Mô hình hóa, mô phỏng và tối ưu hóa các quá trình hóa học

Modeling, simulation and optimization for chemical process

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Bộ môn QT&TB

Curriculum/syllabi

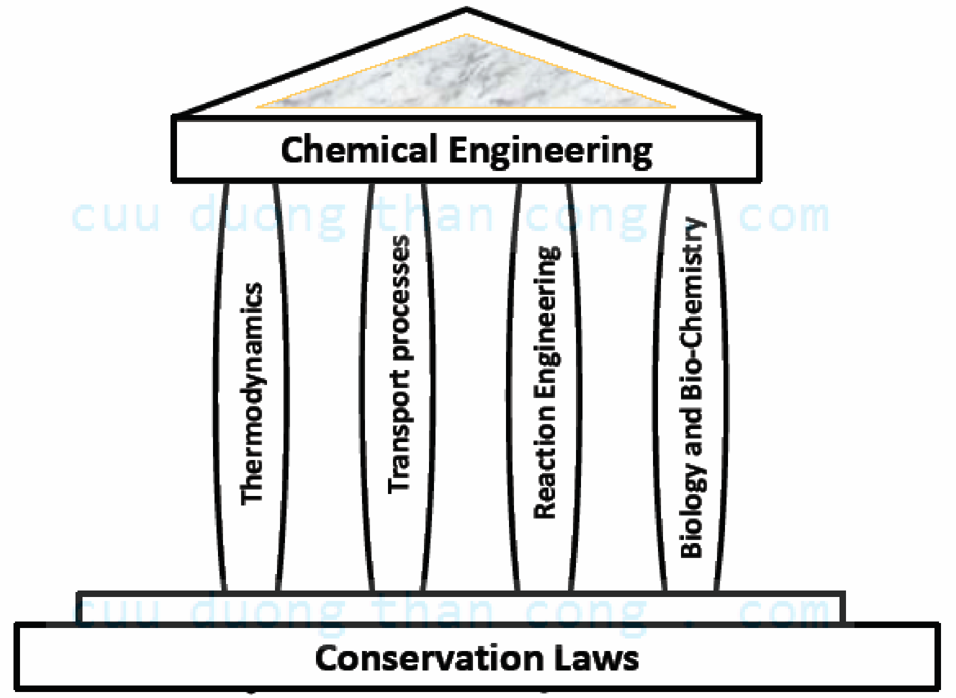
Seminar group

Outline

- General introduction
  - Structure and operation of chemical engineering systems
  - What is a chemical process?
  - Motivation examples
- Part I: Process modeling
- Part II: Computer simulation
- Part III: Optimization of chemical processes

General introduction

- Structure of chemical engineering system



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General introduction

- Conservation laws:
  - Give some balance equations such as mass balance (or the molar number by species), energy balance and momentum equation of the system under consideration
- Equilibrium thermodynamics
  - The extensive variables/intensive variables
  - The laws of thermodynamics
- Reaction engineering
  - Reaction mechanism
  - The rate of a chemical reaction
- Transport processes
  - How materials and energy move from one position to another (heat conductivity, diffusion and convection…)
- Biological processes
  - Transform material from one form to another (enzyme process) or remove pollutants (environmental engineering)

General introduction

- References (complements) :

1. Sandler S. I. (1999). Chemical and Engineering Thermodynamics. Wiley and Sons, 3rd edition.
2. H.B. Callen. Thermodynamics and an introduction to thermostatics. JohnWiley & Sons Inc, 2nd ed. New York, 1985.
3. De Groot S. R. and P. Mazur (1962) Non-equilibrium thermodynamics. Dover Pub. Inc., Amsterdam.
4. Vũ Bá Minh. (tập 4) Kỹ thuật phản ứng. NXB ĐHQG Tp. Hồ Chí Minh, 2004
5. Nguyễn Bin, (tập 5) Các quá trình hóa học. NXB Khoa học và Kỹ thuật, 2008

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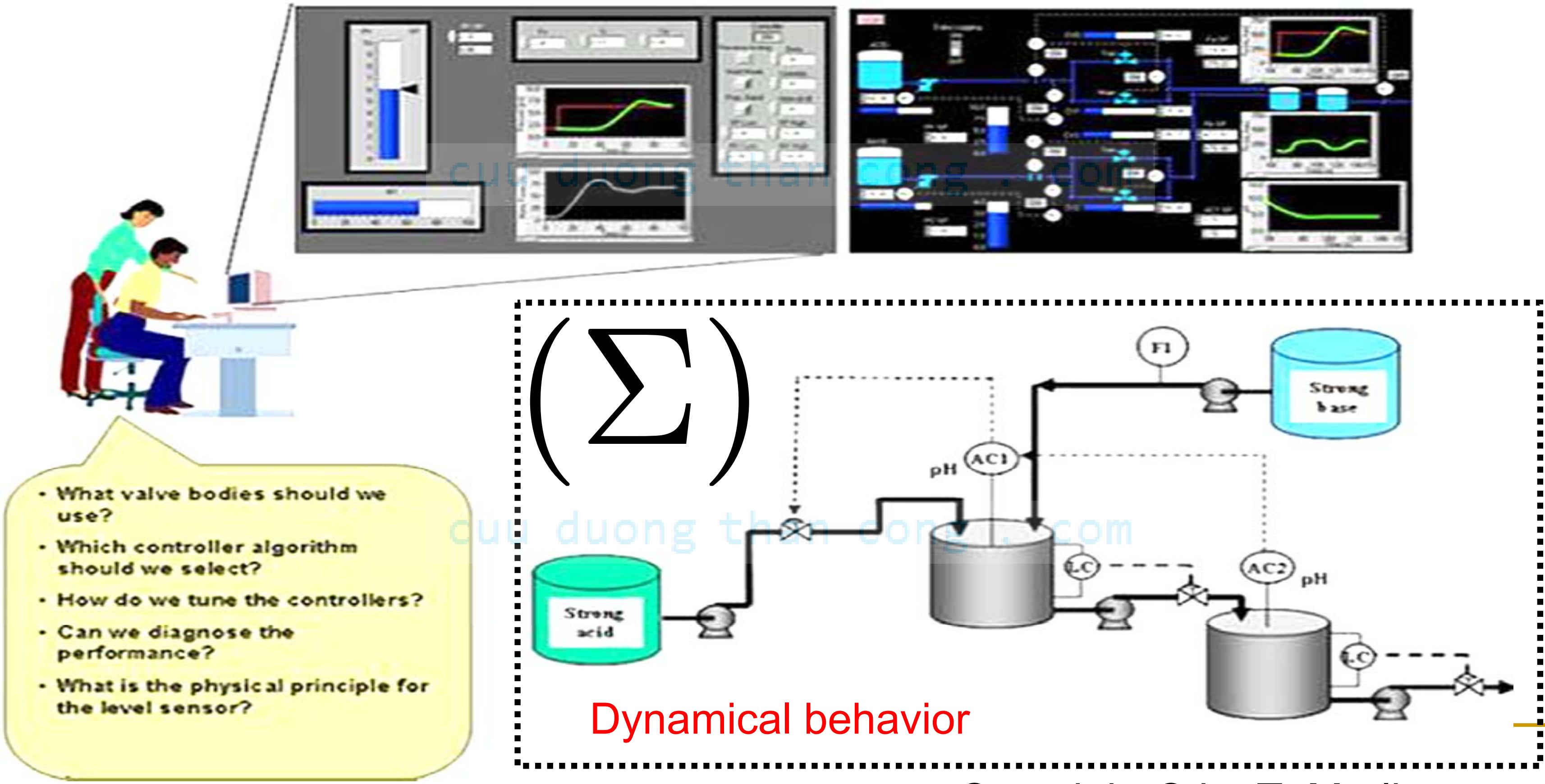
General introduction

