

# Modelling & Simulation of Chemical Engineering Systems

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٥٠١ هـم : تمثيل الأنظمة الهندسية على الحاسب الآلي

Department of Chemical Engineering  
King Saud University

# LECTURE #2



# Last Lecture

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- Modeling and simulation
- System Classifications
- Models Classifications
- Models: steady and dynamic, Lumped and distributed, Deterministic and stochastic
- Model Building
- Process: batch, continuous

# Lumped vs. Distributed

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## Lumped Operations:

(Almost) **perfect mixing** – at any particular time instant, the values of operating conditions are (approximately) the **same at all points** within the unit

## Distributed Operations:

Imperfect mixing will result in different operating conditions at different points even at the same time → existence of **distributions of conditions over spatial domains**

# Lumped vs. Distributed: Mathematical Considerations

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## Lumped Operations:

- Characterised by a **single independent variable** (time)
- Their modelling can be effected in terms of ordinary differential equations (**ODEs**)

## Distributed Operations:

- Introduce **additional independent variables** (e.g., one or more spatial co-ordinates, particle size, molecular weight, etc.)
- Involves partial differential equations (**PDEs**) in time

# Lumped vs. Distributed: How do I decide?

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Deciding on whether to model a system as lumped or distributed operations is a **matter of judgement** for the modeller.

## Must Consider:

- Objectives of the model being constructed (control, optimisation, operating procedures)
- Required predictive accuracy
- Information available for model validation

# Conservation Laws

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## Mathematical Modelling:

- Encoding physical behaviour as a set of mathematical relations
- Involves application of fundamental physical laws
- Consider a subset of the universe as a system of interest – the position of the boundary separating the system and its surroundings may vary with time

# Conservation Laws: General Form

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Conservation laws describe the **variation** of the amount of a “**conserved quantity**” within the system **over time**:

$$\left( \begin{array}{c} \text{rate of} \\ \underline{\text{accumulation}} \\ \text{of conserved} \\ \text{quantity} \\ \text{within system} \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{flow of} \\ \text{conserved} \\ \text{quantity} \\ \underline{\text{into system}} \end{array} \right) - \left( \begin{array}{c} \text{rate of} \\ \text{flow of} \\ \text{conserved} \\ \text{quantity} \\ \underline{\text{from system}} \end{array} \right) + \left( \begin{array}{c} \text{rate of} \\ \underline{\text{generation of}} \\ \text{conserved} \\ \text{quantity} \\ \text{within system} \end{array} \right)$$

(1.1)

# Conserved Quantities

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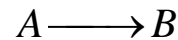
Typical conserved quantities:

- Total mass (kg)
- Mass of an individual species (kg)
- Number of molecules/atoms (mol)
- Energy (J)
- Momentum (kg.m/s)

# Conservation Laws: Comments

- Conservation laws provide a **simple and systematic “balance”**
- With a generation term, conservation laws may be written for any physical quantity
- The **usefulness** of a particular law depends on whether or not we possess the necessary **physical knowledge** to quantify each term
- Often, the rate of generation of one quantity is related to the rate of generation (or consumption) of another – this may affect the quantities to which we can apply a conservation law

– *e.g.*,



$$\left( \begin{array}{c} \text{rate of} \\ \text{generation} \\ \text{of B} \end{array} \right) = \left( \begin{array}{c} \text{rate of} \\ \text{consumption} \\ \text{of A} \end{array} \right)$$

- If we cannot characterise the either rate, a conservation law will not prove to be useful
- A conservation law on **(A+B)** will since it does not involve a generation term

# Accumulation Terms in Conservation Laws

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**Extensive variables:** mass, volume

**Intensive variables:** mass fraction, temperature, pressure, specific volume

Accumulation terms should be formulated in terms of **a single extensive** variable, with use of additional algebraic relations used to express relationships between the extensive variables used and the intensive properties

