Introduction to Microkinetic Modelling

Ivo Filot / i.a.w.filot@tue.nl

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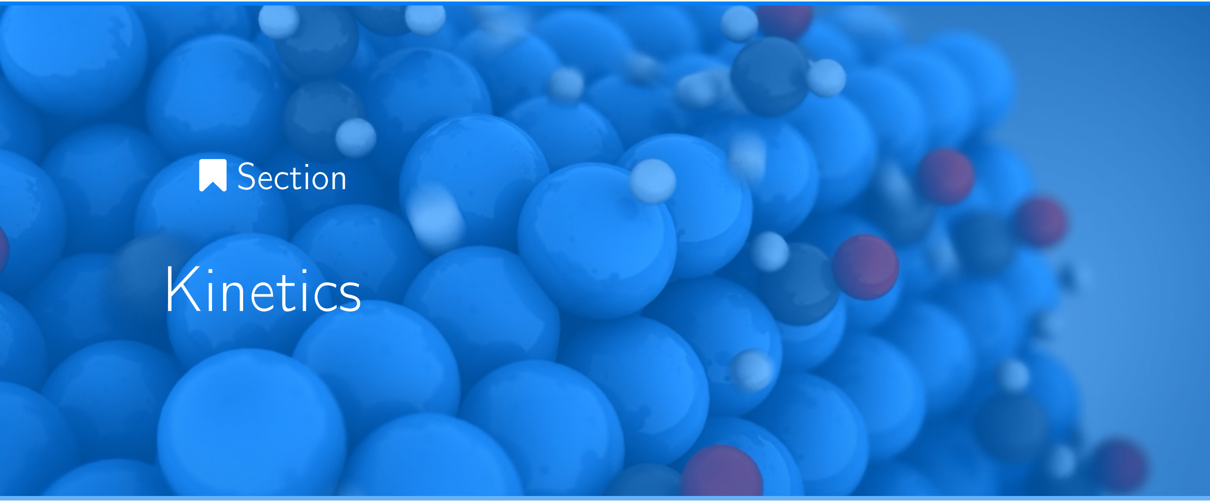


Section

Kinetics

Kinetics

Targets

- Describe rate of transformation
- Elucidate reaction mechanisms
- Essential in reactor modeling and process control

Challenges

- Inherently complex multiscale process
- Balance between model accuracy and system accuracy

Simple kinetic models

First order:

$$r = kC \tag{1}$$

Second order:

$$r = kC^2 \tag{2}$$

Variable order:

$$r = \frac{kC}{1 + KC} \tag{3}$$

Power laws:

$$r = kC_A^{n_A} C_B^{n_B} \tag{4}$$

Elementary reaction steps

If a reaction event has a single transition state that connects reactant and product state, then the rate of change is given by (e.g. for $A \rightarrow B$:

$$-\frac{\partial[A]}{\partial t} = \frac{\partial[B]}{\partial t} = k_f[A] - k_b[B] \tag{5}$$

This is based on the law of mass-action, which can be microscopically justified.

Law of Mass Action

Idea: Reaction rate $\propto$ product of reactant concentrations.

Microscopic basis:

- Collision frequency $(A \rightarrow B) \Rightarrow r \propto [A][B]$
- Probability of multi-molecule events $\Rightarrow [A]^a[B]^b$

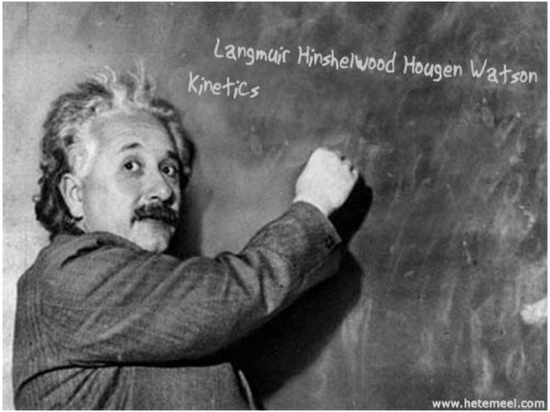
Equilibrium:

