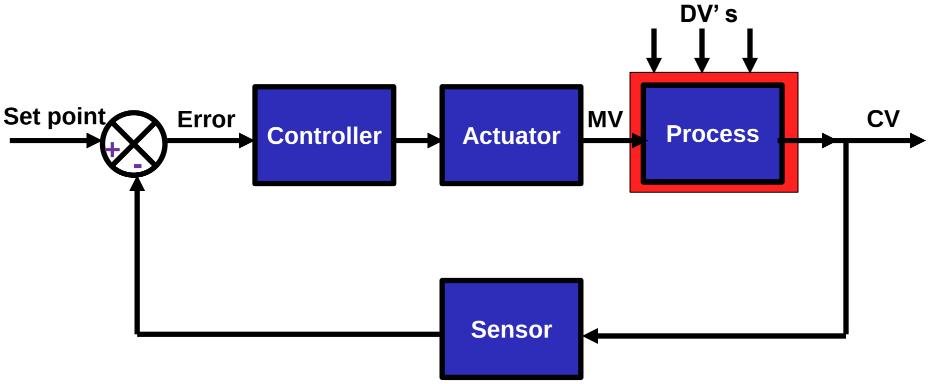
Mathematical Modeling of Chemical Processes



- **Basic concepts and definitions**
- **Steady-state model vs. dynamic model**
- **Degree of freedom analysis**
- **Models of representative processes**

Mathematical Modeling of Chemical Processes

➢Basic concepts and definitions:

- **Mathematical Modeling :** mathematical representation of the essential aspects of an existing process (or a process to be constructed) in a usable form.
- Process modeling is both **an art and a science**. Creativity is required to make **safe assumptions** that result in an appropriate model. Note that the mathematical model should be made **as simple as possible, but no simpler**.
- The model equations are at best an **approximation** to the real process.
- ***Adage*:** “**All models are wrong, but some are useful.**”

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- Modeling inherently involves a compromise between model accuracy and complexity on one hand, and the cost and effort required to develop the model, on the other hand.
- Where to use mathematical modeling:
  - To improve understanding of the process
  - To train plant operating personnel
  - To design the control strategy for a new process
  - To select the controller setting
  - To design the control law
  - To optimize process operating conditions

Mathematical Modeling of Chemical Processes

- **Classification of Models:**
  - **Theoretical models**
  - **Empirical (experimental) models**
  - **Semi-empirical models** (combined approach)

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➢ Theoretical Model:

– Based on physical/chemical/biological relationships and conservation laws:
  - Material/energy balances
  - Heat, mass, and momentum transfer
  - Thermodynamics, chemical kinetics
  - Physical property relationships

– Difficult to develop and it can become quite complex.

– Variables and parameters have physical meaning.

– Can be computationally expensive (not real-time).

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➢ Theoretical Model:

– Extrapolation is usually valid thus it can be used for rigorous prediction of the process behavior.

– Does not require experimental data to obtain (data required for validation and fitting)

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- **Conservation Laws**

Conservation of Mass

$$\left\{\begin{array}{c}\text{rate of mass}\\\text{accumulation}\end{array}\right\}=\left\{\begin{array}{c}\text{rate of mass}\\\text{in}\end{array}\right\}-\left\{\begin{array}{c}\text{rate of mass}\\\text{out}\end{array}\right\}$$

Conservation of Component i

$$\left\{\begin{array}{c}\text{rate of component i}\\\text{accumulation}\end{array}\right\}=\left\{\begin{array}{c}\text{rate of component i}\\\text{in}\end{array}\right\}$$

$$-\left\{\begin{array}{c}\text{rate of component i}\\\text{out}\end{array}\right\}+\left\{\begin{array}{c}\text{rate of component i}\\\text{produced}\end{array}\right\}$$

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Conservation of Energy:

The general law of energy conservation is also called the First Law of Thermodynamics. It can be expressed as:

$$\left\{\begin{array}{c}\textbf{rate of energy}\\\textbf{accumulation}\end{array}\right\}=\left\{\begin{array}{c}\textbf{rate of energy in}\\\textbf{by convection}\end{array}\right\}-\left\{\begin{array}{c}\textbf{rate of energy out}\\\textbf{by convection}\end{array}\right\}$$

$$+\left\{\begin{array}{c}\textbf{net rate of heat addition}\\\textbf{to the system from}\\\textbf{the surroundings}\end{array}\right\}+\left\{\begin{array}{c}\textbf{net rate of work}\\\textbf{performed on the system}\\\textbf{by the surroundings}\end{array}\right\}$$

The total energy of a thermodynamic system is the sum of its internal energy, kinetic energy, and potential energy.