# Conservation Law: Mass

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- **Total mass balance**

Rate of mass in = rate of mass out + rate of mass accumulation

- **Component balance**

flow of moles (A) in + Rate of Generation of moles of (A) =

Flow of moles of (A) out + Rate of Accumulation of moles of (A)

# Conservation Law: Momentum

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- linear momentum ( $\pi$ ) of a mass ( $m$ ) moving with velocity ( $v$ ) is

$$\pi = mv$$

- Rate of momentum in + Rate of Generation of momentum = Rate of momentum out + Rate of Accumulation of momentum
- Newton's second law

$$\frac{d(mv)}{dt} = \sum F$$

# Conservation Laws: Energy

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- Rate of energy in + Rate of Generation of energy = Rate of energy out + Rate of accumulation of energy  $\pm$  amount of energy exchanged with the surrounding

# Conservation Laws: Energy

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**Accumulation:** takes account of all forms of energy

**Internal energy** random movement of molecules/atoms of fluid;  
intermolecular/interatomic forces

**Kinetic energy** bulk motion of the liquid (e.g., agitation)

**Potential energy** by virtue of its position in a gravitational force  
field

**Inlet/Outlet:** make contributions proportional to their flowrate

**Specific enthalpy** (rather than internal energy) is used – the  
difference between them accounts for the energy (work) required to  
force an element of fluid in the inlet stream into the fluid in the  
system.

# Conservation Laws: Energy

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Interaction with Surroundings: account for mechanical work

- (i) Mechanical agitation device  
rate of energy addition  $\approx$  power output of device
- (ii) Work done on the system by the atmosphere (open systems)

$$-P_{atm} \frac{dV}{dt} = \text{work imparted to system}$$

+ve if level moves downwards (atmosphere carries out work on the system)

-ve if level moves upwards (system is pushing back the atmosphere)

# Assumptions in Modelling

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Assumptions should be introduced only when not introducing them results in:

1. Substantial increase in computational complexity (*i.e.*, perfect mixing → CFD)
2. Need to characterise phenomena which are not well understood and/or cannot easily be quantified

# Perfect Mixing Assumption

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All *intensive* properties of the stream(s) leaving a perfectly mixed system are *identical* to those inside the system.

# Macroscopic balance

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For lumped parameter systems the process state variables are uniform over the entire system, that is each state variable  $V$  do not depend on the spatial variables, i.e.  $x, y$  and  $z$  in cartesian coordinates but only on time  $t$ .

In this case the balance equation is written over the whole system using macroscopic modeling.

# Distributed Systems: Microscopic balance

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- The balance equation is written over a differential element within the system to account for the variation of the state variables from point to point in the system, besides its variation with time.
- Each state variable  $V$  of the system is assumed to depend on the three coordinates  $x, y$  and  $z$  plus the time. i.e.  $V = V(x, y, z, t)$ .
- The selection of the appropriate coordinates depends on the geometry of the system under study. It is possible to convert from one coordinate system to another.

# Elements of Conservation Laws

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- **Transport rates**
- **Thermodynamic relations**
- **Phase Equilibrium**
- **Chemical kinetics**
- **Control Laws**

# Transport rates: Mass

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- Bulk and diffusion flow :  $n_{Au} = j_{Au} + \rho_A V_u$
- Total flux = diffusive flux + bulk flux
- Diffusive Flux: Fick's law for binary mixture

$$j_{Au} = -\rho D_{AB} \frac{dw_A}{du}$$

$$j_{Au} = -D_{AB} \frac{d\rho_A}{du}$$

$$J_{Au} = -CD_{AB} \frac{dx_A}{du}$$

$$J_{Au} = -D_{AB} \frac{dC_A}{du}$$

# Transport rates: Momentum

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- Total flux  $\pi_{yx}$  of the x-component in the y-direction is the sum of the convection term and diffusive term  $\tau_{yx}$

