

Geofluids — Part IV

Introduction to Geochemical and Reactive Transport Modeling

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June 2, 2021

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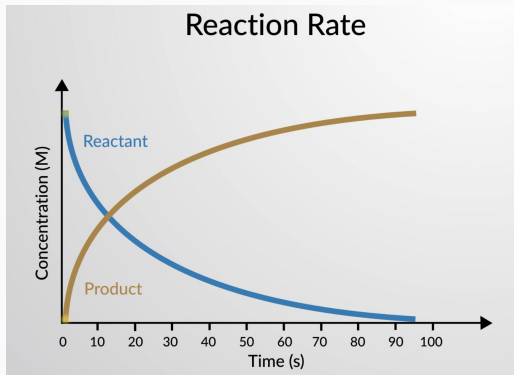
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Chemical kinetic calculation

Chemical kinetics

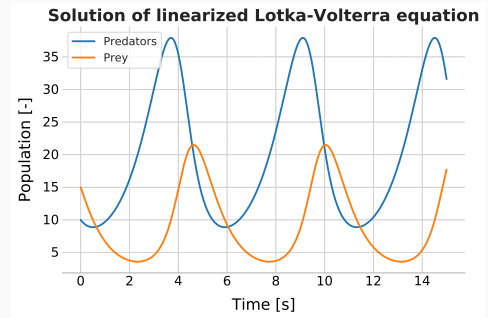
- **Chemical kinetics / reaction kinetics** studies **the rate of chemical reactions** and **factors that influence them**.
- Chemical processes can be described by detailed **kinetic reaction mechanisms** consisting of several hundreds or even thousands of reaction steps.



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 \Rightarrow higher the rate of reaction)
- **Temperature** (higher the temperature \Rightarrow higher the molecule thermal energy \Rightarrow 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 \Rightarrow higher the number of collisions between reactants \Rightarrow 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 [†]	Half-times
<i>Solute-solute</i>	
$\text{H}_2\text{CO}_3^0 = \text{H}^+ + \text{HCO}_3^-$ (acid-base)	$\sim 10^{-6}$ s
<i>Solute-water</i>	
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^0$ (hydration/hydrolysis)	~ 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>	
$\text{Cd}^{2+} + \text{CaX} = \text{Ca}^{2+} + \text{CdX}$ (X^{-2} 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>	
$\text{Al}_{(n+m)}(\text{OH})_{3n+2m}^{n+m} + m\text{H}_2\text{O} \rightarrow (n+m)\text{Al}(\text{OH})_3(\text{s}) + m\text{H}^+$	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>	
$\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}(\text{am}) \rightarrow \alpha\text{-FeOOH}(\text{goethite}) + (n+1)\text{H}_2\text{O}$	y
<i>Radioactive decay</i>	
$^{14}\text{C} \rightarrow ^{14}\text{N} + e^-$	5570 y

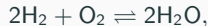
[†]Note: Other descriptions or explanations of the reactions are given parenthetically.

Chemical kinetic calculation

Reaction stoichiometry, rates, and orders

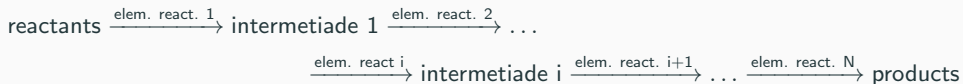
Reaction stoichiometry

- 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 H_2 has stoichiometric coefficient 2, O_2 has coefficient 1, and H_2O has coefficient 2.

- Chemical systems described by a single chemical reaction (reactants \rightarrow 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 $A = (A_1, A_2, A_3) = (\text{H}_2, \text{O}_2, \text{H}_2\text{O})$ is a vector of species, and $\nu = (\nu_1, \nu_2, \nu_3) = (-2, -1, 2)$ is a vector of multiplication factors, then we obtain

$$0 = \sum_{i=1}^3 \nu_i A_i.$$

- 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,
- ν_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
 - $\text{hydrocarbon} + \text{OH} \rightarrow \text{alkyl radical} + \text{H}_2\text{O}$,
 - $\text{alkyl radical} + \text{O}_2 (^3\Sigma) \rightarrow \text{alkylperoxy radical}$,
 - $\text{alkylperoxy radical} + \text{NO} \rightarrow \text{alkoxy radical} + \text{NO}_2$,
 - $\text{alkoxy radical} + \text{O}_2 (^3\Sigma) \rightarrow \text{aldehyde} + \text{HO}$.
- The ratio of hydrocarbons changes dependent on the type of pollution source.
- No single species can be identified as reactants or products.

