Multiphase and Reactive Flow Modelling

BMEGEÁT(MW17|MG27)

Part 1

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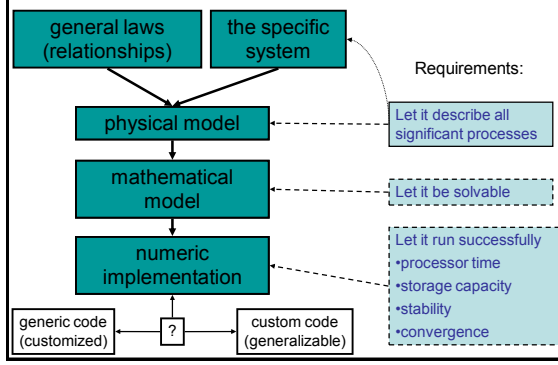
Contents

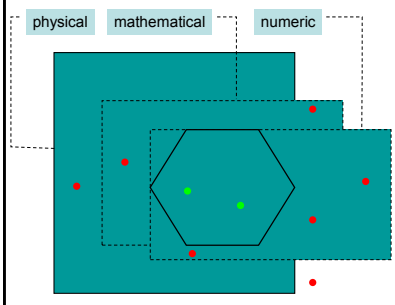
What is modelling?

- Experimental modelling
- Theoretical modelling
  - Physical model layer
  - Mathematical model layer
- Numerical model

Model layers



Relating model layers properly



self consistence

validity

- good models
- wrong models

Validation/verification is unavoidable in the modelling process!

•mistakes can be *proven*,

•reliability can only be *substantiated* by empirical probability

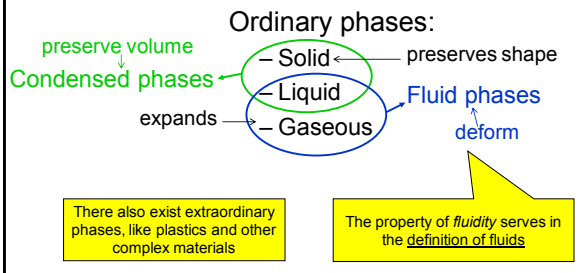
Creating a physical model

What are the significant processes?

- Include all the significant processes
- Get rid of non-significant ones

  The dimensionless numbers help us with these!
- Classify the system based on the above

Basic notions and terminology



Properties and physical models of solids

Properties of solids:

- Mass (inertia), position, translation → Mass point model
- Extension (density, volume), rotation, inertial momentum → Rigid body model
- Elastic deformations (small, reversible and linear), deformation and stress fields → The simplest continuum model
- Inelastic deformations (large, irreversible and nonlinear), dislocations, failure etc. → Even more complex models

Modelled features:

1. Mechanics
   - Statics: mechanical equilibrium is necessary
   - Dynamics: governed by deviation from mechanical equilibrium
2. Thermodynamics of solids

Properties and physical models of fluids

Key properties of fluids:

- Large, irreversible deformations
- Density, pressure, viscosity, thermal conductivity, etc.

Only continuum models are appropriate!

Features to be modelled:

1. Statics
   - Hydrostatics: definition of fluid (pressure and density can be inhomogeneous)
   - Thermostatics: thermal equilibrium (homogenous state)
2. Dynamics
   1. Mechanical dynamics: motion governed by deviation from equilibrium of forces
   2. Thermo*dynamics* of fluids:
      - Deviation from global thermodynamic equilibrium often governs processes multiphase, multi-component systems
      - Local thermodynamic equilibrium is (almost always) maintained

Mathematical model of simple fluids

- Inside the fluid:
  - Transport equations

    Mass, momentum and energy balances

    5 PDE's for $p(t,\vec{\mathbf{r}})$, $\vec{\mathbf{u}}(t,\vec{\mathbf{r}})$ and $T(t,\vec{\mathbf{r}})$ ← Primary (direct) field variables
  - Constitutive equations

    Algebraic equations for $\rho(p,T), \eta(p,T), k(p,T), \ldots$ ← Secondary (indirect) field variables
- Boundary conditions