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➢ Empirical Model:

- Based on curve fitting and analysis of experimental data.
- Requires well-designed experiments.
- Easy to develop and usually quite simple.
- The behavior is usually correct only around the experimental conditions considered (dangerous to extrapolate).
- Parameters of the model may not have physical meaning.
- Used for control design and simplified prediction model.

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➢ Dynamic Versus Steady-State Models

• Dynamic (unsteady) model:

- Describes time behavior of a process.
- Dynamic models of chemical processes consist of ordinary differential equations (ODE) and/or partial differential equations (PDE), plus related algebraic equations.

• Steady-state model:

- Steady state: No further changes in all variables with time.
- Can be obtained by setting the time derivative term zero.
- Steady-state model of chemical processes consist of:
  - Algebraic equations (AE) if all variables do NOT change in space.
  - DE and AE if some variables do change in space.

In this course, we will NOT going to consider spatial variations.

Mathematical Modeling of Chemical Processes

➢ **Linear versus Nonlinear Models:** based on the linearity of the dependent variable.

- **Linear model:** No nonlinear terms of dependent variable.

Examples:

-First-order linear ODE:

$$\tau \frac{dy(t)}{dt} = -y(t) + Ku(t) \qquad \tau \text{ and } K \text{ are constants}$$

- nth-order linear ODE:

$$\frac{d^n y(t)}{dt^n} + a_{n-1}\frac{d^{n-1} y(t)}{dt^{n-1}} + \ldots + a_0 y(t) = b_m \frac{d^m u(t)}{dt^m} + b_{m-1}\frac{d^{m-1} u(t)}{dt^{m-1}} + \ldots + b_0 u(t)$$

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- **Nonlinear Linear model:** there are nonlinear terms of dependent variables.

Examples:

$$\tau \frac{dy(t)}{dt} = -y(t)^2 + Ku(t)$$

$$\tau \frac{dy(t)}{dt} = -y(t) + K\sqrt{u(t)}$$

$$\tau \frac{dy(t)}{dt} y(t) = -y(t)\sin(y) + Ku(t)$$

$$\tau \frac{dy(t)}{dt} = -e^{-y(t)} + Ku(t)$$

Mathematical Modeling of Chemical Processes

➢Systematic Approach for Developing Dynamic Models:

1. State the modeling objectives.
2. Draw a schematic diagram of the process and label all process variables.
3. Make safe assumptions (The model should be no more complicated than necessary to meet the modeling objectives).
4. Determine whether spatial variations of process variables are important. If so, a partial differential equation model will be required.

Mathematical Modeling of Chemical Processes

5. Write appropriate conservation equations (mass, component, energy, ….etc).
6. Introduce equilibrium relations and other algebraic equations (from thermodynamics, transport phenomena, chemical kinetics, equipment geometry, ..etc).
7. Perform a degrees of freedom analysis to ensure that the model equations can be solved.
8. Simplify the model. It is often possible to arrange the equations so that the dependent variables (outputs) appear on the left side and the independent variables (inputs) appear on the right side. This model form is convenient for computer simulation and subsequent analysis.
9. Classify inputs as disturbance variables or as manipulated variables.

Mathematical Modeling of Chemical Processes

➢ Degree of Freedom (N_F) Analysis:

$$N_F = N_V - N_E$$

N_F : Degree of freedom (# of input variable to be specified).
N_V : Number of variables
N_E : Number of independent equations (# of output variables to be found/controlled)

– If **$N_F = 0$** : system is ***exactly specified***. Unique solution exists.