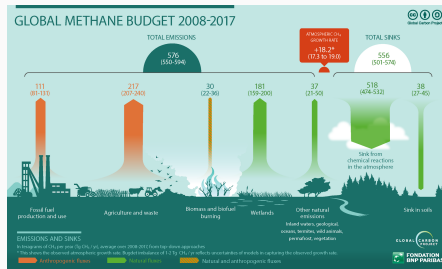


Figure 1: Diagram showing the main sources of methane for the decade 2008-2017, produced by a global report on global methane emissions by the Global Carbon Project (source [Wikipedia](#)).

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

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

we obtain

$$r = \frac{1}{\nu_i} \frac{d[A_i]}{dt}.$$

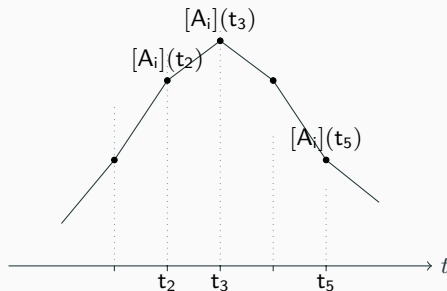


Figure 2: Time-dependent behaviour of the chemical system: the molar concentrations of species A_i measured at consecutive time points.

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.,

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

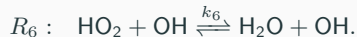
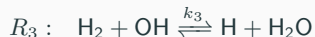
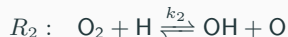
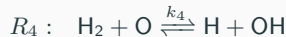
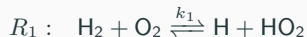
- For elementary reactions, **the reaction orders and the absolute value of the stoichiometric coefficients** of the reactants are **commonly the same**.

Example:

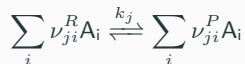
- for unimolecular decomposition $\text{A} \xrightleftharpoons{r} \text{B}$: $r = [\text{A}]$
- for bimolecular reaction
 - $\text{A} + \text{B} \xrightleftharpoons{r} \text{C}$: $r = [\text{A}] \cdot [\text{B}]$, or
 - $\text{A} + \text{A} \xrightleftharpoons{r} \text{C}$: $r = [\text{A}]^2$.

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 1).
- 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	$-\frac{d[A]}{dt} = k [A] [B]$	$k t = \frac{1}{[B]_0 + [A]_0} \ln \frac{[B]_0 [A]}{[B] [A]_0}$	$t_{1/2} = \frac{1}{k [A]_0} (B = A)$

Table 1: 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,
 - ν_{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** $\frac{d[A_i]}{dt}$ and **reaction rates** r_j :

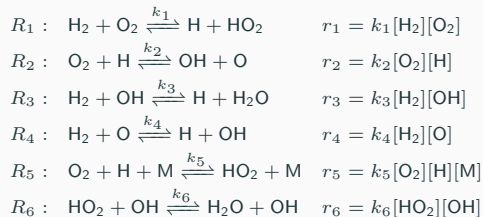
$$\frac{d[A_j]}{dt} = \sum_{j=1}^N \nu_{ji} r_j, \quad j = 1, \dots, M.$$

- 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 $\nu \in \mathbb{R}^{6 \times 8}$