- Operation of a chemical engineering plant

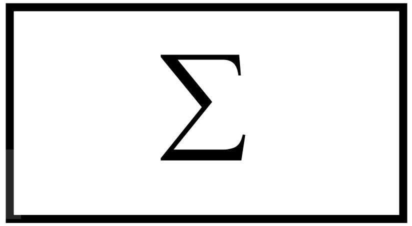


General introduction

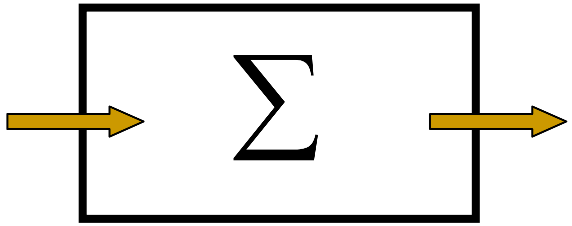
- Oil and gas production plant

General introduction

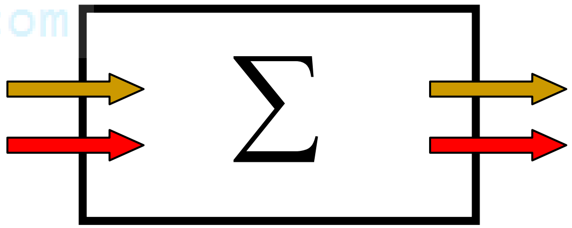
- The system may be
  - Isolated: There is no transfer of mass or energy with the environment



  - Closed: There may be transfer of mechanical energy and heat

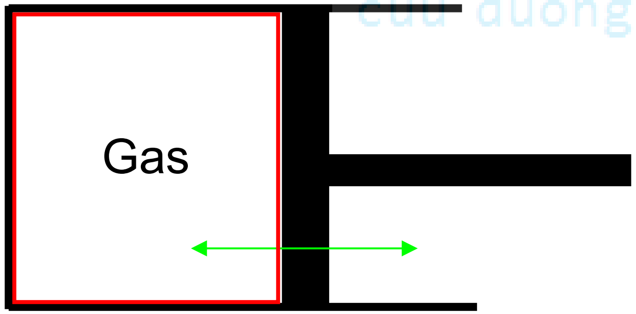


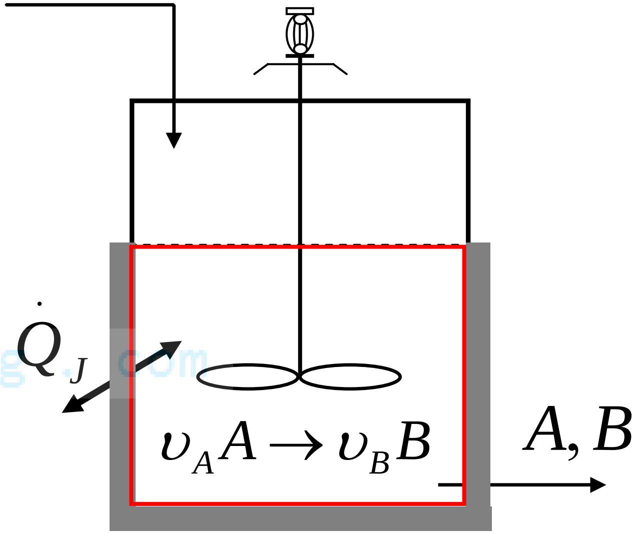
  - Open: There is mass transfer with the environment



General introduction

Question: determinate physical volume of the following systems?





General introduction

- What is a chemical process?
  - Process: A set of actions performed intentionally in order to reach some result (*Longmans Dictionary of Contemporary English*)
  - Processes that involve energy conversion, reaction, separation and transport are called chemical processes (*Prof. Erik Ydstie at CMU, USA*)
  - Definition: **Chemical processes are a special subclass of processes since their behavior is constrained by a range of laws and principles which may not apply in other circumstances (mechanical/electrical systems…)**
  - Properties:
    - **Highly nonlinear**
    - **Complex network**
    - **May be distributed**

General introduction

- Chemical processes
  - Thermal conductivity process
  - Transport (reaction) process
  - …

General introduction

- Why we need informations about dynamical behavior?

