Model building using engineering principles
Dynamic chemical and biochemical models

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Lecture overview

1. Chemical and biochemical systems
   - Characterization of chemical and biochemical systems
2. Balance equations in chemical and biochemical systems
   - Overall mass balances
   - Component mass balances
   - Energy balances
3. Constitutive equations in chemical and biochemical systems
   - Extensive-intensive relationships
   - Reaction rate equations
   - Chemical property relations
4. State space model form of dynamic chemical and biochemical models
   - Component mass balance equations in intensive variable form

Characterization of chemical and biochemical systems

Characterization: through modelling objects and mechanisms

- Modelling objects: spatially homogeneous (perfectly stirred) balancing volumes with chemical reactions as the simplest case
- Mechanisms
  We have the mechanisms that characterize thermal energy systems, and the following special ones:
  - *Chemical reactions*: the rate expression is a polynomial function of the concentrations (mass action law), or it is a rational function of the concentration (biochemical kinetics).
  - *Chemical reactions have a thermal effect*
    (i) the reaction rate depends on the temperature through k (a physico-chemical property)– an exponential type relationship.
    (ii) chemical reactions produce/consume energy that is proportional to the reaction rate – an induced energy term in the energy balance

Balance equations in chemical and biochemical systems

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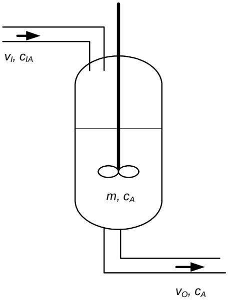
Balance volumes and conserved extensive quantities

Balance volumes: perfectly stirred



Conserved extensive quantities:

- overall mass m
- component masses m_{X_k}, $k = 1, ..., K$
- energy U

Overall mass balances

For **perfectly stirred balance volumes**

- no source or sink term if the balance volume is connected to the environment only. Otherwise, the phase changes (evaporation, boiling, melting, etc.) may generate a mass source or sink through the interphase boundary.
- convective terms are the in- and out-flows entering or leaving the balance volume, that are mass flows $[kg/s]$.

$$\frac{dm}{dt} = v_I - v_O$$

Associated measurable quantity: level (e.g. with constant cross section)

Component mass balances

For **perfectly stirred balance volumes**

- induced component in- and out-flow terms are the inlet and outlet component mass flows entering or leaving the balance volume, that are mass flows $[kg/s]$
- source or sink term: reaction rates R_i, $i = 1, ..., \mathcal{R}$ in units $[mol/(kg \cdot s)]$ caused by the chemical reactions

$$\frac{d(m \cdot c_A)}{dt} = v_I \cdot c_{IA} - v_O \cdot c_A - m \cdot R$$

Associated measurable quantity: concentrations c_{X_k}, $k = 1, ..., K$ in units $[mol/kg]$ (or $[mol/m^3]$)

Energy balances

For **perfectly stirred balance volumes**

- induced convective energy flows induced by the convective mass flows of a balance volume (in unit $[J/s]$),
- source or sink terms caused by the chemical reaction of reaction enthalpy ΔH (in unit $[J/kg]$) together with the usual external (e.g. electrical) heating/cooling or heat transfer terms Q (again in unit $[J/s]$).

$$\frac{dU}{dt} = c_{pI} v_I T_I - c_p v_O T - \Delta H \cdot m \cdot R + Q$$

Associated measurable quantity: temperature

Constitutive equations in chemical and biochemical systems

Constitutive equations – Extensive-intensive relationships

For **perfectly stirred balance volume with constant pressure** and for the component A

$$m_A = m \cdot c_A$$

where m is the overall mass, m_A is the component mass, and c_A is the concentration of component A measured in unit $[mol/kg]$.

$$m = V \cdot \rho$$

where V is the volume, m is the overall mass and ρ is the density of the balance volume.

Constitutive equations – Reaction rate equations 1.