  On explicitly or implicitly specified surfaces
- Initial conditions

Expressing local thermodynamic equilibrium in fluid dynamics:
the use of intensive and extensive state variables

- Integral forms: intensive and extensive (X)
- Differential forms (PDE's):
  - fixed control volume (V=const): intensive and densities of the extensive ones ($x=X/V$)
  - advected fluid parcel (m=const): intensive and specific values of the extensive ones ($x=X/m$)

Thermodynamical representations

Representation (independent variables)	TD potential
entropy and volume (s,1/ρ)	internal energy
temperature and volume (T,1/ρ)	free energy
entropy and pressure (s,p)	enthalpy
temperature and pressure (T,p)	free enthalpy

- All of these are equivalent:
  can be transformed to each other by appropriate formulæ
- Use the one which is most practicable:
  e.g., (s,p) in acoustics: $s = const \Rightarrow \rho(s,p) \rightarrow \rho(p)$.

  We prefer (T,p)

Note

Some models of simple fluids

- $\rho = const,\ \mu = const$ → Stoksean fluid
- $\rho(p),\ \mu = const$ → compressible (or barotropic) fluid

  In both of these, the heat transport problem can be solved separately (one-way coupling):

  fluid dynamical equations → heat transport equation (1 PDE)
- $\rho(p,T),\ \mu(p,T),\ k(p,T),\ \ldots$ → general simple fluid

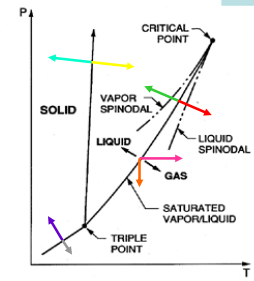
  Mutually coupled thermo-hydraulic equations:

  fluid dynamical equations ↔ heat transport equation
- Non-Newtonian behaviour etc. → models for complex fluids

Phase transitions
in case of a single compound

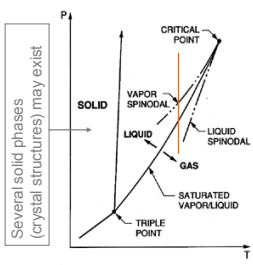
- Evaporation, incl.
  - Boiling
  - Cavitation
- Condensation, incl.
  - Liquefaction
  - Solidification
- Sublimation
- Freezing
- Melting

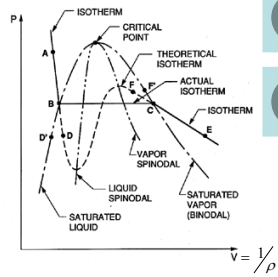
All phase transitions involve latent heat deposition or release



Typical phase diagrams of a *pure* material:

Several solid phases (crystal structures) may exist





In equilibrium 1, 2 or 3 phases can exist together

→ Complete mechanical and thermal equilibrium

Material properties in multi-phase, single component systems

One needs explicit constitutional equations for each phase.

For each phase (p) one needs to know:

- the thermodynamic potential $\mu^{(p)}(p,T)$
- the thermal equation of state $\rho^{(p)}(p,T)$
- the viscosity $\eta^{(p)}(p,T)$
- the heat capacity $c_p^{(p)}(p,T)$
- the thermal conductivity. $k^{(p)}(p,T)$

Conditions of local phase equilibrium in a contact point in case of a pure material

- 2 phases:

  $T^{(1)}=T^{(2)}=:T$

  $p^{(1)}=p^{(2)}=:p$

  $\mu^{(1)}(T,p)=\mu^{(2)}(T,p)$

  Locus of solution: a line $T_s(p)$ or $p_s(T)$, the saturation temperature or pressure (e.g. 'boiling point').
- 3 phases:

  $T^{(1)}=T^{(2)}=T^{(3)}=:T$

  $p^{(1)}=p^{(2)}=p^{(3)}=:p$

  $\mu^{(1)}(T,p)=\mu^{(2)}(T,p)=\mu^{(3)}(T,p)$

  Locus of solution: a point (T_t,p_t), the triple point.