  - Research and development
  - Process design
  - Process control
  - Plant operation
  - …

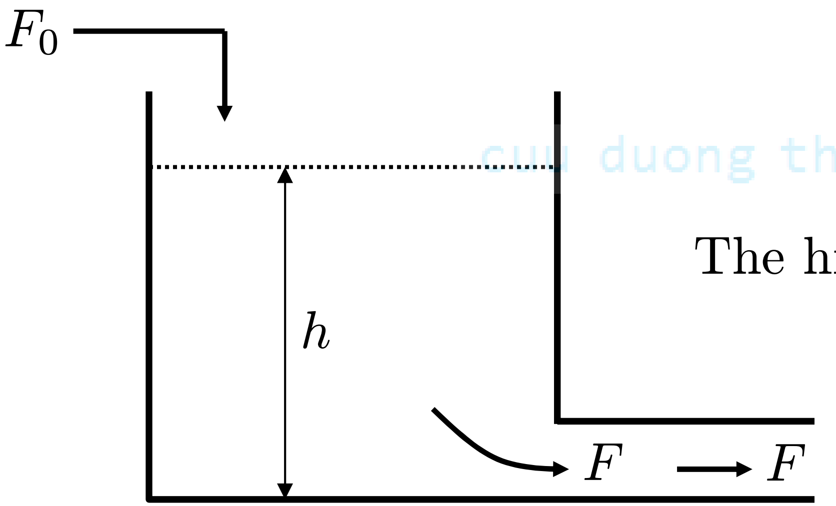
Process modeling, computer simulation and optimization

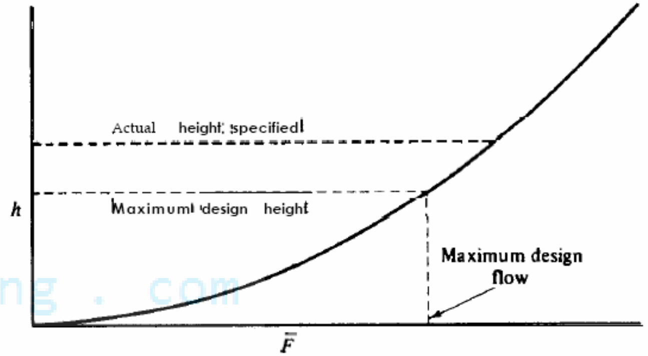
$$\left(\sum\right)$$

Ordinary Differential Equations (ODEs) or Partial Differential Equations (PDEs) or Differential and Algebraic Equations (DAEs)

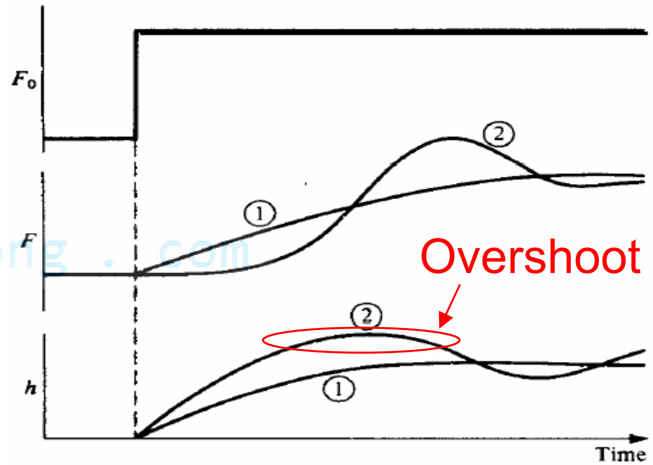
Motivation examples

- Example 1: Gravity-flow tank





The higher the flow rate $\bar{F}$, the higher $\bar{h}$ will be



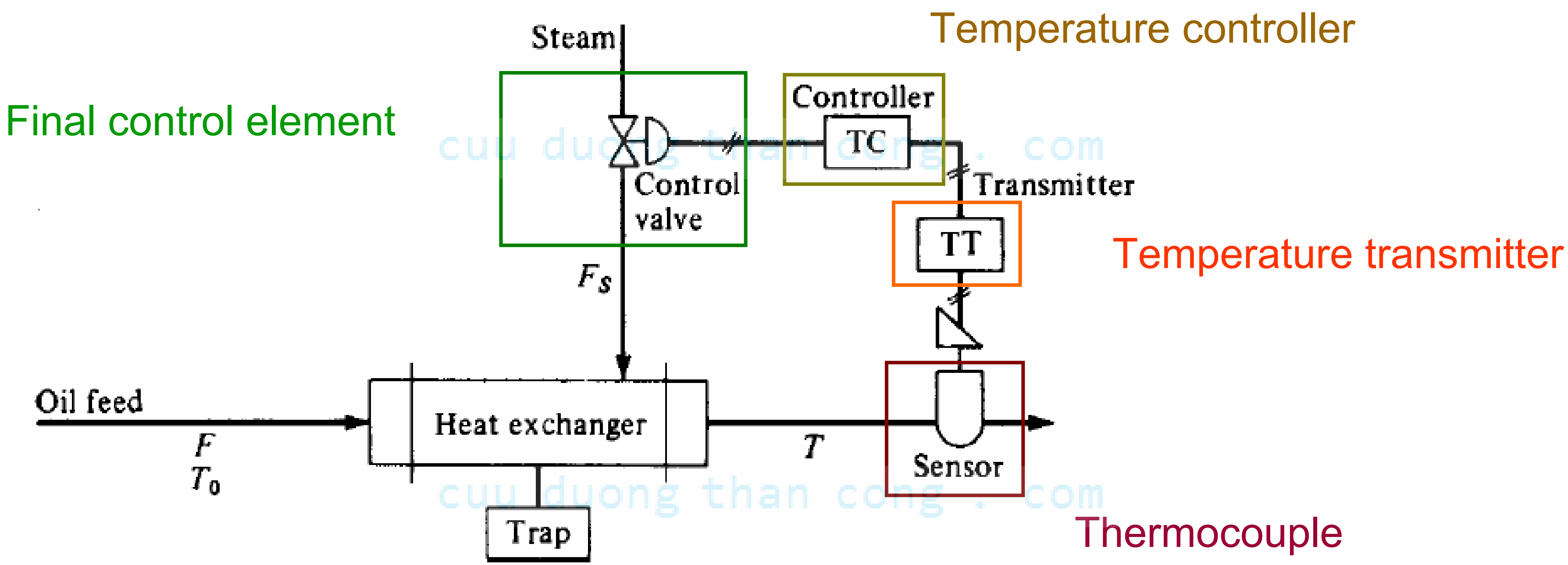
$F_0 = F_0(t)$, $h = h(t)$ and $F = F(t)$