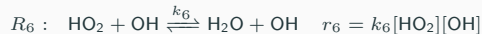
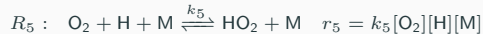
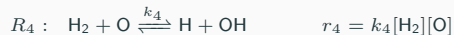
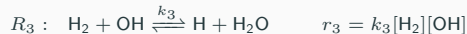


$$\nu = \begin{bmatrix} R_1 \\ R_2 \\ R_3 \\ R_4 \\ R_5 \\ R_6 \end{bmatrix} \begin{matrix} \text{H} & \text{H}_2 & \text{HO}_2 & \text{H}_2\text{O} & \text{O} & \text{O}_2 & \text{OH} & \text{M} \end{matrix} \begin{bmatrix} 1 & -1 & 1 & 0 & 0 & * & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 & * & 1 & 0 \\ 1 & -1 &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

$$\nu = \begin{bmatrix} R_1 \\ R_2 \\ R_3 \\ R_4 \\ R_5 \\ R_6 \end{bmatrix} \begin{matrix} \text{H} & \text{H}_2 & \text{HO}_2 & \text{H}_2\text{O} & \text{O} & \text{O}_2 & \text{OH} & \text{M} \end{matrix} \begin{bmatrix} 1 & -1 & 1 & 0 & 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 & -1 & 1 & 0 \\ 1 & -1 & 0 & 1 & 0 & 0 & -1 & 0 \\ 1 & -1 & 0 & 0 & -1 & 0 & 1 & 0 \\ -1 & 0 & 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \end{bmatrix}_{19}$$

- Quiz:** What are the coefficients in the column with the O₂?

Example, Kinetics law of mass action for hydrogen combustion



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

- The production rates can be formulated as follows:

$$\begin{aligned} \frac{d\text{H}}{dt} &= 1 r_1 - 1 r_2 + 1 r_3 + 1 r_4 - 1 r_5 + 0 r_6 \\ &= k_1[\text{H}_2][\text{O}_2] - k_2[\text{O}_2][\text{H}] + k_3[\text{H}_2][\text{OH}] + k_4[\text{H}_2][\text{O}] - k_5[\text{H}][\text{O}_2][\text{M}] + 0 k_6[\text{HO}_2][\text{OH}] \end{aligned}$$

- Quiz:** What is the right-hand side for the $\frac{d\text{HO}_2}{dt}$? <http://etc.ch/xREb> or



- Answer:** $\frac{d\text{HO}_2}{dt} = 1 r_1 + 1 r_5 - 1 r_6 = k_1[\text{H}_2][\text{O}_2] + k_5[\text{H}][\text{O}_2][\text{M}] - k_6[\text{HO}_2][\text{OH}].$

Chemical kinetic calculation

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 $\ln A$:

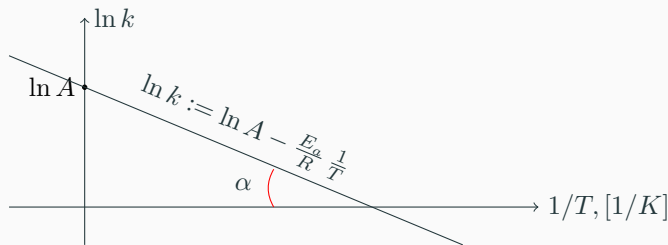


Figure 3: Linear function $\ln k := \ln A - \frac{E_a}{R} \frac{1}{T}$.

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 $C \neq E_a$.

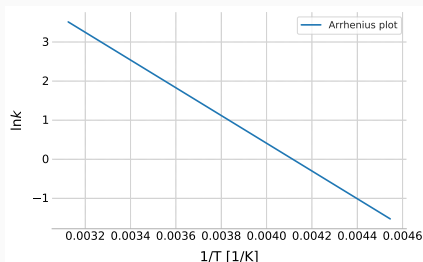
- For some **gas-phase kinetic elementary reactions**, the temperature dependence of the rate coefficient is described by a **truncated form of the extended Arrhenius equation**

$$k = A T^n.$$

Example of methane reaction, Arrhenius plots comparison

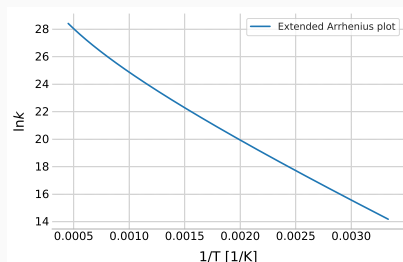
- Reaction of **methane consumption in the troposphere**

$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$, 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:

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

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_{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_{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

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 C₄H₆ from ethanol

- **Butadiene** C₄H₆ 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**:

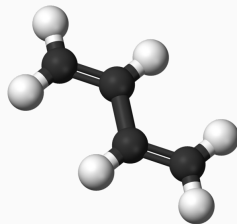
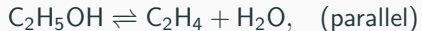


Figure 4: Organic compound of (CH₂ = CH)₂.

