub> <sup>-</sup> (aq)	
CO <sub>3</sub> <sup>2-</sup> (aq)	
CO <sub>2</sub> (aq)	

## Example of the chemical system when $\text{H}_2\text{O}$ and $\text{CaCO}_3$ are involved

- Assume water ( $\text{H}_2\text{O}$ ) and calcite ( $\text{CaCO}_3$ ) are mixed at some given temperature  $T$  and pressure  $P$ .
- A simple (but reasonable) chemical system for this problem is:

Aqueous Phase	Calcite Phase
$\text{H}_2\text{O}(\text{aq})$	$\text{CaCO}_3(\text{s, calcite})$
$\text{H}^+(\text{aq})$	
$\text{OH}^-(\text{aq})$	
$\text{HCO}_3^-(\text{aq})$	
$\text{CO}_3^{2-}(\text{aq})$	
$\text{CO}_2(\text{aq})$	
$\text{Ca}^{2+}(\text{aq})$	

## Example of the chemical system when H<sub>2</sub>O, NaCl, and CO<sub>2</sub> are involved

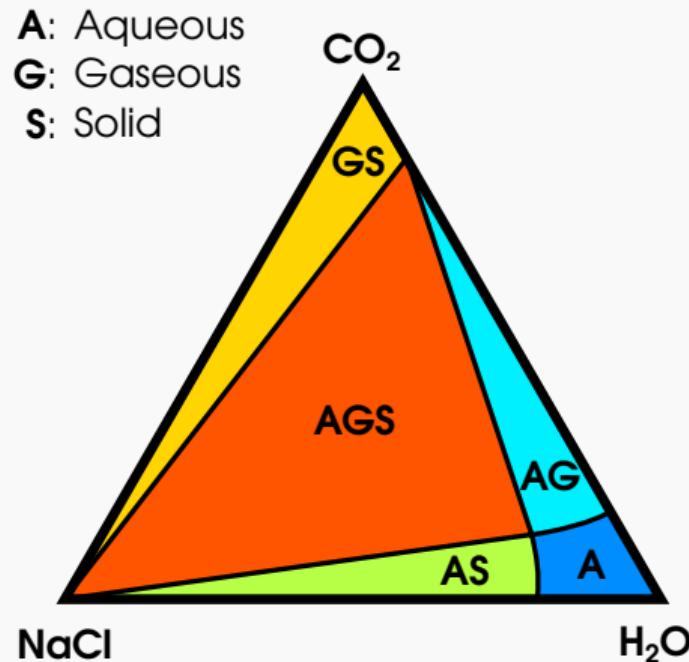
- Assume water (H<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and sodium chloride (NaCl), are mixed at some given temperature T and pressure P.
- A simple (but reasonable) chemical system for this problem is:

Aqueous Phase	Gaseous Phase	Halite Phase
H <sub>2</sub> O(aq)	CO <sub>2</sub> (aq)	CO <sub>2</sub> (g)
H <sup>+</sup> (aq)	HCO <sub>3</sub> <sup>-</sup> (aq)	H <sub>2</sub> O(g)
OH <sup>-</sup> (aq)	CO <sub>3</sub> <sup>2-</sup> (aq)	
Na <sup>+</sup> (aq)	NaCl(aq)	
Cl <sup>-</sup> (aq)		

- **We want 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 ( $T = 200 \text{ }^{\circ}\text{C}$ , critical temperatures and pressures of gases used in Peng-Robinson's EOS)
  - ColdChem.dat (a low-temperature aqueous thermodynamic model)

# **Chemical equilibrium from a thermodynamic and mathematical perspective**

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# **Chemical equilibrium from a thermodynamic and mathematical perspective**

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**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 thermodynamics* 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.

## 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<sub>2</sub>O and 2 moles of CO<sub>2</sub> and **calculate the equilibrium state of the system.**
- these two substances will react and form several species (H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> 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  $n = [n_{\text{H}^+}, n_{\text{HCO}_3^-}, \dots]$ ) 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.,  $b = [b_{\text{H}}, b_{\text{O}}, b_{\text{C}}, b_{\text{Z}}]$ .

# Chemical equilibrium problem for the H<sub>2</sub>O–CO<sub>2</sub> 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 <sub>2</sub> O(aq)	CO <sub>2</sub> (g)
H <sup>+</sup> (aq)	H <sub>2</sub> O(g)
OH <sup>-</sup> (aq)	
CO <sub>3</sub> <sup>2-</sup> (aq)	
HCO <sub>3</sub> <sup>-</sup> (aq)	
CO <sub>2</sub> (aq)	

## Questions:

- What are the amounts of each chemical species at equilibrium?
- Which phases exist at equilibrium?
- How much carbon dioxide, CO<sub>2</sub>(g), dissolved as carbon-bearing aqueous species?
- How much solvent water, H<sub>2</sub>O(aq), evaporated to the gas phase as vapor H<sub>2</sub>O(g)?
- What is the concentration of H<sup>+</sup>(aq), which is related to pH (acidity)?

## Mass conservation constraints for the H<sub>2</sub>O–CO<sub>2</sub> system at equilibrium

- At equilibrium, the amounts of the species:

$$n = (n_{\text{H}_2\text{O(aq)}}, n_{\text{H}^+(\text{aq})}, n_{\text{OH}^-(\text{aq})}, n_{\text{CO}_3^{2-}(\text{aq})}, n_{\text{HCO}_3^-(\text{aq})}, n_{\text{CO}_2(\text{aq})}, n_{\text{CO}_2(\text{g})}, n_{\text{H}_2\text{O(g)}})$$

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

$$2n_{\text{H}_2\text{O(aq)}} + n_{\text{H}^+(\text{aq})} + n_{\text{OH}^-(\text{aq})} + n_{\text{HCO}_3^-(\text{aq})} + 2n_{\text{H}_2\text{O(g)}} = b_{\text{H}} \quad (1)$$

$$n_{\text{H}_2\text{O(aq)}} + n_{\text{OH}^-(\text{aq})} + 3n_{\text{CO}_3^{2-}(\text{aq})} + 3n_{\text{HCO}_3^-(\text{aq})} + 2n_{\text{CO}_2(\text{aq})} + 2n_{\text{CO}_2(\text{g})} + n_{\text{H}_2\text{O(g)}} = b_{\text{O}} \quad (2)$$

$$n_{\text{CO}_3^{2-}(\text{aq})} + n_{\text{HCO}_3^-(\text{aq})} + n_{\text{CO}_2(\text{aq})} + n_{\text{CO}_2(\text{g})} = b_{\text{C}} \quad (3)$$

$$n_{\text{H}^+(\text{aq})} - n_{\text{OH}^-(\text{aq})} - 2n_{\text{CO}_3^{2-}(\text{aq})} - n_{\text{HCO}_3^-(\text{aq})} = b_{\text{Z}} \quad (4)$$

- 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
- $n = (n_1, \dots, n_N)$  is the **vector of species amounts**
- $b = (b_1, \dots, b_E)$  is the **vector of element amounts**

## Constructing the formula matrix for the H<sub>2</sub>O–CO<sub>2</sub> system i

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

Index	Species	Index	Element
0	H <sub>2</sub> O(aq)	0	H
1	H <sup>+</sup> (aq)	1	O
2	OH <sup>-</sup> (aq)	2	C
3	CO <sub>3</sub> <sup>2-</sup> (aq)	3	Z
4	HCO <sub>3</sub> <sup>-</sup> (aq)		
5	CO <sub>2</sub> (aq)		
6	CO <sub>2</sub> (g)		
7	H <sub>2</sub> O(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<sub>2</sub>O-CO<sub>2</sub> system ii

Answer:

$$A = \begin{matrix} & \text{H}_2\text{O(aq)} & \text{H}^+(\text{aq}) & \text{OH}^-(\text{aq}) & \text{CO}_3^{2-}(\text{aq}) & \text{HCO}_3^-(\text{aq}) & \text{CO}_2(\text{aq}) & \text{CO}_2(\text{g}) & \text{H}_2\text{O(g)} \\ \text{H} & 2 & 1 & 1 & 0 & 1 & 0 & 0 & 2 \\ \text{O} & 1 & 0 & 1 & 3 & 3 & 2 & 2 & 1 \\ \text{C} & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 \\ \text{Z} & 0 & 1 & -1 & -2 & -1 & 0 & 0 & 0 \end{matrix}$$

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



<http://etc.ch/oyhr> or

- (1) row(Z) = row(H) - 2 row(O)
- (2) row(Z) = row(H) - 2 row(O) + 2 row(C)
- (3) row(Z) = row(H) - 2 row(O) + 4 row(C)
- (4) row(Z) = row(H) - 2 row(O) + 6 row(C)

Answer: (3)

## Calculating the amounts of elements from species amounts

**Exercise:** Given

$$n = \begin{bmatrix} n_{\text{H}_2\text{O}(\text{aq})} \\ n_{\text{H}^+(\text{aq})} \\ n_{\text{OH}^-(\text{aq})} \\ n_{\text{CO}_3^{2-}(\text{aq})} \\ n_{\text{HCO}_3^-(\text{aq})} \\ n_{\text{CO}_2(\text{aq})} \\ n_{\text{CO}_2(\text{g})} \\ n_{\text{H}_2\text{O}(\text{g})} \end{bmatrix} = \begin{bmatrix} n_0 \\ n_1 \\ n_2 \\ n_3 \\ n_4 \\ n_5 \\ n_6 \\ n_7 \end{bmatrix} = \begin{bmatrix} 55.4551 \\ 1.23485 \cdot 10^{-4} \\ 8.39739 \cdot 10^{-11} \\ 4.93648 \cdot 10^{-11} \\ 1.23484 \cdot 10^{-4} \\ 0.032861 \\ 1.96702 \\ 0.0531732 \end{bmatrix}, \quad \text{calculate } b = \begin{bmatrix} b_{\text{H}} \\ b_{\text{O}} \\ b_{\text{C}} \\ b_{\text{Z}} \end{bmatrix} = An.$$

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](https://repl.it/languages/python)
- Python source code can be downloaded from [\*mass-balance-with-blanks.py\*](#).

## Calculating the amounts of elements using Python – Source i

```
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

```
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))
```

## Calculating the amounts of elements using Python – Source iii

```
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 2:** 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 HC03- 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 3:** 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  $b = (b_1, \dots, b_E)$ , find the amounts of species  $n = (n_1, \dots, n_N)$  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  $n = (n_1, \dots, n_N)$  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  $\mu_i$  is the **chemical potential** of the  $i$ th species.

- $G$  has units of J, and  $\mu_i$  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**  $\mu_i$  is a measure of its tendency to transform into other substances.
- In the following reaction:



- $\mu_A > \mu_B$ : 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  $\mu_A$ , the higher the tendency for A to transform to B.

# Chemical potential and its interpretation, Example

- Consider the following reaction:



- We have the following three cases:

**Case I**

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{aq})} = -390.347 \text{ kJ/mol}$$

**Case II**

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{aq})} = -517.800 \text{ kJ/mol}$$

**Case III**

$$\mu_{\text{CO}_2(\text{g})} = -389.185 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{aq})} = -383.861 \text{ kJ/mol}$$

- Quiz:** what is the tendency for  $\text{CO}_2(\text{g})$  in each of cases?

- Answer:**

- Case I:** Since  $\mu_{\text{CO}_2(\text{g})} = \mu_{\text{CO}_2(\text{aq})}$ , the reaction is in **equilibrium**.

- Case II:** Since  $\mu_{\text{CO}_2(\text{g})} > \mu_{\text{CO}_2(\text{aq})}$ ,  $\text{CO}_2(\text{g})$  tends to **dissolve**.

- Case III:** Since  $\mu_{\text{CO}_2(\text{g})} < \mu_{\text{CO}_2(\text{aq})}$ ,  $\text{CO}_2(\text{g})$  tends to form, **exsolve**.

## Chemical potentials and direction of reactions

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



- $\mu_A + \mu_B > \mu_C + 2\mu_D$ : 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!



# Chemical potentials and direction of reactions, Exercise i

Consider the following reaction and the subsequent three cases:



## Case I

$$\mu_{\text{H}_2\text{O}(\text{aq})} = -239.614 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{HCO}_3^-(\text{aq})} = -610.019 \text{ kJ/mol}$$

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

## Case II

$$\mu_{\text{H}_2\text{O}(\text{aq})} = -239.614 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{HCO}_3^-(\text{aq})} = -717.639 \text{ kJ/mol}$$

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

## Case III

$$\mu_{\text{H}_2\text{O}(\text{aq})} = -239.614 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{g})} = -389.185 \text{ kJ/mol}$$

$$\mu_{\text{HCO}_3^-(\text{aq})} = -606.776 \text{ kJ/mol}$$

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

## Quiz:

- What is the direction of the reaction in each case?
- In each case, is  $\text{CO}_2(\text{g})$  tending to dissolve or exsolve?



## Chemical potentials and direction of reactions, Exercise ii

### Case I:

$$\mu_{\text{H}_2\text{O}(\text{aq})} = -239.614 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{HCO}_3^-(\text{aq})} = -610.019 \text{ kJ/mol}$$

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

$$\mu_{\text{H}_2\text{O}(\text{aq})} + \mu_{\text{CO}_2(\text{g})} = -629.961$$

$$\mu_{\text{HCO}_3^-(\text{aq})} + \mu_{\text{H}^+(\text{aq})} = -629.961$$

$$\boxed{\mu_{\text{H}_2\text{O}(\text{aq})} + \mu_{\text{CO}_2(\text{g})} = \mu_{\text{HCO}_3^-(\text{aq})} + \mu_{\text{H}^+(\text{aq})}}$$

The reaction is in **equilibrium**.

# Chemical potentials and direction of reactions, Exercise iii

## Case II:

$$\mu_{\text{H}_2\text{O(aq)}} = -239.614 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{HCO}_3^-(\text{aq})} = -717.639 \text{ kJ/mol}$$

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

$$\mu_{\text{H}_2\text{O(aq)}} + \mu_{\text{CO}_2(\text{g})} = -629.961$$

$$\mu_{\text{HCO}_3^-(\text{aq})} + \mu_{\text{H}^+(\text{aq})} = -759.093$$

$$\boxed{\mu_{\text{H}_2\text{O(aq)}} + \mu_{\text{CO}_2(\text{g})} > \mu_{\text{HCO}_3^-(\text{aq})} + \mu_{\text{H}^+(\text{aq})}}$$

The reaction is proceeding to the right, and CO<sub>2</sub> is tending to **dissolve**.

## Chemical potentials and direction of reactions , Exercise iv

### Case III:

$$\mu_{\text{H}_2\text{O(aq)}} = -239.614 \text{ kJ/mol}$$

$$\mu_{\text{CO}_2(\text{g})} = -390.347 \text{ kJ/mol}$$

$$\mu_{\text{HCO}_3^-(\text{aq})} = -717.639 \text{ kJ/mol}$$

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

$$\mu_{\text{H}_2\text{O(aq)}} + \mu_{\text{CO}_2(\text{g})} = -628.799$$

$$\mu_{\text{HCO}_3^-(\text{aq})} + \mu_{\text{H}^+(\text{aq})} = -623.475$$

$$\boxed{\mu_{\text{H}_2\text{O(aq)}} + \mu_{\text{CO}_2(\text{g})} < \mu_{\text{HCO}_3^-(\text{aq})} + \mu_{\text{H}^+(\text{aq})}}$$

The reaction is proceeding to the left, and CO<sub>2</sub> 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 4:** Chemical potentials and direction of reactions using Python

Source code: *chemical-potential.py*.

## Chemical potential $\mu_i$ and Gibbs energy

- The **chemical potential of a species  $\mu_i$**  is equivalent to

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

- Thus, the infinitesimal change in Gibbs energy  $dG$  following an infinitesimal change in the  $i$ th species amount  $i$

$$dG = \mu_i dn_i$$

at constant temperature  $T$  and pressure  $P$ .

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

$$\sum_{i=1}^N \mu_i dn_i = 0.$$

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

## Chemical potential $\mu_i$ and its definition

- The **chemical potential**  $\mu_i$  of a species  $i$  is defined as

$$\boxed{\mu_i = \mu_i^o + RT \ln a_i.}$$

- $\mu_i^o$  is the **standard chemical potential** of the species at  $(T, P)$ ;
- $R$  is the **universal gas constant**,  $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ ;
- $T$  and  $P$  are given temperature and pressure;
- $a_i$  is the **activity** of the species at  $(T, P, n_\Phi)$ , where  $n_\Phi$  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 $\mu_i^o$

- The **standard chemical potential**  $\mu_i^o$  of a species is its chemical potential at a **standard reference state**, in which  $a_i = 1$  is assumed.
- For a gas:
  - $\mu_i^o$  is the chemical potential of the gas at a hypothetical ideal state with  $P^o = 1$  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  $\mu_i^o$  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

$\mu_i^o$ [kJ/mol]	$T$ [°C]	$P$ [bar]		
		1	50	100
$\text{H}_2\text{O}(\text{aq})$	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
$\text{H}^+(\text{aq})$	25	0	0	0
	50	0	0	0
	75	0	0	0
	100	—	0	0

## Standard chemical potential tables ii

$\mu_i^o$ [kJ/mol]	$T$ [°C]	$P$ [bar]		
		1	50	100
CO <sub>2</sub> (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 <sub>3</sub> (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

- For a general reaction

- Consider the following reaction

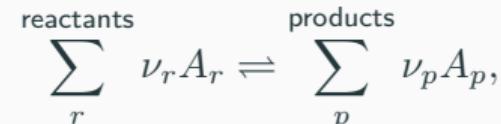


- At equilibrium, the following mass action equation must be satisfied:

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

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).



where

- $A_r, A_p$  are reactant and product species
- $\nu_r, \nu_p$  are the stoichiometric coefficients,

the general mass action equation is

$$K = \frac{\prod_p a_p^{\nu_p}}{\prod_r a_r^{\nu_r}}.$$

- 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:



**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

```
1 from math import *
2
3 R = 8.314
4 T = 100 + 273.15
5 mu_H2O = -242.992 * 1e3
6 mu_OH = -155.559 * 1e3
7
8 lnK = -1/R/T *(mu_OH - mu_H2O)
9
10 print("lnK = ", lnK)
11 print("log10K = ", lnK * log10(e))
```

**Listing 5:** Calculating equilibrium constant of reactions using Python

## Exercise, Mass action and mass conservation equations i

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

Index	Species	Index	Element		
1	$\text{CO}_2(\text{aq})$	1	C	$\text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$	(1)
2	$\text{CO}_3^{2-}(\text{aq})$	2	Cl	$\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq})$	(2)
3	$\text{Cl}^-(\text{aq})$	3	H	$\text{H}_2\text{O}(\text{aq}) + \text{CO}_2(\text{aq}) \rightleftharpoons \text{CO}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq})$	(3)
4	$\text{H}^+(\text{aq})$	4	Na	$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq})$	(4)
5	$\text{H}_2\text{O}(\text{l})$	5	OI	$\text{NaCl}(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	(5)
6	$\text{HCO}_3^-(\text{aq})$				
7	$\text{Na}^+(\text{aq})$				
8	$\text{OH}^-(\text{aq})$				
9	$\text{CO}_2(\text{g})$				
10	$\text{NaCl}(\text{s})$				

### 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

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

where  $n = (n_1, \dots, n_N)$  is the vector of molar amounts of the species.

- The **chemical potential** of the  $i$ th species is defined as

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

- The **standard chemical potentials** of the species  $\mu_i^o$  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  $n_\Phi$ .

**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 substance 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)



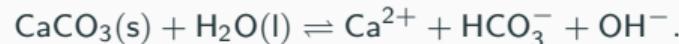
- Let  $[C]$  and  $[D]$  denote the molarities (mol/Lw) or concentrations (mol/kgw) of the products (C and D), then  $K_{sp}$  is defined as

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

**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



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

$$K_{sp} = [\text{Ca}^{2+}]^1 \cdot [\text{HCO}_3^-]^1 \cdot [\text{OH}^-]^1 \approx 10^{-12},$$

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

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

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

$$[\text{CaCO}_3(\text{aq})] = [\text{Ca}^{2+}] = 10^{-4} \text{ mol/L}$$

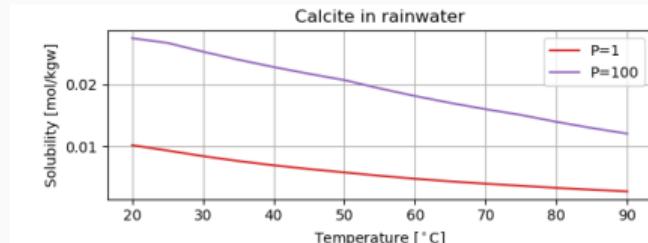
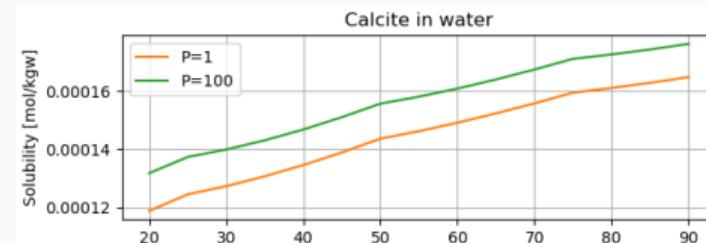
or, using molar mass of calcite 100.09 g/mol,

$$[\text{CaCO}_3(\text{aq})] \approx 10^{-4} \text{ mol/L} \cdot 100 \text{ g/mol} \approx 10^{-2} \text{ g/L} = 10 \text{ mg/L},$$

which is relatively small in comparison to other minerals.

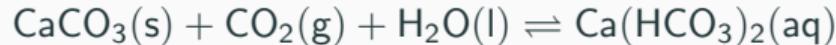
# Dependence of calcite solubility on different factors

- Solubility of  $\text{CaCO}_3$  **increases** as the pressure of the water **increases**.
- Demonstration of these properties can be found in Jupyter notebook tutorial *Calcite solubility in water and  $\text{CO}_2$ -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  $\text{CO}_2$ -saturated water as the temperature **increases** (**unusual!!**).



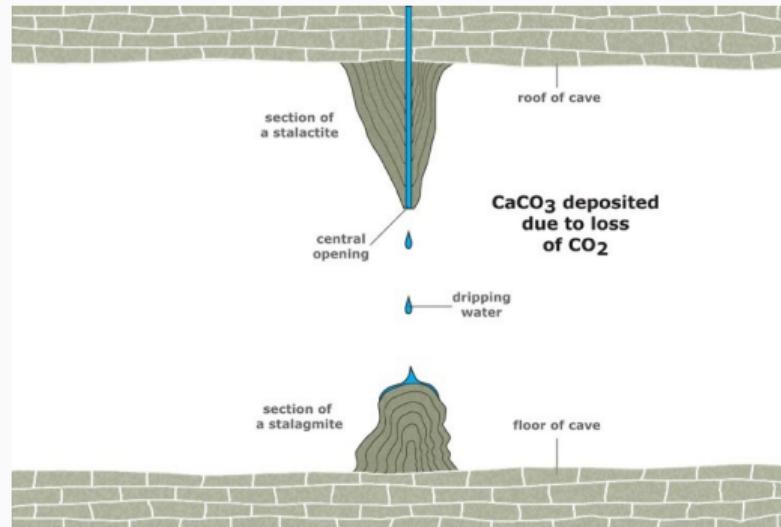
Calcite solubility in water and rain water w.r.t. temperature.

# Calcite solubility example, Stalagmites and stalactites



→ Rainwater meets with limestone to form a solution of calcium bicarbonate.

← The bicarbonate-rich water drips from the ceiling of the cave and partially evaporates, leaving behind a calcium carbonate deposit.



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**Figure 1:** Diagram of cave showing formation of stalagmites and stalactites.

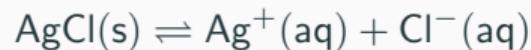
## Calcite solubility example, Limestone fizzing



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

## Solubility of chlorargyrite, Example

- Consider dissolution reaction of chlorargyrite



- Quiz:** What is solubility of  $\text{AgCl(s)}$  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  $\text{AgCl(s)}$  at room temperature.  
**Note:** Compared with other types of salts,  $\text{AgCl}$  is also poorly soluble in water.  
In contrast, table salt  $\text{NaCl}$  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

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

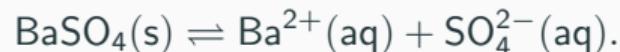
where

- $Q$  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*.

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

## Saturation index, Exercise

- Consider dissolution reaction of barium sulfate



- Solubility product of barium sulfate is  $1.08 \cdot 10^{-10}$  at  $25^\circ\text{C}$ .
- Quiz:** What can be said about the water w.r.t. to barium sulfate if  $[\text{Ba}^{2+}] = 2.9 \cdot 10^{-4}$  molal  $[\text{SO}_4^{2-}] = 1.8 \cdot 10^{-4}$  molal?

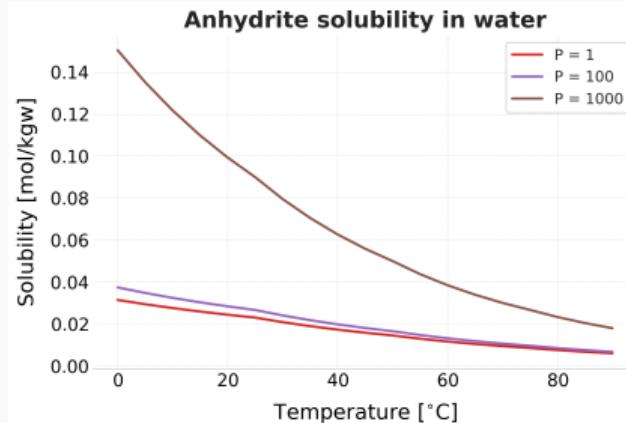


<http://etc.ch/oyhr> or

- Answer:** Water will be supersaturated with  $\text{BaSO}_4(\text{s})$ .

# 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).*



Injection well with SW:

low  $\text{Ba}^{2+}$ , high  $\text{SO}_4^{2-}$



Mixing:



## 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

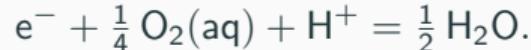
$$\sum_i Z_i m_i = 0,$$

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  $\text{Na}^+$  and 0.1 molal  $\text{Cl}^-$ .

# Reduction/oxidation potential, pE

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



- **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

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

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.

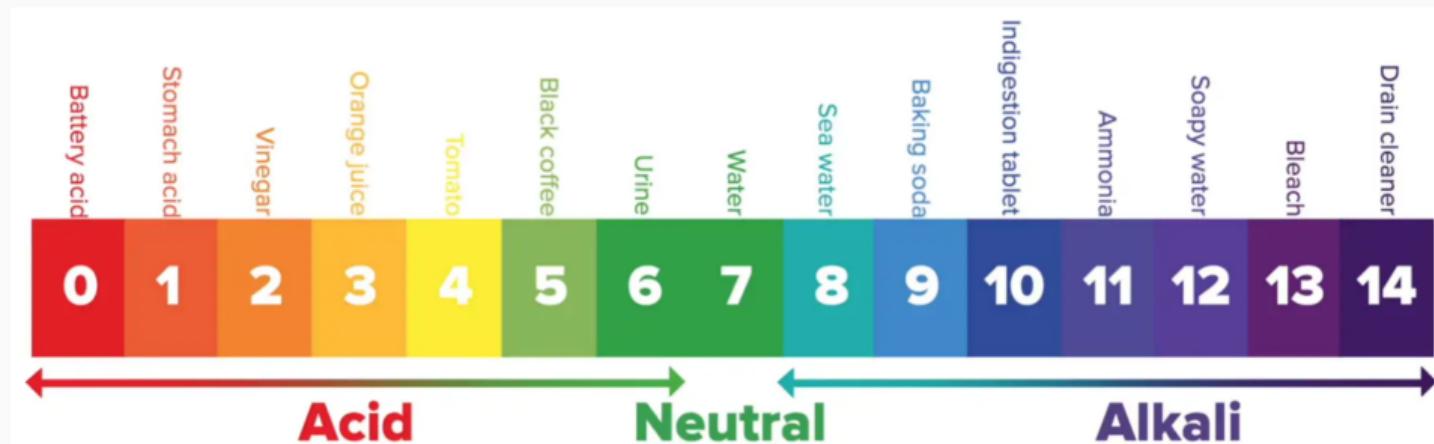
- A solution with a **higher pE / lower pE** will have a tendency to **gain electrons from / lose electrons to** the new species.

# 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  $\text{HCl(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  and it produced the solution with pH = 1.
- **Hint 1:** let the concentration  $[\text{H}^+]$  (measured in mol/L) and  $a_{\text{H}^+}$  be the same (i.e., activity is considered as effective concentration).
- **Hint 2:**  $m_{\text{HCl}} = M_{\text{HCl}} \cdot n_{\text{HCl}}$ , 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  $M_{\text{HCl}} = 36.458 \text{ g/mol}$ .
- **Quiz:** What was the mass of dissolved HCl?



<http://etc.ch/oyhr> or

- **Answer:** 1.09374 g.

## pH, Examples i

- 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.

## pH, Examples ii

- CO<sub>2</sub> added to the seawater influences the pH according to the reaction

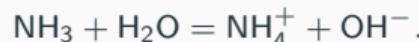


See tutorial *Dependence of the pH on the CO<sub>2</sub>(g) amount in seawater.*

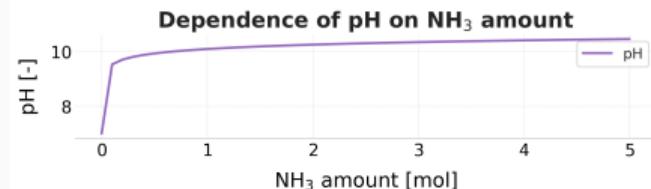
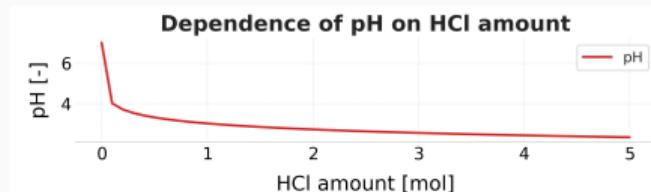
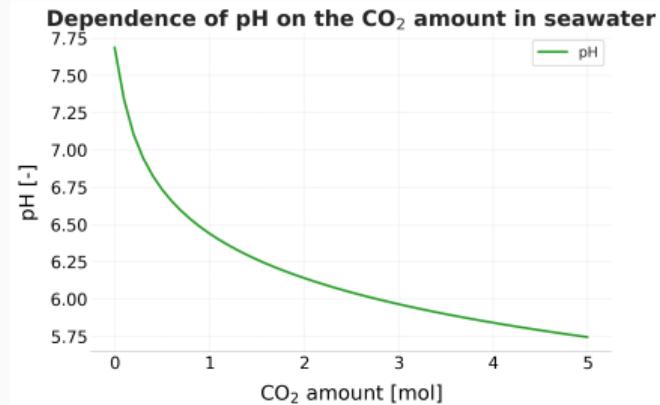
- Adding HCl into water increases free H<sup>+</sup> ions and decreases pH according to the reaction



whereas adding ammonia removes H<sup>+</sup> from water and increases it to produce ammonium and hydroxide, i.e.,



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



# **Thermodynamic models of aqueous, gaseous, and mineral phases**

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## Activities – the effective concentrations of the species

- Let  $c_i$  denote concentration of species  $i$  (**Note:** sometime in literature it is denoted by  $[i]$ , but is different to species amount  $n_i$ ).
- If we would use  $c_i$  instead of activities  $a_i$  to calculate the chemical potentials, then

$$\mu_i = \mu_i^o + RT \ln a_i \quad \text{can be reformulated by} \quad \mu_i = \mu_i^o + RT \ln(c_i/c_i^o)$$

where  $c_i^o$  is a reference concentration

- **But!** This simplification provides **accurate predictions only in some limited cases:**
  - gases at low pressures and high temperatures (close to ideal gas behavior)
  - very dilute electrolyte solutions (close to ideal solution behavior)

## Activities – corrected species “concentrations” in non-ideal mixtures

- Because of the **non-ideal behavior of the mixtures**, the concentrations of the species must be corrected:

$$a_i = \gamma_i(T, P, c) \frac{c_i}{c_i^0},$$

where  $\gamma_i$  is an **activity coefficient**, a function of  $(T, P, c)$ , with  $c$  denoting a **vector of concentrations of all species in the solution**.