– If **$N_F > 0$** : system is ***underspecified***. Infinity number of solutions exist.

– If **$N_F < 0$** : system is ***overspecified*****.** No solutions exist.

Mathematical Modeling of Chemical Processes

➢ A Systematic Approach for N_F Analysis:

1. List the model parameters: quantities in the model that are *known* constants (or parameters that can be specified) on the basis of equipment dimensions, known physical properties, etc.
2. Determine the number of equations N_E and the number of process variables, N_V. **Note that time *t* is *not* considered to be a process variable because it is neither a process input nor a process output**.
3. Calculate the number of degrees of freedom, $N_F = N_V - N_E$.
4. Identify the N_E output variables that will be obtained by solving the process model.
5. Identify the N_F input variables that must be specified as either disturbance variables or manipulated variables, in order to utilize the N_F degrees of freedom.

Mathematical Modeling of Chemical Processes

➢ Solution of Model:

- **ODE model**

  – Linear case: find the analytical solution via Laplace transform, or other methods of calculus.

  – Nonlinear case: analytical solution is difficult or usually does not exists.

  - Use a numerical integration, such as Runge-Kutta (RK) method, by defining initial condition, time behavior of input/disturbance.
  - **Linearize** around some condition (usually steady state) and then find the analytical solution.

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➢ Solution of Model:

Linearization of non-linear term is performed using Taylor Series expansion around equilibrium (steady state):

$$\mathrm{f(x)} = \mathrm{f(\bar{x})} + \left.\frac{\mathrm{df}}{\mathrm{dx}}\right|_{\mathrm{x}=\bar{\mathrm{x}}} (\mathrm{x} - \bar{\mathrm{x}})$$

Where overbar denotes the steady-state.

- **If PDE model:** Convert to ODE by discretization of spatial variables using finite difference approximation and etc. **Example:**

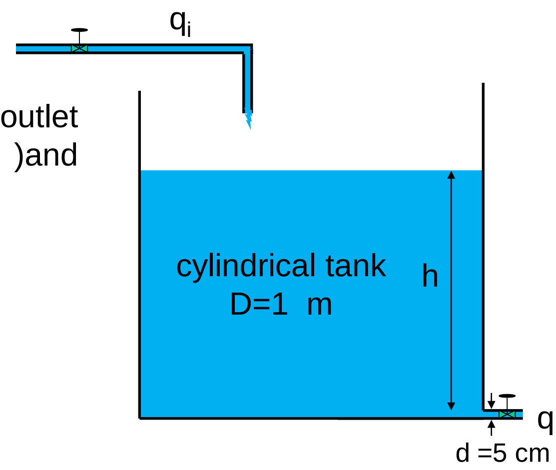
$$\frac{\partial T_L}{\partial t} = -v\frac{\partial T_L}{\partial z} + \frac{1}{\tau_{HL}}(T_w - T_L) \longrightarrow \frac{dT_L(j)}{dt} = -\frac{v}{\Delta z}T_L(j-1) - \left(\frac{v}{\Delta z} + \frac{1}{\tau_{HL}}\right)T_L(j) + \frac{1}{\tau_{HL}}T_w$$

$$\frac{\partial T_L}{\partial z} \approx \frac{T_L(j) - T_L(j-1)}{\Delta z} \qquad (j = 1, \cdots N)$$

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

(a) Find the steady-state outlet volumetric flow rate($\bar{q}$)and liquid height ($\bar{h}$)



Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

Assumptions:

- Adiabatic and isothermal process.
- Incompressible fluid (Liquid).
- Friction in the outlet pipe segments is negligible (short segment).
- Steady-state Mechanical Energy Balance (MEB) is applicable for this unsteady flow.
- The valve loss coefficient , C_v, does not vary with flow rate.