Chain reactions, Ignition of hydrogen example

- **Chain reactions** are defined by reactive 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_2 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 2: Important reactions for the hydrogen ignition mechanism.

Chemical kinetic calculation

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 CO₂;
 - batteries in electronics rely on redox reactions;
 - combustion reactions in the car engines, e.g., combustion of octane (hydrocarbon)



- The H₂O can be
 - (or oxygen in it) **oxidized**, losing electron, $\text{H}_2\text{O}(\text{l}) = \text{O}_2(\text{aq}) + 2 \text{e}^- + 2 \text{H}^+$, or
 - (or hydrogen in it) **reduced**, accepting electron, $\text{H}_2\text{O}(\text{l}) + \text{e}^- = \frac{1}{2} \text{H}_2(\text{aq}) + \text{OH}^-$.
- **Self-redox** is the reaction, where the same element undergoes oxidation and reduction simultaneously,



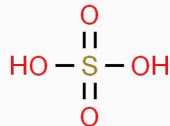
where Cl⁰ with oxidation number 0, becomes Cl⁻¹ in NaCl and Cl⁺¹ in NaClO.

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 H_2O : $\text{H}^+ - \text{O}^{-2} - \text{H}^+$;
- sulfuric acid H_2SO_4 : with H^+ , S^{6+} , and O^{-2} .



- **Oxidizer** causes the oxidation and receives electron:
 - halogens, such as F_2 and Cl_2 ;
 - oxyacid and oxyanions, such as NO_3^- , IO_3^- , and MnO_4^- ;
 - forms of oxygen, such as O_3 ; and
 - peroxides, such as H_2O_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 $\text{NOX} = 0$.
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 $\text{NOX} = +1$.
6. Alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) and zinc (Zn) have $\text{NOX} = +2$.
7. In compounds, aluminum (Al) has $\text{NOX} = +3$.
8. In compounds, hydrogen (H) has $\text{NOX} = +1$, except for metal hydrides, where it has $\text{NOX} = -1$.
9. Oxygen (O_2) has $\text{NOX} = -2$, except for peroxides, where the $\text{NOX} = -1$, and superoxide, where $\text{NOX} = -0.5$.
10. In the right side of the chemical formula, the halogens (F, Cl, Br, and I) have $\text{NOX} = -1$.

Figure 5: From *Modeling and Simulation of Reactive Flows* by Bortoli, Andreis, and Pereira, 2015.

Concepts of half-reaction

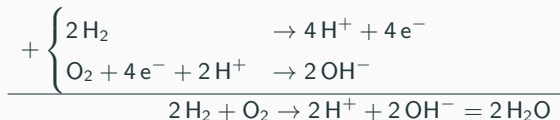
- The redox reactions can be expressed as a combination of two partial ionic reactions:
 - an **oxidation half-reaction**



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

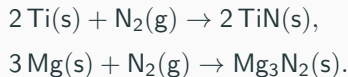
Hence, Zn is oxidized and acts as the reducing agent. H^+ ion is reduced and acts as the oxidizing agent.

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 :



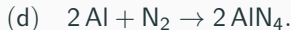
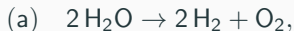
- Many chemicals can 'burn' in **other environments**.
Example 1: metals like titanium and magnesium can burn in nitrogen:



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?



<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 O_2 and (d) uses N_2 instead.

Chemical kinetic calculation

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?