- To calculate  $\gamma_i$ , there are different (theoretical) **activity models**:
  - Davies equation,
  - Debye-Hückel equation,
  - Pitzer equations, etc.

# **Thermodynamic models of aqueous, gaseous, and mineral phases**

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**Aqueous phase**

# Activities of aqueous solute species

- The **activity of aqueous solute species**, such as  $\text{H}^+(\text{aq})$ ,  $\text{HCO}_3^-(\text{aq})$ ,  $\text{CO}_2(\text{aq})$ , is defined as:

$$a_i = \gamma_i m_i,$$

where:

- $\gamma_i$  is the **activity coefficient** of solute species  $i$ ; and
- $m_i$  is the **molality** of solute species  $i$ .

- The **molality**  $m_i$  of the  $i$ th aqueous species is form of describing concentrations and is defined as follows:

$$m_i = \frac{n_i}{\text{mass of solvent species } \text{H}_2\text{O}(\text{aq})},$$

or equivalently:

$$\begin{aligned} m_i &= \frac{n_i}{\text{molar mass}(\text{H}_2\text{O}(\text{aq})) \cdot n_{\text{H}_2\text{O}(\text{aq})}} \\ &= \frac{n_i}{18.01528 \cdot 10^{-3} \cdot n_{\text{H}_2\text{O}(\text{aq})}} \\ &= 55.508 \frac{n_i}{n_{\text{H}_2\text{O}(\text{aq})}}. \end{aligned}$$

## Molarity vs. molality

- The **molarity**  $c_i$  of the  $i$ th species is:

$$c_i = \frac{n_i}{\text{volume of solvent species H}_2\text{O(aq)}} \\ = \frac{n_i \cdot \rho_{\text{H}_2\text{O(aq)}}}{\text{mass of solvent species H}_2\text{O(aq)}},$$

where  $\rho_{\text{H}_2\text{O(aq)}}$  is **water density** at given  $T$  and  $P$ .

- Measured in units of **molar** = **mol/L** (or **mol/L<sub>w</sub>** or  $10^3\text{mol/m}^3$ ).

- The **molality**  $m_i$  of the  $i$ th species is:

$$m_i = \frac{n_i}{\text{mass of solvent species H}_2\text{O(aq)}}.$$

- Measured in units of **molal** = **mol/kg** (or **mol/kgw**).

# Ionic strength of aqueous solutions

- Most activity models for aqueous solutions depends on the **ionic strength**:

$$I = \frac{1}{2} \sum_{i=1}^{\text{solute}} m_i Z_i^2,$$

where:

- $m_i$  is the **molality** of species  $i$ ; and
- $Z_i$  is the **electric charge** of species  $i$ .

- $I$  is a measure (in molal) of *how much concentrated is the solution with ionic species*,
- Note:** Neutral species play no role in  $I$ , just the ions.

- Question:** What is the ionic strength  $I$  of a solution obtained by mixing 1 kg of H<sub>2</sub>O and:

- a) 2 mol of NaCl?
- b) 1 mol of CaCl<sub>2</sub>?

<http://etc.ch/paWu> or



- Answer:** a) 2 molal, b) 3 molal

## Calculating species molalities and ionic strength, Exercise

Index	Species	Amount (mol)
1	$\text{H}_2\text{O}(\text{aq})$	55.4551
2	$\text{H}^+(\text{aq})$	$1.23485 \cdot 10^{-4}$
3	$\text{OH}^-(\text{aq})$	$8.39739 \cdot 10^{-11}$
4	$\text{Na}^+(\text{aq})$	0.92
5	$\text{Cl}^-(\text{aq})$	0.92
6	$\text{CO}_3^{2-}(\text{aq})$	$4.93648 \cdot 10^{-11}$
7	$\text{HCO}_3^-(\text{aq})$	$1.23484 \cdot 10^{-4}$
8	$\text{CO}_2(\text{aq})$	0.032861
9	$\text{CO}_2(\text{g})$	1.96702
10	$\text{H}_2\text{O}(\text{g})$	0.0531732

### Exercise:

- Calculate the mass  $M_w$  of solvent water  $\text{H}_2\text{O}(\text{aq})$  (in kg). Use 18.0154 g/mol as an approximated molar mass of water.
- Calculate the molalities  $m_i$  of the aqueous solute species (in molal).
- Calculate the ionic strength  $I$  of aqueous solution (in molal).

## Calculating species molalities and ionic strength using Python i

```
1 import numpy
2
3 # Create a list with names of aqueous species of interest
4 aqueous_species = ['H2O(aq)', 'H+', 'OH-', 'Na+', 'Cl-', 'CO3--', 'HCO3-', 'CO2(aq)']
5
6 # The index of species H2O(aq) used in the calculation of molalities
7 iH2O = 0
8
9 # Create a list with the electrical charges of each species
10 Z = []
11
12 # Create a list with the amounts (in moles) of each species
13 n = []
14
15 # Transform the list n into a Numpy array for numerical calculations
16 n = numpy.array(n)
```

## Calculating species molalities and ionic strength using Python ii

```
17  
18 # Calculate the molalities of all species  
19 m =  
20  
21 # Calculate the ionic strength of the aqueous solution  
22 I =  
23  
24 # Print the calculated ionic strength  
25 print('Ionic strength of solution is %f molal.' % I)  
26  
27 # Print the calculated molality of each species  
28 for i in range(len(aqueous_species)):  
    print('Molality of %s is %f molal.' % (aqueous_species[i], m[i]))
```

**Listing 6:** Calculating species molalities and ionic strength using Python

Source code: *polybox*.

## Calculating species molalities and ionic strength using Python – Output

```
1 Ionic strength of solution is 0.921001 molal.  
2 Molality of H2O(aq) is 55.508000 molal.  
3 Molality of H+ is 0.000124 molal.  
4 Molality of OH- is 0.000000 molal.  
5 Molality of Na+ is 0.920878 molal.  
6 Molality of Cl- is 0.920878 molal.  
7 Molality of CO3-- is 0.000000 molal.  
8 Molality of HC03- is 0.000124 molal.  
9 Molality of CO2(aq) is 0.032892 molal.
```

**Listing 7:** Calculating species molalities and ionic strength using Python – Output

**Answer:** To check the correctness of gaps in the code, use the [source code](#).

## Activity coefficient of aqueous ionic species, Davies model

- The **Davies activity coefficient model** calculates  $\gamma_i$  using:

$$\log_{10} \gamma_i = -A_\gamma Z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right),$$

where  $A_\gamma$  is the **Debye–Hückel parameter** defined as

$$A_\gamma = 1.824928 \cdot 10^6 \rho_{\text{H}_2\text{O}}^{1/2} (\epsilon_{\text{H}_2\text{O}} T)^{-3/2},$$

where  $\rho_{\text{H}_2\text{O}}$  and  $\epsilon_{\text{H}_2\text{O}}$  are the **density** and **dielectric constant of pure water**.

- For 25 °C and 1 bar,  $A_\gamma = 0.5095$ .
- Limitations of the model:** It is accurate for  $I$  is in the range 0.1–0.7 molal, which is equivalent to 1 kg of water mixed with 5.8–40.9 grams of NaCl (0.5-4 teaspoons of table salt).

## Activity coefficient of aqueous ionic species, Davies model, Exercise

- **Quiz:** What is the activity coefficient of species  $\text{Na}^+$  in an aqueous solution with ionic strength  $I = 0.1$  molal using the *Davies activity coefficient model*:

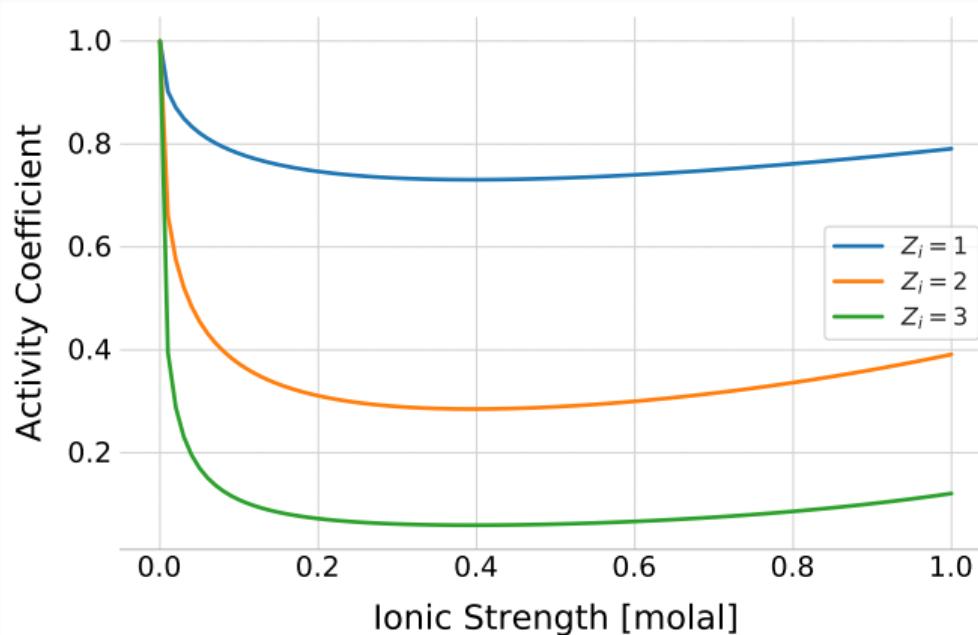
$$\log_{10} \gamma_{\text{Na}^+} = -A_\gamma Z_{\text{Na}^+}^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right), \quad \text{where } A_\gamma = 0.5095?$$



<http://etc.ch/paWu> or

- **Answer:** 0.7814.
  - **Note:** In an ideal solution,  $\gamma_i = 1$  for all species.
- Question:** Based calculated  $\gamma_{\text{Na}^+}$ , is an *ideal solution assumption* reasonable one?

## Activity coefficient as a function of $I$ , Davies model



**Figure 4:** Activity coefficient  $\gamma_i$  for aqueous ions with charge  $Z_i = 1, 2, 3$  as a function of  $I$ .

**Question:** How would these curves look like if the charges would be  $Z_i = -1, -2, -3$ ?

## Activity coefficient calculation in Python, Davies model i

```
1 import numpy
2 import matplotlib.pyplot as plt
3
4 # Function calculating activity coefficient according to the Davis model
5 def gamma_davies(Zi, I):
6     # Debye-Hückel parameter
7     Agamma = 0.5095
8     # Vector of ionic strength in the power 1/2
9     sqrtI = numpy.sqrt(I)
10    return 10**(-Agamma * Zi**2 * (sqrtI / (1.0 + sqrtI) - 0.3 * I))
11
12 # Create array with values of ionic strength in a range from 0.0 to 1.0
13 I = numpy.linspace(0.0, 1.0, 101)
14
15 # Calculate activity coefficients for different charges of the aqueous species
16 gammaZ1 = gamma_davies(1.0, I)
17 gammaZ2 = gamma_davies(2.0, I)
```

## Activity coefficient calculation in Python, Davies model ii

```
18 gammaZ3 = gamma_davies(3.0, I)
19
20 # Plot an activity coefficient as a function an ionic strength for different
   charges
21 plt.xlabel('Ionic Strength [molal]')
22 plt.ylabel('Activity Coefficient')
23 plt.plot(I, gammaZ1, label=r'$Z_i=1$')
24 plt.plot(I, gammaZ2, label=r'$Z_i=2$')
25 plt.plot(I, gammaZ3, label=r'$Z_i=3$')
26
27 # Position the legend and save the figure
28 plt.legend(loc='center right')
29 plt.savefig('activity-coefficient-davies.pdf', bbox_inches='tight')
```

**Listing 8:** Davies activity model calculation in Python

Source code: *davies-activity-model.py*

## Activity model for H<sub>2</sub>O(aq), Davies model

- The activity of H<sub>2</sub>O(aq) can be calculated using the following **Davies model**:

$$\ln a_{\text{H}_2\text{O}(\text{aq})} = \frac{\ln 10}{55.5084} A_\gamma \left[ 2 \left( \frac{I + 2\sqrt{I}}{1 + \sqrt{I}} \right) - 4 \ln(1 + \sqrt{I}) - 0.3I^2 \right] - \frac{1 - x_{\text{H}_2\text{O}(\text{aq})}}{x_{\text{H}_2\text{O}(\text{aq})}},$$

where  $x_{\text{H}_2\text{O}(\text{aq})}$  is the mole fraction of H<sub>2</sub>O(aq):

$$x_{\text{H}_2\text{O}(\text{aq})} = \frac{n_{\text{H}_2\text{O}(\text{aq})}}{\text{sum of moles of all aqueous species}}.$$

- Question:** Consider pure water as a solution. What is the value of ionic strength  $I$  and the activity of water  $a_{\text{H}_2\text{O}}$  ?



<http://etc.ch/paWu> or

- Answer:**  $I = 0$ ,  $a_{\text{H}_2\text{O}} = 1$ .

## Activity model for H<sub>2</sub>O(aq), Ideal model

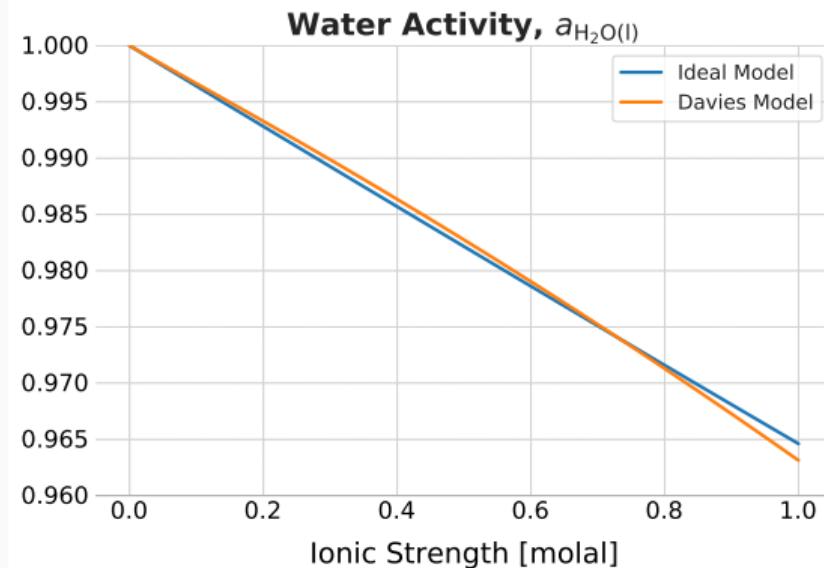
- For an **ideal solution**, all contribution arising from ionic strength can be eliminated:

$$\ln a_{\text{H}_2\text{O}(\text{aq})} = \frac{\ln 10}{55.5084} A_\gamma \left[ 2 \left( \frac{I + 2\sqrt{I}}{1 + \sqrt{I}} \right) - 4 \ln(1 + \sqrt{I}) - 0.3I^2 \right] - \frac{1 - x_{\text{H}_2\text{O}(\text{aq})}}{x_{\text{H}_2\text{O}(\text{aq})}} \quad (5)$$

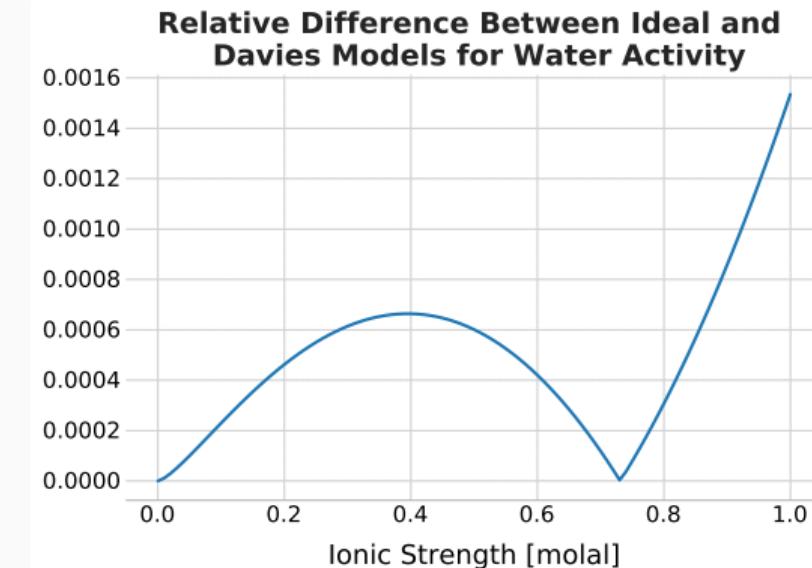
$$= -\frac{1 - x_{\text{H}_2\text{O}(\text{aq})}}{x_{\text{H}_2\text{O}(\text{aq})}}. \quad (6)$$

- Let's investigate how accurate this approximation is?
- Source code: *activity-water-davies-vs-ideal.py*.

## Activity model for $\text{H}_2\text{O}(\text{aq})$ : Davies vs. Ideal model



**Figure 5:** Activities of aqueous solvent species  $\text{H}_2\text{O}(\text{aq})$  as a function of ionic strength  $I$  calculated using the Ideal and Davies models.



**Figure 6:** Relative difference between the Ideal and Davies models for activity of water as a function of ionic strength,  $I$ .

## Activity coefficient model for CO<sub>2</sub>(aq), Drummond model

- The activity of the aqueous species CO<sub>2</sub>(aq) can be calculated using

$$a_{\text{CO}_2(\text{aq})} = \gamma_{\text{CO}_2(\text{aq})} m_{\text{CO}_2(\text{aq})},$$

with  $\gamma_{\text{CO}_2(\text{aq})}$  calculated using the **Drummond model**

$$\ln \gamma_{\text{CO}_2(\text{aq})} = \left( c_1 + c_2 T + \frac{c_3}{T} \right) I - (c_4 + c_5 T) \frac{I}{I+1},$$

where  $T$  is temperature,  $I$  is the ionic strength of the aqueous solution, and  $c_1 = -1.0312$ ,  $c_2 = 1.2806 \cdot 10^{-3}$ ,  $c_3 = 255.9$ ,  $c_4 = 0.4445$  and  $c_5 = -1.606 \cdot 10^{-3}$ .

- Limitations of the model:** This equation is valid within the temperature and salinity ranges 20–400 °C and 0–6.5 molal, respectively.

# Calculating CO<sub>2</sub>(aq) activity coefficient using Drummond model in Python i

```
1 # Import array and plotting libraries
2 import numpy
3 import matplotlib.pyplot as plt
4
5 # Function calculating activity of CO2(aq) according to the Drummond model
6 def gamma_drummond_co2(T, I):
7     c1, c2, c3, c4, c5 = -1.0312, 1.2806e-3, 255.9, 0.4445, -1.606e-3
8     return numpy.exp((c1 + c2*T + c3/T)*I - (c4 + c5*T)*I/(1 + I))
9
10 # Create an array with values of ionic strength in a range from 0.0 to 1.0
11 I = numpy.linspace(0.0, 1.0, 101)
12
13 # Define the temperatures for activity calculation
14 T1, T2, T3 = 50, 150, 250 # in celsius
15 # Calculate CO2(aq) activity for Drummond model for selected temperatures (in
16 # Kelvin)
16 gammaT1 = gamma_drummond_co2(T1 + 273.15, I)
```

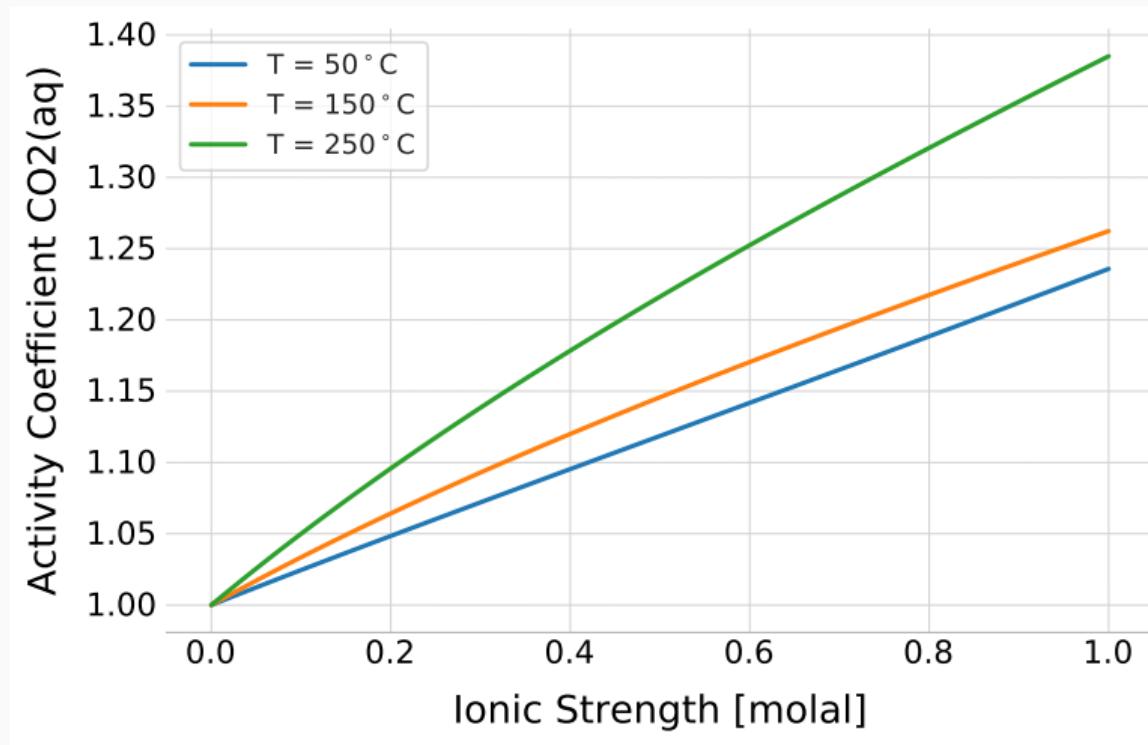
## Calculating CO<sub>2</sub>(aq) activity coefficient using Drummond model in Python ii

```
17 gammaT2 = gamma_drummond_co2(T2 + 273.15, I)
18 gammaT3 = gamma_drummond_co2(T3 + 273.15, I)
19
20 # Plot CO2(aq) activity for Drummond model as a function an ionic strength for
21 # different T
22 plt.xlabel('Ionic Strength [molal]')
23 plt.ylabel('Activity Coefficient CO2(aq)')
24 plt.plot(I, gammaT1, label=r'T = %d^\circ C' % T1)
25 plt.plot(I, gammaT2, label=r'T = %d^\circ C' % T2)
26 plt.plot(I, gammaT3, label=r'T = %d^\circ C' % T3)
27 plt.legend(loc='best')
28 plt.savefig('activity-coefficient-co2-drummond.pdf', bbox_inches='tight')
```

**Listing 9:** Calculating CO<sub>2</sub>(aq) activity coefficient in Python

**Source code:** *activity-coefficient-co2-drummond.py*.

## Activity coefficient model for CO<sub>2</sub>(aq), Drummond model



**Figure 7:** Activity coefficient of CO<sub>2</sub>(aq) calculated using Drummond model at temperatures 50, 150, and 250 °C as a function of ionic strength.

# Salting-out effect

- Consider the dissolution reaction for  $\text{CO}_2(\text{g})$ :



- At equilibrium, the following **mass action equation** is satisfied, i.e.,  $K(T, P) := \frac{a_{\text{CO}_2(\text{aq})}}{a_{\text{CO}_2(\text{g})}}$ .
- Combining  $a_{\text{CO}_2(\text{aq})} = K(T, P) a_{\text{CO}_2(\text{g})}$  and  $a_{\text{CO}_2(\text{aq})} = \gamma_{\text{CO}_2(\text{aq})} m_{\text{CO}_2(\text{aq})}$ , we obtain

$$m_{\text{CO}_2(\text{aq})} = \frac{1}{\gamma_{\text{CO}_2(\text{aq})}} K(T, P) a_{\text{CO}_2(\text{g})}(T, P) \approx \frac{1}{\gamma_{\text{CO}_2(\text{aq})}} f(T, P).$$

- Quiz:** What happens to  $m_{\text{CO}_2(\text{aq})}$  when  $\gamma_{\text{CO}_2(\text{aq})}$  increases with  $I$  for constant  $(T, P)$ ?



<http://etc.ch/paWu> or

- Answer:**  $m_{\text{CO}_2(\text{aq})}$  decrease.

# Summary on the calculation of activities of aqueous species

- The activities of aqueous solute species

$$a_i = \gamma_i m_i.$$

- The molality of the species

$$m_i = 55.508 \frac{n_i}{n_{\text{H}_2\text{O(aq)}}}.$$

- The ionic strength of the aqueous solution

$$I = \frac{1}{2} \sum_i m_i Z_i^2.$$

- The activity coefficient  $\gamma_i$  for ionic species (e.g.,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ , etc.) according to the Davies model:

$$\log_{10} \gamma_i = -A_\gamma Z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right).$$

- The activity coefficient  $\gamma_i$  for  $\text{CO}_2(\text{aq})$  according to the Drummond model:

$$\ln \gamma_i = \left( c_1 + c_2 T + \frac{c_3}{T} \right) I - (c_4 + c_5 T) \frac{I}{I + 1}.$$

- The activity of  $\text{H}_2\text{O(aq)}$  according to the Davies model:

$$\ln a_{\text{H}_2\text{O(aq)}} = -\frac{1 - x_{\text{H}_2\text{O(aq)}}}{x_{\text{H}_2\text{O(aq)}}}.$$

# **Thermodynamic models of aqueous, gaseous, and mineral phases**

---

**Gaseous phase**

## Activities of species in a gaseous solution

- The **activity of gaseous species  $i$**  can be calculated using:

$$a_i = \varphi_i x_i \frac{P}{P^o},$$

where

- $\varphi_i$  is the **fugacity coefficient** of the gaseous species,
- $x_i$  is the **mole fraction** of the gaseous species,
- $P$  is pressure (in units of bar, with  $1\text{ bar} = 10^5\text{ Pa}$ ), and
- $P^o$  is a reference pressure,  $P^o = 1\text{ bar}$ .

- The **fugacity coefficients of ideal gases** are  $\varphi_i = 1$ . **But:** the gases rarely behave ideal.

## Activity of CO<sub>2</sub>(g) using a cubic equation of state

- An **ideal gas** solution has **a PVT behavior** defined by the equation:

$$\frac{PV}{RT} = 1,$$

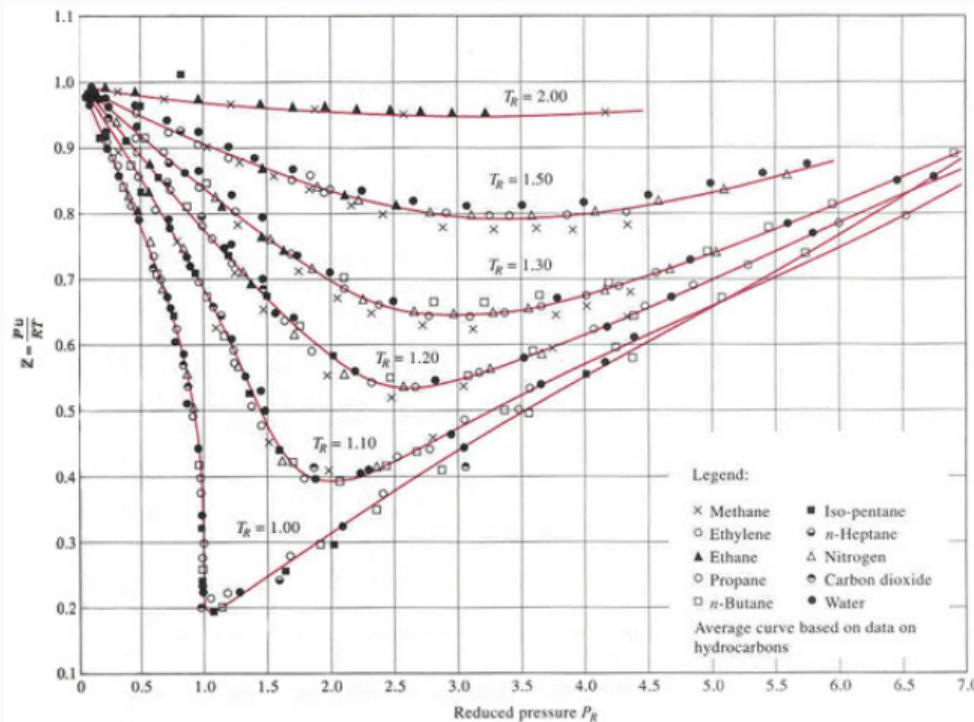
where  $P$  is pressure (in units of Pa),  $T$  is temperature (in units of K),  $V$  is molar volume (in units of m<sup>3</sup>/mol), and  $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$ .

- For **real gases**, we introduce a **compressibility factor**  $Z$  defined as

$$Z = \frac{PV}{RT} < 1.$$

- For **real gases**,  $Z \rightarrow 1$  only when
  - temperatures are very high or
  - pressures are very low.