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

Let us first model the dynamic behavior of this process

- **Apply Mass Balance (MB) :**

$$\begin{Bmatrix}\text{rate of accumulation}\\ \text{of mass in the tank}\end{Bmatrix}=\begin{Bmatrix}\text{rate of}\\ \text{mass in}\end{Bmatrix}-\begin{Bmatrix}\text{rate of}\\ \text{mass out}\end{Bmatrix}$$

$$\frac{dm}{dt}=\dot{m}_i-\dot{m}_o$$

$$\frac{d\left(\rho\pi\frac{D^2}{4}h\right)}{dt}=\rho q_i-\rho q \qquad \textbf{(1)}$$

$$\frac{dh}{dt}=\frac{4}{\pi D^2}q_i-\frac{4}{\pi D^2}q$$

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

- **Apply Mechanical Energy Balance (MEB)** between a point at liquid free surface(point 1) and at the outlet section (point 2):

$$g(z_2-z_1)+\frac{p_2-p_1}{\rho}+\frac{u_2^2-u_1^2}{2}=w_{shaft}-w_{losses}$$

$$p_2=p_1=p_{atm}\ ;\ u_1\approx 0\ ;\ z_2-z_1=-h\ ;\ w_{shaft}=0$$

$$\Rightarrow -gh+\frac{u_2^2}{2}=-w_{losses}$$

→ **Energy losses (w_{losses}) are due to:**

- Valve; its loss coefficient is C_v
- Sudden contraction; its loss coefficient is C_c

$$\Rightarrow w_{losses}=(C_c+C_v)\frac{u_2^2}{2}$$

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

$\Rightarrow$ **MEB** becomes: $u_2 = \sqrt{\dfrac{2gh}{1+C_c+C_v}} = \sqrt{\dfrac{2g}{1+C_c+C_v}}\sqrt{h}$

But: $q = A_2 u_2 = \dfrac{\pi d^2}{4} u_2 = \dfrac{\pi d^2}{4}\sqrt{\dfrac{2g}{1+C_c+C_v}}\sqrt{h}$ **(2)**

$\therefore$ **The process has the following 1st-order nonlinear dynamic model:**

$$\frac{dh}{dt} = \frac{4}{\pi D^2} q_i - \frac{4}{\pi D^2} q \qquad \textbf{(1)}$$

$$q = \frac{\pi d^2}{4}\sqrt{\frac{2g}{1+C_c+C_v}}\sqrt{h} \qquad \textbf{(2)}$$

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

$\rightarrow$ **Now, Degree of Freedom Analysis:**

- ***Parameters:*** *D, d, and* ρ, C_v , C_c

$$N_F = N_V - N_E$$

N_V = 3 (q_i, q, h)
N_E = 2 (MB, MEB)

N_F = 3-2 = 1→ one input variable should be specified.

The output variables: *q* and *h*

Input variables: q_i

Mathematical Modeling of Chemical Processes

Example 1: **Liquid storage tank**

Input variables and parameters must be specified:

Let: q_i = 6 L/s, C_v = 0.9 , and C_c = 0.5

d = 0.05 and D=1 m (given parameters)

- To find the **steady-state values** of *h* and *q*, set the time derivative equals to zero:

$$\frac{dh}{dt}=0=\frac{4}{\pi D^2}q_i-\frac{4}{\pi D^2}q \Rightarrow \bar{q}=\bar{q}_i=6\,\mathrm{L/s}=0.006\,\mathrm{m^3/s}$$

$$\bar{q}=\frac{\pi d^2}{4}\sqrt{\frac{2g}{1+C_c+C_v}}\sqrt{\bar{h}}=0.0056\sqrt{\bar{h}}=0.006\,\mathrm{m^3/s}$$

$$\Rightarrow \bar{h}=1.148\,\mathrm{m}$$

Mathematical Modeling of Chemical Processes

Example 1: **Liquid storage tank**

(b) Suppose that inlet volumetric flow rate, q_i, changes suddenly from 6 to 9 L/s and remains at this new value (step change in q_i), how the liquid height varies with time. How long does it take to reach the new steady state value?