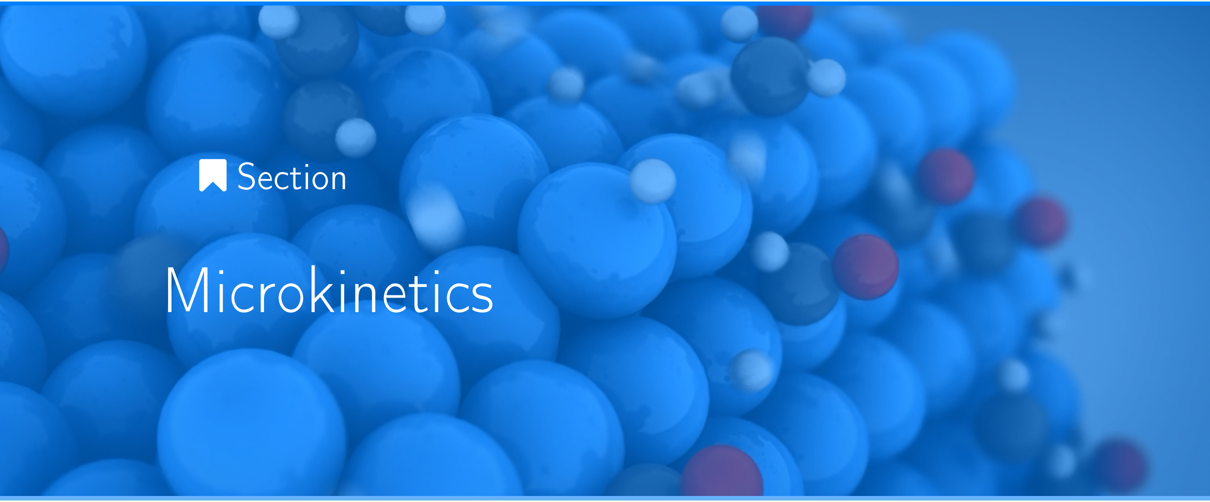
$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{6}$$

Overall rate expressions

- Synthesized from many elementary reaction steps
- Set of elementary reaction steps is the kinetic network, describing reaction mechanism
- Analytical expressions possible by using assumptions
    - Rate-determining step approximation
    - Pseudo-equilibrium approximation
    - (optional) Zero-conversion approximation
    - (catalysis) site-balance

Derivation: LHHW kinetics





Section

Microkinetics

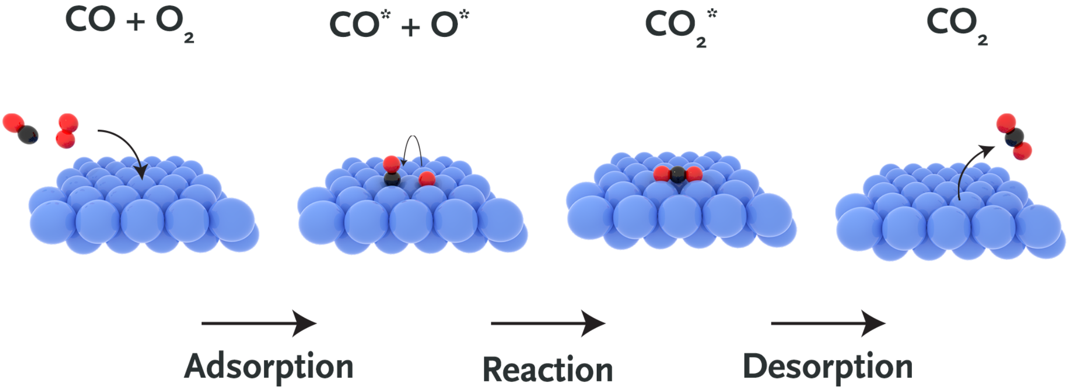
Definition

Definition

Microkinetics is the detailed, mechanistic description of a chemical reaction network, where each elementary step is represented explicitly and assigned its own rate law and rate constant.

In a way, Langmuir-Hinshelwood-Hougen-Watson kinetics already does this.