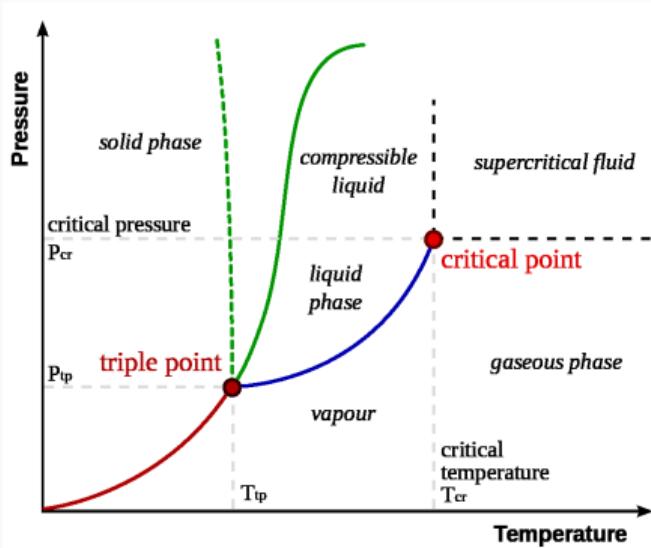
# Compressibility factor of gases i



**Figure 8:** The compressibility factor  $Z$  as a function of reduced pressure  $P_R = P/P_{\text{critical}}$  for several reduced temperatures  $T_R = T/T_{\text{critical}}$  (Cengel and Boles, 2011).

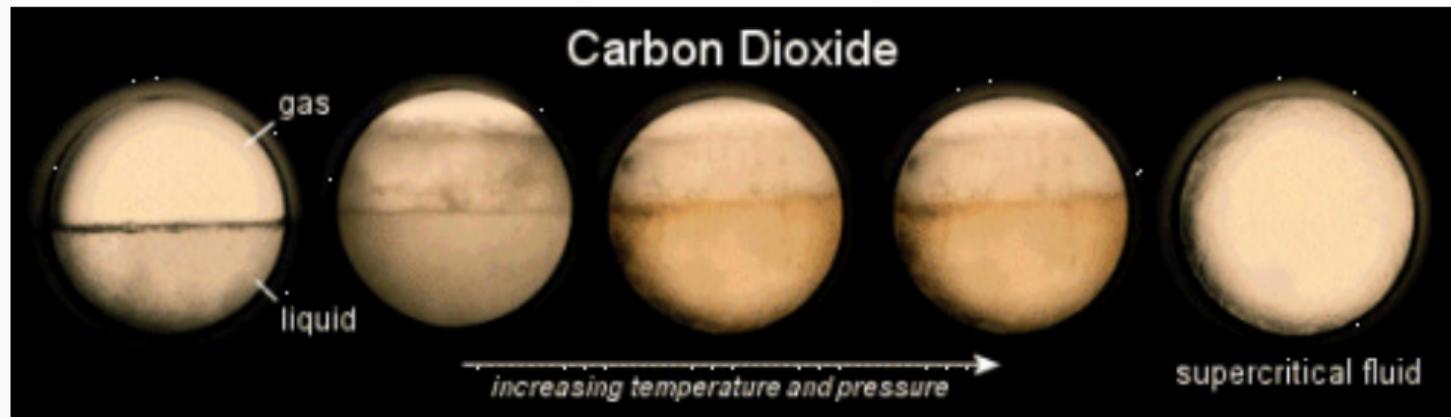
## Compressibility factor of gases ii

- Different gases have similar thermodynamic behavior when  $T$  and  $P$  are normalized by their critical values  $T_{\text{critical}}$  and  $P_{\text{critical}}$ , respectively.
- This allows us to use **single equation of state** to model the  $PVT$  behavior of a gas.



**Figure 9:** A typical phase diagram of a substance. The critical point is the limit point in the liquid-vapor saturation curve.

## Supercritical carbon dioxide $\text{CO}_2(\text{g})$



**Figure 10:**  $\text{CO}_2$  initially existing in two phases: liquid and gas. As temperature and pressure increase, it transitions to a state in which there is only one phase in the **supercritical state**.

- As a **supercritical fluid**, the substance flows like a gas (less viscous than liquid) and is dense like a liquid.
- In geologic  $\text{CO}_2$  sequestration, the supercritical state is more advantageous because of its **high mobility and high density**.

## Cubic equation of state

- A **general cubic equation of state** can be written in terms of  $Z$  (Smith et al., 2005) as

$$1 = \frac{1}{Z - \beta} - q\beta \frac{1}{(Z + \epsilon\beta)(Z + \sigma\beta)},$$

where

- $\epsilon$  and  $\sigma$  are pure numbers (same for all substances),
- $\beta$  and  $q$  are parameters specific to substances and defined as

$$\beta = \Omega \frac{P_r}{T_r} \quad \text{and} \quad q = \frac{\Psi}{\Omega} \frac{\alpha(T_r, \omega)}{T_r}$$

with specific to a **particular equation of state**  $\Omega$ ,  $\Psi$ , and  $\alpha(T)$ ,

- the **reduced temperature and pressure**  $T_r = \frac{T}{T_c}$  and  $P_r = \frac{P}{P_c}$  are defined via **critical temperature and pressure**  $T_c$  and  $P_c$ , and
- $\omega$  is a **acentric factor** that depends on the substance.

- **Note:** For CO<sub>2</sub>(g),  $T_c = 304.2$  K,  $P_c = 73.83$  bar,  $\omega = 0.224$ .

## Cubic equation of state, Different models i

Equation of State	$\epsilon$	$\sigma$	$\Omega$	$\Psi$
Ideal Gas	0	0	0	0
van der Waals (vdW) <sup>1</sup> (1873)	0	0	1/8	27/64
Redlich/Kwong (RK) <sup>2</sup> (1949)	0	1	0.08664	0.42748
Soave/Redlich/Kwong (SRK) <sup>3</sup> (1972)	0	1	0.08664	0.42748
<b>Peng/Robinson (PR)<sup>4</sup> (1976)</b>	$1 - \sqrt{2}$	$1 + \sqrt{2}$	<b>0.07780</b>	<b>0.45724</b>

<sup>1</sup>van der Waals (1873); <sup>2</sup>Redlich & Kwong (1949); <sup>3</sup>Soave (1972), commonly known as Soave–Redlich–Kwong;

<sup>4</sup>Peng & Robinson (1976).

**Table 1:** The parameters  $\epsilon$ ,  $\sigma$ ,  $\Omega$ , and  $\Psi$  for different equation of states.

## Activity of CO<sub>2</sub>(g) using a cubic equation of state iii

Equation of State	$\alpha(T_r, \omega)$
Ideal Gas	0
van der Waals (vdW) <sup>1</sup> (1873)	1
Redlich/Kwong (RK) <sup>2</sup> (1949)	$T_r^{-1/2}$
Soave/Redlich/Kwong (SRK) <sup>3</sup> (1972)	$\left[1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})\right]^2$
<b>Peng/Robinson (PR)</b> <sup>4</sup> (1976)	$\left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{1/2})\right]^2$

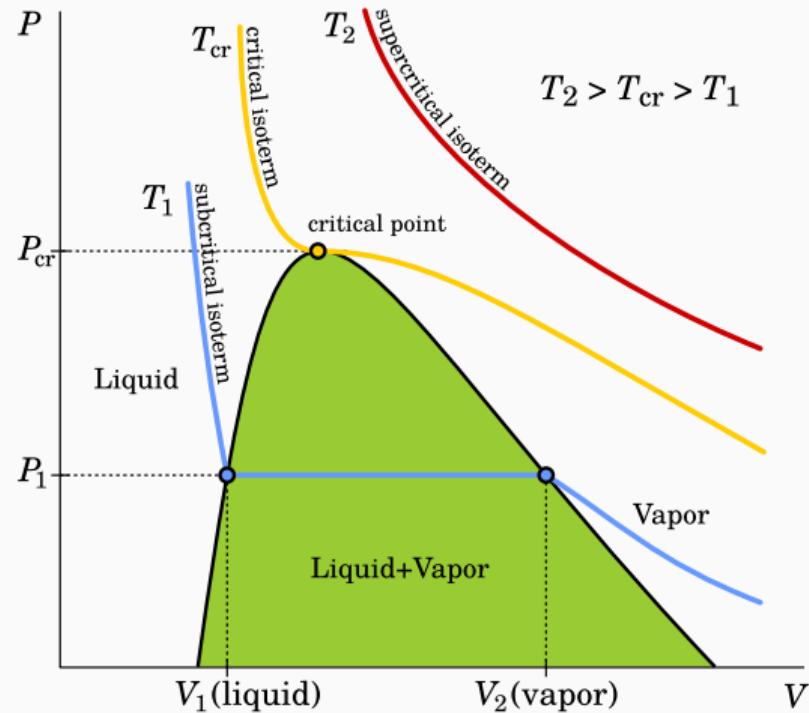
<sup>1</sup>van der Waals (1873); <sup>2</sup>Redlich & Kwong (1949); <sup>3</sup>Soave (1972), commonly known as Soave–Redlich–Kwong;

<sup>4</sup>Peng & Robinson (1976).

**Table 2:** The function  $\alpha(T_r, \omega)$  for different equations of state.

# PV phase diagram with isotherms

- The area in **green** is a region in which **liquid and vapour coexist**.
- There are three **isotherms**: **subcritical**, **critical**, and **supercritical**.
- The horizontal **blue segment** corresponds to the fluid change from liquid to vapour at a constant  $T$  and  $P$ .



**Figure 11:** Illustration of a  $PV$  phase diagram of a substance.

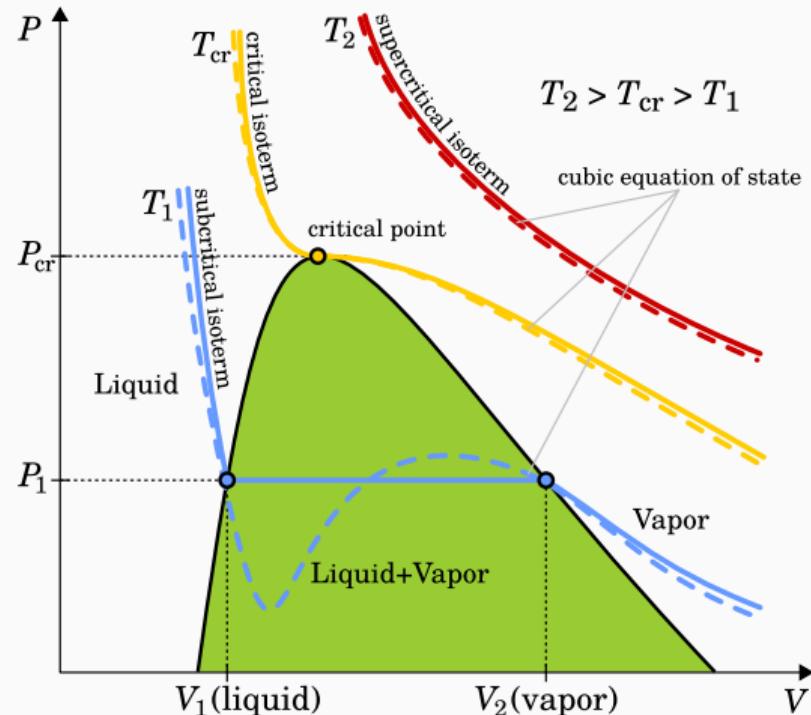
## PV phase diagram with isotherms, Roots of cubic EOS i

- Because we are modeling the *PVT* behavior of a substance using a **cubic equation of state**:

$$Z^3 + AZ^2 + BZ + C = 0,$$

where  $Z = \frac{PV}{RT}$  is compressibility factor, “spurious” behavior can happen as shown on the next figure.

- This equation of state has **utmost three roots**.

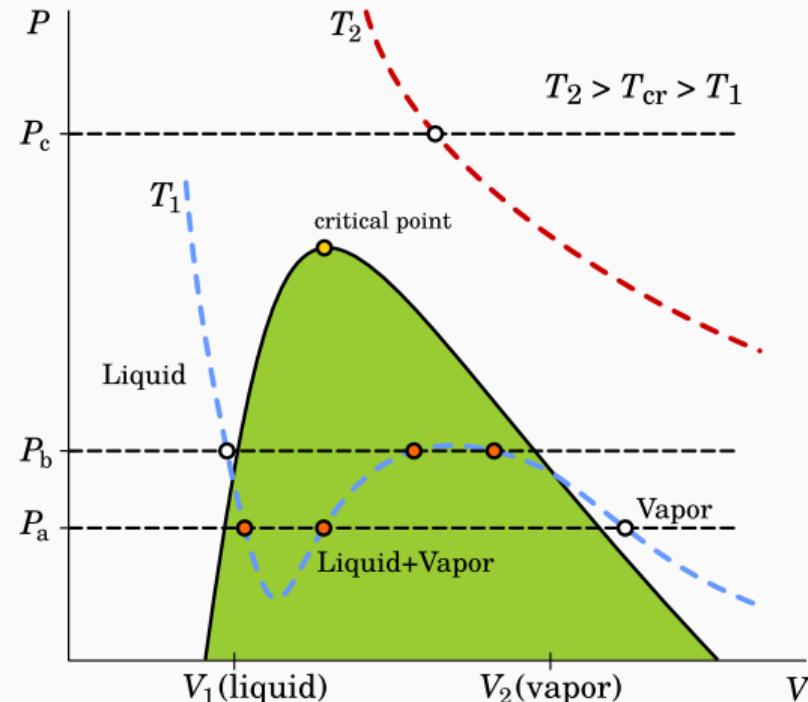


**Figure 12:** Illustration of a *PV* phase diagram of a substance.

## PV phase diagram with isotherms, Roots of cubic EOS ii

- When three real roots exists for cubic equation of state
  - the **smallest real value** possibly corresponds to the **liquid state** and
  - the **largest real value** possibly corresponds to the **gaseous state**.
- Any root inside the green region is a **mathematical artefact** of the cubic model.
- Quiz:** Which value of  $Z$  are we interested in for  $\text{CO}_2(\text{g})$ ?

<http://etc.ch/paWu> or



**Figure 13:** Illustration of a  $PV$  phase diagram of a substance with roots of cubic equation of state.

## Calculating the compressibility factor of CO<sub>2</sub>, Fixed point iteration

- The equation of state is non-linear in  $Z$ , so that its solution requires an **iterative procedure**.
- We rearrange it to a more convenient form for **the largest root** computation (Smith et al., 2005)

$$Z = f(Z) = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

and apply simplest iterative approach, the so-called **fixed-point iteration method**:

- the **initial guess**

$$Z^0 = 1,$$

- the  $i^{\text{th}}$  **iteration**

$$Z^{i+1} = f(Z^i) = 1 + \beta - q\beta \frac{Z^i - \beta}{(Z^i + \epsilon\beta)(Z^i + \sigma\beta)},$$

- the **acceptance criterion**  $|Z^{i+1} - Z^i| < \varepsilon$ , where  $\varepsilon$  is selected tolerance.

## Calculating the compressibility factor of CO<sub>2</sub>, Python code i

```
1 from numpy import *
2 import matplotlib.pyplot as plt
3
4 # Function that calculates the fixed point of equation x = f(x)
5 def fixed_point(f, x0):
6     """
7         :param f: the function
8         :param x0: the initial guess for the fixed point
9         :return x: the fixed point of the equation x = f(x)
10    """
11
12    # Tolerance and max number of iterations
13    maxiters = 100
14    tolerance = 1e-4
15
16    # Counter for the number of iterations
17    counter = 0
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code ii

```
18
19     # Initial guess
20     x = x0
21
22     # Perform one or more fixed point iterations
23     for counter in range(maxiters):
24
25         # Calculate the new approximation for x
26         x_new = f(x)
27
28         # Check the new value for convergence
29         if abs(x_new - x) < tolerance:
30             return x # return x if the calculation converged
31
32         # Update x with x_new
33         x = x_new
34
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code iii

```
35     # Raise an error if the calculation did not converge.
36     raise RuntimeError('Could not calculate the \
37         solution of the nonlinear equation in %d iterations.' % counter)
38
39 # Function to calculate Z using fixed point method
40 def compressibility_factor_fixedpoint(T, P, omega, Tc, Pc):
41     """
42     :param T: temperature
43     :param P: pressure
44     :param omega: the acentric factor
45     :param Tc: critical temperature
46     :param Pc: critical pressure
47     :return Z: compressibility factor
48     """
49
50     # Parameters of Peng-Robinson EOS
51     epsilon = 1 - sqrt(2.0)
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code iv

```
52     sigma = 1 + sqrt(2.0)
53     Omega = 0.07780
54     Psi = 0.45724
55
56     # Reduced temperature and pressure
57     Tr = T / Tc
58     Pr = P / Pc
59
60     # Evaluation of the alpha(Tr, omega) function
61     alpha = (1 + (0.37464 + 1.54226 * omega - 0.26992 * omega**2) * (1 - sqrt(
62     Tr)))**2
63
64     # Contants beta and q
65     beta = Omega * Pr/Tr
66     q = Psi/Omega * alpha/Tr
67
68     # Initial guess for Z
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code v

```
68     Z0 = 1.0
69
70     # Define the function f that represents the nonlinear equation x = f(x)
71     def f(Z):
72         return (1 + beta - q*beta*(Z - beta)/((Z + epsilon*beta)*(Z + sigma*
73             beta)))
74
75         return fixed_point(f, Z0) # use fixed point function to perform the
76         calculation of Z
77
78 # The array with temperature values in K
79 temperatures = linspace(60.0, 300.0, 9) + 273.15
80
81 # The array with pressure values in bar
82 pressures = linspace(1.0, 400.0, 101)
83
84 # The critical temperature and pressure of CO2
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code vi

```
83 TcCO2 = 304.2
84 PcCO2 = 73.83
85
86 # The acentric factor of CO2
87 omegaCO2 = 0.224
88
89 # Create a plot
90 plt.xlabel('Pressure [bar]')
91 plt.ylabel(r'$Z = \frac{PV}{RT}$')
92 plt.ylim(0.05, 1.05)
93 plt.title('Compressibility Factor of CO2(g)\nUsing Fixed Point Method')
94
95 # Plot one curve for each temperature in array temperatures
96 for T in reversed(temperatures):
97     # Create a list with Z values at current T and P from the array pressures
98     Z = [compressibility_factor_fixedpoint(T, P, omegaCO2, TcCO2, PcCO2) for P
99         in pressures]
```

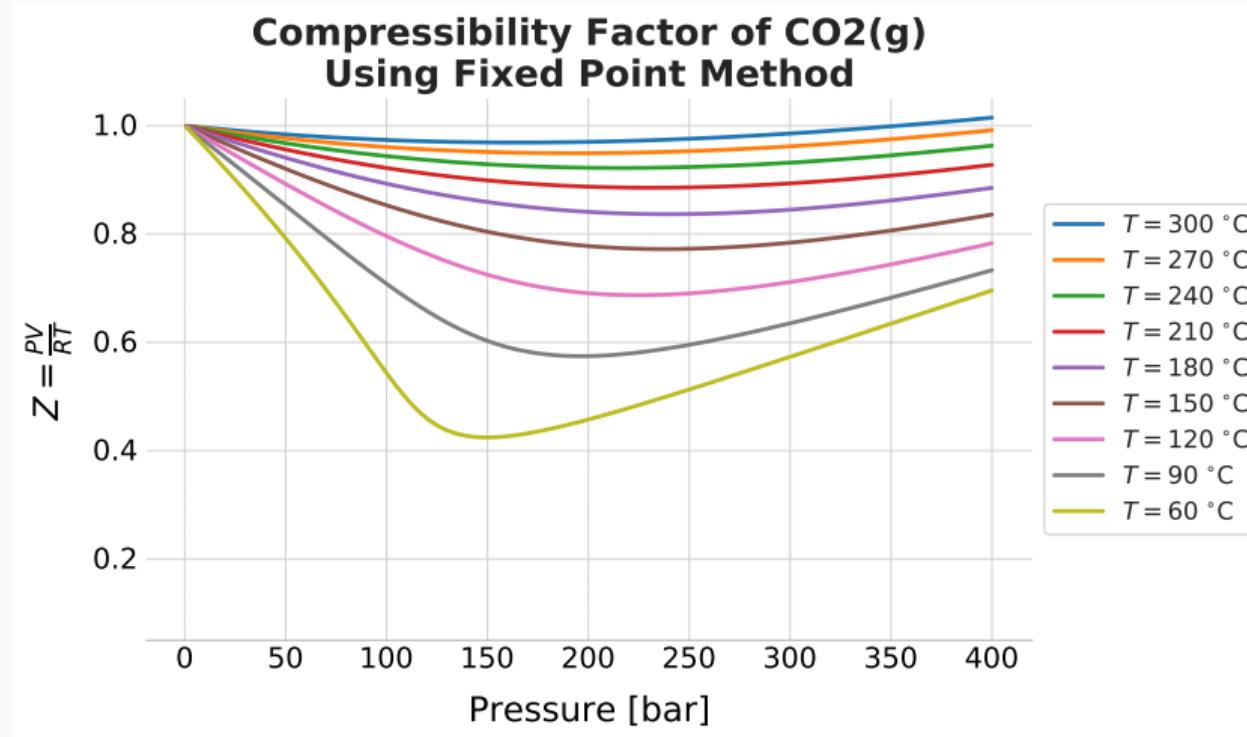
## Calculating the compressibility factor of CO<sub>2</sub>, Python code vii

```
99      # Plot the values of Z over all pressure points and current temperature T
100     plt.plot(pressures, Z, label=r'$T=%.\mathbf{0f}^{\circ}\mathrm{C}$' % (T -
101           273.15))
102     # Position the legend and save the figure
103     plt.legend(loc='center left', bbox_to_anchor=(1, 0.5))
104     plt.savefig('co2-compressibility-factor-fixed-point.pdf', bbox_inches='tight')
```

**Listing 10:** Calculating the compressibility factor of CO<sub>2</sub> using fixed point method in Python

Source code: *co2-compressibility-factor-fixed-point.py*.

# Calculating the compressibility factor of CO<sub>2</sub>, Fixed point iteration i



**Figure 14:** The compressibility factor  $Z$  of CO<sub>2</sub> for temperatures 60–300 °C and 1–400 bar calculated using fixed point iteration method.

# Calculating the compressibility factor of CO<sub>2</sub>, Fixed point iteration ii

- Disadvantages of the fixed point method:
  - slow, requiring many iterations; and
  - unstable, failing to converge.
- The fixed point method failed at regions close to the liquid-vapor saturation curve, for temperatures below  $T_{cr} = 31.04^{\circ}\text{C}$  and pressures close to the saturation pressure (i.e., near the blue curve).
- This is due to discontinuity of derivative in the function of Z at  $T = T_{cr}$ , whereas fixed point requires its **continuity**.
- **Solution:** Newton's method.

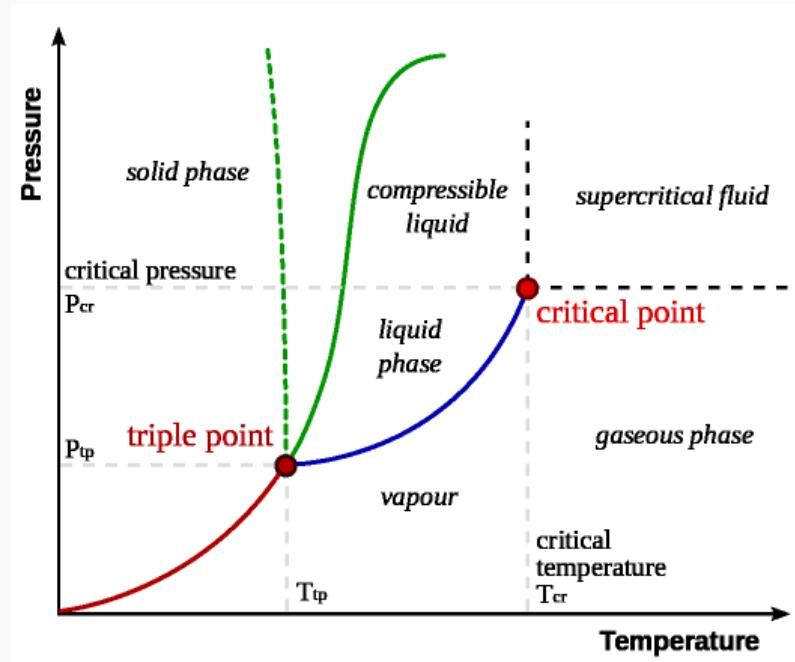
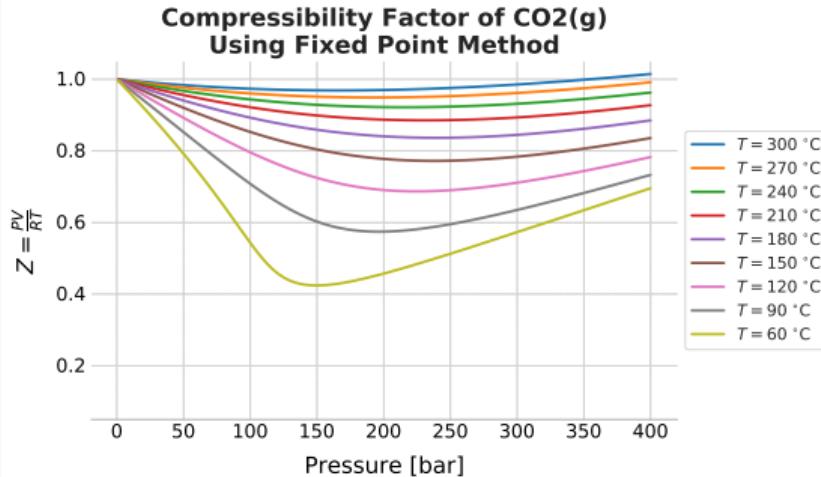
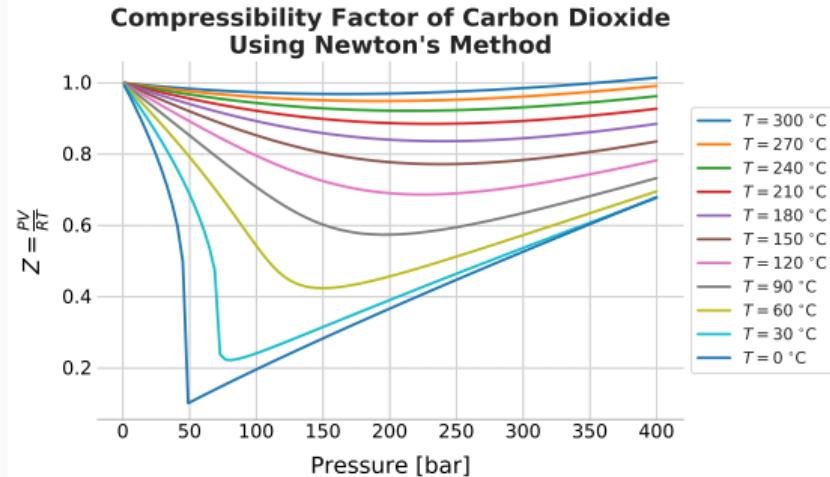


Figure 15: The phase diagram of a substance.

# Compressibility factor of CO<sub>2</sub>, Newton vs. Fixed point method



**Figure 16:** The compressibility factor  $Z$  of CO<sub>2</sub> for temperatures 60–300 °C and 1–400 bar using **fixed point iteration method**. Failed computations for temperatures 0 and 30 °C!



**Figure 17:** The compressibility factor  $Z$  of CO<sub>2</sub> for temperatures 0–300 °C and 1–400 bar using **Newton's method**. Newton's method had no trouble for temperatures 0 and 30 °C!

## Calculating the compressibility factor of CO<sub>2</sub>, Newton's method

- In **Newton's method**, we transform the non-linear equation  $Z = 1 + \beta - q\beta \frac{Z-\beta}{(Z+\epsilon\beta)(Z+\sigma\beta)}$  into the form  $r(Z) = 0$ , where  $r$  is the **residual function**

$$r(Z) = f(Z) - Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} - Z.$$

- Newton's method requires **first order derivative** of  $r(Z)$  in its iterative process:
  - the **initial guess**

$$Z^0 = 1,$$

- $i^{\text{th}}$  **iteration**

$$Z^{i+1} = Z^i - r(Z^i)/r'(Z^i),$$

where

$$r'(Z) = -\frac{q\beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \left\{ 1 - (Z - \beta) \frac{2Z + (\epsilon + \sigma)\beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \right\} - 1,$$

- and **acceptance criterion**  $|r(Z^{i+1})| < \varepsilon$ , where  $\varepsilon$  is selected tolerance.

## Calculating the compressibility factor of CO<sub>2</sub>, Python code i

```
1 from numpy import *
2 import matplotlib.pyplot as plt
3
4 # Function that solves the nonlinear equation r(x) = 0
5 def newton(r, rprime, x0):
6     """
7         :param r: the function
8         :param rprime: the first derivative of f
9         :param x0: the initial guess for the root
10        :return x: the root of the equation f(x) = 0
11    """
12
13    # Tolerance and max number of iterations
14    maxiters = 100
15    tolerance = 1e-4
16
17    # Counter for the number of iterations
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code ii

```
18     counter = 0
19
20     # Initial guess
21     x = x0
22
23     # Perform one or more Newton iterations
24     for counter in range(maxiters):
25
26         # Calculate the new approximation for x
27         x = x - r(x) / rprime(x)
28
29         # Check the new value for convergence
30         if abs(r(x)) < tolerance:
31             return x # return x if the calculation converged
32
33     # Raise an error if the calculation did not converge.
34     raise RuntimeError('Could not calculate the \\\'
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code iii

```
35         solution of the nonlinear equation in %d iterations.' % counter)
36
37 # Function to calculate Z using Newton's method
38 def compressibility_factor_newton(T, P, omega, Tc, Pc):
39     """
40     :param T: temperature
41     :param P: pressure
42     :param omega: the acentric factor
43     :param Tc: critical temperature
44     :param Pc: critical pressure
45     :return Z: compressibility factor
46     """
47
48     # Parameters of Peng-Robinson EOS
49     epsilon = 1 - sqrt(2.0)
50     sigma = 1 + sqrt(2.0)
51     Omega = 0.07780
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code iv

```
52     Psi = 0.45724
53
54     # Reduced temperature and pressure
55     Tr = T / Tc
56     Pr = P / Pc
57
58     # Evaluation of the alpha(Tr, omega) function
59     alpha = (1 + (0.37464 + 1.54226*omega - 0.26992*omega**2)*(1 - sqrt(Tr)))
60             **2
61
62     # Contants beta and q
63     beta = Omega * Pr / Tr
64     q = Psi/Omega * alpha/Tr
65
66     # Residual function r that represents the nonlinear equation r(x) = 0
def r(Z):
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code v

```
67         return (1 + beta - q*beta*(Z - beta)/((Z + epsilon*beta)*(Z + sigma*  
68 beta))) - Z  
69  
70     # First order derivative of function r'(x)  
71     def rprime(Z):  
72         aux = (Z + epsilon*beta)*(Z + sigma*beta)  
73         return -q*beta/aux * (1.0 - (Z - beta)*(2*Z + (epsilon + sigma)*beta)/  
74 aux) - 1  
75  
76     # Initial guess for Z  
77     Z0 = 1.0  
78  
79     return newton(r, rprime, Z0) # use newton function to perform the  
80 # calculation of Z  
81  
82 # The array with temperature values in K  
83 temperatures = linspace(0.0, 300.0, 11) + 273.15
```

## Calculating the compressibility factor of CO<sub>2</sub>, Python code vi