$\bar{F}_0$, $\bar{h}$ and $\bar{F}$: steadystate values

How to understand dynamical behavior to design the system avoiding « Overshoot »?

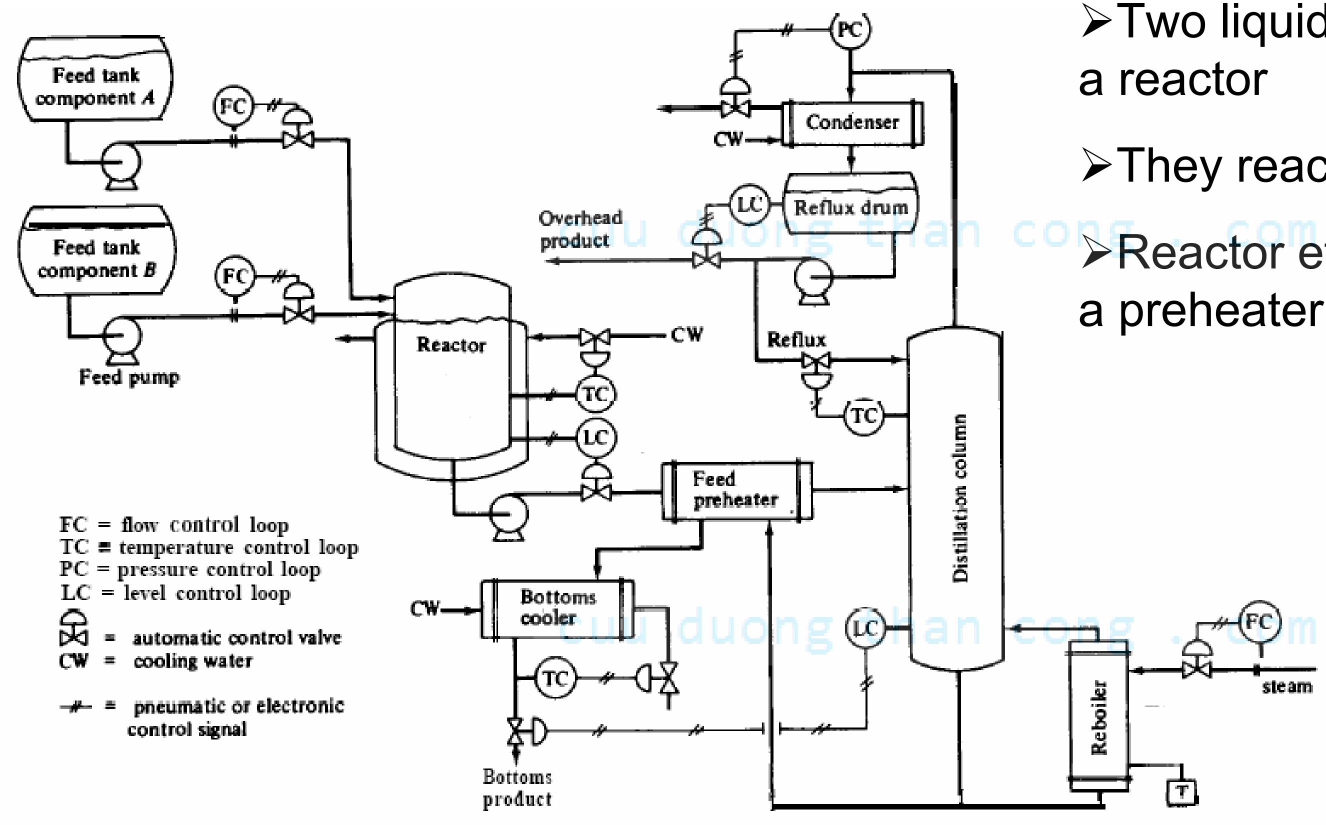
Motivation examples

- Example 2: Heat exchanger



Motivation examples

- Example 3: Typical chemical plant and control system



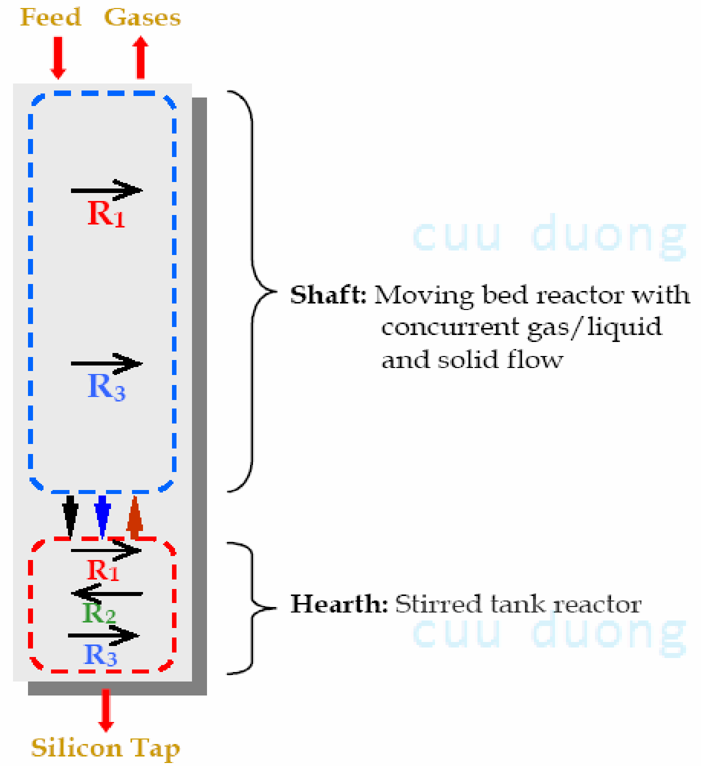
- ➢Two liquids feeds are pumped into a reactor
- ➢They react to form products
- ➢Reactor effluent is pumped through a preheater into a distillation