1 mass action law reaction rates

- elementary reaction steps: ***irreversible reactions***:

$$\sum_{i=1}^{K} \alpha_{ij} \mathbf{X}_i \to \sum_{i=1}^{K} \beta_{ij} \mathbf{X}_i \quad j = 1, ..., r \tag{1}$$

  where $\mathbf{X}_i$ denotes a *chemical component* and the
- *stoichiometric coefficients* α_{ij} *and* β_{ij} *are always non-negative integers*
- reaction rate expression

$$R_j = k_j \prod_{i=1}^{n} c_i^{\alpha_{ij}}$$

- $k_j > 0$ is the *reaction rate coefficient* of the jth reaction, that is *always positive*

Example – MAL reaction rate equations

- Simple linear example
  Let us assume a simple reaction kinetic system with two irreversible steps and three components

$$\mathbf{X}_1 \to \mathbf{X}_2 \to \mathbf{X}_3$$

  Then the reaction rate equations are

$$R_1 = k_1 c_1 \quad , \quad R_2 = k_2 c_2$$

- Simple nonlinear example
  Now we consider a simple elementary reaction step

$$2\mathbf{A} + \mathbf{B} \to \mathbf{C}$$

  Then the reaction rate equation is

$$R = k c_A^2 c_B$$

Constitutive equations – Reaction rate equations 2.

2 biochemical reaction rates

- elementary reaction

$$\mathbf{X} + \mathbf{X}_B \rightarrow$$

where $\mathbf{X}_B$ is the biologically active component (e.g. the biomass), $\mathbf{X}$ is the substrate

- "monod type" reaction rate expression

$$R(c, c_B) = k \cdot c \cdot \frac{c_B}{k_B + c_B}$$

c_B is the concentration of the biologically active component, c is that of the substrate with k and k_B being positive constant coefficients

- second order "monod type" reaction rate expression

$$R(c, c_B) = k \cdot c \cdot \frac{c_B}{k_B + c_B + k_{B1} c_B^2}$$

where k_{B1} is also a positive constant

Constitutive equations – Chemical property relations

i Reaction rate coefficient relations – Arrhenius law

$$k = k_0 \cdot e^{-\frac{E}{RT}}$$

where $k_0 > 0$ is the pre-exponential factor, $E > 0$ is the activation energy and R is the universal gas constant

ii Reaction enthalpy relations – only the temperature dependence is considered

$$\Delta H = H_0 \cdot \left(1 + c_{H1}(T - T_0) + c_{H1}(T - T_0)^2\right)$$

where T_0 is a suitable reference temperature, H_0 is the reaction enthalpy at the reference temperature, and $c_{Hi}, i = 1, 2$ are constants

Transformation to state space model form

From the **extensive form of the dynamic component mass balance equation**

1. The conservation balance equations should be transformed to have measurable (mostly intensive) quantities in them.
2. The constitutive algebraic equations should be substituted into the differential ones (if possible).

Component mass balance equations in intensive form – 1

Assumptions for the transformation steps

F1 A single perfectly stirred balance volume with a single $\mathbf{A} \rightarrow \mathbf{B}$ type chemical reaction is considered with overall mass m and internal energy U.

F2 One in- (v_I) and one out-flow (v_O) is assumed, that are mass flows $[kg/s]$.

F3 Constant thermodynamical properties are assumed.

F4 The component concentrations c_A and c_B are measured in $[mol/kg]$, and the unit of the reaction rate R is $[mol/kg/s]$, accordingly.

Original equations

Mass balance

$$\frac{dm}{dt} = v_I - v_O$$

Component mass balance

$$\frac{d(m \cdot c_A)}{dt} = v_I \cdot c_{IA} - v_O \cdot c_A - m \cdot R$$

Component mass balance equations in intensive form – 2

Original equations

Mass balance

$$\frac{dm}{dt} = v_I - v_O$$

Component mass balance

$$\frac{d(m \cdot c_A)}{dt} = v_I \cdot c_{IA} - v_O \cdot c_A - m \cdot R$$

with

$$m\frac{dc_A}{dt} + c_A\frac{dm}{dt} = v_I \cdot c_{IA} - v_O \cdot c_A - m \cdot R$$

State equation originating from the component mass balance

$$\frac{dc_A}{dt} = \frac{v_I}{m} \cdot (c_{IA} - c_A) - R$$

State space model in chemical and biochemical systems

- **State equations**: overall mass balances, component mass balances and energy balances in intensive form
- **State variables**: for each balance volume i

$$x = [\ m_i, (c_{X_k,i}, k = 1, ..., K), T_i \mid i = 1, ..., N]^T$$

- **Output variables**: non-input variables that we can directly measure