Catalytic cycle



$CO + O_2$ $\rightarrow$ $CO^* + O^*$ $\rightarrow$ CO_2^* $\rightarrow$ CO_2

Adsorption

Reaction

Desorption

Example: CO oxidation

The overall reaction is

$$2\mathrm{CO} + \mathrm{O}_2 \rightarrow 2\mathrm{CO}_2 \tag{7}$$

and constitutes the following elementary reaction steps

$$\mathrm{CO} + * \rightleftarrows \mathrm{CO}* \tag{8}$$
$$\mathrm{O}_2 + 2* \rightleftarrows 2\mathrm{O}* \tag{9}$$
$$\mathrm{CO} * + \mathrm{O}* \rightleftarrows \mathrm{CO}_2 * + * \tag{10}$$
$$\mathrm{CO}_2 + * \rightleftarrows \mathrm{CO}_2* \tag{11}$$

Each of the compounds in the system give an ordinary differential equation.

Example: CO oxidation

If we assume that CO recombination on the catalytic surface is the rate-determining step and we operate at zero conversion, we can readily derive the overall reaction rate by employing the pseudo-equilibrium assumption:

$$r = \frac{k_{\mathrm{rds}} K_{\mathrm{CO}} p_{\mathrm{CO}} \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}}{\left(1 + K_{\mathrm{CO}} p_{\mathrm{CO}} + \sqrt{K_{\mathrm{O_2}} p_{\mathrm{O_2}}}\right)^2} \tag{12}$$

But what if we cannot make such assumptions?

Example: CO oxidation

Set of ordinary differential equations:

$$\frac{\partial \theta_{\mathrm{CO}}}{\partial t} = k_{1,\mathsf{ads}}\theta_* - k_{1,\mathsf{des}}\theta_{\mathrm{CO}} - k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} + k_{3,b}\theta_{\mathrm{CO_2}}\theta_* \tag{13}$$

$$\frac{\partial \theta_{\mathrm{O}}}{\partial t} = 2k_{2,\mathsf{ads}}\theta_*^2 - 2k_{2,\mathsf{des}}\theta_{\mathrm{O}}^2 - k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} + k_{3,b}\theta_{\mathrm{CO_2}}\theta_* \tag{14}$$

$$\frac{\partial \theta_{\mathrm{CO_2}}}{\partial t} = k_{4,\mathsf{ads}}\theta_* - k_{4,\mathsf{des}}\theta_{\mathrm{CO_2}} + k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} - k_{3,b}\theta_{\mathrm{CO_2}}\theta_* \tag{15}$$

$$\begin{aligned}\frac{\partial \theta_*}{\partial t} &= -k_{1,\mathsf{ads}}\theta_* + k_{1,\mathsf{des}}\theta_{\mathrm{CO}} - 2k_{2,\mathsf{ads}}\theta_*^2 + 2k_{2,\mathsf{des}}\theta_{\mathrm{O}}^2 \\ &\quad + k_{3,f}\theta_{\mathrm{CO}}\theta_{\mathrm{O}} - k_{3,b}\theta_{\mathrm{CO_2}}\theta_* - k_{4,\mathsf{ads}}\theta_* + k_{4,\mathsf{des}}\theta_{\mathrm{CO_2}}\end{aligned} \tag{16}$$

Initial values and boundary conditions

The partial pressures of the reactants (and possibly of the products if we do not work at zero-conversion) are the boundary conditions. The surface concentrations at $t = 0$ act as initial values.