```
81
82 # The array with pressure values in bar
83 pressures = linspace(1.0, 400.0, 101)
84
85 # The critical temperature and pressure of CO2
86 TcCO2 = 304.2
87 PcCO2 = 73.83
88
89 # The acentric factor of CO2
90 omegaCO2 = 0.224
91
92 # Create a plot
93 plt.xlabel('Pressure [bar]')
94 plt.ylabel(r'$Z = \frac{PV}{RT}$')
95 plt.title('Compressibility Factor of Carbon Dioxide\nUsing Newton\'s Method')
96
97 # Plot one curve for each temperature in array temperatures
```

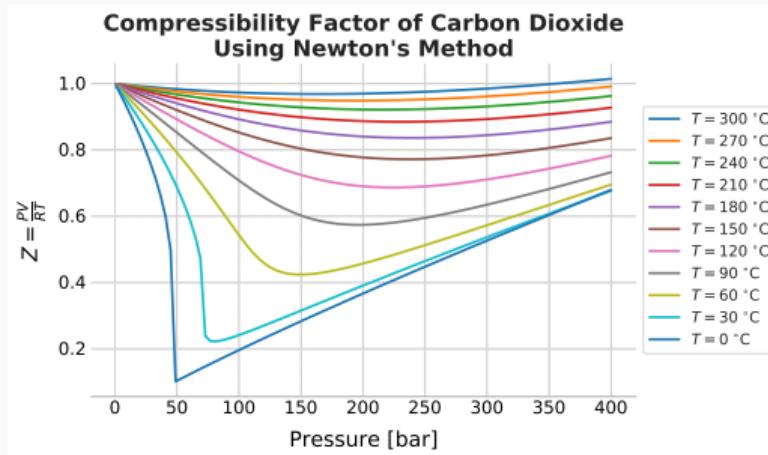
## Calculating the compressibility factor of CO<sub>2</sub>, Python code vii

```
98 for T in reversed(temperatures):
99     # Create a list with Z values at current T and P from the array pressures
100    Z = [compressibility_factor_newton(T, P, omegaCO2, TcCO2, PcCO2) for P in
101        pressures]
102    # Plot the values of Z over all pressure points and current temperature T
103    plt.plot(pressures, Z, label=r'$T=%.\mathfrak{0f}\circ\mathrm{C}$' % (T -
104        273.15))
105
106    # Position the legend and save the figure
107    plt.legend(loc='center left', bbox_to_anchor=(1, 0.5))
108    plt.savefig('co2-compressibility-factor-newton.pdf', bbox_inches='tight')
```

**Listing 11:** Calculating the compressibility factor of CO<sub>2</sub> using Newton's method in Python

Source code: [polybox](#).

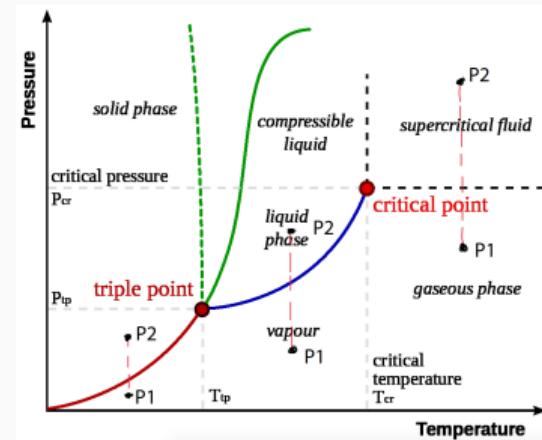
# Calculating the compressibility factor of CO<sub>2</sub>, Newton's method



**Figure 18:** For  $T < T_{\text{cr}}(\text{CO}_2) = 31.04 \text{ }^\circ\text{C}$ , the increase in pressure results in a phase transition from vapor to liquid.

**Quiz:** To which part of the phase diagram does the blue lines correspond to, if we are increasing P1 to P2?

**Answer:** to the middle.



**Figure 19:** The phase diagram of a substance.  $T_{\text{cr}}(\text{CO}_2) = 31.04 \text{ }^\circ\text{C}$ .



## Activity of CO<sub>2</sub>(g) using a cubic equation of state

- Once  $Z$  is calculated, the **fugacity coefficient of the gas** is computed using:

$$\ln \varphi_i := Z - 1 - \ln(Z - \beta) - q\theta,$$

where  $\theta$  is defined as:

$$\theta := \begin{cases} \frac{1}{\sigma - \epsilon} \ln \left( \frac{Z + \sigma\beta}{Z + \epsilon\beta} \right) & \epsilon \neq \sigma \\ \frac{\beta}{Z + \epsilon\beta} & \epsilon = \sigma \end{cases}$$

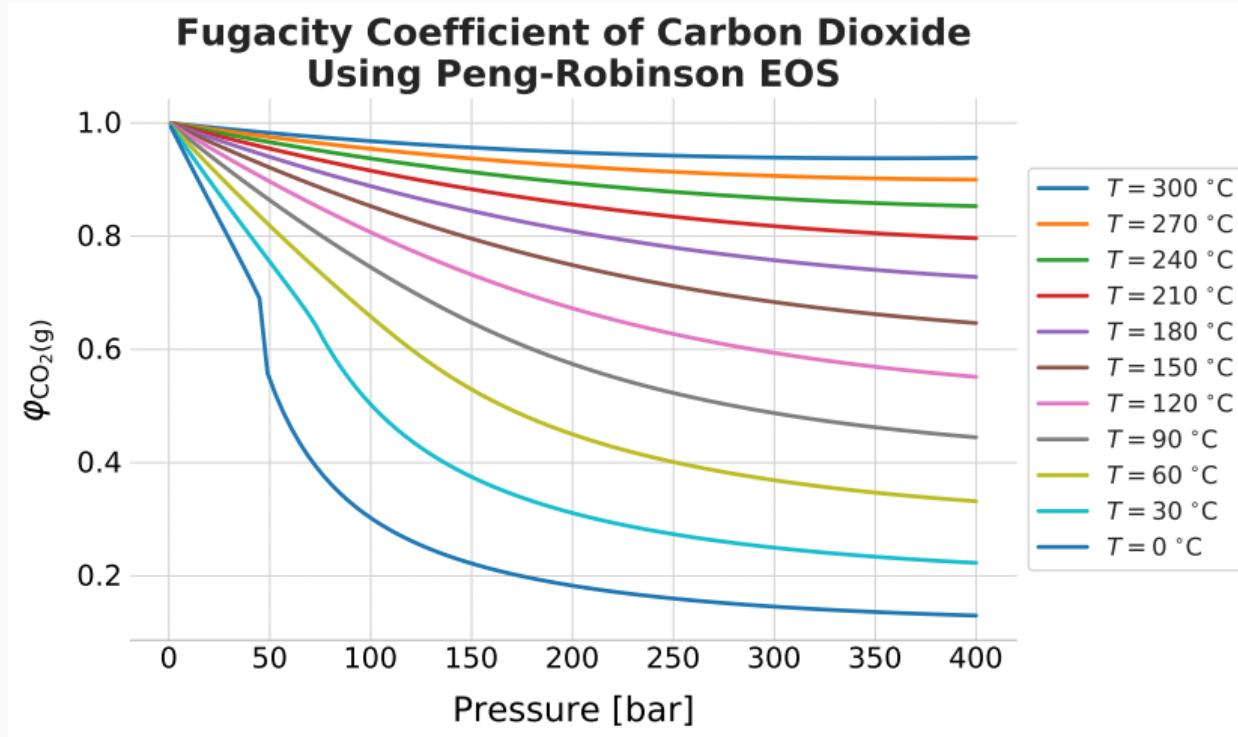
dependent on the equation of state.

- The **activity of CO<sub>2</sub>(g)** is calculated using:

$$a_{\text{CO}_2(\text{g})} = \varphi_{\text{CO}_2(\text{g})} \frac{P}{P^o},$$

with  $P$  measured in bar and  $P^o = 1$  bar.

## Fugacity coefficient of CO<sub>2</sub> following the calculation of Z



**Figure 20:** The fugacity coefficient of CO<sub>2</sub> using Peng–Robinson equation of state (EOS) for temperatures 0–300 °C and 1–400 bar.

## Summary on the calculation of activities of gaseous species

- The activities of gaseous species:

$$a_i = \frac{\varphi_i x_i P}{P^o}.$$

- The compressibility factor

$$Z = \frac{PV}{RT} < 1$$

- The fugacity coefficient of the CO<sub>2</sub>(g):

$$\ln \varphi_i = Z - 1 - \ln(Z - \beta) - q\theta$$

with  $Z \equiv 1$  **only** when the substance is an **ideal gas**.

- Calculation of  $Z$  requires the solution of the **cubic equation of state**

$$Z = \frac{Z}{Z - \beta} - q\beta \frac{Z}{(Z + \epsilon\beta)(Z + \sigma\beta)}$$

by *fixed point method* or *Newton's method*.

# **Thermodynamic models of aqueous, gaseous, and mineral phases**

---

**Mineral phase**

## Summary on the calculation of activities of mineral species

- The activities of pure minerals (e.g., mineral phases composed by a single mineral only) is

$$a_i = 1.$$

## **Numerical method for chemical equilibrium calculation**

---

# Recap of a chemical equilibrium problem

- Calculate the amounts of the species in each phase at equilibrium at given:
  - **temperature** (e.g., 100 °C);
  - **pressure** (e.g, 300 bar); and
  - **amounts of elements H, O, C, Na, Cl**
  - **Note:** the latter is rather given as a recipe that determine the values of H, O, C, Na, Cl by formula matrix  $b = A \cdot n$ , e.g.,
    - 1 kg of  $\text{H}_2\text{O}$ ,
    - 1 mol  $\text{CO}_2$ ,
    - 0.1 mol of NaCl.

Aqueous Phase	Gaseous Phase	Mineral Phases
$\text{H}_2\text{O}(\text{aq})$	$\text{CO}_2(\text{g})$	$\text{NaCl}(\text{s, halite})$
$\text{H}^+(\text{aq})$	$\text{H}_2\text{O}(\text{g})$	
$\text{OH}^-(\text{aq})$		
$\text{Na}^+(\text{aq})$		
$\text{Cl}^-(\text{aq})$		
$\text{CO}_2(\text{aq})$		
$\text{HCO}_3^-(\text{aq})$		
$\text{CO}_3^{2-}(\text{aq})$		

# Chemical equilibrium equations, Fundamental condition

Fundamental condition for chemical equilibrium reads as follows:

## Gibbs energy minimization (GEM) problem

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

$$\min_n G(n) \quad \text{subject to (s.t.)} \quad An = b \quad \text{and} \quad n \geq 0.$$

How do we transform it into a system of equations from which species amounts  $n = (n_1, \dots, n_N)$  can be calculated?

# **Numerical method for chemical equilibrium calculation**

---

**Unconstrained minimization**

## Chemical equilibrium equations, Finding the minimum

- Assume there were **no constraints** of mass conservation and non-negative bounds.
- Then, the **chemical equilibrium equations** would result from the condition

$$\frac{\partial G}{\partial n_i} = 0 \quad (i = 1, \dots, N),$$

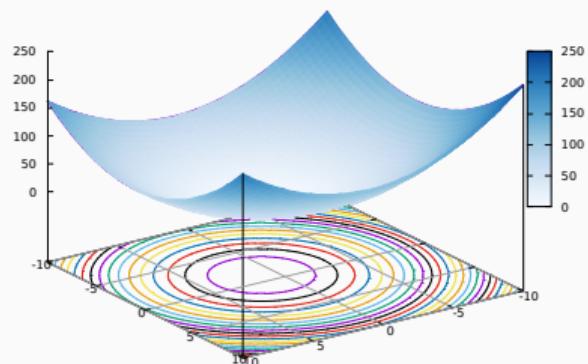
which corresponds to a state in which the **Gibbs energy does not change with infinitesimal changes in the amounts of the species**.

- **But!** some care would still be needed to ensure that a **minimum is found**, and not a **maximum or saddle point**.

## Example of finding the minimum

- Consider the function  $f$  defined as:

$$f(x, y) = (x - 1)^2 + (y + 1)^2.$$



- The values of  $(x, y)$  that minimizes  $f$  can be found using:

$$\frac{\partial f}{\partial x} = 0 \implies 2(x - 1) = 0 \implies x = 1$$

$$\frac{\partial f}{\partial y} = 0 \implies 2(y + 1) = 0 \implies y = -1.$$

- Question:** How can we tell, mathematically, that the solution above corresponds to a minimum?



<http://etc.ch/cKvh> or

- Answer:** Check if the derivatives  $\partial^2 f / \partial x^2$  and  $\partial^2 f / \partial y^2$  at  $(1, -1)$  are non-negative.

## Distinguishing between minimum, maximum, saddle point values

- In general, one checks the **eigenvalues of Hessian matrix**

$$H = \begin{bmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} \end{bmatrix}$$

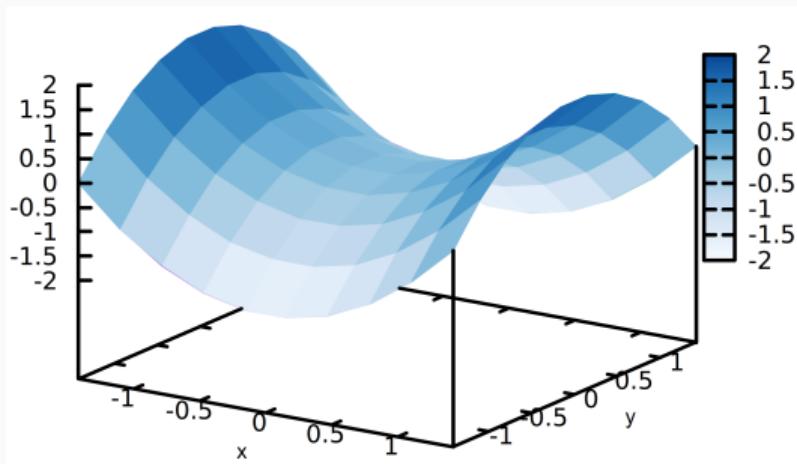
at obtained stationary point  $(x_*, y_*)$ .

- If the eigenvalues are **non-negative** at the  $(x_*, y_*)$  (or Hessian is a positive semi-definite matrix at  $(x_*, y_*)$ ), this point is indeed a **local minimum**.
- If the eigenvalues are **negative** at the  $(x_*, y_*)$  (or Hessian is negative-definite at  $(x_*, y_*)$ ), this point is a **local maximum**.
- If the eigenvalues are of different signs at the  $(x_*, y_*)$ , this point is a **saddle point**.

## Example of saddle point problem

- Consider the function  $f$  defined as:

$$f(x, y) = x^2 - y^2.$$



- At  $(x, y) = (0, 0)$ :

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = 0,$$

but  $f(0, 0) = 0$  is **neither a minimum nor a maximum**.

- Quiz:** What are the signs of  $\partial^2 f / \partial x^2$  and  $\partial^2 f / \partial y^2$  for this example?

<http://etc.ch/cKvh> or



- Answer:** The values of  $\partial^2 f / \partial x^2 > 0$  and  $\partial^2 f / \partial y^2 < 0$  at  $(0, 0)$ , which implies a **saddle point**.

# **Numerical method for chemical equilibrium calculation**

---

**Constrained minimization**

## Lagrangian function of chemical equilibrium problem

- Because of the **mass conservation constraints**,  $An = b$ , and the **non-negative constraints**,  $n \geq 0$ , we need to write the **Lagrange function**  $L$  for the Gibbs energy minimization problem:

$$L(n, y, z) := G(n) - (An - b)^T y - n^T z,$$

where the **unknowns**  $n$ ,  $y$ , and  $z$  correspond to

- the vector of *species amounts*  $n = (n_1, \dots, n_N)$ ,
- the vector of *Lagrange multipliers*  $y = (y_1, \dots, y_E)$ , and
- the vector of *complementary variables*  $z = (z_1, \dots, z_N)$  that satisfy

$$n_i z_i = 0, \quad n_i \geq 0, \quad z_i \geq 0.$$

- Note:** The above form of the Lagrangian function is called **matrix form** but one can write it explicitly for each unknown  $n_i$ ,  $y_j$ , and  $z_i$ .

## System of equation corresponding to minimization of Lagrangian

- Instead of finding **only**  $n = (n_1, \dots, n_N)$  that solves

$$\frac{\partial G}{\partial n_i} = 0 \quad (i = 1, \dots, N),$$

we find  $n = (n_1, \dots, n_N)$ ,  $y = (y_1, \dots, y_E)$ , and  $z = (z_1, \dots, z_N)$  that solves

$$\frac{\partial L}{\partial n_i} = 0 \quad (i = 1, \dots, N),$$

$$\frac{\partial L}{\partial y_j} = 0 \quad (j = 1, \dots, E),$$

$$n_i z_i = 0 \quad (i = 1, \dots, N),$$

$$n_i, z_i \geq 0 \quad (i = 1, \dots, N).$$

## System of equation corresponding to minimization of Lagrangian ii

We rewrite the system of equations

using the definition of  $\mu_i := \partial G / \partial n_i$ :

$$\frac{\partial L}{\partial n_i} = 0 \quad (i = 1, \dots, N),$$

$$\mu_i - \sum_{j=1}^E A_{ji} y_j - z_i = 0 \quad (i = 1, \dots, N),$$

$$\frac{\partial L}{\partial y_j} = 0 \quad (j = 1, \dots, E),$$

$$\sum_{i=1}^N A_{ji} n_i - b_j = 0 \quad (j = 1, \dots, E),$$

$$n_i z_i = 0 \quad (i = 1, \dots, N),$$

$$n_i z_i = 0 \quad (i = 1, \dots, N),$$

$$n_i, z_i \geq 0 \quad (i = 1, \dots, N),$$

$$n_i, z_i \geq 0 \quad (i = 1, \dots, N).$$

**Note:** Since  $\mu_i$  is a function of unknown  $n_i$ , we obtain **non-linear system of equation**.

## **Interior-point method for constrained minimization**

---

# Abstract constrained minimization formulation

- Solve the following general **constrained minimization problem**:

$$\min_x f(x) \quad \text{subject to} \quad Ax = b \quad \text{and} \quad x \geq 0.$$

- Quiz:** What would be  $f(x)$  and  $x$  in a context of chemical equilibrium problem?



<http://etc.ch/cKvh> or

- Answer:** We will define  $f$  as our Gibbs energy function

$$f(x) = G(x; T, P),$$

where

- $x = (x_1, \dots, x_n)$  represents the **unknown species amounts**,  $n = (n_1, \dots, n_N)$ ,
- $A$  specifies the **formula matrix of the system**, and
- $b$  stands for the **vector of element amounts**.

## Lagrangian of general minimization formulation

- First, we write the **Lagrange function for the general minimization problem**:

$$L(x, y, z) = f(x) - (Ax - b)^T y - x^T z.$$

- Then, we formulate its **first-order necessary conditions for the minimum**:

$$\partial f / \partial x - A^T y - z = 0,$$

$$Ax - b = 0,$$

$$x_i z_i = 0 \quad (i = 1, \dots, n),$$

$$x_i, z_i \geq 0 \quad (i = 1, \dots, n).$$

## Complementarity conditions

- The **complementarity conditions**

$$x_i z_i = 0$$

$$x_i \geq 0$$

$$z_i \geq 0$$

are **challenging to solve numerically**.

- They are sharp conditions, in which

$$x_i \geq 0 \quad \text{and} \quad z_i = 0$$

or

$$x_i = 0 \quad \text{and} \quad z_i \geq 0.$$

## **Interior-point method for constrained minimization**

---

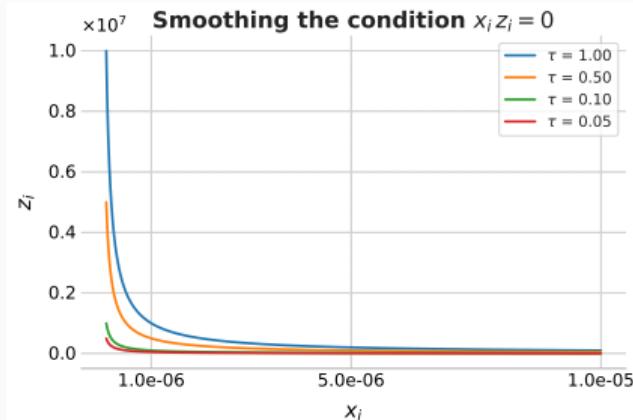
**Interior-point perturbation approach**

# Interior-point perturbation approach

- Perturb  $x_i z_i = 0$  with a **small and constant number**

$$x_i z_i = \tau.$$

- Note:** the choice of  $\tau$  affects the smallest amount a species that can exist in equilibrium.
- Example:** the choice  $\tau = 10^{-20}$  causes species in **unstable phases** to have amounts around this value.
  - Quiz:** What can we say about the amount of mineral dissolved in water?



<http://etc.ch/cKvh> or



- Answer:** The amount will be of order  $\tau$ .

## Interior-point Newton method

- We'll use **Newton's method** to solve the obtained system of non-linear equations:

$$\frac{\partial f}{\partial x} - A^T y - z = 0,$$

$$Ax - b = 0,$$

$$x_i z_i = \tau \quad (i = 1, \dots, n),$$

$$x_i, z_i \geq 0 \quad (i = 1, \dots, n).$$

- Define the **residual function**  $F$  as follows:

$$F(x, y, z) := \begin{bmatrix} \frac{\partial f}{\partial x} - A^T y - z \\ Ax - b \\ XZe - \tau \end{bmatrix},$$

where

- $e = (1, \dots, 1)^T$ ,
- $X = \text{diag}(x)$ , and
- $Z = \text{diag}(z)$ .

The resulting problem: find  $(x, y, z)$ , with  $x, z \geq 0$ , so that:

$$F(x, y, z) = 0.$$

## Jacobian matrix for the interior-point Newton method

- Newton's method require the Jacobian  $J$  of the residual function:

$$F(x, y, z) := \begin{bmatrix} \frac{\partial f}{\partial x} - A^T y - z \\ Ax - b \\ XZe - \tau \end{bmatrix},$$

which is defined as

$$J := \begin{bmatrix} \frac{\partial F_1}{\partial x} & \frac{\partial F_1}{\partial y} & \frac{\partial F_1}{\partial z} \\ \frac{\partial F_2}{\partial x} & \frac{\partial F_2}{\partial y} & \frac{\partial F_2}{\partial z} \\ \frac{\partial F_3}{\partial x} & \frac{\partial F_3}{\partial y} & \frac{\partial F_3}{\partial z} \end{bmatrix}.$$

- Answer:

$$J = \begin{bmatrix} H & -A^T & -I \\ A & 0 & 0 \\ Z & 0 & X \end{bmatrix}.$$

where

- $I$  be the identity matrix and
- $H$  represent the Hessian matrix of  $f$  (second derivatives of  $f$ )

$$H := \frac{\partial^2 f}{\partial x^2}.$$

- Exercise:** derive the matrix blocks in Jacobian of  $J$ .

- How can we calculate Hessian matrix  $H$ ?**

## **Interior-point method for constrained minimization**

---

**Hessian matrix of the Gibbs energy  
function**

## Hessian matrix of the Gibbs energy function

- The **Hessian matrix of the Gibbs energy** is

$$H := \frac{\partial^2 G}{\partial n^2} \quad \text{or in element-wise notation} \quad H := \{H_{ij}\}_{ij} := \left\{ \frac{\partial^2 G}{\partial n_i \partial n_j} \right\}_{ij}$$

- Recall that

$$\frac{\partial G}{\partial n_i} = \mu_i \quad \text{and} \quad \mu_i = \mu_i^o + RT \ln a_i.$$

- Thus,

$$H_{ij} = \frac{\partial \mu_i}{\partial n_j} = \frac{\partial}{\partial n_j} (\mu_i^o + RT \ln a_i) = RT \frac{\partial \ln a_i}{\partial n_j}.$$

- Expressions for  $\partial \ln a_i / \partial n_j$  can be derived for all previous activity models.

## Partial molar derivatives of activities

- Instead of exact calculation of partial molar derivatives, we **derive them for ideal models**.
- We use activity models to **correct for the non-ideal behavior** of the aqueous and gaseous solutions.
- We use the partial molar derivatives of ideal activity models as it is **simpler to derive**.
- So, in

$$\begin{aligned}\mu_i - \sum_{j=1}^N A_{ji}y_j - z_i &= 0 \quad (i = 1, \dots, N), \\ \sum_{i=1}^E A_{ji}n_i - b_j &= 0 \quad (j = 1, \dots, E), \\ n_i z_i &= 0 \quad (i = 1, \dots, N), \\ n_i, z_i &\geq 0 \quad (i = 1, \dots, N),\end{aligned}$$

$\mu_i$  will be calculated exactly. But the Jacobian will be approximated.

- Ideally, an **automatic differentiation** scheme should be used to compute these derivatives (beyond the scope of this course).

## Partial molar derivatives of activities of aqueous solutes

- Recall that the **activity of an aqueous solute** is

$$a_i = \gamma_i m_i, \text{ where } m_i = 55.508 \frac{n_i}{n_w}.$$

- Its ideal activity model is  $a_i = m_i$ , with  $\gamma_i = 1$ .
- Thus,

$$\begin{aligned}\frac{\partial \ln a_i}{\partial n_j} &\approx \frac{\partial \ln m_i}{\partial n_j} = \text{Exercise} \\ &= \frac{\partial 55.508}{\partial n_j} + \frac{\partial \ln n_i}{\partial n_j} - \frac{\partial \ln n_w}{\partial n_j} = \begin{cases} \frac{1}{n_i} & j = i, \\ -\frac{1}{n_w} & j = w, \\ 0 & \text{otherwise.} \end{cases}\end{aligned}$$

## Partial molar derivatives of activities of aqueous solvent, H<sub>2</sub>O(aq)

- Recall that the **ideal activity of water**, H<sub>2</sub>O(aq), is

$$a_w = -\frac{1 - x_w}{x_w}, \quad \text{where} \quad x_w = \frac{n_w}{\sum n_i}.$$

- Thus,

$$\begin{aligned}\frac{\partial \ln a_w}{\partial n_j} &= \text{Exercise} \\ &= \frac{\partial \ln(x_w - 1)}{\partial n_j} - \frac{\partial \ln x_w}{\partial n_j} = \begin{cases} -\frac{1}{n_w} & j = w, \\ -\frac{1}{n_w} \frac{x_w}{x_w - 1} & j \neq w. \end{cases}\end{aligned}$$

## Partial molar derivatives of activities of CO<sub>2</sub>(g)

- Recall that the **activity of CO<sub>2</sub>(g)** was calculated using

$$a_{\text{CO}_2(\text{g})} = \varphi_{\text{CO}_2(\text{g})} \frac{P}{P^o},$$

where the fugacity coefficient  $\varphi_{\text{CO}_2(\text{g})}$  was only a function of  $T$  and  $P$ , i.e.,

$$\varphi_{\text{CO}_2(\text{g})} = \varphi_{\text{CO}_2(\text{g})}(T, P).$$

- Thus, the value of the following derivative

$$\begin{aligned}\frac{\partial \ln a_{\text{CO}_2(\text{g})}}{\partial n_j} &= \text{Exercise} \\ &= 0.\end{aligned}$$

## Partial molar derivatives of activities – pure minerals

- Recall that the **activities of pure minerals** (e.g., mineral phases with only one mineral end-member),

$$a_i = 1.$$

- Thus, for mineral species,

$$\frac{\partial \ln a_i}{\partial n_j} = 0.$$

## Calculation of the Hessian matrix of the Gibbs energy function in Python i

- Have a look in the Python code of the project to see the implementation of these formulas for when calculating the Hessian matrix  $H$  with entry  $H_{ij}$  given by:

$$H_{ij} = RT \frac{\partial \ln a_i}{\partial n_j} \quad \text{used in} \quad J = \begin{bmatrix} H & -A^T & -I \\ A & 0 & 0 \\ Z & 0 & X \end{bmatrix}.$$

```
1 # Define the function that calculates:  
2 #   - G, the Gibbs energy of the system;  
3 #   - u, the gradient of the Gibbs energy, or chemical potentials of the  
4 #     species  
5 #   - H, the Hessian of the Gibbs energy, or partial molar derivatives of  
6 #     activities  
7 # These quantities are normalized by RT for numerical reasons.  
8 def gibbs_energy(T, P, n):
```

## Calculation of the Hessian matrix of the Gibbs energy function in Python ii

```
7     RT = R*T
8     u = chemical_potentials(T, P, n)/RT
9     H = chemical_potentials_ddn(T, P, n)/RT
10    G = n.dot(u)/RT
11    return G, u, H
12
13 # Define the function that calculates the partial molar derivatives of the
14 # chemical potentials of the species.
15 def chemical_potentials_ddn(T, P, n):
16     return R*T*ln_activities_ddn(T, P, n)
17
18 # Define the function that calculates the partial molar derivatives of the
19 # ln activities of all species
20 def ln_activities_ddn(T, P, n):
21     # Create an array with the entries in n corresponding to aqueous species
22     n_aqueous = n[slice_aqueous]
23
```

## Calculation of the Hessian matrix of the Gibbs energy function in Python iii

```
24 # The matrix with partial molar derivatives of the activities
25 ln_a_ddn = zeros((num_species, num_species))
26
27 ln_a_ddn[slice_aqueous, slice_aqueous] = ln_activities_aqueous_species_ddn(T
28 , P, n_aqueous)
29
30
31 # Define the function that calculates the activities of the aqueous species.
32 # Parameters:
33 # - T is temperature in units of K
34 # - P is pressure in units of Pa
35 # - nphase is an array with the mole amounts of the aqueous species
36 # Return:
37 # - an array with the ln activities of aqueous species
38 def ln_activities_aqueous_species_ddn(T, P, nphase):
39 # The molar amount of H2O(l)
```

## Calculation of the Hessian matrix of the Gibbs energy function in Python iv