$$\pi_{yx} = \tau_{yx} + (\rho v_x)v_y$$

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y}$$

# Transport rates: Energy

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- total energy flux  $e_u$  ( $J/s.m^2$ ) of a fluid at constant pressure flowing with a velocity  $v_u$  in the  $u$ -direction can be expressed as:
- $e_u = q_u + (\rho C_p T) v_u$
- *Heat Diffusion, conduction  $q$ :*

$$q_u = -k \frac{\partial T}{\partial u}$$

# One-dimensional Transport laws for molecular diffusion

Transport Type	Law	Flux	Transport property	gradient
Mass	Fick's	$J_{Au}$	$D$	$\frac{dC_A}{du}$
Heat	Fourrier	$q_u$	$k$	$\frac{dT}{du}$
Momentum	Newton	$\tau_{ux}$	$\mu$	$\frac{dv_x}{du}$

# Macroscopic Transfer Rates

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- gradient is the difference between the bulk properties, i.e. concentration or temperature in two medium in contact

$$J_A = K \times \Delta C_A$$

$$q = U \times \Delta T$$

# Thermodynamic relations

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- Equation of state

$$PV = nRT$$

- Enthalpies

$$\tilde{h} = \bar{C}_p (T - T_{ref})$$

$$\tilde{H} = \bar{C}_p (T - T_{ref}) + \lambda$$

- Internal energy

# Phase equilibrium

- $y_{Ai} = F(x_{Ai})$
- Henry's law
- Raoult's law

$$y_i \phi_i P = x_i \gamma_i P_i^S$$

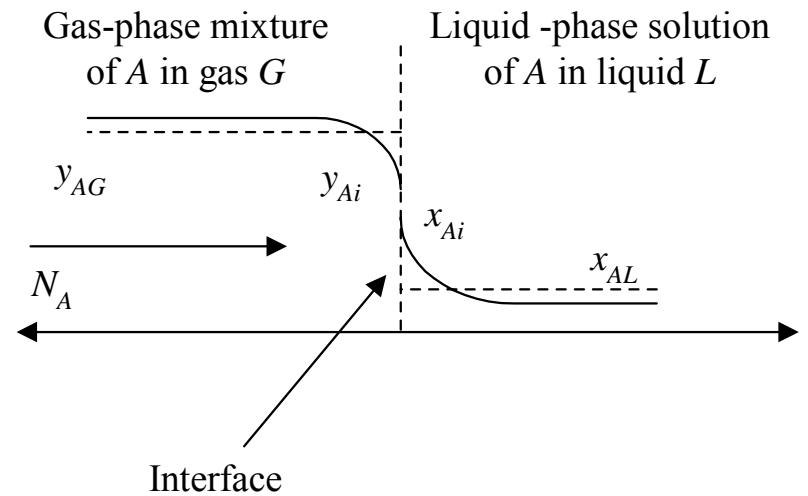


Figure 1.7: Equilibrium at the interface

# Chemical kinetics

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The overall rate  $R$  in *moles/m<sup>3</sup>s* of a chemical reaction is defined by:

$$R = \frac{1}{v_i V} \frac{dn_i}{dt}$$

Simple Reaction:  $A + B \rightarrow C$

$$R = k C_A C_B$$

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

# Degree of Freedom

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- For a processing system described by a set of  $N_e$  independent equations and  $N_V$  variables, the degree of freedom  $f$  is
- $F = N_V - N_e$
- $f = 0$ . The system is exactly determined (specified) system . Thus, the set of balance equation has a finite number of solutions (one solution for linear systems)
- $f < 0$ . The system is over-determined (over-specified) by  $f$  equations.  $f$  equations have to be removed for the system to have a solution.
- $f > 0$ . The system is under-determined (under-specified) by  $f$  equations. The set of equation, hence, has infinite number of solution .