To specify the various pieces of equipment:

- •Fluid mechanics
- •Heat transfer
- •Chemical kinetics
- •Thermodynamics and mass transfer

Motivation examples

- Example 4: Optimization of a silicon process



$$R1: 2C(s) + SiO(g) = SiC(s) + CO(g)$$

$$R2: Si + SiO_2 = 2SiO(g)$$

$$R3: SiC(s) + SiO(g) = 2Si(l) + CO(g)$$

The silicon reactor

Motivation examples

- Example 4: Optimization of a silicon process

(1) The process models (dynamic and static material balances).

(2) A method to reconcile the model to process data and estimate process parameters and states.

(3) Tools for process optimization to find best operating conditions (setpoints).

(4) Process control methods to stabilize the process at the optimal operating points.

$$\min_{\theta \in \Theta} \sum_{k=1}^{N} \|y(k) - h(x(k), z(k), \theta\|^2$$

subject to

$$0 = f(x, z, \theta)$$

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Process modeling

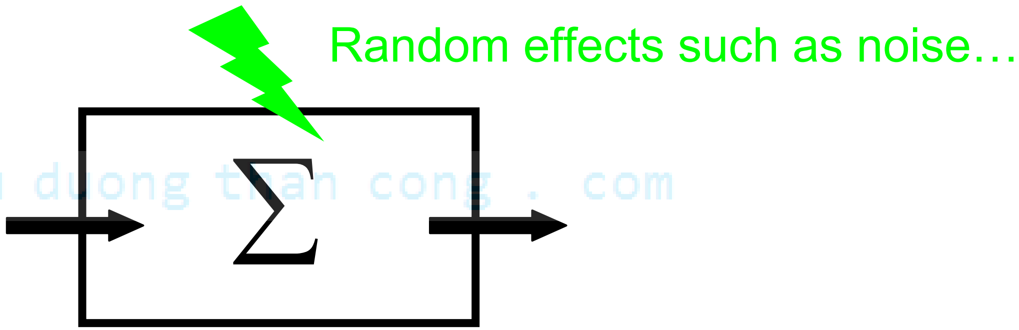
- Introduction
- Fundamental laws
  - Continuity equations
  - Energy equation
  - Equations of motion

Introduction

- Uses of mathematical models
  - Can be useful in all phases of chemical engineering, from research and development to plant operations, and even in business and economic studies
    - Research and development:
      - Determinating chemical kinetic mechanisms and parameters from lab. or pilot-plant reaction data
      - Exploring the effects of different operating conditions
      - Adding in scale-up calculations…
    - Design
      - Exploring the sizing and arrangement of processing equipment
      - Studying the interactions of various parts…
    - Plant operation
      - Cheaper, safer and faster
      - Troubleshooting and processing problems…

Introduction

- Scope of course
  - A deterministic system is a system in which no randomness is involved in the evolution of states of the system
  - A stochastic system is non-deterministic system



Introduction

- Principles of formulation
  - Basis
    - Fundamental physical and chemical laws such as laws of conservation of mass, energy and momentum
  - Assumptions
    - Impose limitations « reasonable » on the model
  - Mathematical consistency of model
    - Number of variables equals the number of equations (degrees of freedom)
    - Units of all terms in all equations are consistent

Introduction

- Solution of the model equations
  - Initial and/or boundary conditions
  - Available numerical solution techniques and tools
  - Solutions are physically acceptable…?

- Verification
  - The mathematical model is proving that the model describes the "real-world" situation
    - Real challenge

Fundamental laws

- Continuity equations
  - Total continuity equations (total mass balance)

$$\begin{bmatrix}\text{Mass flow} \\ \text{into system}\end{bmatrix} - \begin{bmatrix}\text{mass flow} \\ \text{out of system}\end{bmatrix} = \begin{bmatrix}\text{time rate of change} \\ \text{of mass inside system}\end{bmatrix}$$

  - Component continuity equations (component balance)

$$\begin{bmatrix}\text{Flow of moles of jth} \\ \text{component into system}\end{bmatrix} - \begin{bmatrix}\text{flow of moles of jth} \\ \text{component out of system}\end{bmatrix} + \begin{bmatrix}\text{rate of formation of moles of jth} \\ \text{component from chemical reactions}\end{bmatrix} = \begin{bmatrix}\text{time rate of change of moles of jth} \\ \text{component inside system}\end{bmatrix}$$

EXERCISE ?

Fundamental laws

- Energy balance

$$\begin{bmatrix}\text{Flow of internal, kinetic, and} \\ \text{potential energy into system} \\ \text{by convection or diffusion}\end{bmatrix} - \begin{bmatrix}\text{flow of internal, kinetic, and} \\ \text{potential energy out of system} \\ \text{by convection or diffusion}\end{bmatrix}$$

$$+ \begin{bmatrix}\text{heat added to system by} \\ \text{conduction, radiation, and} \\ \text{reaction}\end{bmatrix} - \begin{bmatrix}\text{work done by system on} \\ \text{surroundings (shaft work and} \\ \text{PV work)}\end{bmatrix}$$

$$= \begin{bmatrix}\text{time rate of change of internal, kinetic,} \\ \text{and potential energy inside system}\end{bmatrix}$$

EXERCISE ?