```
40 nH2O = nphase[iH2O]
41
42 # The mole fraction of H2O(l)
43 xH2O = nH2O/sum(nphase)
44
45 # Calculate the partial molar derivatives of the solute activities
46 ddn = diag(1.0/nphase)      # 1/ni, j = i
47 ddn[:, iH2O] = -1.0/nH2O   # -1/nw, j = w
48
49 # Calculate the partial molar derivatives of the solvent water activity
50 ddn[iH2O, :] = -1.0/nH2O * xH2O/(xH2O - 1.0) # -1/nw, j = w
51 ddn[iH2O, iH2O] = -1.0/nH2O                      # 1/nw*xw/(xw -1), j<>w
52
53 return ddn
```

**Listing 12:** Calculating Jacobian using Python

## **Interior-point method for constrained minimization**

---

**Numerical solution by the interior-point  
Newton method**

# Numerical solution by the interior-point Newton method

**Newton method algorithm** at step 1:

- At the first Newton iteration, start with **initial guess**

$$x^0 = (x_1^0, \dots, x_n^0), y^0 = (y_1^0, \dots, y_m^0) \text{ and } z^0 = (z_1^0, \dots, z_n^0).$$

- Compute  $x^1 = (x_1^1, \dots, x_n^1)$ ,  $y^1 = (y_1^1, \dots, y_m^1)$  and  $z^1 = (z_1^1, \dots, z_n^1)$  using

$$x^1 = x^0 + \alpha_x^0 \Delta x^0$$

$$y^1 = y^0 + \Delta y^0$$

$$z^1 = z^0 + \alpha_z^0 \Delta z^0$$

where  $\alpha_x$  and  $\alpha_z$  are introduced parameters to ensure  $x_i^1 > 0$  and  $z_i^1 > 0$ .

- How do we calculate variations  $\Delta x^0$ ,  $\Delta y^0$ ,  $\Delta z^0$ ?

- To calculate the Newton variations  $\Delta x^0 = (\Delta x_1^0, \dots, \Delta x_n^0)$ ,  $\Delta y^0 = (\Delta y_1^0, \dots, \Delta y_m^0)$  and  $\Delta z^0 = (\Delta z_1^0, \dots, \Delta z_n^0)$ , we solve the matrix equation

$$\underbrace{\begin{bmatrix} H^0 & -A^T & -I \\ A & 0 & 0 \\ Z^0 & 0 & X^0 \end{bmatrix}}_{J^0} \begin{bmatrix} \Delta x^0 \\ \Delta y^0 \\ \Delta z^0 \end{bmatrix} = -\underbrace{\begin{bmatrix} g^0 - A^T y^0 - z^0 \\ Ax^0 - b \\ X^0 Z^0 e - \tau \end{bmatrix}}_{F^0}$$

where  $J^0$ ,  $F^0$ ,  $H^0$ ,  $Z^0$ ,  $X^0$  represent to evaluation of respective matrices using the values of  $x$ ,  $y$ ,  $z$  at the 0th iteration, i.e.,

- $- J^0 := J(x^0, y^0, z^0)$ ,
- $- F^0 := F(x^0, y^0, z^0)$ , etc.

**Newton method algorithm** at the step  $k + 1$ :

- The vector steps  $\Delta x^k, \Delta y^k, \Delta z^k$  at the iteration  $k$  is calculated by

$$J^k \begin{bmatrix} \Delta x^k \\ \Delta y^k \\ \Delta z^k \end{bmatrix} = -F^k$$

- New approximations  $x^{k+1}, y^{k+1}, z^{k+1}$  is obtained by

$$x^{k+1} = x^k + \alpha_x^k \Delta x^k,$$

$$y^{k+1} = y^k + \Delta y^k,$$

$$z^{k+1} = z^k + \alpha_z^k \Delta z^k.$$

- How do we calculate  $\alpha_x^k$  and  $\alpha_z^k$  reassuring positivity of  $x_i^{k+1}$  and  $z_i^{k+1}$ ?

- Start with  $\alpha_x^k \leftarrow 1$ .
- Check if

$$x_i^k + \Delta x_i^k \leq 0 \quad \text{for } i = 1, \dots, n$$

- if so,  $\alpha_x^k \leftarrow (\delta - 1) \frac{x_i^k}{\Delta x_i^k}$ , where  $\delta \in (0, 1)$ , e.g.,  $\delta = 10^{-4}$ ;
- otherwise, go to next component with index  $i$ .
- It results into either a **full Newton step** (for  $\alpha_x^k = 1$ ) or a **partial Newton step** (for  $\alpha_x^k < 1$ ).
- If for certain index  $i$ , parameter  $\alpha_x^k < 1$ , then

$$x_i^{k+1} = \delta x_i^k,$$

and for all other indices

$$x_j^{k+1} = x_j^k + \alpha_x^k \Delta x_j^k, \quad j = 1, \dots, n, j \neq i.$$

## Summary of the Newton method algorithm:

- With initial guess  $x^0$ ,  $y^0$ , and  $z^0$ , repeat

$$\begin{aligned}x^{k+1} &= x^k + \alpha_x^k \Delta x^k \\y^{k+1} &= y^k + \Delta y^k \quad \text{iteration } k \\z^{k+1} &= z^k + \alpha_z^k \Delta z^k\end{aligned}$$

until

$$\|F^k\|_\infty = \|F(x^k, y^k, z^k)\|_\infty < \epsilon_{\text{tol}},$$

where

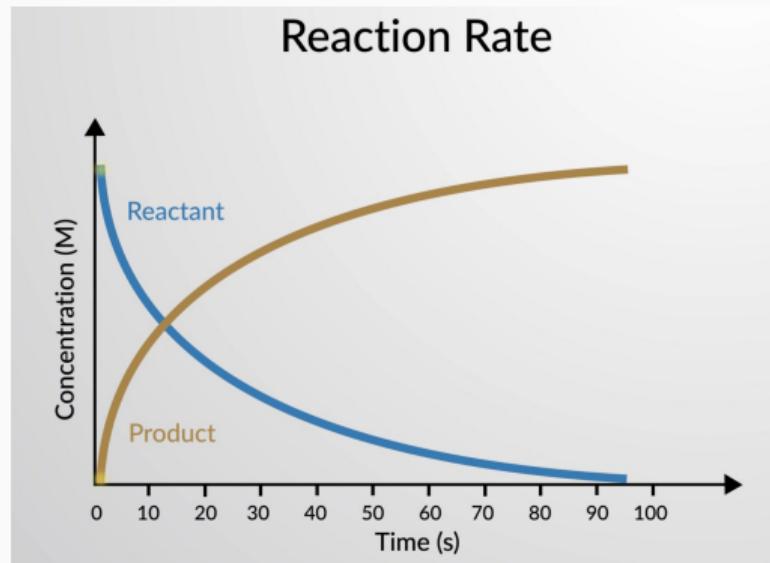
- $\epsilon_{\text{tol}} = 10^{-6}$  is **selected tolerance** and
- the **norm of a vector  $v$**  is defined by  $\|v\|_\infty = \max(|v_i|)$ .

## Chemical kinetic calculation

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# Chemical kinetics

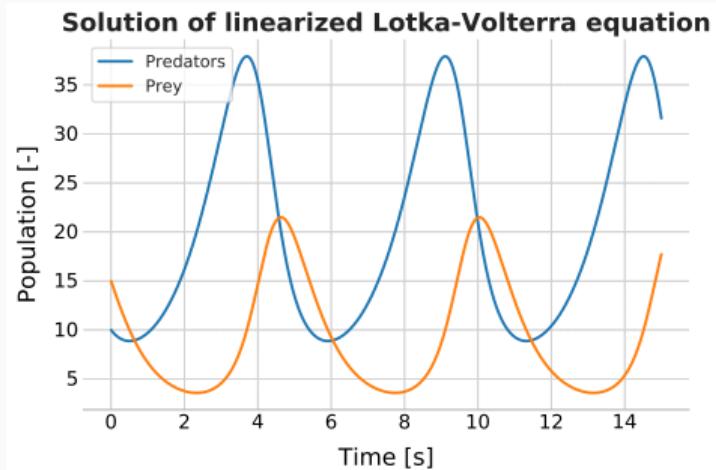
- Chemical kinetics / reaction kinetics studies the rate of chemical reactions and factors that influence them.
- Chemical processes can be described by detailed kinetic reaction mechanisms consisting of several hundreds or even thousands of reaction steps.



# Application of kinetic reactions

**Reaction mechanisms** are used in many fields of science and technology:

- combustion (turbulent combustion modeling),
- atmospheric chemistry,
- environmental/ecological modeling (e.g., Lotka–Volterra model),
- process engineering, and
- systems biology (e.g., cell cycle, metabolism networks and molecular signal transfer).



# Global and elementary chemical kinetics reaction

- Kinetic mechanisms are described in a **single global step**.
- **But!** In reality, such reaction happen in a series of elementary steps, **sequence of one or more elementary reactions**:
  - *unimolecular reaction*: dissociation of one reagent molecule;
  - *bimolecular reaction*: collisions between two molecules; or
  - *trimolecular reaction*: collision of three reactant molecules (occurs less frequently).
- **Elementary chemical reactions** is a transition between two atomic / molecular states.



- The **activation energy** between these two states determines **the rate at which reactions occur**:
  - for *low activation energy*  $\Rightarrow$  *reaction is rapid*,
  - for *higher activation energy*  $\Rightarrow$  *reaction is slower*.

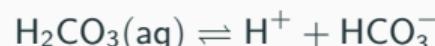
## Factors affecting reaction rates

- **Nature of the reactants** (strength of bonds, size of the product)
- **Physical state** (solid, gas, or liquid phase)
- **Surface area of solid state** (surface that can be involved in a reaction)
- **Concentration** (higher the concentration ⇒ higher the rate of reaction)
- **Temperature** (higher the temperature ⇒ higher the molecule thermal energy ⇒ higher )
- **Catalysts**, a substance that alters the rate of a chemical reaction but remains unchanged itself (increases the rate of the reaction)
- **Pressure** (higher the pressure ⇒ higher the number of collisions between reactants ⇒ higher the rate of reaction)
- **Absorption of light** (light absorption provide activation energy)

## Time scale of kinetics reactions, Examples

- **The time scale**, on which the chemical reactions occur, spans many orders of magnitude (from microseconds to years).
- Reactions are characterized by the so-called **half-time**.
- The range of time scales can differ by several orders of magnitude:

- 



is acid–base reaction involving only solutes has **half-time of about  $10^{-6}$  s**

- 



is a solute–water hydration reaction has a **half-time of 0.1 s**

- 



mineral dissolution reaction can be in the **order of weeks at low temperatures**

# Half-times of some reactions

**TABLE 2.1** General reaction types and example reactions at low temperatures and pressures, with approximate reaction half-times.

Reaction type and example <sup>†</sup>		Half-times
<i>Solute-solute</i>		
$\text{H}_2\text{CO}_3^{\circ} = \text{H}^+ + \text{HCO}_3^-$	(acid-base)	$\sim 10^{-6}$ s
<i>Solute-water</i>		
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^{\circ}$	(hydration/hydrolysis)	$\sim 0.1$ s
$\text{Cu}^{2+} + \text{H}_2\text{O} = \text{CuOH}^+ + \text{H}^+$	(hydrolysis/complexation)	$\sim 10^{-10}$ s
$\text{Fe}(\text{H}_2\text{O})_6^{2+} = \text{Fe}(\text{H}_2\text{O})_5^{2+} + \text{H}_2\text{O}$	(hydrolysis/complexation)	$\sim 10^{-7}$ s
<i>Adsorption-desorption</i>		
$\text{Cd}^{2+} + \text{CaX} = \text{Ca}^{2+} + \text{CdX}$	( $\text{X}^-$ is the surface site)	$\sim \text{s-hr}$
<i>Gas-water or gas solution-exsolution</i>		
$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$		$\sim \text{min}$
<i>Oxidation-reduction</i>		
$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2(\text{g}) + \frac{5}{2}\text{H}_2\text{O} = \text{Fe}(\text{OH})_3(\text{ppt}) + 2\text{H}^+$		min-hr
<i>Hydrolysis of multivalent ions</i>		
$\text{Al}_{n+m}(\text{OH})_{3n+2m}^{+m} + m\text{H}_2\text{O} \rightarrow (n+m)\text{Al}(\text{OH})_3(\text{s}) + m\text{H}^+$		hr-y
<i>Mineral-water equilibria</i>		
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaCO}_3 + \text{H}^+$		week-y
<i>Isotopic exchange</i>		
${}^{34}\text{SO}_4^{2-} + \text{H}{}^{32}\text{S}^- = \text{H}{}^{34}\text{S}^- + {}^{32}\text{SO}_4^{2-}$		y
<i>Mineral recrystallization</i>		
$\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}(\text{am}) \rightarrow \alpha\text{-FeOOH(goethite)} + (n+1)\text{H}_2\text{O}$		y
<i>Radioactive decay</i>		
${}^{14}\text{C} \rightarrow {}^{14}\text{N} + e^-$		5570 y

<sup>†</sup>Note: Other descriptions or explanations of the reactions are given parenthetically.

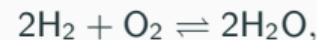
# **Chemical kinetic calculation**

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**Reaction stoichiometry, rates, and  
orders**

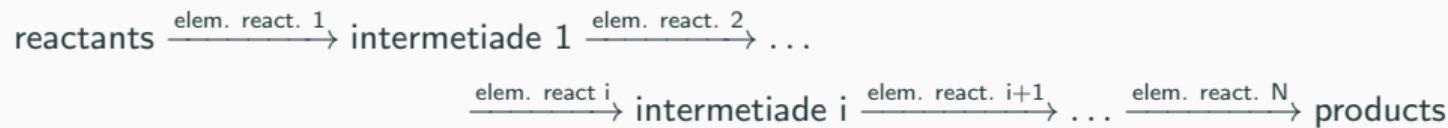
# Reaction stoichiometry

- Chemical process can be described by the **single stoichiometric equation**, also called **overall reaction equation**.
- **Stoichiometric equation** defines the molar ratio of the reacting species and the reaction products / the number of moles of each reactant and the product that appears in the overall reaction equation.
- **Example:** the overall reaction equation for the **combustion (oxidation) of hydrogen**:



where  $\text{H}_2$  has stoichiometric coefficient 2,  $\text{O}_2$  has coefficient 1, and  $\text{H}_2\text{O}$  has coefficient 2.

- Chemical systems described by a single chemical reaction (reactants → products) are **very rare**.
- In reality, we are dealing with a network of **elementary reactions**



# Reaction stoichiometry, generalization

- Equation  $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$  can be rearranged as follows

$$0 = -2\text{H}_2 - \text{O}_2 + 2\text{H}_2\text{O},$$

- If  $\mathbf{A} = (\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3) = (\text{H}_2, \text{O}_2, \text{H}_2\text{O})$  is a vector of species, and  $\boldsymbol{\nu} = (\nu_1, \nu_2, \nu_3) = (-2, -1, 2)$  is a vector of multiplication factors, then we obtain

$$0 = \sum_{i=1}^3 \nu_i \mathbf{A}_i.$$

- The **general stoichiometric equation of chemical reaction** is defined by

$$0 = \sum_{i=1}^N \nu_i A_i,$$

where

- $N$  is the number of species,
- $\nu_i$  is the stoichiometric coefficient of the  $i$ th species ( $\nu_i < 0$  for reactants and  $\nu_i > 0$  for products), and
- $A_i$  is the formula of the  $i$ th species in the overall reaction equation.

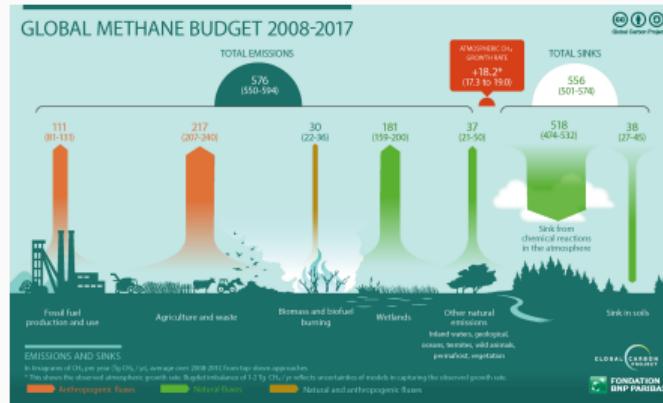
# Complexity of finding single overall reaction equation

There are **many chemical processes** for which a **single overall reaction equation** that describes the stoichiometry of the process **cannot be found**.

- Example: **oxidation of hydrocarbons sourced from exhaust gases in the troposphere**, with the sequence of reactions

- hydrocarbon + OH → alkyl radical + H<sub>2</sub>O,
- alkyl radical + O<sub>2</sub> (<sup>3</sup>Σ) → alkylperoxy radical,
- alkylperoxy radical + NO → alkoxy radical + NO<sub>2</sub>,
- alkoxy radical + O<sub>2</sub> (<sup>3</sup>Σ) → aldehyde + HO.

- The ratio of hydrocarbons changes dependent on the type of pollution source.
- No single species can be identified as reactants or products.



**Figure 21:** Diagram showing the main sources of methane for the decade 2008-2017, produced by a global report on global methane emissions by the Global Carbon Project (source [Wikipedia](#)).

# Reaction rate as production/consumption rate

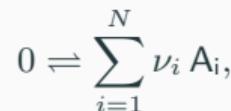
- The reaction rate is the rate at which reactants are consumed, or the rate at which products are formed,  $\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}$ .
- The reaction rate can be defined as the rate of change of concentration of a reactant/product divided by its stoichiometric coefficient.

- Example: for hydrogen oxidation

$2 \text{H}_2 + \text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O}$ , the reaction rate is defined as

$$r = \frac{1}{2} \frac{d[\text{H}_2\text{O}]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2]}{dt} = -\frac{d[\text{O}_2]}{dt}.$$

- For more general reaction



we obtain

$$r = \frac{1}{\nu_i} \frac{d[\text{A}_i]}{dt}.$$

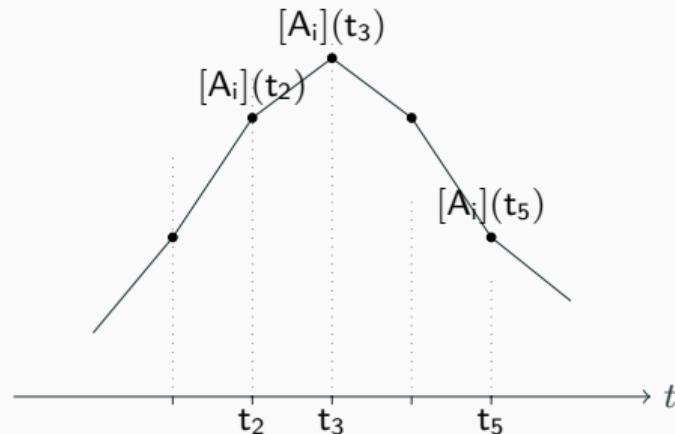


Figure 22: Time-dependent behaviour of the chemical system: the molar concentrations of species  $\text{A}_i$  measured at consecutive time points.

## Example, Production/consumption rate

- Knowing that  $r = \frac{1}{\nu_i} \frac{d[A_i]}{dt} = \frac{1}{\nu_i} r(A_i)$ , where  $\nu_i > 0$  for products and  $\nu_i < 0$  for reactants.
- Consider the reaction



**Quiz** (multiple choice): Which statements about reaction/production rates are correct?



<http://etc.ch/xREb> or

- **Answer:** the correct relations on the reaction/production rates are

$$-\frac{1}{a} r(A) = \frac{1}{d} r(D) \quad \Rightarrow \quad r(A) = -\frac{a}{d} r(D),$$

$$-\frac{1}{b} r(B) = \frac{1}{d} r(D),$$

$$\frac{1}{c} r(C) = \frac{1}{d} r(D) \quad \Rightarrow \quad r(C) = \frac{c}{d} r(D).$$

# Reaction rate via concentrations of reactants

- Reaction rate for general equation

$$0 \rightleftharpoons \sum_{i=1}^N \nu_i A_i,$$

can be defined **proportional to the concentrations of the reactants raised to a power**:

$$r := k \prod_{i=1}^N [A_i]^{\alpha_i},$$

where

- $k > 0$  is the rate coefficient,
- $[A_i]$  is a molar concentrations ( $\frac{\text{mol}}{\text{m}^3}$ ),
- $\alpha_i > 0$  is the order of reaction with respect to species  $A_i$ , and
- $N$  is the number of species.

## Order of reaction vs. stoichiometry

- For the overall reaction equation, **the order does not necessarily reflect the stoichiometry**, i.e.,  $\alpha_i \neq \nu_i$ , because of the **intermediate steps** hidden in the overall reaction.

**Example:** in the reaction  $\text{CO} + \text{Cl}_2 \xrightleftharpoons{r} \text{COCl}_2$ , the reaction rate  $r = [\text{CO}]^2 \cdot [\text{Cl}_2]^{3/2}$ .

- The sum of the powers is **the overall order of the reaction**, i.e.,

$$\alpha = \sum_{i=1}^N \alpha_i.$$

- For elementary reactions, **the reaction orders and the absolute value of the stoichiometric coefficients of the reactants are commonly the same**.

**Example:**

- for unimolecular decomposition  $\text{A} \xrightleftharpoons{r} \text{B}$ :  $r = [\text{A}]$

- for bimolecular reaction

- $\text{A} + \text{B} \xrightleftharpoons{r} \text{C}$ :  $r = [\text{A}] \cdot [\text{B}]$ , or

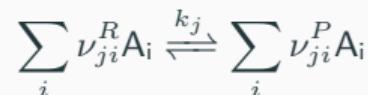
- $\text{A} + \text{A} \xrightleftharpoons{r} \text{C}$ :  $r = [\text{A}]^2$ .

# Stoichiometry in intermediate reactions

- The overall **reaction of hydrogen combustion**  $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$  should contain the following intermediate steps (among total 30-40 steps):



- Each **elementary reaction step**  $j$  can be characterized by the stoichiometric equation



- The **stoichiometric coefficient belonging to species  $A_i$  in a reaction step  $j$**  can be calculated by

$$\nu_{ji} = \nu_{ji}^P - \nu_{ji}^R.$$

## Differential & integral forms for the reaction rate, Half-time

- To establish the relationship between the **rate of change of the concentration of a reactant/product** and **reaction rate** over time, i.e.,

$$r := \frac{1}{\nu_i} \frac{d[A_i]}{dt} \quad \text{and} \quad r := k \prod_{i=1}^N [A_i]^{\alpha_i},$$

the **differential equation** is used.

- For simple cases, it may be analytically integrated (see Table 3).
- The half-life of the reaction** is the time required for the reagent concentration be reduced to half of its initial value.

Reaction	Order	Differential Form	Integrated form	Half-time
$A \rightarrow B$	0	$-\frac{d[A]}{dt} = k$	$[A] = [A]_0 - k t$	$t_{1/2} = \frac{[A]_0}{2k}$
$A \rightarrow C$	1	$-\frac{d[A]}{dt} = k [A]$	$\ln [A] = \ln [A]_0 - k t$	$t_{1/2} = \frac{\ln 2}{k}$
$A + B \rightarrow C$	2	$-\frac{d[A]}{dt} = k [A] [B]$	$k t = \frac{1}{[B]_0 + [A]_0} \ln \frac{[B]_0 [A]}{[B] [A]_0}$	$t_{1/2} = \frac{1}{k [A]_0} \quad (B = A)$

**Table 3:** Differential and integral forms for the reaction rate as well as half-time, where  $[A]_0$  and  $[B]_0$  correspond to the initial concentrations of A and B, respectively.

## Example, Differential & integral forms for the reaction rate, Half-time

- **Quiz:** Given a first-order reactant and rate constant  $k = 1.5\text{e-}4 \text{ 1/min}$ , what is the half-life of the reactant if the time is defined by  $t_{1/2} = \frac{\ln 2}{k}$ ?



<http://etc.ch/xREb> or

- **Answer:**  $\ln 2 / 1.5\text{e-}4 \text{ min} = \ln 2 / 0.0000025 \text{ s} \approx 27.73\text{e}4 \text{ s}$

# Mass action kinetics and corresponding kinetic system of ODEs

- The law of mass action kinetics for elementary reactions can be formulated as

$$r_j := k_j \prod_{i=1}^N [A_i]^{\nu_{ji}}, \quad j = 1, \dots, M,$$

where

- $r_j$  is the kinetic rate of  $j$ th reaction step and  $k_j$  is the  $j$ th rate coefficient,
- $N$  and  $M$  are the number of species and the number of reactions, respectively,
- $\nu_{ji}$  is the stoichiometric coefficient of the  $i$ th species, and
- $A_i$  is the formula of the  $i$ th species, and  $[A_i]$  is its corresponding concentration.

- Kinetic system of ordinary differential equations ODEs defines the relationship between production rates of the species  $\frac{d[A_j]}{dt}$  and reaction rates  $r_j$ :

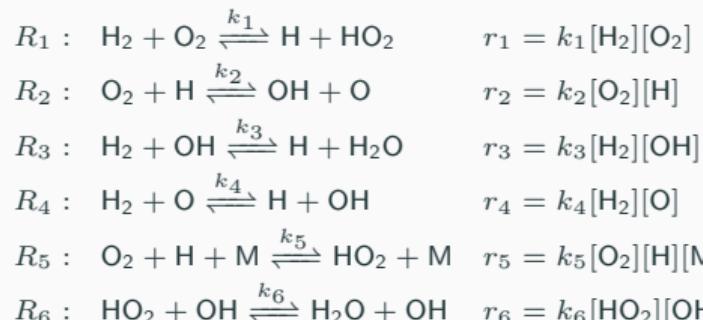
$$\frac{d[A_j]}{dt} = \sum_{j=1}^N \nu_{ji} r_j, \quad j = 1, \dots, M.$$

- The kinetic system of ODEs and its initial values together provide the following initial value problem

$$\frac{d[A_j]}{dt} = \sum_{j=1}^N \nu_{ji} r_j, \quad [A_j](0) = [A_j]_0, \quad j = 1, \dots, M.$$

## Example, Kinetics law of mass action for hydrogen combustion

- The overall reaction  $2 \text{H}_2 + \text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O}$  can be decomposed into the following  $M = 6$  elementary steps with corresponding the stoichiometry matrix  $\nu \in \mathbb{R}^{6 \times 8}$

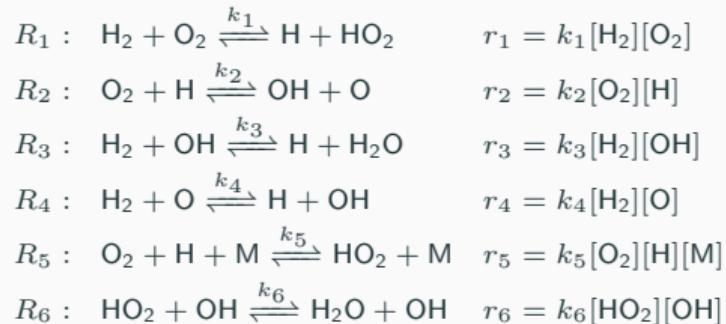


$$\nu = \begin{bmatrix}
 R_1 & \begin{matrix} 1 & -1 & 1 & 0 & 0 & 0 & * & 0 & 0 \end{matrix} \\
 R_2 & \begin{matrix} -1 & 0 & 0 & 0 & 1 & 0 & * & 1 & 0 \end{matrix} \\
 R_3 & \begin{matrix} 1 & -1 & 0 & 1 & 0 & 0 & * & -1 & 0 \end{matrix} \\
 R_4 & \begin{matrix} 1 & -1 & 0 & 0 & -1 & 0 & * & 1 & 0 \end{matrix} \\
 R_5 & \begin{matrix} -1 & 0 & 1 & 0 & 0 & 0 & * & 0 & 0 \end{matrix} \\
 R_6 & \begin{matrix} 0 & 0 & -1 & 1 & 0 & 0 & * & 0 & 0 \end{matrix}
 \end{bmatrix}$$

$$\nu = \begin{bmatrix}
 R_1 & \begin{matrix} \text{H} & \text{H}_2 & \text{HO}_2 & \text{H}_2\text{O} & \text{O} & \text{O}_2 & \text{OH} & \text{M} \end{matrix} \\
 R_2 & \begin{matrix} 1 & -1 & 1 & 0 & 0 & -1 & 0 & 0 \end{matrix} \\
 R_3 & \begin{matrix} -1 & 0 & 0 & 0 & 1 & -1 & 1 & 0 \end{matrix} \\
 R_4 & \begin{matrix} 1 & -1 & 0 & 1 & 0 & 0 & -1 & 0 \end{matrix} \\
 R_5 & \begin{matrix} 1 & -1 & 0 & 0 & -1 & 0 & 1 & 0 \end{matrix} \\
 R_6 & \begin{matrix} -1 & 0 & 1 & 0 & 0 & -1 & 0 & 0 \end{matrix} \\
 R_7 & \begin{matrix} 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \end{matrix}
 \end{bmatrix}$$

- Quiz:** What are the coefficients in the column with the  $\text{O}_2$ ?

## Example, Kinetics law of mass action for hydrogen combustion



$$\nu = \begin{bmatrix} H & H_2 & HO_2 & H_2O & O & O_2 & OH & M \\ R_1 & 1 & -1 & 1 & 0 & 0 & -1 & 0 & 0 \\ R_2 & -1 & 0 & 0 & 0 & 1 & -1 & 1 & 0 \\ R_3 & 1 & -1 & 0 & 1 & 0 & 0 & -1 & 0 \\ R_4 & 1 & -1 & 0 & 0 & -1 & 0 & 1 & 0 \\ R_5 & -1 & 0 & 1 & 0 & 0 & -1 & 0 & 0 \\ R_6 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}$$

- The production rates can be formulated as follows:

$$\begin{aligned}
 \frac{dH}{dt} &= 1r_1 - 1r_2 + 1r_3 + 1r_4 - 1r_5 + 0r_6 \\
 &= k_1[H_2][O_2] - k_2[O_2][H] + k_3[H_2][OH] + k_4[H_2][O] - k_5[H][O_2][M] + 0k_6[HO_2][OH]
 \end{aligned}$$



- Quiz:** What is the right-hand side for the  $\frac{dHO_2}{dt}$ ? <http://etc.ch/xREb> or

- Answer:**  $\frac{dHO_2}{dt} = 1r_1 + 1r_5 - 1r_6 = k_1[H_2][O_2] + k_5[H][O_2][M] - k_6[HO_2][OH]$ .

## **Chemical kinetic calculation**

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**Reaction rate and its dependence on  
temperature and pressure**

## Temperature dependence of rate coefficients, Arrhenius equation

- The temperature dependence of rate coefficient  $k$  is described by the **(classic) Arrhenius equation**:

$$k := A e^{-\frac{E_a}{RT}},$$

where

- $A$  is the pre-exponential factor or A-factor,
  - $E_a$  is the activation energy ( $\frac{\text{J}}{\text{mol}}$ ),
  - $R = 8.314$  is the gas constant ( $\frac{\text{J}}{\text{mol K}}$ ), and
  - $T$  is the temperature (K).
- $E_a$  is the **minimum energy** that the reactant molecules must possess before the reaction can occur (bigger  $E$  is  $\Rightarrow$  smaller is the reaction rate  $\Rightarrow$  slower the reaction will proceed).
  - $E_a$  is **determined experimentally** by performing the reaction at several temperatures.

## Temperature dependence of rate coefficients, Arrhenius plot

- After taking the **natural logarithm of the Arrhenius equation**, one obtains

$$\ln k := \ln A - \frac{E_a}{R} \frac{1}{T},$$

- Assume that  $y := \ln k$  and  $x := \frac{1}{T}$ .
- Then, the graph of  $y = \ln A - \frac{E_a}{R} x$  is a **linear function** with slope  $\tan \alpha = -\frac{E_a}{R}$  and intersect  $\ln A$ :

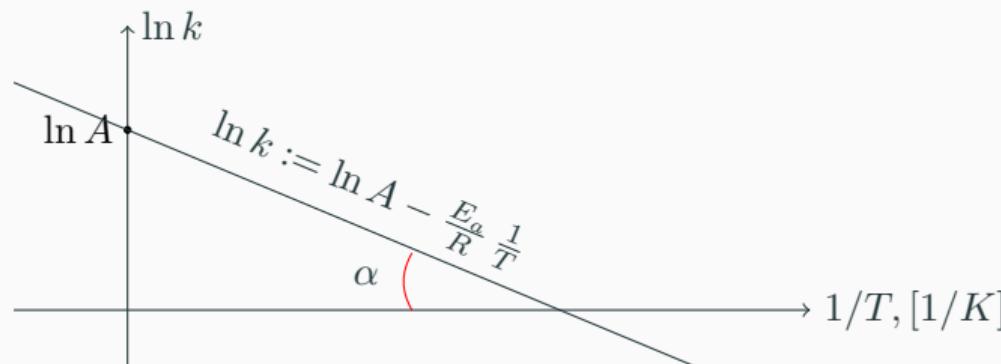


Figure 23: Linear function  $\ln k := \ln A - \frac{E_a}{R} \frac{1}{T}$ .

## Alternative forms of Arrhenius equation

- In **high-temperature gas-phase kinetic systems** (e.g., combustion and pyrolytic systems) the temperature dependence of the rate coefficient is described by the **modified / extended Arrhenius equation**:

$$k := B T^n e^{-\frac{C}{RT}},$$

where  $B \neq A$  and  $C \neq E_a$ .

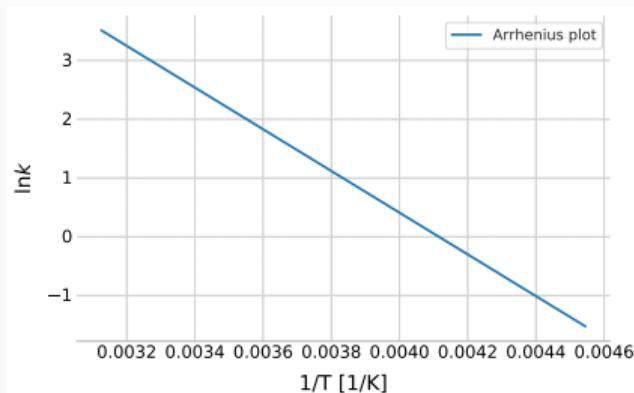
- For some **gas-phase kinetic elementary reactions**, the temperature dependence of the rate coefficient is described by a **truncated form of the extended Arrhenius equation**

$$k = A T^n.$$

# Example of methane reaction, Arrhenius plots comparison

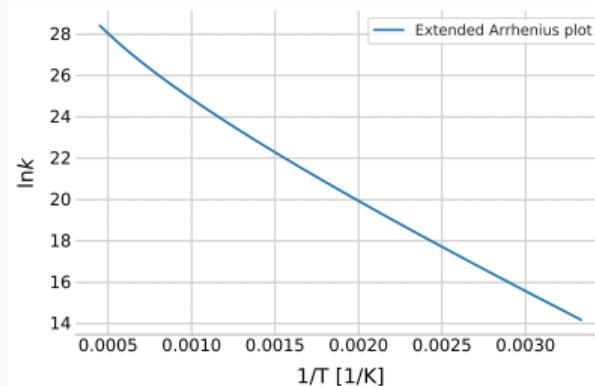
- Reaction of **methane consumption in the troposphere**

$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$ , happens in a range between 220 K (-53 °C) and 320 K (+47 °C).



(a) Arrhenius plot

- In **methane flames**, it is one of the main consuming reactions of the **fuel molecules**, where  $T$  ranges between 300 K (27 °C) and 2,200 K (maximum temperature of a laminar premixed methane-air flame).



(b) Extended Arrhenius plot

## Pressure dependence of rate coefficients, Lindemann model i

- According to **Lindemann model**, a unimolecular decomposition is only possible if **the energy in the molecule is sufficient to break the bond**.
- Before decomposition, the energy must be added to A by means of collision with M (representation of the pressure) to obtain excited molecule  $A^*$ :



- The **production rates** can be written as:

$$\frac{d[C]}{dt} = k_3 [A^*]$$

$$\frac{d[A^*]}{dt} = \sum_{i=1,\dots,3} \nu_i r_i = r_1 - r_2 - r_3 = k_1 [A][M] - k_2 [A^*][M] + k_3 [A^*]$$