# Model solution

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- It would be ideal to be able to solve the model analytically, that is to get closed forms of the state variables in term of the independent variables.
- Unfortunately this seldom occurs for chemical processes. why? The reason is that the vast majority of chemical processes are nonlinear.
- Solution of process models is usually carried out numerically

# Validation

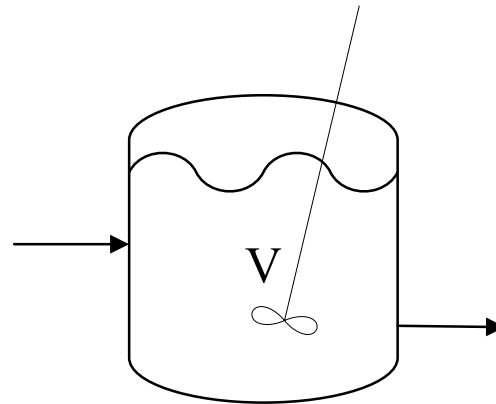
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- Model verification (validation) is the last and the most important step of model building. Reliability of the obtained model depends heavily on faithfully passing this test. Implementation of the model without validation may lead to erroneous and misleading results.

# Examples of Mathematical Models for Chemical Processes Lumped Parameter Systems

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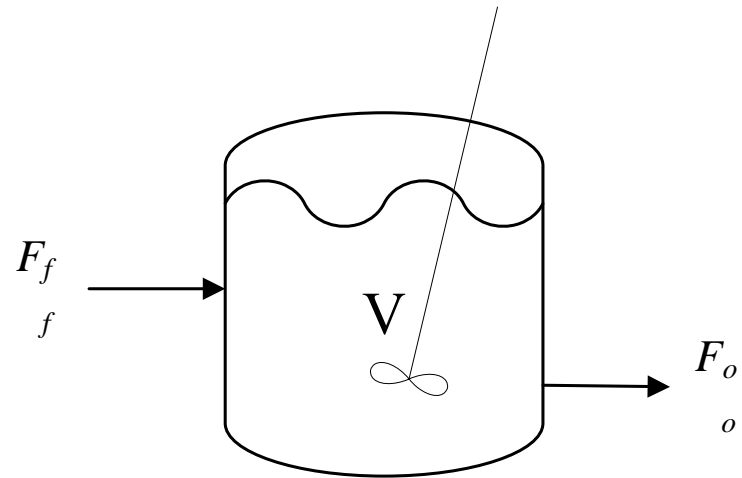
- Liquid Storage Tank
- Our objective is to develop a model for the variations of the tank holdup, i.e. volume of the tank



# Liquid Storage Tank Assumptions

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- Perfectly mixed (Lumped) → density of the effluent is the same as that of tank content.
- Isothermal



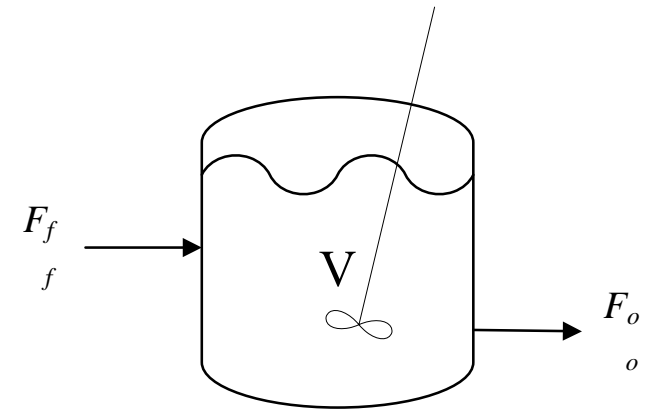
# Liquid Storage Tank Model

Rate of mass accumulation = Rate of mass in - rate of mass out

$$m|_{t+\Delta t} - m|_t = \rho_f F_f \Delta t - \rho_o F_o \Delta t$$

$$\lim_{\Delta t} \frac{m|_{t+\Delta t} - m|_t}{\Delta t} = \rho_f F_f - \rho_o F_o$$

$$\frac{dm}{dt} = \frac{d(\rho V)}{dt} = \rho_f F_f - \rho_o F_o$$



# Liquid Storage Tank Model

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- Under isothermal conditions we assume that the density of the liquid is constant.