Multiple components

- Almost all systems have more than 1 (chemical) components
- Phases are typically *multi-component mixtures*

Concentration(s): measure(s) of composition

There are lot of practical concentrations in use, e.g.

- Mass fraction (we prefer this!)
  $c_1 = m_1/m,\quad c_2 = m_2/m, \ldots \quad c_k = m_k/m, \ldots \quad \sum_k c_k = \sum_k m_k/m = 1$
- Volume fraction (used in CFD and if volume is conserved upon mixing!)
  $\alpha_1 = V_1/V,\quad \alpha_2 = V_2/V, \ldots \quad \alpha_k = V_k/V, \ldots \quad \sum_k \alpha_k = \sum_k V_k/V = 1$
- Mole fraction (used in case of chemical reactions and diffusion)
  $y_1 = n_1/n,\quad y_2 = n_2/n, \ldots \quad y_k = n_k/n, \ldots \quad \sum_k y_k = \sum_k n_k/n = 1$

Multiple components

Concentration fields appear as new primary field variables in the mathematical model
One of them (usually that of the solvent) is redundant, not used.

$c_k(t,\vec{\mathbf{r}})$ for $k = 2,\ldots,K$

Notations to be used (or at least attempted)

- Phase index (upper):
  - (p) or
  - (s), (ℓ), (g), (v), (f) for solid, liquid, gas , vapour, fluid
- Component index (lower): k
- Coordinate index (lower): i, j or t

Examples: $\rho^{(s)},\ c_k^{(p)},\ u_i^{(p)}$

- Partial differentiation:

$\partial_t,\ \partial_i\ (\partial_1 = \partial_x, \partial_2 = \partial_y, \partial_3 = \partial_z)$

Note

Material properties in multi-component mixtures

- One needs constitutional equations for each phase
- These algebraic equations depend also on the concentrations

For each phase (p) one needs to know:

- the thermodynamic potential $\mu^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the thermal equation of state $\rho^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the heat capacity $c_p^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the viscosity $\eta^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the thermal conductivity $k^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$
- the diffusion coefficients $D_{k,t}^{(p)}\left(p,T,c_1^{(p)},c_2^{(p)},\ldots\right)$

Conditions of local phase equilibrium in a contact point in case of multiple components

- Suppose N phases and K components:
- Thermal and mechanical equilibrium on the interfaces:

  $T^{(1)}=T^{(2)}=\ldots=T^{(N)}=:T$

  $p^{(1)}=p^{(2)}=\ldots=p^{(N)}=:p$ $\quad 2N \rightarrow$ only 2 independent unknowns
- Mass balance for each component among all phases:

$$\mu_1^{(1)}\left(T,p,\cancel{c_1^{(1)}},c_2^{(1)},\ldots,c_K^{(1)}\right)=\mu_1^{(2)}\left(T,p,\cancel{c_1^{(2)}},c_2^{(2)},\ldots,c_K^{(2)}\right)=\ldots=\mu_1^{(N)}\left(T,p,\cancel{c_1^{(N)}},c_2^{(N)},\ldots,c_K^{(N)}\right)$$
$$\mu_2^{(1)}\left(T,p,\cancel{c_1^{(1)}},c_2^{(1)},\ldots,c_K^{(1)}\right)=\mu_2^{(2)}\left(T,p,\cancel{c_1^{(2)}},c_2^{(2)},\ldots,c_K^{(2)}\right)=\ldots=\mu_2^{(N)}\left(T,p,\cancel{c_1^{(N)}},c_2^{(N)},\ldots,c_K^{(N)}\right)$$
$$\vdots$$
$$\mu_K^{(1)}\left(T,p,\cancel{c_1^{(1)}},c_2^{(1)},\ldots,c_K^{(1)}\right)=\mu_K^{(2)}\left(T,p,\cancel{c_1^{(2)}},c_2^{(2)},\ldots,c_K^{(2)}\right)=\ldots=\mu_K^{(N)}\left(T,p,\cancel{c_1^{(N)}},c_2^{(N)},\ldots,c_K^{(N)}\right)$$