## Pressure dependence of rate coefficients, Lindemann model ii

- Assuming steady-state for  $[A^*]$ , meaning that  $\frac{d[A^*]}{dt} = 0$ , we obtain

$$[A^*] = \frac{k_1 [A] [M]}{k_2 [M] + k_3} \quad \text{and} \quad \frac{d[C]}{dt} = \frac{k_1 k_3 [A] [M]}{k_2 [M] + k_3},$$

where M represents applied pressure.

- Under low pressure**,  $[M]$  is very small ( $k_2 M \ll k_3$ ), then

$$\frac{d[C]}{dt} = k_{\text{low}} [A] [M],$$

where  $k_{\text{low}}$  is the **reaction rate coefficient at low pressure**.

- For high pressure**,  $[M]$  is large ( $k_2 M \gg k_3$ ), then

$$\frac{d[C]}{dt} = k_{\text{high}} [A],$$

where  $k_{\text{high}}$  is the **reaction rate coefficient at high pressure**.

## Summary on reactions, their rates, rate coefficients, and orders

- The **overall reaction mechanism** is the result of **all the elementary reactions** in the mechanism.
- The **reaction rate** and the **reaction rate coefficient** are **determined by experiments**.
- **The units of the reaction rate coefficients**  $k$  depend on the relation  $[k] = \frac{1}{\text{s} [\text{mol}/\text{m}^3]^{n-1}}$ , where  $n$  is the order of reaction.
- The orders are generally **not equal** to the stoichiometric coefficients of the overall reaction equation.
- **The order of reaction** is determined **experimentally** or by **means of mathematical models**.
- The **most important reactions** are of:
  - zero order,
  - first order, and
  - second order.
- Third-order reactions **are quite rare**, reactions of order greater than three are **not known**.

# **Chemical kinetic calculation**

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**Reaction mechanisms**

# Reaction mechanisms

- The **kinetic mechanisms** can contain basically **three types of reactions**:
  - in series (consecutive reactions),
  - in parallel (competitive reactions), and
  - independent.
- **In series occurring reactions** (consecutive reactions), reactant forms an **intermediate product**, which subsequently reacts to form another product:



- **In parallel reactions** (competitive reactions), the reagent is consumed by two different reaction paths to form **different products**:



- Usually, kinetic mechanisms involve a **combination of both reactions in series or parallel**.

## Example, Formation of butadiene C<sub>4</sub>H<sub>6</sub> from ethanol

- **Butadiene** C<sub>4</sub>H<sub>6</sub> is the organic compound, colorless gas that is easily condensed to a liquid.
- It is important industrially as a monomer in the **production of synthetic rubber**.
- In South America, Eastern Europe, China, and India, butadiene is **produced from ethanol**:

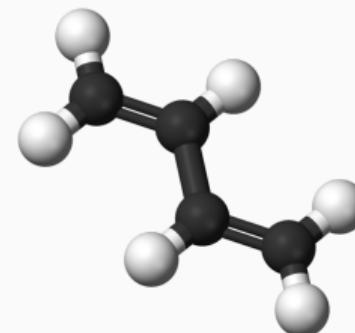


Figure 24: Organic compound of (CH<sub>2</sub> = CH)<sub>2</sub>.

## Chain reactions, Ignition of hydrogen example

- **Chain reactions** are defined by reactives intermediate reacting to produce another intermediates, have complex kinetics, and occur quickly.
- The intermediate species in a chain reaction is **a chain propagator**:



- They are the basis of **combustion processes**, rapid reactions of species with O<sub>2</sub> generating heat.

N	Reaction	Step
1	$\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{OH}^*$	initiation of the step
2	$\text{OH}^* + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}^*$	propagation of the chain
3	$\text{H}^* + \text{O}_2 \rightleftharpoons \text{OH}^* + \text{O}^*$	branch of the chain
4	$\text{O}^* + \text{H}_2 \rightleftharpoons \text{OH}^* + \text{H}^*$	branch of the chain
5	$\text{H}^* \rightleftharpoons 0.5\text{H}_2$	termination of the chain
6	$\text{H}^* + \text{O}_2 + \text{M} \rightleftharpoons \text{HO}_2^* + \text{M}^*$	propagation of the chain

**Table 4:** Important reactions for the hydrogen ignition mechanism.

# Chemical kinetic calculation

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Redox reaction

# Redox reaction

- **Redox (or reduction-oxidation) reaction** is a type of chemical reaction that involves a transfer of electrons between two species.
- **Examples:**
  - body uses redox reactions to convert food and oxygen to energy plus water and CO<sub>2</sub>;
  - batteries in electronics rely on redox reactions;
  - combustion reactions in the car engines, e.g., combustion of octane (hydrocarbon)



- The H<sub>2</sub>O can be
  - (or oxygen in it) **oxidized**, losing electron,  $\text{H}_2\text{O(l)} = \text{O}_2(\text{aq}) + 2\text{e}^- + 2\text{H}^+$ , or
  - (or hydrogen in it) **reduced**, accepting electron,  $\text{H}_2\text{O(l)} + \text{e}^- = \frac{1}{2}\text{H}_2(\text{aq}) + \text{OH}^-$ .
- **Self-redox** is the reaction, where the same element undergoes oxidation and reduction simultaneously,



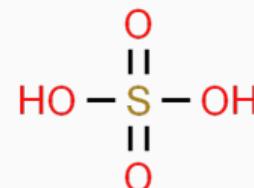
where Cl<sup>0</sup> with oxidation number 0, becomes Cl<sup>-1</sup> in NaCl and Cl<sup>+1</sup> in NaClO.

# Oxidation number, Oxidizers and reducers

- **Oxidation number** (NOX) of a chemical element is the number of charges that an atom would possess if the electrons were not shared but located entirely on a single atom.

- **Examples:**

- water  $\text{H}_2\text{O}$ :  $\text{H}^+ - \text{O}^{-2} - \text{H}^+$  ;
- sulfuric acid  $\text{H}_2\text{SO}_4$ : with  $\text{H}^+$ ,  $\text{S}^{6+}$ , and  $\text{O}^{-2}$ .



- **Oxidizer** causes the oxidation and receives electron:

- halogens, such as  $\text{F}_2$  and  $\text{Cl}_2$ ;
- oxyacid and oxyanions, such as  $\text{NO}_3^-$ ,  $\text{IO}_3^-$ , and  $\text{MnO}_4^-$ ;
- forms of oxygen, such as  $\text{O}_3$ ; and
- peroxides, such as  $\text{H}_2\text{O}_2$ .

- **Reducer** causes the reduction and gives away electron:

- alkali and alkaline earth metals, Li and Na.

## Basic rules of the redox number determination

1. The sum of the oxidation numbers of all atoms that constitute a molecule is equal to zero (electroneutrality rule).
2. The sum of the oxidation numbers of all atoms of a polyatomic ion is always equal to the charge of this ion.
3. Isolated elements and simple substances have  $\text{NO}_X = 0$ .
4. Monatomic ions have the oxidation number equal to its own charge.
5. Alkali metals (Li, Na, K, Rb, Cs, Fr) and silver (Ag) have  $\text{NO}_X = +1$ .
6. Alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) and zinc (Zn) have  $\text{NO}_X = +2$ .
7. In compounds, aluminum (Al) has  $\text{NO}_X = +3$ .
8. In compounds, hydrogen (H) has  $\text{NO}_X = +1$ , except for metal hydrides, where it has  $\text{NO}_X = -1$ .
9. Oxygen ( $\text{O}_2$ ) has  $\text{NO}_X = -2$ , except for peroxides, where the  $\text{NO}_X = -1$ , and superoxide, where  $\text{NO}_X = -0.5$ .
10. In the right side of the chemical formula, the halogens (F, Cl, Br, and I) have  $\text{NO}_X = -1$ .

**Figure 25:** From *Modeling and Simulation of Reactive Flows* by Bortoli, Andreis, and Pereira, 2015.

## Concepts of half-reaction

- The redox reactions can be expressed as a combination of two partial ionic reactions:

- an **oxidation half-reaction**



- and a **reduction half-reaction**

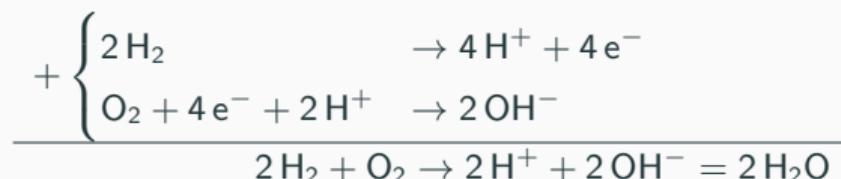


- Example:** reaction  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$  can be decoupled to

- an **oxidation half-reaction** (of hydrogen)  $\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$  and

- a **reduction half-reaction** (of oxygen)  $\text{O}_2 + 4e^- + 2\text{H}^+ \rightarrow 2\text{OH}^-$ .

- In a linear combination of these equations, **the number of donated electrons must be equal to the number of received electrons**:



## Quiz on redox reaction

- **Quiz:** determine what is the oxidizing and reducing agents in the following reaction?



Reminder:

- **reducing agent** is the one that **forces other species to gain electron**, and
- **oxidizing agent** is the one that **forces other species to lose one**):



<http://etc.ch/xREb> or

- **Answer:** The oxidation state of H changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2.

Hence, Zn is oxidized and acts as the reducing agent.  $\text{H}^+$  ion is reduced and acts as the oxidizing agent.

## Combustion reactions

- **Combustion** is the formal terms for 'burning' and typically involves a **substance reacts with oxygen to transfer energy to the surroundings** as light and heat.
- **Example:** internal combustion engines rely on the combustion of organic hydrocarbons  $C_xH_y$  to generate  $CO_2$  and  $H_2O$ :



- Many chemicals can 'burn' in **other environments**.

**Example 1:** metals like titanium and magnesium can burn in nitrogen:



**Example 2:** chemicals can be also oxidized by other chemicals than oxygen, such as  $Cl_2$  or  $F_2$ ; these processes are also considered combustion reactions.

## Quiz on redox reaction

- **Quiz:** which of the following are combustion reactions?

- (a)  $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2,$
- (b)  $4 \text{Fe} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3,$
- (c)  $2 \text{AgNO}_3 + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + 2 \text{NHO}_3,$
- (d)  $2 \text{Al} + \text{N}_2 \rightarrow 2 \text{AlN}_4.$



<http://etc.ch/xREb> or

- **Answer:** Reactions (b) and (d) are combustion reactions with different oxidizing agents. Reaction (b) is the conventional combustion reaction using  $\text{O}_2$  and (d) uses  $\text{N}_2$  instead.

## **Chemical kinetic calculation**

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**Simplification principles in reaction kinetics**

## Simplification/reduction principles in reaction kinetics

- If applied appropriately, the following **kinetic simplification/reduction principles** may provide a nearly identical solution compared to the original system of ODEs:
  - the pool chemical / pool component approximation,
  - the pre-equilibrium approximation,
  - the rate-determining step, and
  - the quasi-steady-state approximation.
- Reduction principles **only valid under certain conditions**, e.g., the results are reliable for certain temperature ranges.

## Pool chemical / pool component approximation

- **Pool chemical / pool component approximation** applicable when
  - the concentration of a reactant species is **much higher** than those of the other species, and, therefore,
  - the concentration change of this species is **considered to be negligible** throughout the simulation period.
- **Example:** a **second-order reaction** step  $A + B \rightarrow C$  can be converted to **first-order** assuming  $[B] \approx \text{const}$  during the simulations.
  - We introduce a new rate coefficient

$$k' := k [B] \approx \text{const.}$$

- Then, the second-order expression can be converted to a first-order one:

$$\frac{d[C]}{dt} = k [A] [B] = k' [A].$$

- This particular case is called a **pseudo-first-order approximation** and  $k'$  is the **pseudo-first-order rate coefficient**.

# Pre-equilibrium / partial equilibrium / fast equilibrium approximation i

- **Partial equilibrium / fast equilibrium approximation** applicable when the **species participating in a pair of fast-equilibrium reactions are consumed by slow reactions.**

- (i) In case of **equilibrium**, the rates of the forward and backward reactions are equal  $\Rightarrow$  the concentrations of the participating species can be calculated from the stoichiometry and the equilibrium constant.

**Example:** consider equilibrium reaction  $A \xrightleftharpoons[k_2]{k_1} B$  with equilibrium  $K_e := \frac{k_1}{k_2}$

$\Rightarrow$  in case of **equilibrium**:  $k_1 [A] = k_2 [B]$ .

- **Quiz:** how can we express concentrations of B?

<http://etc.ch/xREb> or



- **Answer:**  $[B] = K_e [A]$ .

## Pre-equilibrium / partial equilibrium / fast equilibrium approximation ii

- (ii) If the **rates of the equilibrium reactions are much higher than the rates of the other reactions consuming these species**  $\Rightarrow$  concentrations of these species are determined by the equilibrium reactions only.

**Example:** consider equilibrium reaction  $A \xrightleftharpoons[k_2]{k_1} B \xrightarrow{k_3} C$ , where  $k_3 \ll k_1, k_2$   
 $\Rightarrow$  assuming  $[B] = K_e [A]$ , therefore  $\frac{d[C]}{dt} = k_3 [B]$ .

- **Quiz:** how can we express the production rate of C?

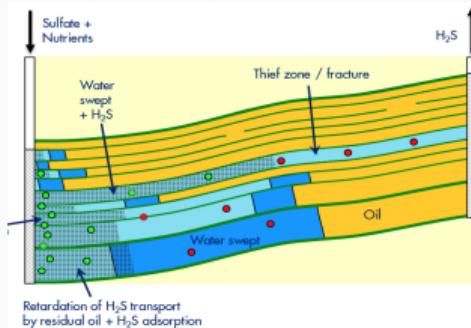


<http://etc.ch/xREb> or

- **Answer:**  $\frac{d[C]}{dt} = k_3 [B] = k_3 K_e [A]$ .

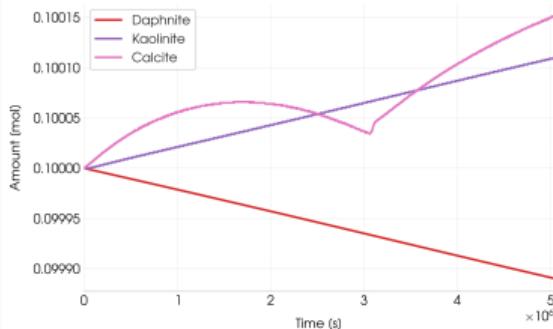
# Example, Complex souring system

- Kinetics modeling of souring of complex system for approx. 58.33 days with minerals:

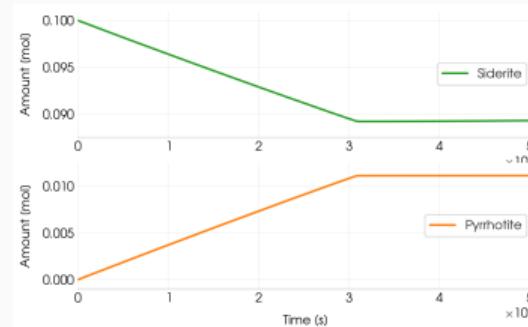


- Calcite,  $k_{\text{Calcite}} \sim 10^{-1}$ ,
- Daphnite,  $k_{\text{Daphnite}} \sim 10^{-9}$ ,
- Kaolinite,  $k_{\text{Kaolinite}} \sim 10^{-11}$ ,
- Siderite,  $k_{\text{Siderite}} \sim 10^{-6}$ ,
- Quartz,  $k_{\text{Quartz}} \sim 10^{-10}$

- Assuming that calcite is controlled by equilibrium, we obtained the speedup of  $\approx 4.24x$ .



(a) Calcite, daphnite, and kaolinite



(b) Pyrrhotite and siderite over time

## Rate-determining step

- For **sequential first-order reactions**, the reaction step having **the smallest rate coefficient is the rate-determining one**.
- **Example:** in the reaction  $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \xrightarrow{k_4} E \xrightarrow{k_5} P$  and  $k_2 \ll k_1, k_3, k_4, k_5$ , then

$$\frac{d[P]}{dt} = k_2 [B].$$

## Quasi-steady-state approximation

- The **quasi-steady-state approximation (QSSA)** is also called the **Bodenstein principle**.
- The assumption of steady-state is valid for the **intermediate species** that are produced by slow reactions and consumed by fast reactions, so that their concentrations remain small.
- For the mechanism  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ , the production rates are

$$\begin{aligned}\frac{d[B]}{dt} &= k_1 [A] - k_2 [B], \\ \frac{d[C]}{dt} &= k_1 [B].\end{aligned}$$

- If  $k_2 \gg k_1$ , then the species B can be assumed in steady-state, i.e.,  $\frac{d[B]}{dt} \approx 0$  and  $[B] = \frac{k_1}{k_2} [A]$ .
- In many engineering problems, it is acceptable assume steady-state for intermediate species with **concentrations lower than 1%**.

**Mathematical point of view  
evolutionary kinetic systems of  
ODE**

---

# Evolutionary system of ODE for kinetically controlled species

- The **evolution of a chemical system with kinetically controlled species** is governed by the system **ODEs**:

$$\frac{dn_i}{dt} = f_i(T, P, n) = \sum_{j=1}^M \nu_{ij} r_j(T, P, n), \quad n_i = n_i^o, \quad i = 1, \dots, N,$$

where

- $n_i = [A_i]$  and  $n_i^o = [A_i]^o$  are *number of moles* and *initial number of moles* of the  $i$ th species,
- $n, n^o \in \mathbb{R}^N$  is the *molar composition* and *initial molar composition* vector of the system, and
- $f_i : \mathbb{R}^{2+N} \rightarrow \mathbb{R}$  is the *production/consumption* of the  $i$ th species in every reaction, and
- $r_j : \mathbb{R}^{2+N} \rightarrow \mathbb{R}$  is the *kinetic rate function* of the  $j$ th reaction.

- System of ODEs can be presented in the **matrix form**

$$\frac{dn}{dt} = f(n) := \nu^T r(n),$$

where

- $f(n) : \mathbb{R}^N \rightarrow \mathbb{R}^N$  is a vector function defined via
- $\nu \in \mathbb{M}^{M \times N}$  is the stoichiometric matrix of reactions, and
- $r : \mathbb{R}^M \rightarrow \mathbb{R}^N$  is the rate function of reactions.

# Mathematical characteristics of kinetic system of ODEs

- Kinetic system of ODEs is a **stiff first-order (usually autonomous) nonlinear system**

$$\frac{dn}{dt} = f(n, p),$$

where

- $n \in \mathbb{R}^N$  is a vector of species concentrations,
- $p \in \mathbb{R}^N$  is a vector of parameters, and
- $f : \mathbb{R}^{2N} \rightarrow \mathbb{R}^N$  is the rate function of reactions.

- **Jacobian matrices**

$$J := \frac{\partial f(n, p)}{\partial n} = \left\{ \frac{\partial f_i}{\partial n_j} \right\}_{ij} \quad \text{or} \quad F := \frac{\partial f(n, p)}{\partial p} = \left\{ \frac{\partial f_i}{\partial p_j} \right\}_{ij}$$

are very frequently used for the following **reduction algorithms**:

- determining local sensitivity analysis of each species (principal reactions),
- analyzing of timescales present in the kinetic system.

## Partial equilibrium assumption

- We **partition the chemical system** to

- **equilibrium species**  $n_e \in \mathbb{R}^{N_e}$  controlled by  $M_e$  **equilibrium reactions**

$$0 \rightleftharpoons \sum_{i=1}^N \nu_{e,ij} B_i, \quad j = 1, \dots, M_e, \quad \nu_e \in \mathbb{R}^{M_e \times N}, \quad \text{and}$$

- **kinetic species**  $n_k \in \mathbb{R}^{N_k}$  controlled by  $M_k$  **kinetics reactions**

$$0 \rightleftharpoons \sum_{i=1}^N \nu_{k,ij} B_i, \quad j = 1, \dots, M_k, \quad \nu_k \in \mathbb{R}^{M_k \times N}.$$

- Then, **the vector of species amount** can be represented by  $n = [n_e; n_k]^T \in \mathbb{R}^N$ ,  $N = N_e + N_k$ , with

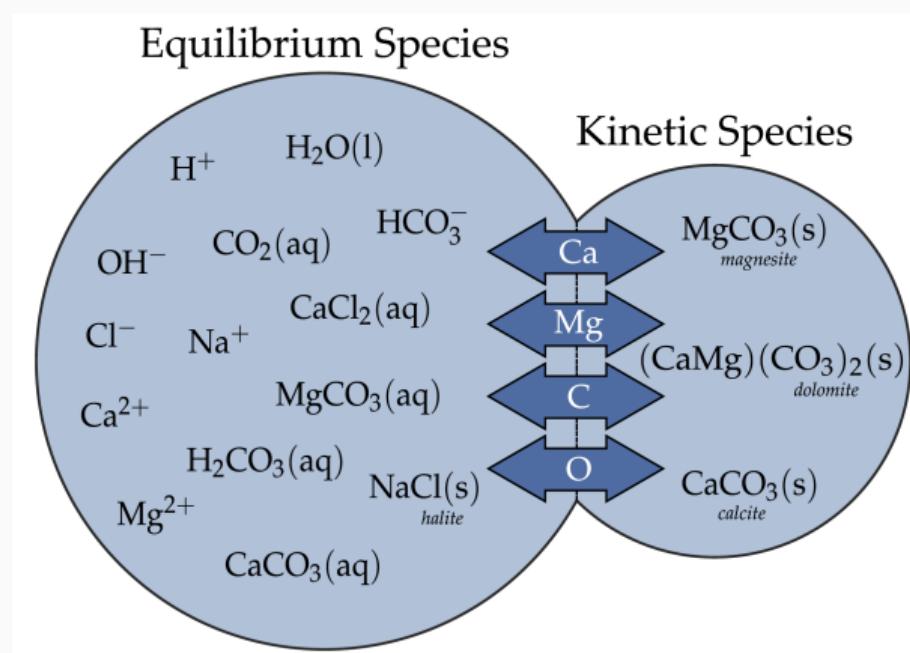
- the formula matrix  $A = \begin{bmatrix} A_e & A_k \end{bmatrix}$  composed of the **formula matrices of the equilibrium and kinetic species**  $A_e \in \mathbb{R}^{E \times N_e}$  and  $A_k \in \mathbb{R}^{E \times N_k}$ , and
  - corresponding elements compositions  $b = b_e + b_k$ , where  $b_e = A_e n_e$  and  $b_k = A_k n_k \in \mathbb{R}^E$ .

# Principle of mass conservation

- The principle of mass conservation:

$$\frac{db}{dt} = \frac{db_e}{dt} + \frac{db_k}{dt} = 0,$$

where  $b_e = A_e n_e$  and  
 $b_k = A_k n_k \in \mathbb{R}^E$ .



From A.M.M. Leal et al., Applied Geochemistry 55 (2015) 46–61.

## Equilibrium- and kinetically controlled system of ODE

- Equilibrium- and kinetically-controlled reactions requires the solution of the **system of ODEs**

$$\frac{db_e}{dt} = f_e(n_e) \quad t > 0, \quad b_e = An_e^o \quad t = 0, \quad (7)$$

$$\frac{dn_k}{dt} = f_k(n_k) \quad t > 0, \quad n_k = n_k^o \quad t = 0,$$

where

- $n_k \in \mathbb{R}^{N_k}$  and  $n_e \in \mathbb{R}^{N_e}$  are the amounts of the equilibrium and kinetic species,
- $n_e^o, n_k^o$  is vector of the *initial amounts of the equilibrium and kinetic species*, respectively.

- How do we calculate  $n_e$  after  $b_e$  is recovered by the system of ODEs?

## Chemical equilibrium calculation

- To calculate  $n_e$ , we solve **the fundamental GEM problem**

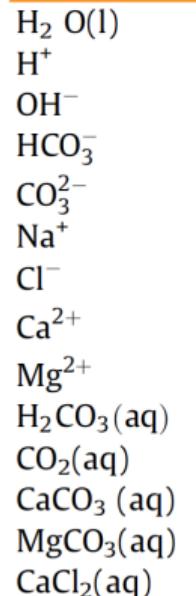
$$n_e = \underset{n_e}{\operatorname{argmin}} G_e = n_e^T \mu_e \quad \text{s.t.} \quad A_e n_e = b_e, n_e \geq 0.$$

- Here,  $\mu_{e,i} = \mu_{e,i}(T, P, n) := \mu_{e,i}^o + RT \ln a_{e,i}$  denotes the **chemical potential** of the  $i$ th species with
  - $R$  is the universal gas constant,
  - $\mu_{e,i}^o = \mu_{e,i}^o(T, P)$  the *standard chemical potential* of the  $i$ th species, and
  - $a_{e,i} = a_{e,i}(T, P, n)$  the *activity* of the  $i$ th species.

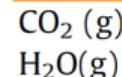
## Example, Partition to kinetic and equilibrium species i

Description of the chemical system H<sub>2</sub>O–CO<sub>2</sub>–Halite–Calcite–Magnesite–Dolomite with their phases and respective chemical species.

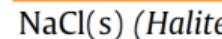
### Aqueous phase



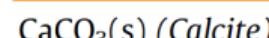
### Gaseous phase



### Mineral phase #1



### Mineral phase #2



### Mineral phase #3



### Mineral phase #4



## Example, Partition to kinetic and equilibrium species ii

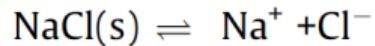
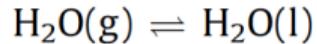
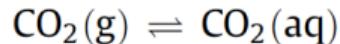
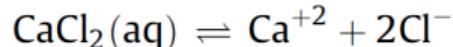
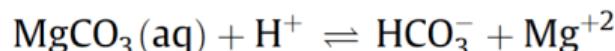
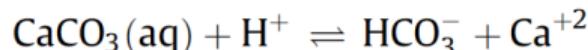
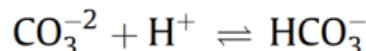
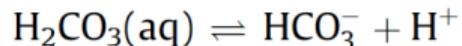
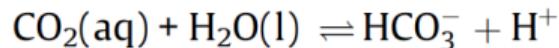
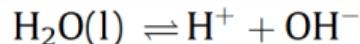
Partition of the chemical system  $\text{H}_2\text{O}-\text{CO}_2$ -Halite-Calcite-Magnesite-Dolomite in equilibrium and kinetic species.

Equilibrium species	Kinetic species
$\text{H}_2\text{O(l)}$	$\text{CaCO}_3(s)$
$\text{H}^+$	$\text{MgCO}_3(s)$
$\text{OH}^-$	$(\text{CaMg})(\text{CO}_3)_2(s)$
$\text{HCO}_3^-$	
$\text{CO}_3^{2-}$	
$\text{Na}^+$	
$\text{Cl}^-$	
$\text{Ca}^{2+}$	
$\text{Mg}^{2+}$	
$\text{H}_2\text{CO}_3(\text{aq})$	
$\text{CO}_2(\text{aq})$	
$\text{CaCO}_3(\text{aq})$	
$\text{MgCO}_3(\text{aq})$	
$\text{CaCl}_2(\text{aq})$	
$\text{CO}_2(\text{g})$	
$\text{H}_2\text{O(g)}$	
$\text{NaCl}(s)$	

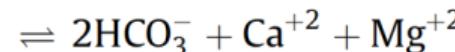
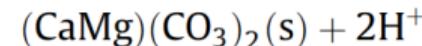
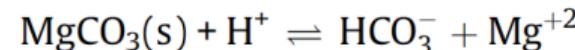
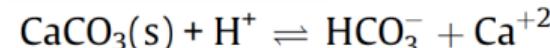
## Example, Partition to kinetic and equilibrium species iii

Description of the equilibrium and kinetic reactions in the chemical system

### Equilibrium reactions



### Kinetic reactions



## Differential-algebraic equations for equilibrium and kinetic chemical system

- The evolution of the chemical state of a system undergoing a **mixed equilibrium and kinetic** process is governed by the following **differential-algebraic equations (DAE)**

$$\begin{aligned}\frac{db_e}{dt} &= f_e(n_e) & t > 0, \quad b_e = An_e^o & \quad t = 0, \\ \frac{dn_k}{dt} &= f_k(n_k) & t > 0, \quad n_k = n_k^o & \quad t = 0, \\ n_e &= \varphi(T, P, b_e) & t > 0.\end{aligned}$$

where  $n^o = [n_e^o, n_k^o]^T$  is a given initial condition with provided on each time-step triple  $(T, P, b_e)$ .

## General rate law for mineral growth or dissolution

- In equation controlling kinetic species

$$\frac{dn_k}{dt} = f_k(n_k) = \nu^T r(n_k),$$

the **general rate law for mineral precipitation and dissolution** (Lasaga, 1981 and Palandri and Kharaka, 2004) can be formulated as

$$r_j(T, P, n) := S_j(n) \sum_m M_{j,m}(T, P, n),$$

where

- $r_j : \mathbb{R}^{2+N} \rightarrow \mathbb{R}$  is a *rate function of the mineral* in the  $j$ th reaction,
- $S_j = S_j(n_j)$  is the corresponding *surface area function* of the mineral [ $\text{m}^2$ ],
- $M_{j,m}$  is the  $m$ -th *kinetic mechanism* function of the mineral [ $\frac{\text{mol}}{\text{s m}^2}$ ].

## Kinetic mechanism function

- **Kinetic mechanism function** of the mineral includes in  $k_{j,m}$  different scenarios (such as acid, neutral, base, carbonate,etc) and is defined as

$$M_{j,m} := k_{j,m} \operatorname{sgn}(1 - \text{SI}) |1 - \text{SI}|^{p_m} |C_{j,m}|^{q_m},$$

where

- SI is the *saturation index* of the  $j$ th mineral,
- $p_i$  and  $q_i$  are *empirical exponents* used to fit the rate law,
- $C_{j,m}$  is a function to model *catalysts and inhibitors* of the mineral reaction,
- 

$$k_{j,m} := k_{j,m}^o e^{-\frac{E_{m,i}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right)}$$

is the **rate constant** of the mineral reaction (according to the **Arrhenius equation**) with

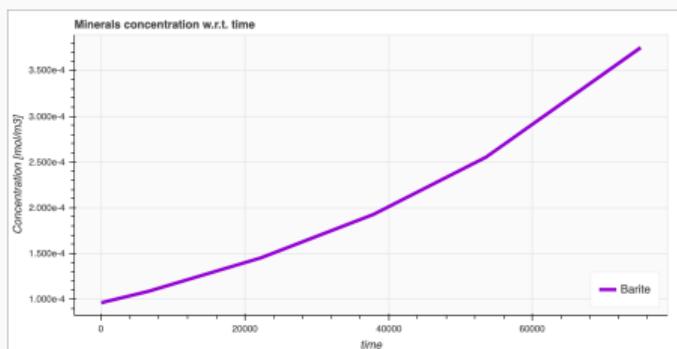
- $k_{j,m}^o$  as the *reaction rate constant at 25 °C*,
- $E_{j,m}$  as the *activation energy*,
- $R$  as the *universal gas constant* and  $T$  as the given temperature,

## Example of barite precipitation using acidic mechanism

In rate law  $r_{\text{Barite}} = S \operatorname{sgn}(1 - \text{SI}) |1 - \text{SI}| k e^{\left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]}$ , we defined  $S$ ,  $k$ , and  $E_a$ :