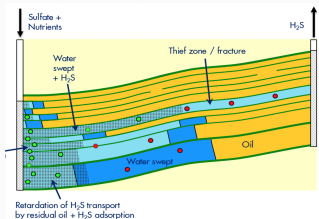


<http://etc.ch/xREb> or

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

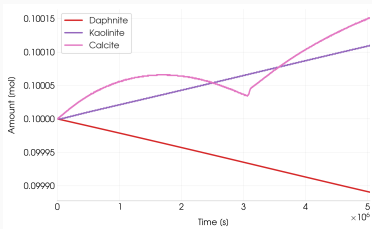
Example, Complex souring system

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

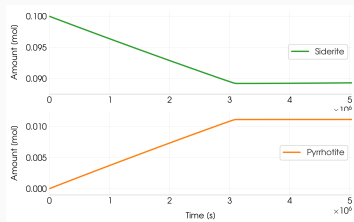


- Calcite, $k_{\text{Calcite}} \sim 10^{-1}$,
- Daphnite, $k_{\text{Daphnite}} \sim 10^{-9}$,
- Kaolinite, $k_{\text{Kaolinite}} \sim 10^{-11}$,
- Siderite, $k_{\text{Siderite}} \sim 10^{-6}$,
- Quartz, $k_{\text{Quartz}} 10^{-10}$

- 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

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B],$$

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

- 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

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

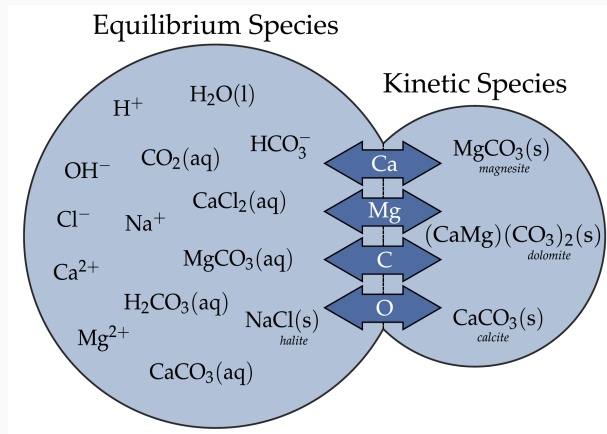
- Then, **the vector of species amount** can be represented by $n = [n_e; n_k]^T \in \mathbb{R}^N$, $N = N_e + N_k$, with
 - the formula matrix $A = \begin{bmatrix} A_e & A_k \end{bmatrix}$ composed of the **formula matrices of the equilibrium and kinetic species** $A_e \in \mathbb{R}^{E \times N_e}$ 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**

$$\begin{aligned}\frac{db_e}{dt} &= f_e(n_e) & t > 0, & & b_e &= An_e^o & t = 0, \\ \frac{dn_k}{dt} &= f_k(n_k) & t > 0, & & n_k &= n_k^o & t = 0,\end{aligned}\tag{1}$$

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**

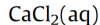
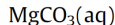
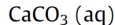
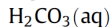
$$n_e = \underset{n_e}{\operatorname{argmin}} G_e = n_e^T \mu_e \quad \text{s.t.} \quad A_e n_e = b_e, n_e \geq 0.$$

- 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_2O – CO_2 –Halite–Calcite–Magnesite–Dolomite with their phases and respective chemical species.

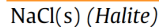
Aqueous phase



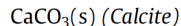
Gaseous phase



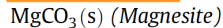
Mineral phase #1



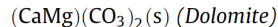
Mineral phase #2



Mineral phase #3



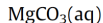
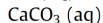
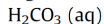
Mineral phase #4



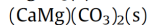
Example, Partition to kinetic and equilibrium species ii

Partition of the chemical system H_2O – CO_2 –Halite–Calcite–Magnesite–Dolomite in equilibrium and kinetic species.