Fundamental laws

- Equations of motion

$$\vec{F} = \frac{d\left(M\vec{v}\right)}{dt}$$

Where $\vec{v}$ = velocity, $\vec{F}$ = total force and M = mass

- Pushing in the *i* direction (*i*=*x*,*y*,*z*)

$$F_i = \frac{d\left(Mv_i\right)}{dt}$$

EXERCISE ?

Fundamental laws

- Consider a system with *n* components
  - Number of equations obtained from the fundamental laws
    - *n* balance equations by species
    - 1 total mass balance equation
    - 1 energy balance equation
    - 3 equations of motion (if the system is under movement)

Not independent

$$\Rightarrow n + 1 + (3) \text{ equations}$$

Constitutive equations

Transport equations

Quantity	Heat	Mass
Flux	4	N_A
	Molecular transport	
Driving force	$\frac{\partial T}{\partial z}$	$\frac{\partial C_A}{\partial z}$
Law	Fourier's	**Fick's**
Property	Thermal conductivity k_T	Diffusivity $\mathcal{D}_A$
	Overall transport	
Driving force	AT	$\Delta C_A \dagger$
Relationship	$q = h_T \Delta T$	$N_A = k_L$ AC,

Reaction kinetics of (bio)chemical reaction…

$$k = k(T, C)$$

Other equations

- As we saw, we need equations that tell us how the physical properties, primarily density and enthalpy, change with temperature, pressure, and composition to rewrite **alternative** mathematical models
  - Equations of state

$$\text{Liquid density} = \rho_L = f_{(P,\,T,\,x_i)}$$

$$\text{Vapor density} = \rho_V = f_{(P,\,T,\,y_i)}$$

$$\textbf{Liquid}\ \text{enthalpy} = h = f_{(P,\,T,\,x_i)}$$

$$\text{Vapor enthalpy} = H = f_{(P,\,T,\,y_i)}$$

Other equations (cont.)

- In some cases, simplification can be made without sacrificing much overall accuracy

$$H = C_p T \text{ (liquid)}$$

$$H = C_p T + \lambda_v \text{ (vapor)}$$

- Or more complex, C_p is considered as a function of temperature

$$H = \int_{T_{ref}}^{T} C_p(T)dT$$

Other equations (cont.)

- A polynomial in T is used for C_p

$$C_p(T) = A_1 + A_2 T$$

- We obtain

$$\begin{aligned} H &= \left[A_1 T + A_2 \frac{T^2}{2} \right]_{T_{ref}}^{T} \\ &= A_1 (T - T_0) + \frac{A_2}{2} (T^2 - T_0^2) \end{aligned}$$

Other equations (cont.)

- If the mixture is composed of components (which we know the pure-component enthalpies) then the total enthalpy can be averaged

$$H = \frac{\sum_{j=1}^{N} x_j h_j M_j}{\sum_{j=1}^{N} x_j M_j}$$

x_j - mole fraction of jth component

M_j - molecular weight of jth component

h_j - pure-component enthalpy of jth component (energy per unit mass)

Other equations (cont.)

- Liquid densities can be assumed constant in many systems
- Vapor densities usually cannot be considered invariant in many systems and the *PVT* relationship is almost always required.
  - The simplest and most often used case is the perfect gas law

$$PV = nRT \quad \Rightarrow \rho_v = \frac{nM}{V} = \frac{PM}{RT}$$

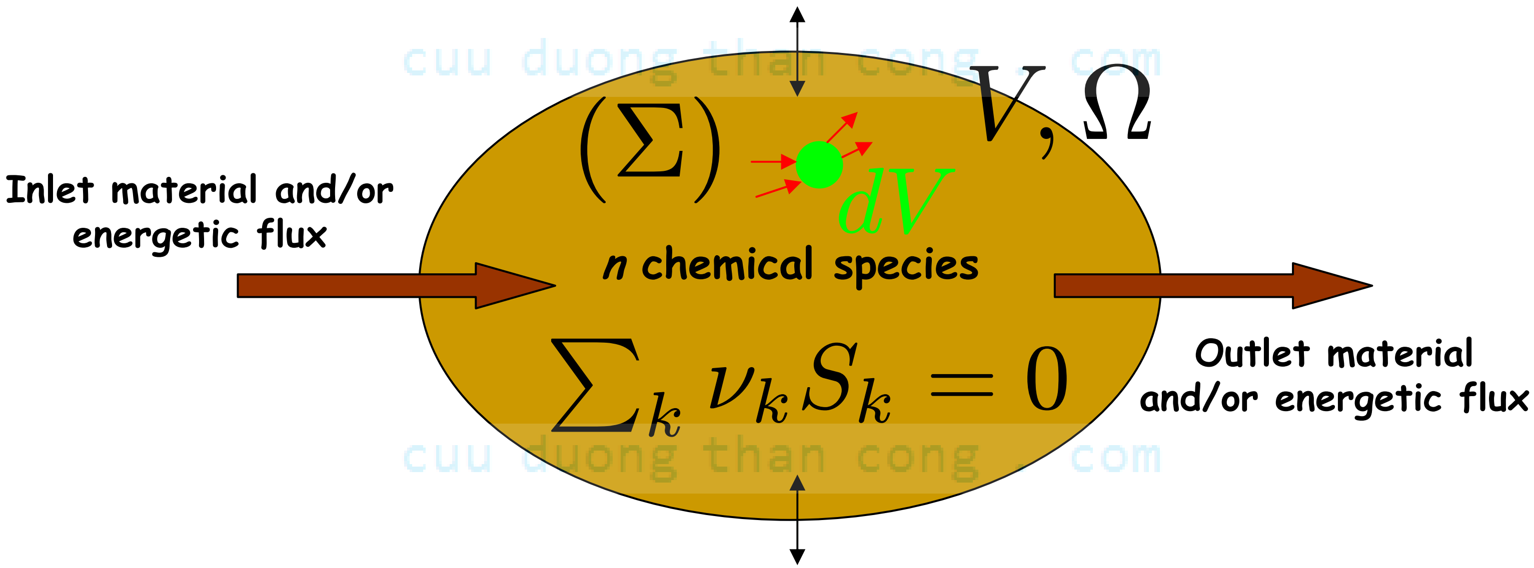
Examples of mathematical modeling of chemical process

(Distributed) Transport reaction systems

De Groot S. R. and P. Mazur (1962) Non-equilibrium thermodynamics. Dover Pub. Inc., Amsterdam.