```
1 eq_str_barite = "Barite = SO4-- + Ba++"
2 min_reaction_barite = editor.addMineralReaction("Barite") \
3     .setEquation(eq_str_barite) \
4     .addMechanism("logk = -8.6615 mol/(m2*s); Ea = 22 kJ/mol") \
5     .setSpecificSurfaceArea(0.006, "m2/g")
```

**Listing 13:** Define barite mineral reaction and its parameters



Barite precipitation.

## Example of hematite kinetic mechanisms in reservoir souring

Hematite mineral reacts according to the reaction



and has the following kinetic rate dependent on neutral, acidic, and sulfide promoted mechanisms:

$$r_{\text{Hematite}} := n S M \left( \frac{n}{n^o} \right)^{2/3} k_{\text{diss}} (1 - \Omega),$$
$$k_{\text{diss}} := k_{\text{neu}} + k_{\text{acid}} + k_{\text{sulfide}},$$
$$k_{\text{neu}} := 2.51\text{e-}15 \cdot e^{\left[ -\frac{66.2}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]},$$
$$k_{\text{acid}} := 4.07\text{e-}10 \cdot e^{\left[ -\frac{66.2}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]} \cdot a(\text{H}^+),$$
$$k_{\text{sulfide}} := 3.5\text{e-}9 \cdot e^{\left[ -\frac{40}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right]} \cdot a^{1/2}(\text{HS}^-),$$

where  $M$  is the molar mass.

## **Numerical method for chemical kinetics calculation**

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## History of stiffness of system of ODEs

- **Stiffness** is the characteristics of “**how hard**” is it to solve a system of ODEs.
- The first identification due to chemical engineers Curtiss and Hirschfelder (1952):

*“Stiff equations are equations where certain implicit methods perform better,  
usually tremendously better, than explicit ones”.*
- **It comes from** the system of coupled equations for combustion has very different time scale characteristics. In geochemistry, the situation is similar, but a little less critical.
- If **nonstiff methods** are employed to solve stiff problems ⇒ **more computational effort is required**.
- This results in **chemical problems being a bottleneck** in reaction kinetics (and other areas, e.g., electrical engineering, mechanical engineering, etc.) for 15 years.
- But, in 1968, a variety of methods began to appear in the literature.

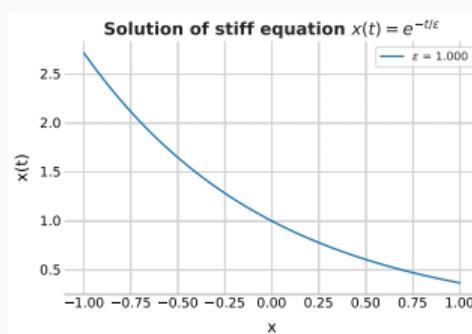
# Example of stiff problem and complication by numerical integration

- The **stiff equations and systems**: let  $\epsilon > 0$  be a small parameter and consider the **initial value problem**

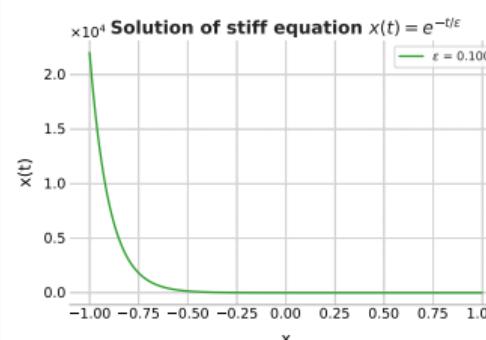
$$\frac{dx(t)}{dt} = -\frac{1}{\epsilon} x(t), \quad x(0) = 1, \quad t \in [0, T],$$

with the **exponential solution** is  $x(t) = e^{-\frac{t}{\epsilon}}$ .

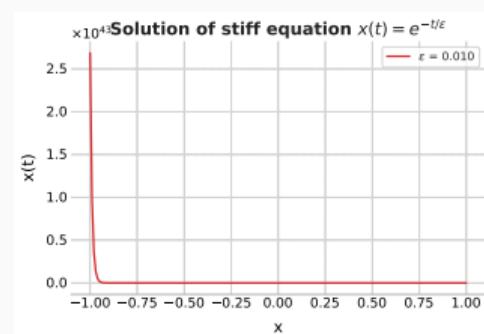
- In order to accurately integrate this problem with Euler method,  $\Delta t$  (**integration time steps**) **must be smaller than  $\epsilon$** .



(c)



(d)



(e)

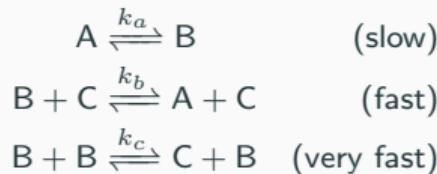
# Numerical integration schemes and codes for stiff systems

- **One-step methods:**
  - implicit Runge-Kutta methods,
    - e.g., Gauss, Radau, Lobatto methods, etc.
  - Rosenbrock methods (semi-implicit / semi-explicit / generalized / adaptive / additive Runge-Kutta methods),
  - semi-implicit extrapolation methods,
- **Multi-step methods** (the first numerical methods to be proposed for stiff differential equations):
  - explicit Adams methods,
  - predictor-corrector schemes,
  - Nystrom methods,
  - backward differentiation formular (BDF) schemes.
- For more details, see Hairer & Wanner (2010).
- In Reaktoro, for the integration of the chemical kinetics, the **CVODE package** **implementing BDF methods** Cohen & Hindmarsh (1996); Hindmarsh et al. (2005) is used.

## Example, Roberts system

Consider the Roberts system modeling **3-species chemical kinetics problem**: find amount  $n = [n_A, n_B, n_C]^T$  on the time-interval  $t \in [0, 4 \cdot 10^3]$  with

- reaction rates  $k_a = 4 \cdot 10^{-2}$ ,  $k_b = 10^4$ ,  $k_c = 3 \cdot 10^7$  and
- initial condition  $n^o = [n_A^o, n_B^o, n_C^o] = [1, 0, 0]$ .



resulting in the system of ODEs

$$\begin{cases} \frac{dn_A}{dt} = -a n_A + b n_B \cdot n_C \\ \frac{dn_B}{dt} = a n_A - b n_B \cdot n_C - c n_B^2 \\ \frac{dn_C}{dt} = c n_B^2 \end{cases}$$

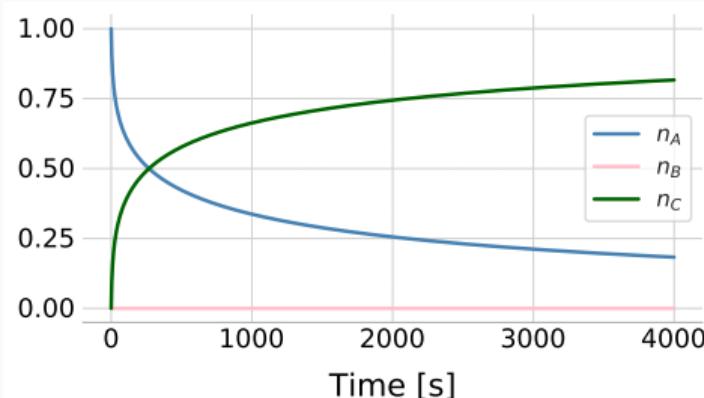
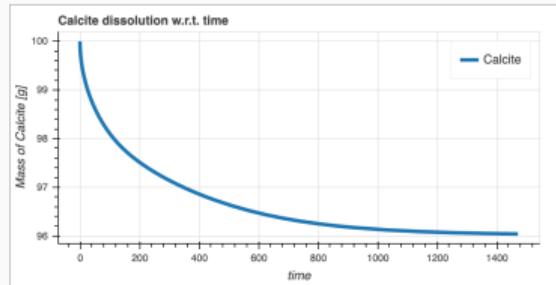


Figure 26: Solution of the Roberts system.

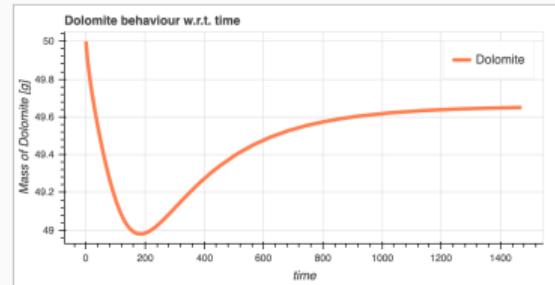
Source code: [polybox](#) using `odeint` function of `scipy.integrate` Python package.

# Example, Calcite dissolution

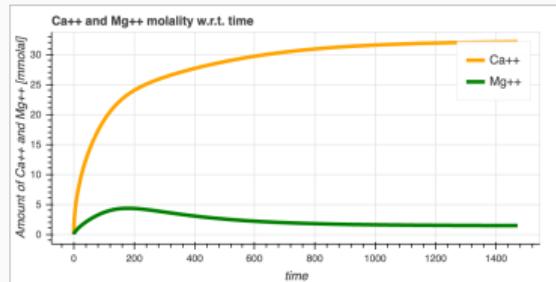
Jupyter notebook tutorial *Kinetic dissolution of carbonate with recording:*



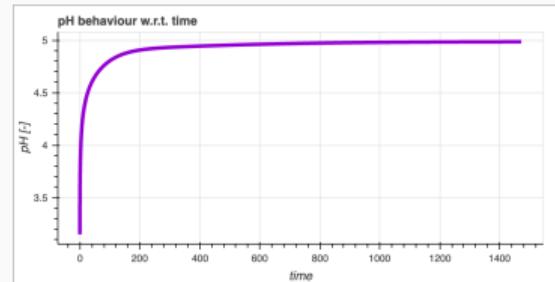
(a) Calcite dissolution



(b) Dolomite dissolution



(c)  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  molality increase



(d) pH

## **Reactive transport modeling**

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# Reactive transport modeling

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## Introduction

# Introduction

- **Reactive transport (RT) modeling** is an essential tool for the **analysis of coupled physical, chemical, and biological processes** in Earth systems.
- **Reactive transport models** have been applied to understand bio-geochemical systems for more than **three decades**.
- Modeling of interactions of processes at a range of spatial and time scales → connecting these process (material capabilities) at the atomic and the macroscopic scales.
- **Reactive transport models** predicts the distribution in space and time of the chemical reactions that occur along a flow-path.
- It is **essential for interpreting** the phenomena occurring in the surface or subsurface systems, as well as engineering and environmental problems:
  - reactive fluid flow (in tanks, reactors, or membranes),
  - solute transport (e.g., particles and species in the atmosphere),
  - geochemical reactions (e.g., gas and oil industry, migrating magma), and
  - bio-geochemical processes.

# Applications

- Description of **elemental and nutrient fluxes between major Earth reservoirs:**
  - understanding the natural waters composition;
  - precipitation / dissolution of rocks (minerals) in geologic formations after injection of industrial wastes / steam / CO<sub>2</sub>;
  - generation of acidic waters and leaching of metals from mine wastes.
- Treatment of **contaminant retardation in the subsurface:**
  - migration of contaminant plumes;
  - the mobility of radionuclides in waste repositories;
  - the bio-degradation of chemicals in landfills.
- Treatment of **deep Earth processes** such as metamorphism and **magma transport**.



(e) Acid mine drainage

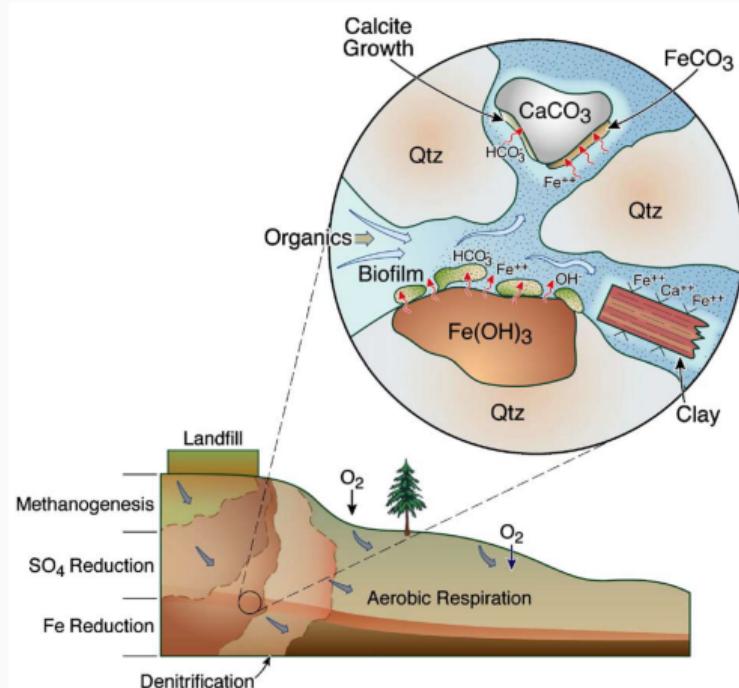


(f) Yellow slime mold



(g) A landfill in Poland

## Example of coupled processes



**Figure 27:** Illustration from Steefel et al. (2005): **coupled geochemical, microbiological, and hydrologic processes operating at both the aquifer and pore scale**, i.e., oxidation-reduction zones developed in an aquifer downstream from an organic-rich landfill.

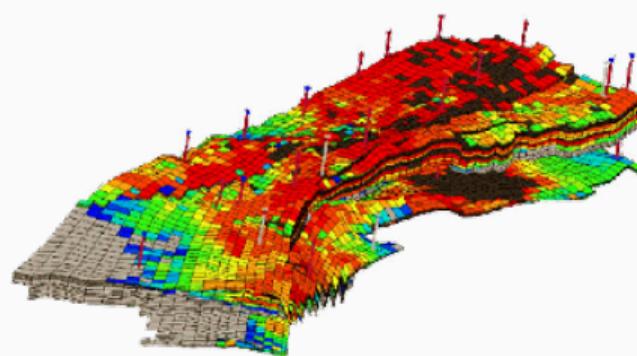
## **Reactive transport modeling**

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**Petroleum reservoir simulation**

# Petroleum reservoir simulation

- **Important characteristics** of reservoir are the nature of the **rock and the fluids** filling it.
- **Reservoir characteristics:**
  - heterogeneous;
  - properties heavily depend on the space location.
- **Example:** **fractured reservoir** is a set of heterogeneous porous media blocks (the matrix) and a net of fractures. **Rock properties** (permeability) in such a reservoir dramatically change:
  - permeability in the matrix is 1 millidarcy;
  - permeability in the fractures is 1000 millidarcy.



# Stages of oil recovery

The nature of the fluids filling in reservoir strongly depends on the **stage of oil recovery**:

- **Early stage / primary recovery:**

- single fluid (gas/oil),
- high pressure,
- gas/oil is produced by natural decompression without pumping effort at the wells,
- stage ends when a pressure equilibrium between the oil field and the atmosphere occurs.

- **Secondary recovery stage** (to recover part of the remaining oil):

- fluid is injected through injection wells,
- oil is produced through production wells,
- high reservoir pressure,
- high flow rates,
- $\begin{cases} P_{\text{reservoir}} \geq P_{\text{bubble}} : \text{ two-phase immiscible flow (water and oil phases),} \\ P_{\text{reservoir}} < P_{\text{bubble}} : \text{ the flow is of the oil type.} \end{cases}$

# Enhanced oil recovery techniques

- **Water flooding**
  - is not very effective: > 50% of hydrocarbons often remain in the reservoir;
  - large amount of oil is trapped in small pores and cannot be washed out;
  - the oil is heavy and viscous, whereas the water is extremely mobile ⇒ with sufficiently high flow rates, the production wells primarily produce water instead of oil.
- **Enhanced recovery techniques** (using complex chemical and thermal effects) is injecting materials that are not normally present in a petroleum reservoir.
- **Main objective** of these techniques is to achieve **miscibility** (and thus **eliminate the residual oil saturation oil**) by
  - increasing temperature (e.g., in situ combustion) or
  - injecting other chemical species (e.g., CO<sub>2</sub>).
- Popular enhanced recovery techniques:
  - **composition flow** (given chemical composition, the rest is dependent on the thermodynamic conditions and the overall concentration of each species);
  - **thermal methods** (steam drive and soak);
  - **chemical flooding** (alkaline, surfactant, polymer, and foam flooding).

## Reactive transport modeling

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Advection-diffusion-reaction equation

## Advection-diffusion-reaction equation (transport equation) i

- Conservation laws permit us to derive the following partial differential equation that governs the **transport of a conservative quantity**  $u$ :

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = f \quad \mathbf{x} \in \Omega, t > 0$$

- **Quiz:** which operator in this equation could be responsible for the reactive part of the modeling?



<http://etc.ch/JTfB/?qr> or

## Advection-diffusion-reaction equation (transport equation) ii

- Conservation laws permit us to derive the following partial differential equation that governs the **transport of a conservative quantity**  $u$ :

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = f \quad \mathbf{x} \in \Omega, \quad t > 0$$

where

- $\frac{\partial u}{\partial t}$  is the **time derivative**;
- $\nabla u = \begin{pmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} & \frac{\partial u}{\partial z} \end{pmatrix}$  is the **gradient operator** of scalar variable  $u$  denoting **flux** and in combination with  $D$  accounting for the **diffusion/dispersion processes**;
- $\nabla \cdot \mathbf{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$  is the **divergence operator** of vector variable  $\mathbf{v}$  accounting **convection/advection**;
- $\rho(u)$  is the **reaction operator**.

## Advection-diffusion-reaction initial boundary value problem (I-BVP)

- Adding initial and boundary condition, we obtain **initial boundary value problem (I-BVP)**

$$\partial u / \partial t + \nabla \cdot (\mathbf{v} u - D \nabla u) + \rho(u) = f \quad \mathbf{x} \in \Omega, t > 0$$

$$u = u_0 \quad \mathbf{x} \in \Omega, t = 0$$

$$u = u_D \quad \mathbf{x} \in \Gamma_D, t > 0$$

$$\mathbf{v} u - D \nabla u = g \quad \mathbf{x} \in \Gamma_N, t > 0$$

- $u$  is some **conservative quantity** (e.g., energy, species amounts) per volume;
- $\mathbf{v}$  is the **velocity field** in which the quantity is advected;
- $D$  is a **dispersion–diffusion tensor**;
- $f$  is a **rate of generation** (e.g., heat generation, reaction rate).
- $u_0$  is the **given initial condition** of  $u$  at time  $t = 0$  at every  $x$  in the domain  $\Omega$ ;
- $u_D$  is the **given value** of  $u$  on a **Dirichlet boundary**  $\Gamma_D$ ;
- $g$  is the **given value** of the flux  $\mathbf{v} u - D \nabla u$  on a **Neumann boundary**  $\Gamma_N$ .

## Exercise, 1D advection-diffusion equation

- **Exercise:** Write the partial differential equation

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = f$$

for the **one dimensional case** with  $u = u(t, x)$  and a scalar velocity  $v$ .

- **Answer:** one dimensional case of the equation above reads as follows:

$$\frac{\partial u}{\partial t} + \frac{\partial}{\partial x} \left( vu - D \frac{\partial u}{\partial x} \right) + \rho(u) = f.$$

Alternatively, we can apply the operator  $\partial/\partial x$  on each term inside parenthesis to get

$$\frac{\partial u}{\partial t} + \frac{\partial(vu)}{\partial x} - \frac{\partial}{\partial x} \left( D \frac{\partial u}{\partial x} \right) + \rho(u) = f.$$

## Exercise, 1D advection-diffusion equation (constant diffusion and velocity)

- **Exercise:** Assume velocity  $v$  and diffusion coefficient  $D$  are constant. How can we simplify

$$\frac{\partial u}{\partial t} + \frac{\partial(vu)}{\partial x} - \frac{\partial}{\partial x} \left( D \frac{\partial u}{\partial x} \right) + \rho(u) = f?$$

- **Answer:** We move both  $v$  and  $D$  outside the derivative

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} + \rho(u) = f.$$

## First-order splitting to transport and reaction equations

- Let us represent

$$\frac{\partial u}{\partial t} + \nabla \cdot (\mathbf{v}u - D\nabla u) + \rho(u) = 0 \quad \text{as} \quad \frac{\partial u}{\partial t} + T(u) + R(u) = 0$$

where  $T(u)$  and  $R(u)$  are transport and reaction operators.

- According to the **first-order splitting**, we first solve the **transport equation** for  $\bar{u}$ , i.e.,

$$\begin{aligned}\frac{\partial \bar{u}}{\partial t} + T(\bar{u}) &= 0, & t > 0, \\ \bar{u} &= u_0, & t = 0,\end{aligned}$$

and next the **reaction equation** with reconstructed  $\bar{u}$  as the initial condition, i.e.,

$$\begin{aligned}\frac{\partial u}{\partial t} + R(u) &= 0, & t > 0, \\ u &= \bar{u}, & t = 0.\end{aligned}$$

## Reaction equation in terms of chemical kinetic-equilibrium problem

- Reaction equation

$$\begin{aligned}\frac{\partial u}{\partial t} + R(u) &= 0, \quad t > 0, \\ u &= \bar{u}, \quad t = 0,\end{aligned}$$

is already discussed **chemical kinetic-equilibrium differential-algebraic equation (DAE)**

$$\begin{aligned}\frac{db_e}{dt} &= f_e(n_e), \quad t > 0, \\ \frac{dn_k}{dt} &= f_k(n_k), \quad t > 0, \\ n_e &= \varphi(T, P, b_e), \quad t > 0, \\ b_e &= An_e^o, \quad t = 0, \\ n_k &= n_k^o, \quad t = 0.\end{aligned}$$

# Numerical solution of the transport equations

- There are many **numerical methods** for the solution of the I-BVP with transport equation

$$\frac{\partial u}{\partial t} + T(u) = f.$$

- **Finite difference method (FDM):**
  - is the **simplest** of all methods,
  - has **disadvantages** when **complex geometries** are involved.
- **Finite volume method (FVM):**
  - forces **conservation of quantities** at discretized level,
  - only needs to do flux evaluation for the cell boundaries,
  - can be used on **unstructured (triangular) grids**,
  - the **higher-order approximations** are not easily constructed.
- **Finite element method (FEM):**
  - applicable to **general boundary conditions**, **complex geometry**, and **variable material properties**,
  - clear **structure and versatility** (e.g., mixed formulation),
  - solid theoretical base to obtain **error estimates**.

## Basics of finite difference method (FDM)

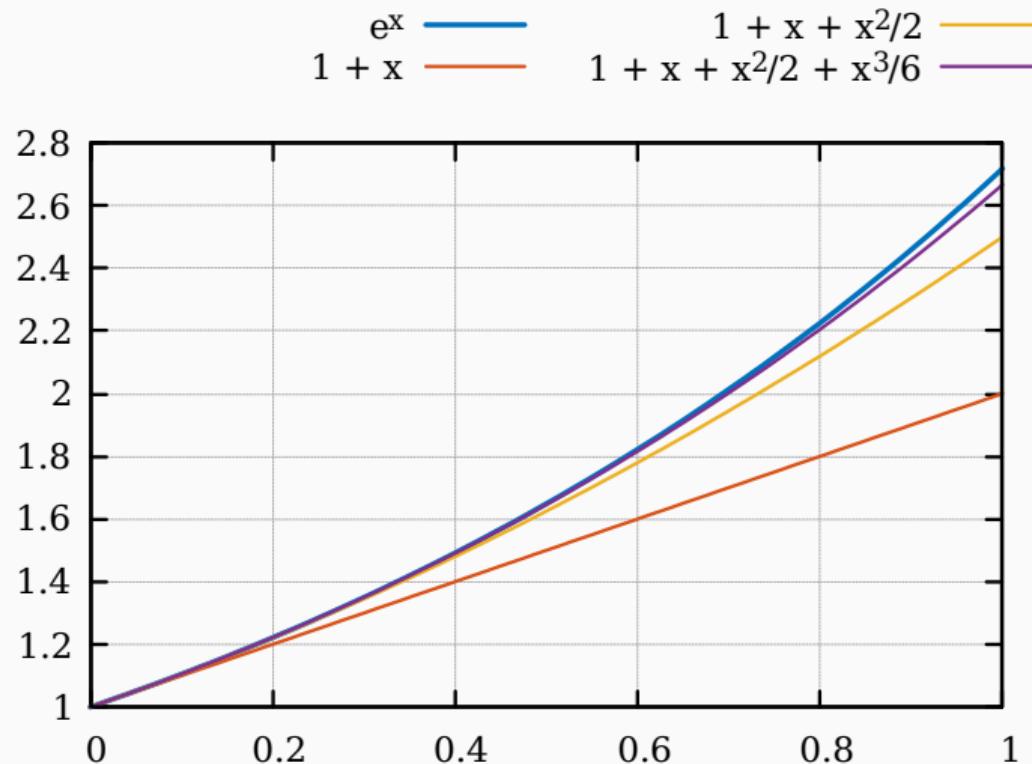
- In the **FDM**, the derivatives are approximated with **finite difference formulas**.
- The **Taylor expansion** is a **polynomial** approximation of function  $f$  around a point  $x_i$

$$f(x_i + \Delta x) = f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + \cdots + \frac{1}{n!} \frac{\partial^n f(x_i)}{\partial x^n} \Delta x^n + \cdots$$

- **Exercise:** Write the Taylor expansion for  $f(x) = e^x$  around  $x_i = 0$ .
- **Answer:**

$$f(x_i + h) = e^{x_i + \Delta x} \approx 1 + \Delta x + \frac{1}{2} \Delta x^2 + \frac{1}{6} \Delta x^3 + \cdots$$

## Approximation of $e^x$ using Taylor series



## First-order FDM scheme

- We can derive **finite difference approximations** for derivatives  $\frac{\partial f(x_i)}{\partial x}$ ,  $\frac{\partial^2 f(x_i)}{\partial x^2}$ , etc by truncating the Taylor expansion

$$f(x_i + \Delta x) = f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + \cdots + \frac{1}{n!} \frac{\partial^n f(x_i)}{\partial x^n} \Delta x^n + \cdots$$

up until the **derivative order**.

- For example, for **1st order approximation**

$$f(x_i + \Delta x) \approx f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + O(\Delta x^2) \implies \frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + h) - f(x_i)}{\Delta x} + O(\Delta x),$$

the error decrease is of order  $O(h)$  with decreasing  $h$ .

- **Exercise:** Derive the **second order approximation**, where the approximation error is proportional to  $O(h^2)$  with a decrease of  $h$ ?

## Second-order FDM scheme, Central difference approximation

- Write the following two **truncated Taylor expansions**:

$$f(x_i + \Delta x) = f(x_i) + \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + O(\Delta x^3)$$

$$f(x_i - \Delta x) = f(x_i) - \frac{\partial f(x_i)}{\partial x} \Delta x + \frac{1}{2} \frac{\partial^2 f(x_i)}{\partial x^2} \Delta x^2 + O(\Delta x^3)$$

- By subtracting the two equations, we can write

$$\frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + \Delta x) - f(x_i - \Delta x)}{2\Delta x} + O(\Delta x^2)$$

which is a **central finite difference approximation** for  $\partial f(x_i)/\partial x$ .

## Usage of FDM to transform differential equation

- We use the **finite difference formulas**

$$\frac{\partial f(x_i)}{\partial x} \approx \frac{f(x_i + \Delta x) - f(x_i - \Delta x)}{2\Delta x}$$

and

$$\frac{\partial^2 f(x_i)}{\partial x^2} \approx \frac{f(x_i + \Delta x) - 2f(x_i) + f(x_i - \Delta x)}{\Delta x^2}$$

to transform the **partial differential equation** (PDE)

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} = f \quad \text{on} \quad [x_L, x_R]$$

into a **system of linear algebraic equations**.

## Discretization of transport equation, Computational domain discretization

- We numerically solve the transport problem

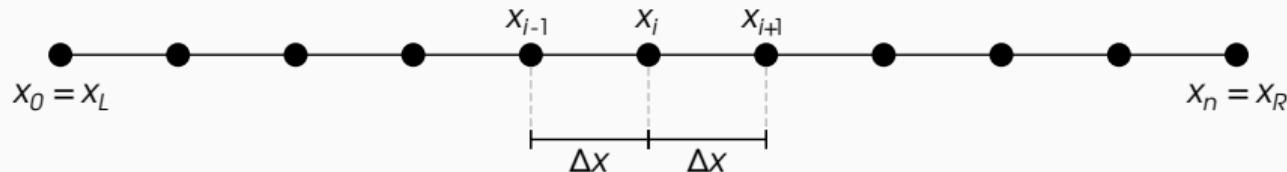
$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} = f \quad x_L < x < x_R, \quad t > 0,$$

$$u = 0 \quad x_L < x < x_R, \quad t = 0,$$

$$u = 1 \quad x = x_L, \quad t > 0,$$

and free boundary at  $x = x_R$  using the finite difference method (FDM).

- Consider the following uniform discretization of computational domain  $[x_L, x_R]$ :



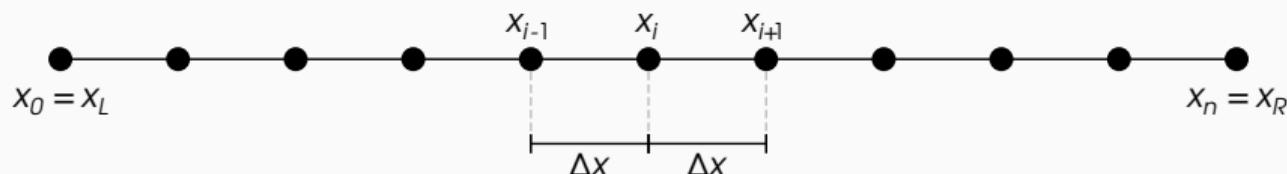
## Discretization of transport equation, Finite difference formulas

- Using **finite difference formulas**, we can approximate the partial derivatives in transport equation as follows:

$$\frac{\partial u}{\partial t} \approx \frac{u_i^{k+1} - u_i^k}{\Delta t} \quad x = x_i, t = t_k$$

$$\frac{\partial u}{\partial x} \approx \frac{u_{i+1}^{k+1} - u_{i-1}^{k+1}}{2\Delta x} \quad x = x_i, t = t_k$$

$$\frac{\partial^2 u}{\partial x^2} \approx \frac{u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1}}{\Delta x^2} \quad x = x_i, t = t_k$$



## Discretization of transport equation: system of algebraic equations

- The differential equation

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial x} - D \frac{\partial^2 u}{\partial x^2} = f$$

becomes a **system of algebraic equations**

$$\left( \frac{u_i^{k+1} - u_i^k}{\Delta t} \right) + v \left( \frac{u_{i+1}^{k+1} - u_{i-1}^{k+1}}{2\Delta x} \right) - D \left( \frac{u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1}}{\Delta x^2} \right) = f_i \quad (i = 1, \dots, n-1)$$

- With **recovered values**  $u_i^k$  ( $u$  on every **discrete point**  $x_i$  at **discrete time**  $t_k$ ), we solve algebraic equations to find  $u_i^{k+1}$  ( $u$  on every  $x_i$  at  $t_{k+1} = t_k + \Delta t$ ):

$$u_i^{k+1} + \frac{v \Delta t}{2\Delta x} \left( u_{i+1}^{k+1} - u_{i-1}^{k+1} \right) - \frac{D \Delta t}{\Delta x^2} \left( u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1} \right) = \Delta t f_i + u_i^k \quad (i = 1, \dots, n-1)$$

## Discretization of transport equation: central vs. upwind scheme

- The **central scheme** for the finite difference approximation of the advection term, i.e.,

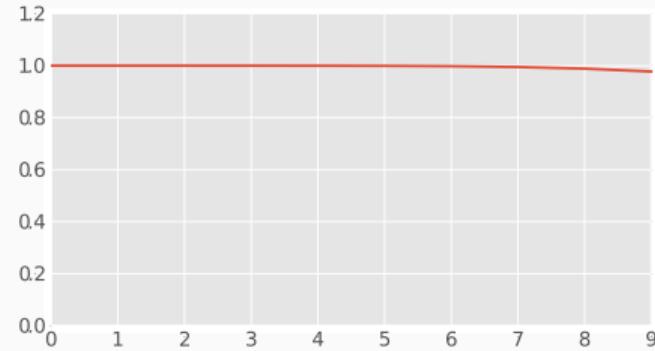
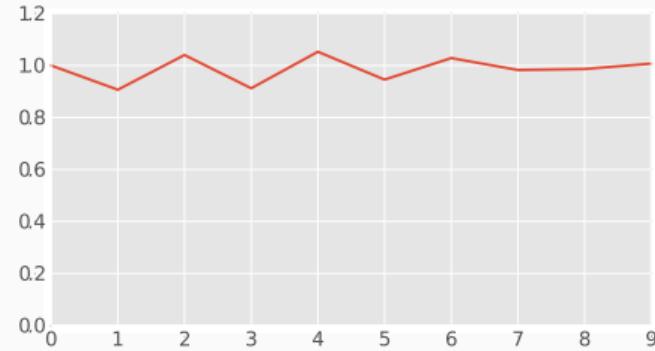
$$v \frac{\partial u}{\partial x} \approx v \left( \frac{u_{i+1}^{k+1} - u_{i-1}^{k+1}}{2\Delta x} \right),$$

can produce **spurious oscillations**.

- One can use instead an **upwind scheme**, i.e.,

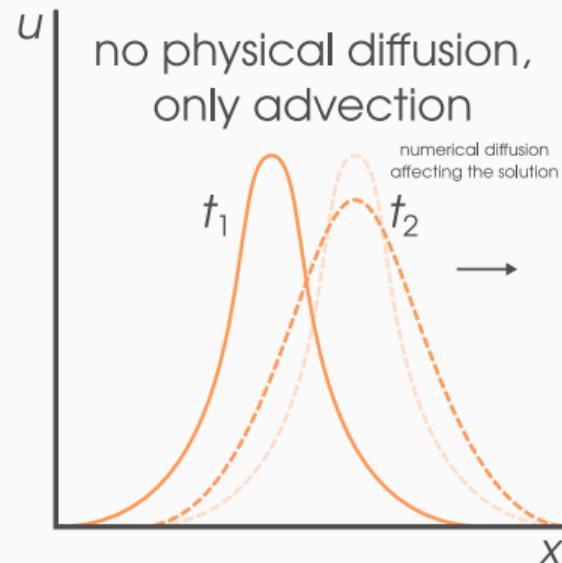
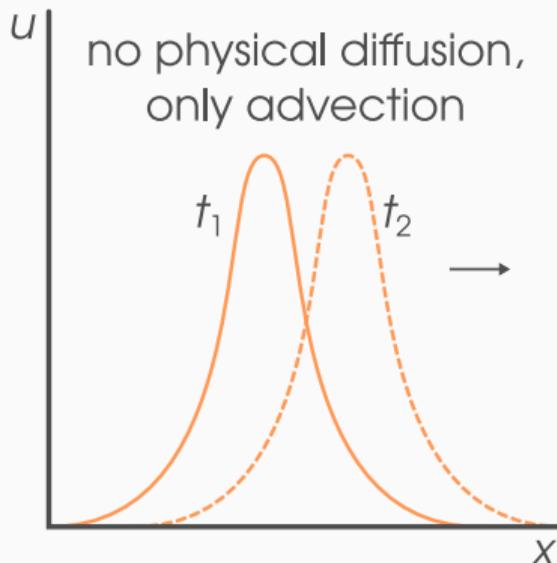
$$v \frac{\partial u}{\partial x} \approx v \left( \frac{u_i^{k+1} - u_{i-1}^{k+1}}{\Delta x} \right),$$

to prevent this.



# Numerical diffusion introduced by the upwind scheme

- **Warning:** the upwind scheme fixes the numerical oscillation, but introduces **numerical diffusion!**



## Discretization of transport equation: tridiagonal formulation

- We write the algebraic equation

$$\left( \frac{u_i^{k+1} - u_i^k}{\Delta t} \right) + v \left( \frac{u_i^{k+1} - u_{i-1}^{k+1}}{\Delta x} \right) - D \left( \frac{u_{i+1}^{k+1} - 2u_i^{k+1} + u_{i-1}^{k+1}}{\Delta x^2} \right) = f_i \quad (i = 1, \dots, n-1)$$

into the the following tridiagonal matrix form:

$$a_i u_{i-1}^{k+1} + b_i u_i^{k+1} + c_i u_{i+1}^{k+1} = d_i \quad (i = 1, \dots, n-1)$$

- **Tridiagonal matrix** is a band matrix that has nonzero elements on the main diagonal and first diagonal below and above it the main one.
- **Exercise:** Find the values of the coefficients  $a_i, b_i, c_i$ , and  $d_i$ .

## Discretization of transport equation: internal points

- For **every internal point**  $x_i$ , we have the system

$$a_i u_{i-1}^{k+1} + b_i u_i^{k+1} + c_i u_{i+1}^{k+1} = d_i \quad (i = 1, \dots, n-1)$$

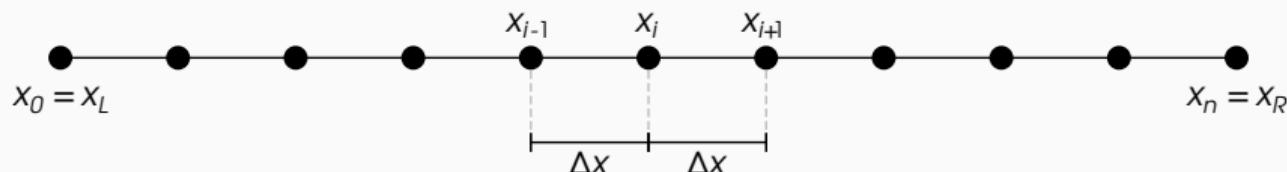
where

$$a_i = -\frac{v\Delta t}{\Delta x} - \frac{D\Delta t}{\Delta x^2}$$

$$b_i = 1 + \frac{v\Delta t}{\Delta x} + 2\frac{D\Delta t}{\Delta x^2}$$

$$c_i = -\frac{D\Delta t}{\Delta x^2}$$

$$d_i = u_i^k + \Delta t f_i$$



## Discretization of transport equation: left boundary condition

- On the **left boundary point**,  $u = 1$ , and thus  $u_0^k = u_0^{k+1} = 1$ .
- **Exercises:** What are the values of  $a_0$ ,  $b_0$ ,  $c_0$  and  $d_0$  in the general equation:

$$a_0 u_{-1}^{k+1} + b_0 u_0^{k+1} + c_i u_1^{k+1} = d_0?$$

- **Answer:**

$$a_0 = 0$$

$$b_0 = 1$$

$$c_0 = 0$$

$$d_0 = 1$$

## Discretization of transport equation: right boundary condition

- On the **right boundary point**, we use the following finite difference representation for the **advection** and **diffusion terms**:

$$\left(v \frac{\partial u}{\partial x}\right)_n^{k+1} = v \frac{u_n^{k+1} - u_{n-1}^{k+1}}{\Delta x} \quad \text{and} \quad \left(D \frac{\partial^2 u}{\partial x^2}\right)_n^{k+1} = 0.$$

- Then, the algebraic equation reads as

$$a_n u_{n-1} + b_n u_n + c_n u_{n+1} = d_n$$

with

$$a_n = -\frac{v\Delta t}{\Delta x}$$

$$b_n = 1 + \frac{v\Delta t}{\Delta x}$$

$$c_n = 0$$

$$d_n = u_n^k + \Delta t f_{n-1}.$$

## Solving a tridiagonal matrix equation

$$\begin{aligned} b_0 u_0 + c_0 u_1 &= d_0 & (i = 0) \\ a_i u_{i-1}^{k+1} + b_i u_i^{k+1} + c_i u_{i+1}^{k+1} &= d_i & (i = 1, \dots, n-1) \\ a_n u_{n-1} + b_n u_n &= d_n & (i = n) \end{aligned}$$

or

$$\begin{bmatrix} b_0 & c_0 & & & & \\ a_1 & b_1 & c_1 & & & \\ & a_2 & b_2 & c_2 & & \\ & & \ddots & \ddots & \ddots & \\ & & & a_{n-1} & b_{n-1} & c_{n-1} \\ & & & & a_n & b_n \end{bmatrix} \begin{bmatrix} u_0 \\ u_1 \\ u_2 \\ \vdots \\ u_{n-1} \\ u_n \end{bmatrix} = \begin{bmatrix} d_0 \\ d_1 \\ d_2 \\ \vdots \\ d_{n-1} \\ d_n \end{bmatrix}$$

- This special linear system can be solved using the **Thomas matrix algorithm**.
- The algorithm is stable for the **diagonally dominant** or **positive definite** matrices.

## Thomas algorithm in Python