Equilibrium species



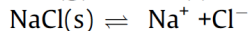
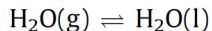
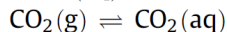
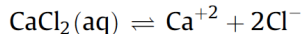
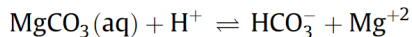
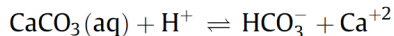
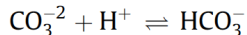
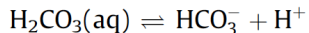
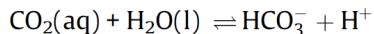
Kinetic species



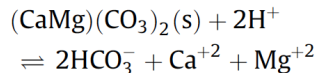
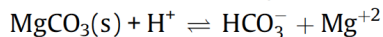
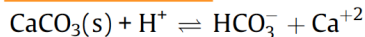
Example, Partition to kinetic and equilibrium species iii

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)**

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

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 [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

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

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,
-

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

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

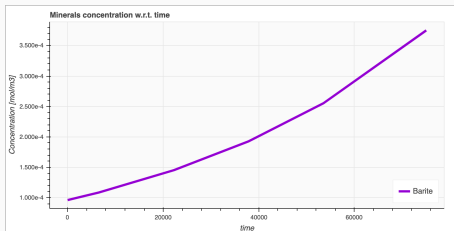
- $k_{j,m}^o$ as the *reaction rate constant* at 25 °C,
- $E_{j,m}$ as the *activation energy*,
- R as the *universal gas constant* and T as the given temperature,

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 1: 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:

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

where M is the molar mass.

Numerical method for chemical kinetics calculation

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 \Rightarrow **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.

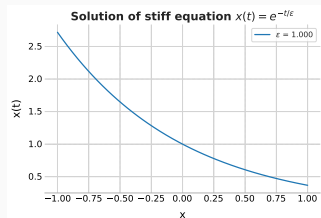
Example of stiff problem and complication by numerical integration

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

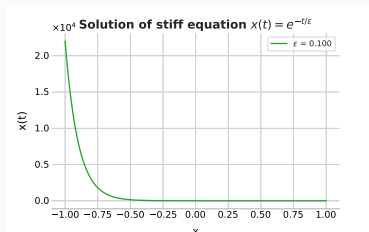
$$\frac{dx(t)}{dt} = -\frac{1}{\epsilon} x(t), \quad x(0) = 1, \quad t \in [0, T],$$

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

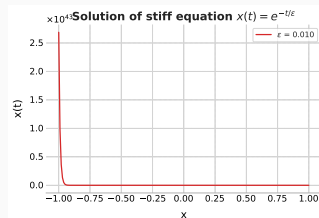
- In order to accurately integrate this problem with Euler method, Δt (**integration time steps**) must be smaller than ϵ .



(c)



(d)



(e)

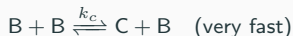
Numerical integration schemes and codes for stiff systems

- **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 formula (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

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

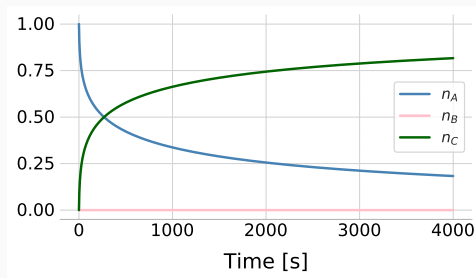
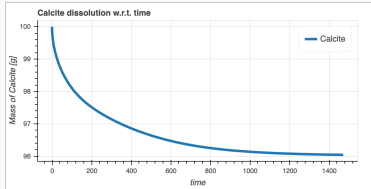


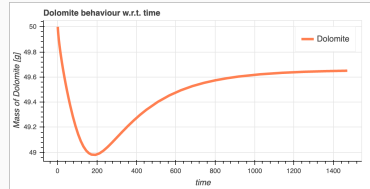
Figure 6: Solution of the Roberts system.

Example, Calcite dissolution

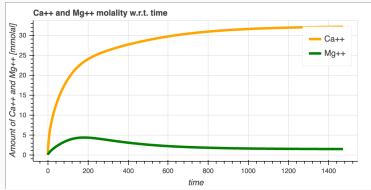
Jupyter notebook tutorial *Kinetic dissolution of carbonate* with *recording*:



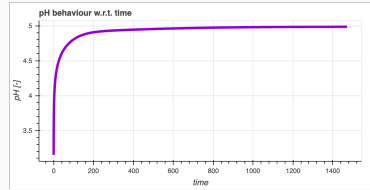
(a) Calcite dissolution



(b) Dolomite dissolution



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



(d) pH

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