Examples of mathematical modeling of chemical process

- Distributed reaction systems (reactor tubular for example)



Examples of mathematical modeling of chemical process

- Mass conservation by species

$$\frac{dm_k}{dt} = \frac{d}{dt}\int_V \rho_k dV = \int_V \frac{\partial \rho_k}{\partial t} dV$$

Total material flux $\rightarrow \mathbf{J}_k = \mathbf{v}_k \rho_k$

$$\int_V \nu_k M_k r_v dV$$

$$-\int_\Omega \mathbf{J}_k \cdot d\mathbf{\Omega} = -\int_V \mathrm{div}(\mathbf{J}_k) dV$$ Gauss theorem

$$\Rightarrow \frac{\partial \rho_k}{\partial t} = -\mathrm{div}(\mathbf{J}_k) + \nu_k M_k r_v$$

Examples of mathematical modeling of chemical process

$$\frac{\partial(\sum_k \rho_k)}{\partial t} = -\mathrm{div}(\sum_k \mathbf{J}_k)$$

$$\rho = \sum_k \rho_k \qquad \mathbf{v} = \frac{\sum_k \mathbf{J}_k}{\rho}$$

$$v = \rho^{-1}$$

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}(\mathbf{v}\rho)$$

$$\underbrace{\frac{\partial v}{\partial t} + \mathbf{v} \cdot \overrightarrow{\nabla} v}_{\frac{Dv}{Dt}} = v\,\mathrm{div}(\mathbf{v})$$

$$\mathbf{J}_k^c = \rho_k \mathbf{v}$$

$$\mathbf{J}_k^d = \rho_k(\mathbf{v}_k - \mathbf{v}) \qquad \Rightarrow \mathbf{J}_k = \mathbf{J}_k^d + \mathbf{J}_k^c$$

Examples of mathematical modeling of chemical process

$$\frac{dU}{dt} = \int_V \frac{\partial \rho u}{\partial t} dV = -\int_\Omega \mathbf{J}_u \cdot d\mathbf{\Omega}$$

$$\frac{\partial \rho u}{\partial t} = -\mathrm{div}\mathbf{J}_u$$

$$\mathbf{J}_u = \rho u \mathbf{v} + p\mathbf{v} + \mathbf{J}_q = \rho \underbrace{\left(u + pv\right)}_{=h} \mathbf{v} + \mathbf{J}_q$$

$$\sum_k h_k \mathbf{J}_k^c \qquad \mathbf{J}_q' \qquad \sum_k h_k \mathbf{J}_k^d$$

Examples of mathematical modeling of chemical process

- Seminar:
  - Nonisothermal CSTR
  - Batch reactor
  - pH systems
  - Distillation column

Examples of mathematical modeling of chemical process

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Phương trình dòng

- Sự vận chuyển trong thiết bị phản ứng của hỗn hợp phản ứng, bao gồm:
  - Dòng vật liệu (khối lượng/nồng độ)
  - Dòng nhiệt năng (năng lượng)
  - Dòng động lượng (xung)

$\Rightarrow$ Được đặc trưng bởi mật độ dòng Γ (lượng/thể tích)

- Có dòng đối lưu, dòng dẫn, dòng cấp và dòng phát sinh
  - Dòng đối lưu hoặc dòng dẫn có thể tồn tại độc lập hoặc đồng thời **nhưng chỉ trong một pha**
  - Sự vân chuyển xảy ra qua lớp biên của **hai pha** là dòng cấp

Phương trình dòng

- Các quá trình vận chuyển trong thiết bị
  - Dòng đối lưu
    - Sự thay đổi vị trí trong không gian của mật độ dòng được gọi là đối lưu (dòng vận chuyển vĩ mô)
    - Mật độ dòng đối lưu được biểu thị

$$\overrightarrow{j}_c = \Gamma \overrightarrow{v}$$ (lượng/thời gian/diện tích)

  - Dòng dẫn (khuếch tán)
    - Chuyển động phân tử trong lòng pha khí hoặc pha lỏng là chuyển động vi mô tạo thành dòng dẫn

$$\overrightarrow{j}_d = -D\overrightarrow{\text{grad}}C$$ (lượng/thời gian/diện tích)

Phương trình dòng

- Các quá trình vận chuyển trong thiết bị (tt)
  - Dòng cấp
    - Sự vận chuyển của đại lượng đặc trưng từ pha này sang pha khác gọi là sự cấp
    - Các quá trình xảy ra giữa các pha thường được mô tả bằng các đại lượng quảng tính

$$\overrightarrow{j} = \epsilon f \Delta\Gamma$$ (lượng/thời gian/diện tích)

ϵ - hệ số cấp, f - bề mặt riêng (xét trên một đơn vị thể tích)