$$\theta_i = 0 \tag{17}$$

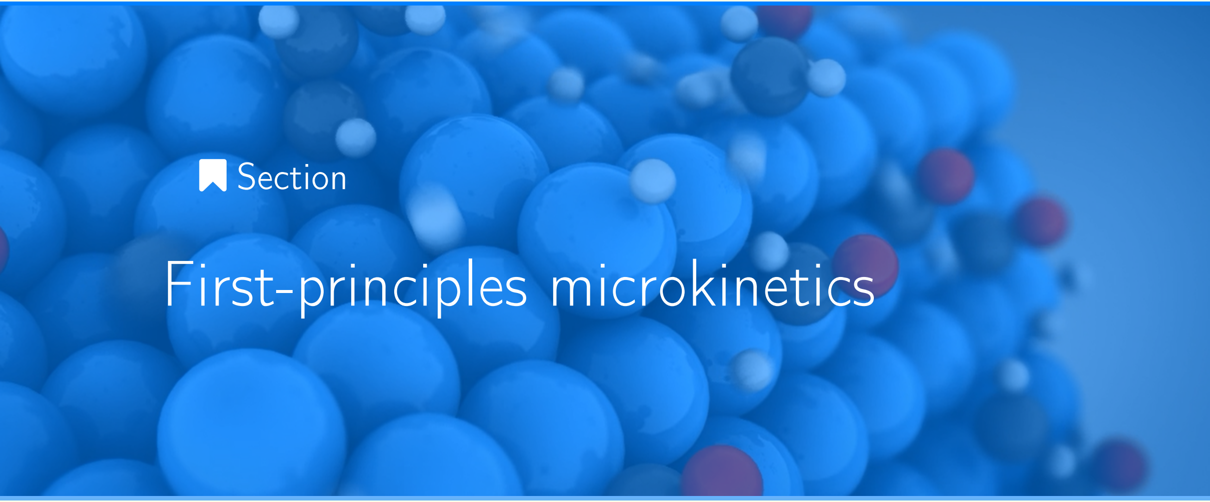
with exception of

$$\theta_* = 1. \tag{18}$$

Time-integration

- Time-integration in microkinetics is done using an ODE solver. In Matlab, `ode15s` is preferred, in Python, we use `scipy.integrate.ode`.
- If speed is important, `Sundials` or `Netlib` libraries are very good options (C and Fortran, respectively).
- Time-integration is done until steady-state is reached:

$$\frac{\partial \theta_i}{\partial t} = 0 \tag{19}$$



Section

First-principles microkinetics

Definition

Definition

First-principles microkinetics combines **first-principles calculations** (DFT) with **microkinetic modeling**. Each elementary step's energetics and rate constants are derived from quantum mechanics and statistical thermodynamics, rather than experiment.

Finding parameters from first principles

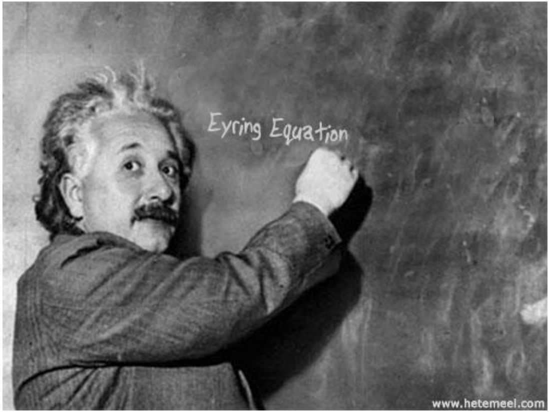
Qualitatively, we can use Arrhenius equation:

$$k(T, \{p_i\}) = \nu \cdot \exp\left(-\frac{\Delta E_{\text{act}}}{RT}\right) \tag{20}$$

More quantitative (using *ab-initio* data), use Eyring equation:

$$k(T, \{p_i\}) = \frac{k_b T}{h} \frac{Q^{\dagger}_{\text{TS}}}{Q_{\text{IS}}} \exp\left(\frac{-\Delta E_{\text{act,elec}}}{RT}\right) \tag{21}$$

Derivation Eyring equation



Elementary reaction types

Adsorption:

$$k_{f,\mathsf{HK}} = \frac{pA}{\sqrt{2\pi m k_b T}} \tag{22}$$

Desorption:

$$k_{b,\mathsf{HK}} = \frac{k_b T^3}{h^3} \frac{A\left(2\pi m k_b\right)}{h^2} \frac{T}{\sigma \Theta_{\mathsf{rot}}} \exp\left(-\frac{\Delta E_{\mathrm{act,zpe}}}{k_b T}\right) \tag{23}$$

Surface reaction:

$$k_{f,\mathsf{arr}} = k_{b,\mathsf{arr}} = \frac{k_b T}{h} \exp\left(-\frac{\Delta E_{\mathrm{act+zpe}}}{k_b T}\right) \tag{24}$$