$K(N\text{-}1)$ independent equations for $2+N(K\text{-}1)$ independent unknowns

Phase equilibrium in a multi-component mixture

Gibbs' Rule of Phases, *in equilibrium*:

$$\#\text{phases} \equiv N \le \#\text{components} + 2 \equiv K + 2$$

TD limit on the # of phases

If there is no (global) TD equilibrium: additional phases may also exist

- in transient metastable state(s) or
- in spatially separated, distant points

Miscibility

The number of phases in a given system is also influenced by the miscibility of the components:

- Gases always mix →
  Typically there is at most 1 contiguous gas phase
- Liquids maybe miscible or immiscible →
  Liquids may separate into more than 1 phases
  (e.g. polar water + apolar oil)

1. Surface tension (gas-liquid interface)
2. Interfacial tension (liquid-liquid interface)

(In general: Interfacial tension on fluid-liquid interfaces)

- Solids typically remain granular

Topology of phases and interfaces

A phase may be
- *Contiguous*
  (more than 1 contiguous phases can coexist)
- *Dispersed:*
  - solid particles, droplets or bubbles
  - of small size
  - usually surrounded by a contiguous phase
- *Compound*

Interfaces are
- 2D interface surfaces separating 2 phases
  - gas-liquid: *surface*
  - liquid-liquid: *interface*
  - solid-fluid: *wall*
- 1D contact lines separating 3 phases and 3 interfaces (at least)
- 0D contact points with (at least) 4 phases, 6 interfaces and 4 contact lines

Topological limit on the # of phases (always local)

Special Features to Be Modelled

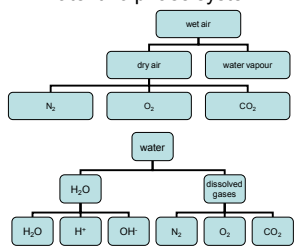
- Multiple components →
  - chemical reactions
  - molecular diffusion of constituents
- Multiple phases → inter-phase processes
  - momentum transport,
  - mass transport and
  - energy (heat) transfer

across interfaces and within each phase.
(Local deviation from total TD equilibrium is typical)

Are components = chemical species?

Not always:
- Major reagents in chemical reactions has to be modelled separately,
- but similar materials can be grouped together and treated as a single component
  - The grouping can be refined in the course of the modelling

Example:
components in an air-water two phase system



Multi-component transport

We set up transport equations for single-phase multi-component fluids

Multi-component advection and diffusion model

necessary → Modelling chemical reactions

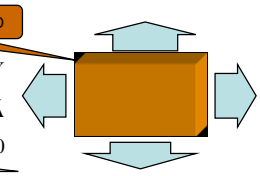
conceptual and mathematical analogy → Multi-phase transport equations

Multi-component transport
Outline

- Balance equations
- Mass balance — equation of continuity
- Component balance
- Advection
- Molecular diffusion
- Chemical reactions

Mass balance for a control volume

Eulerian (fixed) control volume in 3D



Mass inside: $m(t) = \iiint \rho(t,\vec{\mathbf{r}})\,dV$

Outflow rate: $J(t) = \oiint \vec{\mathbf{j}}(t,\vec{\mathbf{r}}) \cdot \mathbf{d}\vec{\mathbf{A}}$

Mass production rate: $Q(t) = 0$

Mass is a conserved quantity (in 3D): no production (sources) and decay (sinks) inside

This is a conservation law

Integral form: $\frac{dm}{dt} = -J(t) + Q(t)$

Mass balance equation

By definition:

Differential form: $\partial_t \rho + \vec{\nabla}(\rho\,\vec{\mathbf{u}}) = 0$ ← $\vec{\mathbf{u}}(t,\vec{\mathbf{r}}) := \vec{\mathbf{j}}/\rho$

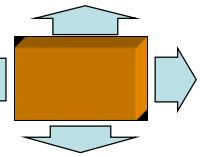
Component mass balance

For each component:

Mass inside: $m_k(t) = \iiint \rho_k(t,\vec{\mathbf{r}})\,dV$

Outflow rate: $J_k(t) = \oiint \vec{\mathbf{j}}_k(t,\vec{\mathbf{r}})\cdot d\vec{\mathbf{A}}$

Mass production rate: $Q_k(t) = 0$



If component masses are also conserved, **then** no production (sources) and decay (sinks) inside

These are also conservation laws

Integral form: $\frac{dm_k}{dt} = -J_k(t) + Q_k(t)$

Mass balance equations ↕ ↕ ↕ By definition:

Differential form: $\partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}_k) = 0 \leftarrow \vec{\mathbf{u}}_k(t,\vec{\mathbf{r}}) := \vec{\mathbf{j}}_k / \rho_k$

The mass transport equations

$\partial_t \rho + \vec{\nabla}(\rho \vec{\mathbf{u}}) = 0$

$\sum_k \Uparrow$

$\forall k:\ \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}_k) = 0$

$\Downarrow$

$\partial_t(c_k\rho) + \vec{\nabla}(c_k \rho \vec{\mathbf{u}}) = -\vec{\nabla}(\rho_k \vec{\mathbf{w}}_k) = -\vec{\nabla}\vec{\mathbf{j}}_{\text{diff }k} \Leftarrow \vec{\mathbf{j}}_{\text{diff }k} := \rho_k \vec{\mathbf{w}}_k$

$\sum_k \rho_k = \rho,\quad \sum_k \vec{\mathbf{j}}_k = \sum_k \rho_k \vec{\mathbf{u}}_k = \vec{\mathbf{j}}$

$\rho_k = c_k \rho,\quad \vec{\mathbf{j}}_k = \rho_k \vec{\mathbf{u}}_k = c_k \rho \vec{\mathbf{u}}_k$

$\vec{\mathbf{u}}_k = \vec{\mathbf{u}} + (\vec{\mathbf{u}}_k - \vec{\mathbf{u}}) = \vec{\mathbf{u}} + \vec{\mathbf{w}}_k$

advection ***diffusion***

$c_k\left[\partial_t \rho + \vec{\nabla}(\rho \vec{\mathbf{u}})\right] + \rho\left[\partial_t c_k + \vec{\mathbf{u}}\vec{\nabla} c_k\right] = -\vec{\nabla}\vec{\mathbf{j}}_{\text{diff }k}$

$\forall k: D_t c_k = \partial_t c_k + \vec{\mathbf{u}}\vec{\nabla} c_k = -\frac{1}{\rho}\vec{\nabla}\vec{\mathbf{j}}_{\text{diff }k}$

$\sum_k \vec{\mathbf{j}}_{\text{diff }k} = \sum_k \rho_k \vec{\mathbf{w}}_k = \vec{\mathbf{0}}$

Notations to be used (or at least attempted)

- Material derivative of a specific quantity:

$$\frac{Df}{Dt} := \frac{\partial f}{\partial t} + \left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)f \rightarrow D_t f := \partial_t f + \left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)f$$

Note

Two ways of resolving redundancy

1. Pick exactly *K* mass transport equations and choose the *K* primary variables as follows:

$k = 1,\ldots K:\ \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}) = -\vec{\nabla}\vec{\mathbf{j}}_{\text{diff }k}$

$\partial_t \rho + \vec{\nabla}(\rho \vec{\mathbf{u}}) = 0$

$k = 2,\ldots K:\ D c_k = -(1/\rho)\vec{\nabla}\vec{\mathbf{j}}_{\text{diff }k}$

2. If needed, calculate the remaining secondary variable fields from the algebraic relations:

$\rho(t,\vec{\mathbf{x}}) = \sum_k \rho_k(t,\vec{\mathbf{x}})$

$c_k(t,\vec{\mathbf{x}}) = \rho_k(t,\vec{\mathbf{x}}) / \rho(t,\vec{\mathbf{x}})$

$c_1(t,\vec{\mathbf{x}}) = 1 - \sum_{k=2}^{K} c_k(t,\vec{\mathbf{x}})$

$\rho_k(t,\vec{\mathbf{x}}) = \rho(t,\vec{\mathbf{x}}) \cdot c_k(t,\vec{\mathbf{x}})$