$\Delta\Gamma$ - động lực

Phương trình dòng

- Các quá trình vận chuyển trong thiết bị (tt)
  - Dòng phát sinh
    - Dòng phát sinh vật chất do phản ứng hóa học

$$G_j = \sum_{i=1}^{m} \nu_{ji} r_i$$

    - Dòng phát sinh cuả nhiệt năng do phản ứng hóa học

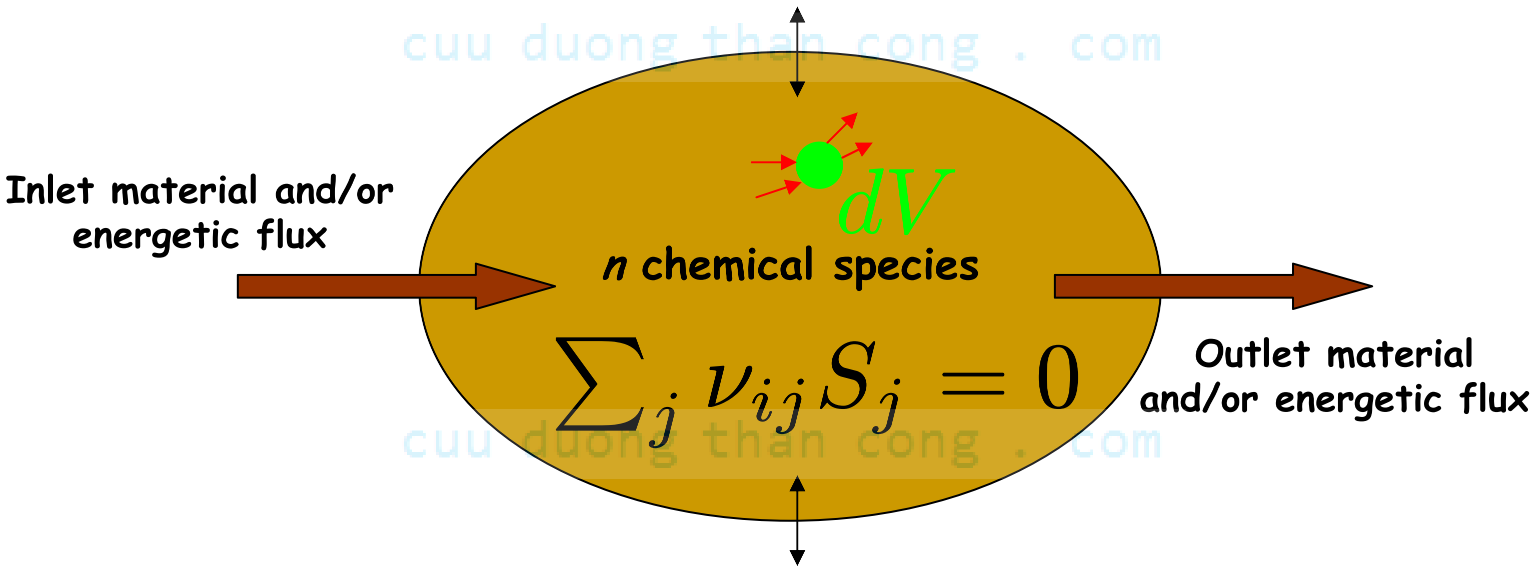
$$G_i = (-\Delta H_i) r_i$$

    - Dòng phát sinh của động lượng do chênh lệch áp suất
      - Được hình thành do sự thay đổi của áp suất trong hệ, tức là có tác dụng của xung lực

$$G = \overrightarrow{\mathrm{grad}} P$$

Phương trình dòng

- Xét trường hợp hệ tổng quát (**đồng thể** hay **dị thể**) có phản ứng hóa học



Phương trình dòng

- Phương trình cân bằng tổng quát có dạng của phương trình vi phân riêng phần được **Damköhler** thiết lập (1936)

$$\frac{\partial \Gamma}{\partial t} = -\mathrm{div}(\overrightarrow{v}\Gamma) + \mathrm{div}(\delta\,\overrightarrow{\mathrm{grad}}\Gamma) - \boxed{\epsilon f \Delta \Gamma} + G$$

$$\overrightarrow{j}_c \qquad \overrightarrow{j}_d$$

Dòng cấp

Dòng phát sinh

$$\Gamma = \rho \quad C_j \quad \rho C_p T \quad \rho\overrightarrow{v}$$

Phương trình dòng

$$\frac{\partial \Gamma}{\partial t} = -\mathrm{div}(\overrightarrow{v}\Gamma) + \mathrm{div}(\delta \overrightarrow{\mathrm{grad}}\Gamma) - \epsilon f \Delta \Gamma + G$$

- Viết lại các phương trình cân bằng

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}(\overrightarrow{v}\rho) + \mathrm{div}(D^\star \overrightarrow{\mathrm{grad}}\rho) - \beta^\star f \Delta \rho + G$$

$$\begin{aligned}\frac{\partial C_j}{\partial t} = & -\mathrm{div}(\overrightarrow{v} C_j) + \mathrm{div}(D \overrightarrow{\mathrm{grad}} C_j) \\ & -\beta_j f \Delta C_j + G_j\end{aligned}$$

$$\begin{aligned}\frac{\partial \rho C_p T}{\partial t} = & -\mathrm{div}(\overrightarrow{v}\rho C_p T) + \mathrm{div}(\alpha_T \overrightarrow{\mathrm{grad}}\rho C_p T) \\ & -\alpha^\star f \Delta \rho C_p T + G\end{aligned}$$

$$\begin{aligned}\frac{\partial \rho \overrightarrow{v}}{\partial t} = & -\mathrm{div}(\overrightarrow{v} \circ \rho \overrightarrow{v}) + \mathrm{div}(\nu \overrightarrow{\mathrm{grad}}\rho \overrightarrow{v}) \\ & -\gamma f \Delta(\rho \overrightarrow{v}) + G\end{aligned}$$

Phương trình dòng

$$\frac{\partial \Gamma}{\partial t} = -\mathrm{div}(\overrightarrow{v}\Gamma) + \mathrm{div}(\delta\overrightarrow{\mathrm{grad}}\Gamma) - \epsilon f \Delta\Gamma + G$$

- Example: xem chương 5, tập 5 (sách Các quá trình, thiết bị **TRONG CÔNG NGHỆ HÓA CHẤT VÀ THỰC PHẨM**, Nguyễn Bin)

  - Mô hình toán cho hệ khuấy lý tưởng
  - Chuỗi thiết bị khuấy lý tưởng
  - Thiết bị khuấy gián đoạn
  - Thiết bị đẩy lý tưởng
  - Các bài toán thực tế

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Ref.: Burden R. L. and Faires J. D. ***Numerical analysis***.