Eyring equation

$$k(T,\{p_i\}) = \frac{k_b T}{h} \frac{Q^{\dagger}_{\mathsf{TS}}}{Q_{\mathsf{IS}}} \exp\left(\frac{-\Delta E_{\mathsf{act,elec}}}{RT}\right) \tag{25}$$

with

$$Q = \prod_i q_i, \in \{q_{\mathsf{t}}, q_{\mathsf{v}}, q_{\mathsf{r}}\} \tag{26}$$

Molecular partition functions ⇔ Degrees of Freedom

Degrees of freedom

General:

- IS, FS → $3N$
- TS → $3N-1$ (extracted to construct crossing frequency)

Gas phase:

- Vibrational DOF: 3N-5 (linear; e.g. H_2, CO_2) or 3N-6 (non-linearr)
- Rotational DOF: 2 (linear), 3 (non-linear), 0 (atom)
- Translational DOF: 3

Surface:

- IS, FS → $3N$ vibrational
- TS → $3N-1$ vibrational

Obtaining parameters

- **Electronic structure calculation:** Electronic (activation) energies
- **Frequency analysis:** Vibrational frequencies → Vibrational partition functions and zero-point energy correction
- **Geometry optimization:** Moment of inertia → Rotational partition function
- **Fundamental properties:** Total mass → Translational partition function

Note: When calculating frequencies for a catalytic system, often the contribution of the support is neglected as the support's atoms are much heavier than of the adsorbates.

Partition Function Assumptions & Alternatives

Fundamental Assumptions (Ideal-Gas, Rigid-Molecule Approx.)

- Separation of modes:

  $$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

  (no coupling)
- No intermolecular interactions (ideal gas)
- Translational motion: particle-in-a-box, continuous levels (MB statistics)
- Rotational motion: rigid rotor, no vib–rot coupling; symmetry number correction
- Energy levels dense enough for classical or quasi-classical treatment

Shomate equation

When these assumptions fail:

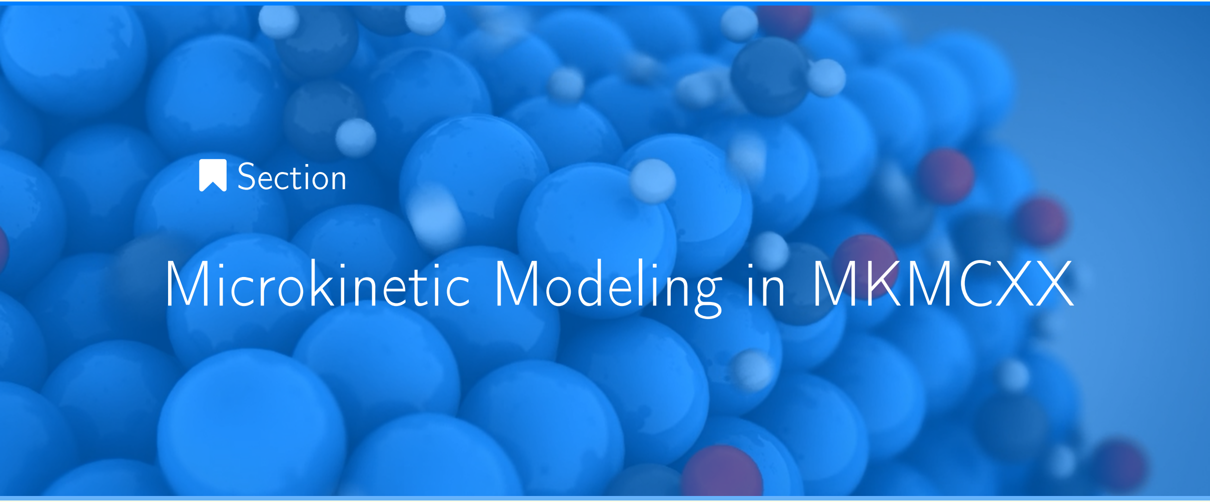
- Coupled modes, anharmonicity, non-rigid rotation, non-ideal gas behavior
- **Use Shomate equations with NIST thermochemical tables:**

$$C_p(T),\ H(T),\ S(T) \text{ directly from fitted coefficients}$$

- Avoids explicit partition-function evaluation; incorporates real-data corrections

$$H^\circ(T) - H^\circ(298) = A\,T + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4 - \frac{E}{T} + F - H \tag{27}$$

$$S^\circ(T) = A \ln T + B\,T + \frac{C}{2}T^2 + \frac{D}{3}T^3 - \frac{E}{2T^2} + G \tag{28}$$