Typically, this is the solvent

For a binary mixture:
$c_2(t,\vec{\mathbf{x}}) =: c(t,\vec{\mathbf{x}})$
$c_1(t,\vec{\mathbf{x}}) = 1 - c(t,\vec{\mathbf{x}})$

Differential forms in balance equations

Conservation of *F*: $F(t) = \iiint \varphi(t,\vec{\mathbf{r}})\,dV = \iiint f(t,\vec{\mathbf{r}})\cdot\rho(t,\vec{\mathbf{r}})\,dV$

- equations for the density (φ)
  - general
  - only convective flux
- equation for the specific value (f)

$\partial_t \varphi + \vec{\nabla}\cdot\vec{\mathbf{j}}_F = 0$

$\Downarrow$ if $\vec{\mathbf{j}}_F = \vec{\mathbf{u}}\cdot\varphi$

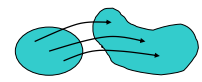
$\partial_t \varphi + \vec{\nabla}(\vec{\mathbf{u}}\cdot\varphi) = 0$

$\Downarrow$ if m is conserved

$D_t f \equiv \partial_t f + \left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)f = 0$

These forms describe passive advection of *F*

Passive advection



- The concentrations of the fluid particles do not change with time:
  $D_t c_k \equiv \partial_t c_k + \left(\vec{\mathbf{u}}\cdot\vec{\nabla}\right)c_k = 0$
- The component densities vary in fixed proportion to the overall density:
  $\partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}) = 0$
- Computational advantage: The component transport equations uncouple from the basic fluid dynamical problem and can be solved separately and *a posteriori*
- The solution requires
  - Lagrangian particle orbits
  - Initial conditions (hyperbolic equations)

Simple diffusion models

- No diffusion → pure advection

$\vec{\mathbf{j}}_{\text{diff }k} = \vec{\mathbf{0}}$ $\quad \begin{cases} \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}) = 0 \\ D_t c_k = 0 \end{cases}$

- Equimolecular counter-diffusion

$\vec{\mathbf{j}}_{\text{diff }k} = -\rho D \vec{\nabla} c_k$ for constant D and $\rho \rightarrow \begin{cases} \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}) = D \nabla^2 \rho_k \\ D_t c_k = D \nabla^2 c_k \end{cases}$

- Fick's 1st Law

for each solute if $c_k << 1 \; (k = 2, \ldots, K)$

$\vec{\mathbf{j}}_{\text{diff }k} = -\rho D_k \vec{\nabla} c_k$ constant D_k and $\rho \rightarrow \begin{cases} \partial_t \rho_k + \vec{\nabla}(\rho_k \vec{\mathbf{u}}) = D_k \nabla^2 \rho_k \\ D_t c_k = D_k \nabla^2 c_k \end{cases}$

but note that $\sum_{k=1}^{K} \vec{\mathbf{j}}_{\text{diff }k} \neq \vec{\mathbf{0}}$

Fick's 2nd Law: $\partial_t c_k = D_k \nabla^2 c_k$

Turbulent mixing

Further diffusion models

Thermodiffusion and/or barodiffusion

Occur(s) at

- high concentrations
- high T and/or p gradients

For a binary mixture:

$\vec{\mathbf{j}}_{\text{diff}} = -\rho D \left(\nabla c + (k_T / T) \nabla T + (k_p / p) \nabla p \right)$

$D \cdot k_T$: coefficient of thermodiffusion

$D \cdot k_p$: coefficient of barodiffusion

Analogous cross effects appear in the heat conduction equation

Further diffusion models

Nonlinear diffusion model

Cross effect among species' diffusion

Valid also at

- high concentrations
- more than 2 components
- low *T* and/or *p* gradients

(For a binary mixture it falls back to Fick's law.)