```
1  def thomas(a, b, c, d):
2      # Size of the matrix
3      n = len(d)
4      # Calculation of new coefficients
5      c[0] /= b[0]
6      for i in range(1, n - 1):
7          c[i] /= b[i] - a[i]*c[i - 1]
8          d[0] /= b[0]
9      # The forward sweep
10     for i in range(1, n):
11         d[i] = (d[i] - a[i]*d[i - 1])/(b[i] - a[i]*c[i - 1])
12     x = d
13     # The backward sweep
14     for i in reversed(range(0, n - 1)):
15         x[i] -= c[i]*x[i + 1]
16     return x
```

**Listing 14:** Thomas algorithm for tridiagonal matrices

## Transport step in Python

```
1  beta, alpha = v * dt / dx, D * dt / dx**2
2  def transport(u):
3      # Coefficients a, b, c
4      a.fill(-beta - alpha)
5      b.fill(1 + beta + 2*alpha)
6      c.fill(-alpha)
7      # Coefficients a, b, c on the left boundary node
8      a[0] = 0.0
9      b[0] = 1.0
10     c[0] = 0.0
11     # Coefficients a, b, c on the right boundary node
12     a[-1] = -beta
13     b[-1] = 1 + beta
14     c[-1] = 0.0
15     # Dirichlet boundary condition for u on the left boundary node
16     u[0] = ul
17     # Solve the tridiagonal matrix equation
18     thomas(a, b, c, u)
```

Listing 15: Transport step in Python

## **Reactive transport modeling**

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**Reactive transport in a single fluid phase**

## Reactive transport in a single fluid phase

- Consider a **single fluid phase** with  $N$  chemical species.
- Each species is transported according to the following  $N$  **reactive transport equations**

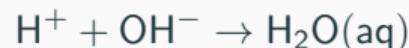
$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} - D \nabla n_i) = r_i \quad (i = 1, \dots, N),$$

where

- $n_i$  is the **concentration** of species  $i$  (in  $\text{mol}/\text{m}^3$ );
- $\mathbf{v}$  is the **fluid velocity** (in  $\text{m}/\text{s}$ );
- $D$  is the **diffusion coefficient** of the species (in  $\text{m}^2/\text{s}$ );
- $r_i$  is the **rate of production/consumption** of species  $i$  (in  $\text{mol}/(\text{m}^3 \cdot \text{s})$ ).

## Local chemical equilibrium assumption i

- The **rates of transport** (advection and diffusion) can sometimes be **considerably slower** than the **rates of chemical reactions**.
- **Advection flux rates** are  $n_i v \approx 10^{-5} \text{ mol}/(\text{m}^2 \cdot \text{s})$ , considering  $v \approx 1 \text{ m/day}$ .
- **Diffusion flux rates** are  $-D \nabla n_i \approx 10^{-9} \text{ mol}/(\text{m}^2 \cdot \text{s})$ , considering  $D \approx 10^{-9} \text{ m}^2/\text{s}$ .
- **Rates of aqueous reactions** are several orders of magnitude higher, e.g., the reaction

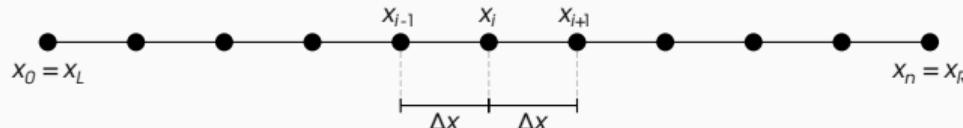


has a rate of  $r_i \approx 10^{11} \text{ mol}/(\text{m}^3 \cdot \text{s})$ .

- Many aqueous reactions **equilibrate** in the order of microseconds to few seconds!

## Local chemical equilibrium assumption ii

- If chemical reactions proceed at a rate much faster than transport rates, we can assume the species react **instantaneously to equilibrium**.
- Then, these chemical species are assumed to be in **local chemical equilibrium** (i.e., at every point in space, they are in chemical equilibrium).
  - As soon as the chemical species are perturbed due to advection and diffusion, they instantaneously react to achieve a new state of equilibrium.
  - For example, as water flows through a reactive porous rock, the fluid gets immediately saturated with the rock minerals.
- We will see that, at every time step, a chemical equilibrium calculation is needed at every node, which could be computationally demanding.



## Simplifying the reactive transport equations

- We will now simplify the reactive transport equations

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} - D \nabla n_i) = r_i \quad (i = 1, \dots, N),$$

using the assumption that the species are in **local chemical equilibrium**.

- Since the species are in equilibrium at all times, the reaction rates  $r_i$  depend on the rates of transport and cannot be calculated in advance.
- However, there is a way to **eliminate** them and **drastically reduce the number of transport equations** to solve!

## Things we need in the simplification

- Contribution of each species to the **concentration of element  $j$** :

$$b_j = \sum_{i=1}^N A_{ji} n_i.$$

- **Rate of production of every chemical element** and according to **the mass conservation condition for the elements**:

$$\sum_{i=1}^N A_{ji} r_i = 0.$$

## Reactive transport combined with aqueous-mineral reactions

- We start from the equation for a **single fluid phase**

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v} - D \nabla n_i) = r_i \quad (i = 1, \dots, N).$$

- If **mineral species** are present, they are **immobile**.
- We **partition the species to fluid and solid species** with corresponding amount of elements  $b^f$  and  $b^s$ , such that the **reactions that occur among aqueous and mineral species** are governed as follows:

$$\frac{\partial n_i^f}{\partial t} + \nabla \cdot (n_i^f \mathbf{v} - D \nabla n_i^f) = r_i^f \quad (i = 1, \dots, N^f),$$

$$\frac{\partial n_i^s}{\partial t} = r_i^s \quad (i = 1, \dots, N^s),$$

where superscript s refers to solid, and f to fluid.

## Reactive transport equations in terms of element concentrations

**Exercise:** Using the fact that

$$b_j = b_j^f + b_j^s = \sum_{i=1}^{N^f} A_{ji} n_i + \sum_{i=1}^{N^s} A_{ji} n_i = \sum_{i=1}^N A_{ji} n_i$$

and

$$\sum_{i=1}^N A_{ji} r_i = 0,$$

derive

$$\frac{\partial b_j^s}{\partial t} + \frac{\partial b_j^f}{\partial t} + \nabla \cdot (b_j^f \mathbf{v} - D \nabla b_j^f) = 0 \quad (j = 1, \dots, E).$$

# Reactive transport equations in terms of element concentrations

To solve

$$\frac{\partial b_j^s}{\partial t} + \frac{\partial b_j^f}{\partial t} + \nabla \cdot (b_j^f \mathbf{v} - D \nabla b_j^f) = 0 \quad (j = 1, \dots, E),$$

we use the following **operator splitting** scheme:

- **Step 1:** Ignore the changes in  $b_j^s$  and calculate  $b_j^f$  in every node using

$$\frac{\partial b_j^f}{\partial t} + \nabla \cdot (b_j^f \mathbf{v} - D \nabla b_j^f) = 0 \quad (j = 1, \dots, E).$$

- **Step 2:** Use the updated amounts of elements in the fluid with the elements in the solid to calculate **the amount of elements**  $b_j = b_j^s + b_j^f$ .

**Update the species concentrations**  $n = [n_e, n_k]$ ,  $n_e \in \mathbb{R}^{N_e}$  and  $n_k \in \mathbb{R}^{N_k}$ , calculated at every node

$$\begin{aligned}\frac{db_e}{dt} &= f_e(n_e) & t > 0, & b_e = b_e^o = b_j & t = 0, \\ \frac{dn_k}{dt} &= f_k(n_k) & t > 0, & n_k = n_k^o & t = 0, \\ n_e &= \varphi(T, P, b_e) & t > 0.\end{aligned}$$

## **Reactive transport modeling**

---

**Example of reactive transport modeling  
of microbial souring**

# SUBPROBLEMS IN MODELLING THE MICROBIAL SOURING OF WATERFLOODED OIL RESERVOIRS

## Microbial souring

Sulfate reducing bacteria produces H<sub>2</sub>S while growing (the result of metabolic activity)



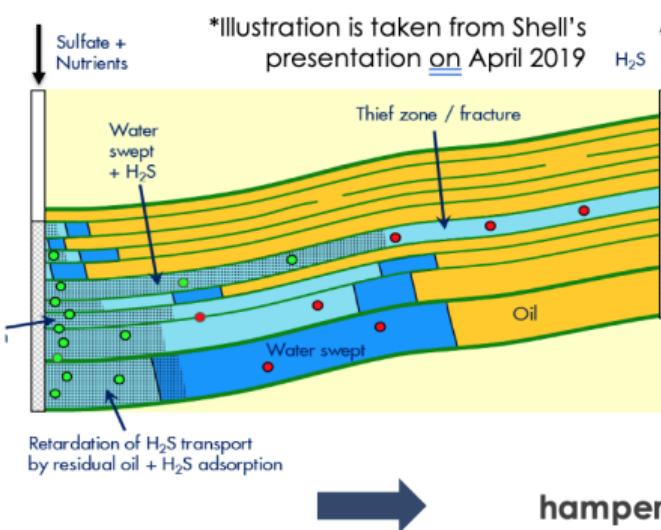
## Hydrogen sulfide (H<sub>2</sub>S) scavenging

'Collection' of the toxic and corrosive H<sub>2</sub>S-gas



## Waterflooding

Injection of the seawater (SW) + nutrients into reservoir with formation water (FW)



## Scaling

Scaled minerals reduce near wellbore permeability and hamper the well productivity/injectivity.

# MODELLING RESERVOIR SOURING

Injecting water into hydrocarbon reservoirs + exposing fluids to foreign microbes causes **the reservoir souring / increase of H<sub>2</sub>S mass**.

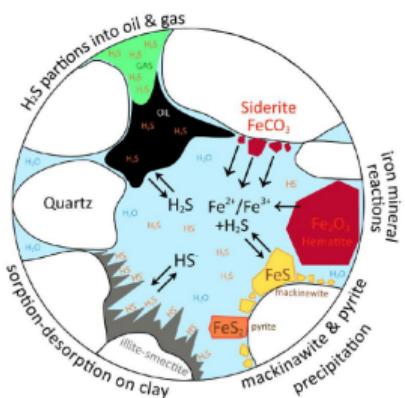


Field level prediction of H<sub>2</sub>S generation and production is important due to

- H<sub>2</sub>S toxicity to human/animals
- H<sub>2</sub>S corrosiveness to most metals causing
  - cracking of drill/transport pipe and tubular goods
  - destruction of testing tools and wire lines

# WHAT IS H<sub>2</sub>S-SCAVENGING?

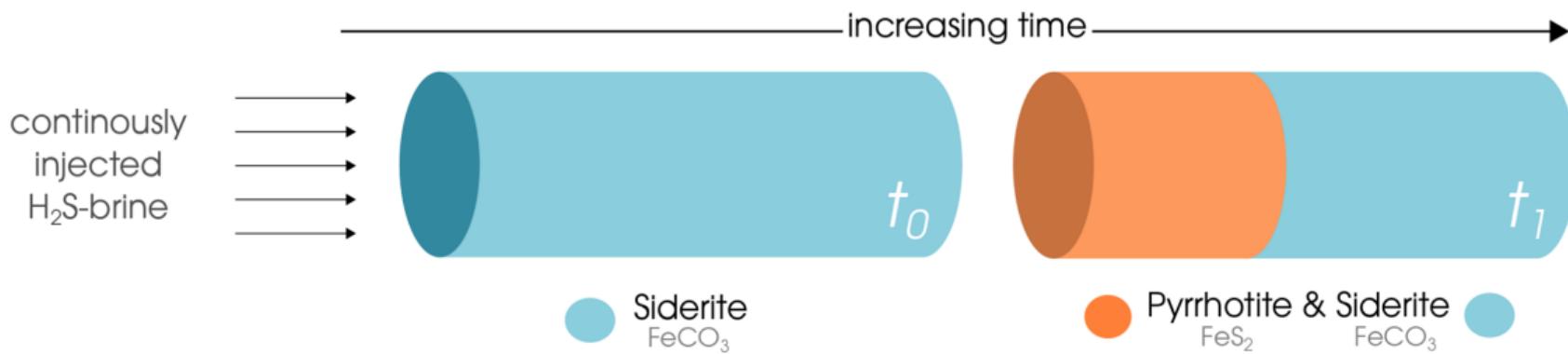
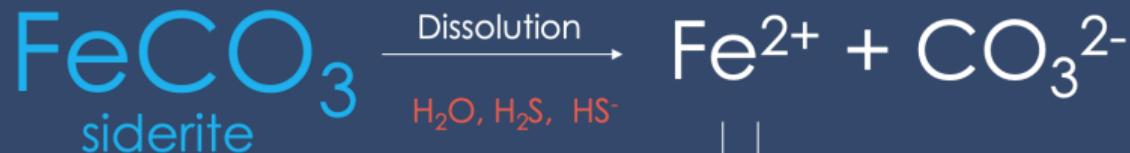
Scavenging is a technique to get rid of hydrogen sulfide.



**Sulfide scavenger** is any chemical that

- **can react** with one or more **sulfide species** (H<sub>2</sub>S, HS<sup>-</sup>, and S<sub>2</sub><sup>-</sup> ect.) and
- **can convert them** to a more **inert form**.

Our scavenger is **siderite/iron(II) carbonate (FeCO<sub>3</sub>)**.



## Discretization Parameters

$\Delta t = 1.2$  hours,  $\Delta x = 1$  m

## Thermodynamic Conditions

$T = 25$  °C,  $P = 1.01325$  bar

## Transport Parameters

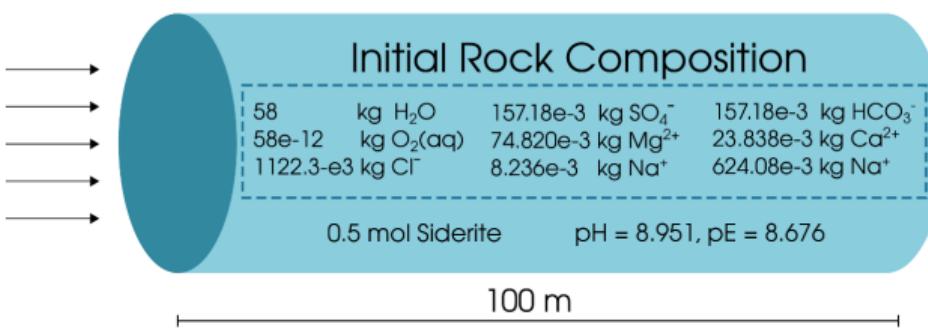
$v = 1.05e-5$  m/s,  $D = 0$

### Injected Fluid Composition

Aqueous species

+

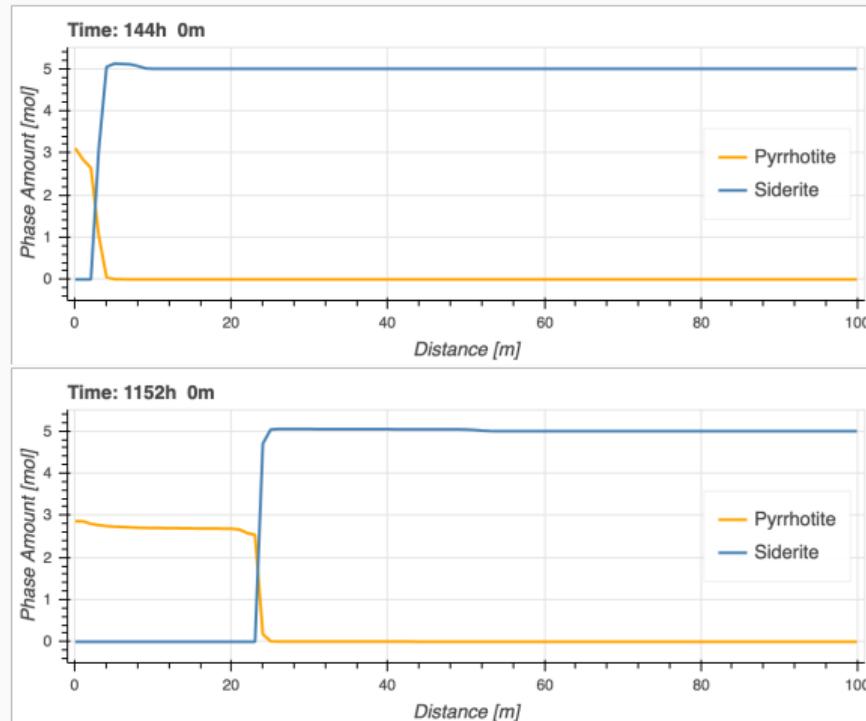
0.0196504 mol HS  
0.167794 mol H<sub>2</sub>S(aq)  
pH = 5.726, pE = 8.220



**Chemical system:** 44 preselected species (incl. minerals) with elements (C, Ca, Cl, Fe, H, K, Mg, Na, O, S)  
**5000 time steps x 100 mesh cells: 500,000 chemical equilibrium calculations**

## Example, Results of souring modeling

Jupyter notebook tutorial *RT modeling of the H<sub>2</sub>S scavenging process along a rock core*:



**Figure 28:** Siderite dissolution and pyrrhotite precipitation.

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