Section

Microkinetic Modeling in MKMCXX

MKMCXX

- C++ based microkinetics software suite
- General purpose
- Build on top of Sundials library
- Very fast and multi-threaded

I/O

- Single input file (some exceptions)
- 5 blocks
  - `&compounds`
  - `&reactions`
  - `&settings`
  - `&runs`
  - `&output`

Compounds

- Defines which species are in the system
- Set their starting concentration (partial pressure)
- Set flags to label compounds (e.g. reactant, product, surface species, etc.)

```
&compounds
# name ; c = concentration ; FLAGS = flags (comma-separated)
A;      c = 1.0; FLAGS = GAS, REACTANT
AB;     c = 0.0; FLAGS = GAS, PRODUCT, KEY

# Adsorbed compounds
A*;         c = 0.0; FLAGS = SURFACE
*;          c = 1.0; FLAGS = SURFACE
&endblock
```

Reactions

Different kinetic models available (Arrhenius, HertzKnudsen, ...)

```
&reactions
{A}     +   {*}         =>  {A*};                       ; model =
    HertzKnudsenDefault; Asite = 1e-20; m = 12; theta = 1.0; sigma = 1; S = 1;
    Edes = 120e3; FLAGS = DRC
{B2}    +   2{*}        =>  2{B*};                      ; model =
    HertzKnudsenDefault; Asite = 1e-20; m = 28; theta = 1.0; sigma = 1; S = 1;
    Edes = 80e3;  FLAGS = DRC
{AB}    +   {*}         =>  {AB*};                      ; model =
    HertzKnudsenDefault; Asite = 1e-20; m = 26; theta = 1.0; sigma = 1; S = 1;
    Edes = 50e3;  FLAGS = DRC
{A*}    +   {B*}        =>  {AB*} + {*};                ; model = ArrheniusDefault;
     Vf = 1e13; Vb = 1e13; Eaf = 120e3; Eab = 80e3; FLAGS = DRC
&endblock
```

Settings

Overall system settings (simulation parameters), such as which sensitivity analyses to conduct.

```
&settings
ORDERS = 1
DRC = 1
EACT = 1
&endblock
```

Runs

Species temperature, simulation time and relative and absolute tolerances.

```
&runs
T = 350;    t = 1e6; atol = 1e-8; rtol = 1e-8
T = 375;    t = 1e6; atol = 1e-8; rtol = 1e-8
T = 400;    t = 1e6; atol = 1e-8; rtol = 1e-8
T = 425;    t = 1e6; atol = 1e-8; rtol = 1e-8
T = 450;    t = 1e6; atol = 1e-8; rtol = 1e-8
T = 475;    t = 1e6; atol = 1e-8; rtol = 1e-8
T = 500;    t = 1e6; atol = 1e-8; rtol = 1e-8
&endblock
```

Output

Specifies which output to write.

```
&output
FORMAT = EXCEL, TABDELIM, HDF5
&endblock
```

Exercise 1

- Perform the example simulation as found here: `https://www.mkmcxx.nl/v3/example_simulation/`
- Construct an analytical solution and compare your results with the analytical solution. Does it match?

Exercise 2

- Model the methanation reaction ($CO + 3H_2 \rightarrow CH_4 + H_2O$)
- Download a DFT-based dataset from: `https://zenodo.org/records/17526594` (use the .mks files)
- Build a microkinetic model using `HertzKnudsenNist` and `ArrheniusQRatio` kinetics models

Note:

- All slab models have two adsorbates to cancel dipole moment
- First check whether overall thermodynamics is correct via PED

Exercise 2 (continued)

- Using data directly from DFT shows very low TOF, why?
- Discuss how results can be improved without performing new DFT calculations.