$$\vec{\mathbf{j}}_{\text{diff }k} = \rho \cdot \sum_{\ell \neq k} \frac{M_k}{M} \cdot \frac{\tilde{K}_{\ell k} - \tilde{K}_{kk}}{\det(\mathbf{K})} \cdot \vec{\nabla} y_k$$

$$\tilde{\mathbf{K}} = \text{adj}(\mathbf{K})$$

$$K_{k\ell} = \frac{y_k}{D_{k\ell}} + \frac{M_\ell}{M_k} \cdot \sum_{s \neq k} \frac{y_s}{D_{ks}} \text{ if } k \neq \ell$$

$$K_{kk} = 0$$

$$y_k = \frac{M}{M_k} \cdot c_k : \text{mole fraction}$$

$$M = \sum_k y_k M_k : \text{mean molar mass}$$

$$D_{k\ell} : \text{binary diffusion coefficient}$$

$$D_{k\ell}(T, n, M_k, M_\ell) = D_{\ell k}$$

Further notes on diffusion modelling

- For internal consistency of the whole model
  - D has to be changed in accordance to the turbulence model (`turbulent diffusivity')
  - Diffusive heat transfer has to be included in the heat transport equation
- In the presence of multiple phases, the formulation can be straightforwardly generalised by introducing the phasic quantities

$c_k \rightarrow c_k^{(p)}, \; \rho_k \rightarrow \rho_k^{(p)}, \; \vec{\mathbf{j}}_k \rightarrow \vec{\mathbf{j}}_k^{(p)}, \; \vec{\mathbf{j}}_{\text{diff }k} \rightarrow \vec{\mathbf{j}}_{\text{diff }k}^{(p)}, \; D_k \rightarrow D_k^{(p)} \ldots$

The advection–diffusion equations

local rate of change | advective flux | diffusive flux

$$\partial_t (\rho \cdot c_k) + \vec{\nabla}(\vec{\mathbf{u}} \cdot \rho \cdot c_k) = -\vec{\nabla} \cdot \vec{\mathbf{j}}_k$$

$\Updownarrow$ since m is conserved

$$D_t c_k \equiv \partial_t c_k + (\vec{\mathbf{u}} \cdot \vec{\nabla}) c_k = -\frac{1}{\rho} \vec{\nabla} \cdot \vec{\mathbf{j}}_k$$ ← e.g. $D \cdot \nabla^2 c_k$

The component masses are *conserved* but *not passive* quantities

The advection–diffusion–reaction equations

local rate of change | advective flux | diffusive flux | reactive source terms

$$\partial_t (\rho \cdot c_k) + \vec{\nabla}(\vec{\mathbf{u}} \cdot \rho \cdot c_k) = -\vec{\nabla} \cdot \vec{\mathbf{j}}_k + (\text{mass production rate density})$$

$\Updownarrow$ since m is conserved

$$D_t c_k \equiv \partial_t c_k + (\vec{\mathbf{u}} \cdot \vec{\nabla}) c_k = -\frac{1}{\rho} \vec{\nabla} \cdot \vec{\mathbf{j}}_k + (\text{local specific production rate})$$

The component masses are *not conserved* quantities

Reaction modelling OUTLINE

Incomplete without class notes

1. Reaction stoichiometry
2. Reaction energetics
3. Reaction kinetics

Effects in the model equations:

- reactive source terms in the advection–diffusion–reaction equations
- reaction heat source terms in the energy (=heat conduction) equation

Chemical reactions

- *Chemical reactions* are stochastic processes in which a molecular configuration of atoms transitions into another configuration

Incomplete without class notes

A figure showing initial and final configurations and explaining the relevant energy changes is missing from here

Energetics

forward reaction: ΔE>0 energy released → *exothermic*
reverse reaction: ΔE<0 energy consumed → *endothermic*