$$\frac{dV}{dt} = F_f - F_o$$

$$A \frac{dL}{dt} = F_f - F_o$$

# Liquid Storage Tank Model

## Degree of Freedom

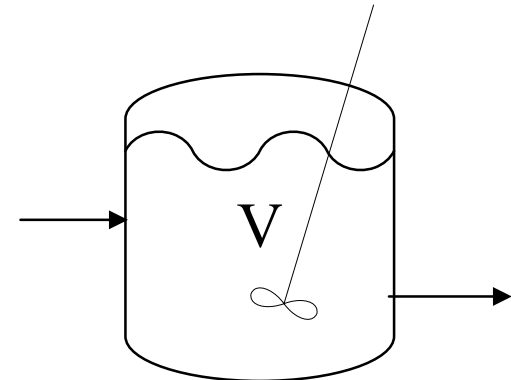
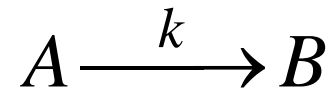
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- Parameter of constant values:  $A$
- Variables which values can be externally fixed (Forced variable):  $Ff$
- Remaining variables:  $L$  and  $F_o$
- Number of equations: 1
- Number of remaining variables – Number of equations =  $2 - 1 = 1$

$$F_o = \alpha\sqrt{L}$$

# Isothermal CSTR

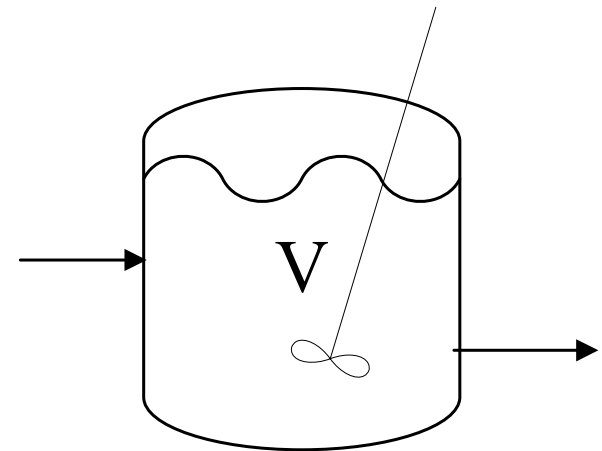
- Our objective is to develop a model for the variation of the volume of the reactor and the concentration of species  $A$  and  $B$ .
- a liquid phase chemical reactions taking place:



# Isothermal CSTR: Assumptions

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- Perfectly mixed
- Isothermal
- The reaction is assumed to be irreversible and of first order.



# Isothermal CSTR: Model

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- Component balance

- Flow of moles of  $A$  in:

$$F_f C_{Af}$$

- Flow of moles of  $A$  out:

$$F_o C_{Ao}$$

- Rate of accumulation:

$$\frac{dn}{dt} = \frac{d(VC_A)}{dt}$$

- Rate of generation:

$$-rV$$

where  $r$  ( $moles/m^3s$ ) is the rate of reaction.

# Isothermal CSTR: Model

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$$\frac{d(VC_A)}{dt} = F_f C_{Af} - F_o C_A - rV$$

$$\frac{d(VC_A)}{dt} = V \frac{d(C_A)}{dt} + C_A \frac{d(V)}{dt} = F_f C_{Af} - F_o C_A - rV$$

$$V \frac{d(C_A)}{dt} = F_f (C_{Af} - C_A) - kC_A V$$

# Isothermal CSTR: Degree of Freedom

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- Parameter of constant values:  $A$
- (Forced variable):  $F_f$  and  $C_{Af}$
- Remaining variables:  $V$ ,  $F_o$ , and  $C_A$
- Number of equations: 2
- The degree of freedom is

$$f = 3 - 2 = 1$$

The extra relation is obtained by the relation between the effluent flow  $F_o$  and the level in open loop