A binary reaction

Stoichiometry

forward reaction

reactant → *products*

$H_2O = H^+ + OH^-$

product ← *reactants*

reverse reaction

$\forall k: |\nu_k| = 1$

Reagents and reaction products	
k	species
1	H_2O
2	H^+
3	OH^-

A template reaction

Stoichiometry

forward reaction

reactants → *product*

$2\,H_2 + O_2 = 2\,H_2O$

products ← *reactant*

reverse reaction

Reagents and reaction products	
k	species
1	H_2O
2	O_2
3	H_2

Reaction stoichiometry

Stoichiometric constants

- *forward reaction:*
  $+2\cdot H_2O - 1\cdot O_2 - 2\cdot H_2 = 0$
  $\nu_1 = +2,\ \nu_2 = -1,\ \nu_3 = -2$
- *reverse reaction:*
  $-2\cdot H_2O + 1\cdot O_2 + 2\cdot H_2 = 0$
  $\nu_1 = -2,\ \nu_2 = +1,\ \nu_3 = +2$
- for reactants: $\nu_k < 0$,
- ror reaction products: $\nu_k > 0$
- for *catalysts*: $\nu_k = 0$

$\sum_k \nu_k \neq 0$

The number of molecules is not conserved

Reagents and reaction products	
k	species
1	H_2O
2	O_2
3	H_2

Stoichiometric constants

- *forward reaction:*
  $+2\cdot H_2O - 1\cdot O_2 - 2\cdot H_2 = 0$
  $\nu_1 = +2,\ \nu_2 = -1,\ \nu_3 = -2$
- *reverse reaction:*
  $-2\cdot H_2O + 1\cdot O_2 + 2\cdot H_2 = 0$
  $\nu_1 = -2,\ \nu_2 = +1,\ \nu_3 = +2$
- for reactants: $\nu_k < 0$,
- ror reaction products: $\nu_k > 0$
- for *catalysts*: $\nu_k = 0$

$\sum_k M_k \cdot \nu_k = 0$

BUT: the total mass is conserved

Reagents and reaction products	
k	species
1	H_2O
2	O_2
3	H_2

Reactive source terms

Incomplete without class notes

One reaction process:

$$\forall k : \frac{dn_k}{dt} = \nu_k \cdot \dot{\xi}$$

reaction rate

Several reactions:

$$\forall k : \frac{dn_k}{dt} = \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]}$$

reaction rate vector

Possible units:
- mol/s,
- (mol/m^3)/s,
- (mol/kg)/s

$$\forall k : \frac{dm_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]} = Q_k(t)$$

$$\forall k : \frac{d\rho_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]}$$

$$\forall k : \frac{dc_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \dot{\xi}_{[r]}$$

reactive source terms

An alternative formulation:
summation over reaction pairs instead of individual reactions

$$\forall k : \frac{dm_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]}\right) = Q_k(t)$$

$$\forall k : \frac{d\rho_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]}\right)$$

$$\forall k : \frac{dc_k}{dt} = M_k \cdot \sum_{[r]} \nu_{k[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]}\right)$$

forward and reverse reaction rates

Reactive heat source terms in the energy transport equation

Energy released (or consumed) in the course of the reactions appear in the system as *reaction heat*.

The corresponding source terms in the energy balance (aka. heat transport) equation are:

$$\sum_{[r]} \Delta E_{[r]} \cdot \dot{\xi}_{[r]}$$

energy released in reaction [r]

or, equivalently

$$\sum_{[r]} \Delta E_{[r]} \cdot \left(\dot{\xi}^{\rightarrow}_{[r]} - \dot{\xi}^{\leftarrow}_{[r]}\right)$$

energy released in forward reaction [r]

Reaction kinetics

For a wide range of reactions the reaction rates look like this

$$\dot{\xi}_{[r]} \propto \left[\prod_i (c_i)^{\gamma_i}\right] \cdot \exp\left(-\frac{E_{\mathrm{act}[r]}}{R \cdot T}\right)$$

probability of the simultaneous presence of all reactant molecules

probability of the transition at the prevailing temperature

Incomplete without class notes

Notational system for local extensive quantities

- For integral description (in control volumes):
  - extensive quantity: F
- For differential description (local values):
  - density: $\varphi = F/V = \rho \cdot f$
  - specific value $f = F/m$
  - molar value $f = F/n$
  - molecular value $F^* = F/N$