→ **Now the dynamic model should be solved**

$$\frac{dh}{dt}=\frac{4}{\pi D^2}q_i-\frac{4}{\pi D^2}q$$

$$q=\frac{\pi d^2}{4}\sqrt{\frac{2g}{1+C_c+C_v}}\sqrt{h}$$

$$\Rightarrow \frac{dh}{dt}=\frac{4}{\pi D^2}q_i-\frac{4}{\pi D^2}\frac{\pi d^2}{4}\sqrt{\frac{2g}{1+C_c+C_v}}\sqrt{h}$$

and q_i =0.009 m³/s

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

$$\therefore \quad \frac{dh}{dt} = 0.01146 - 0.00713\sqrt{h}$$

$$\text{at } t = 0 \,(\text{old steady state}):\quad h = \bar{h}_{old} = 1.148\,\text{m}$$

Remarks:

- Note **that t = 0 does NOT mean startup from rest**, it mean the **old steady-state situation**.
- The above **1st–order nonlinear ODE** can be solved analytically be separation of variables.

Mathematical Modeling of Chemical Processes

Analytical solution:
$$\int_{1.148}^{h} \frac{dh}{0.01146 - 0.00713\sqrt{h}} = \int_{0}^{t} dt = t$$

Integrate by substitution method to have:

$$-450.85\ln(2.9992 - 1.866\sqrt{\text{h}}) + 300.52972 - 280.505\sqrt{\text{h}} = t$$

At q_i= 9 L/s the **new steady-state** value of h is:

$$\Rightarrow \text{MB}: \bar{q} = \bar{q}_i = 9\,\text{L/s}$$

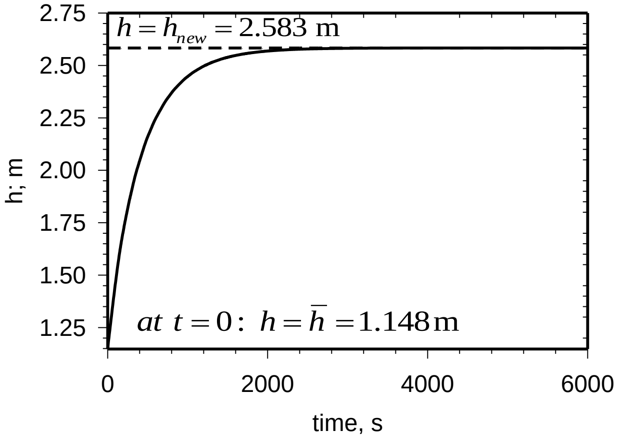
$$\text{MEB}: \bar{q} = 0.0056\sqrt{\bar{h}} = 0.009 \Rightarrow \bar{h}_{new} = 2.583\,\text{m}$$

To know how long does it take to reach this news steady state height:

$$\text{t} = -450.85\ln(2.9992 - 1.866\sqrt{2.583}) + 300.52972 - 280.505\sqrt{2.583} = 3650\,s \approx 1\,\text{hr}$$

Mathematical Modeling of Chemical Processes

Plot h versus t to see the dynamic response:



Remark. Without introducing controller and when q_i changes from 6 to 9 L/s the steady state height will change from 1.148 to 2.583 m during a period of around one hour.

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

- **Approximate solution (linearization of the model) :**

$$\frac{dh}{dt} = 0.01146 - 0.00713\sqrt{h} \quad at\ t = 0 \quad h = \bar{h} = 1.148\,\text{m}$$

Let us linearize the nonlinear term ; $\sqrt{h}$:

Let: $f(h) = \sqrt{h}$

Taylor series expansion around: $h = \bar{h} = 1.148\,\text{m}$

$$f(h) = f(\bar{h}) + \left.\frac{df}{dh}\right|_{\bar{h}} (h - \bar{h})$$

$$= \sqrt{\bar{h}} + \left.\frac{1}{2\sqrt{h}}\right|_{\bar{h}} (h - \bar{h}) = \sqrt{1.148} + \left.\frac{1}{2\sqrt{1.148}}\right|_{\bar{h}} (h - 1.148)$$

$$= 0.535724 + 0.466658h$$

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank

Then, the linearized 1st-order ODE is:

$$\frac{dh}{dt} = 0.01146 - 0.00713(0.535724 + 0.466658h)$$
$$= 0.00764 - 0.00333h$$
$$\Rightarrow \int_{1.148}^{h} \frac{dh}{0.00764 - 0.00333h} = \int_{0}^{t} dt = t$$

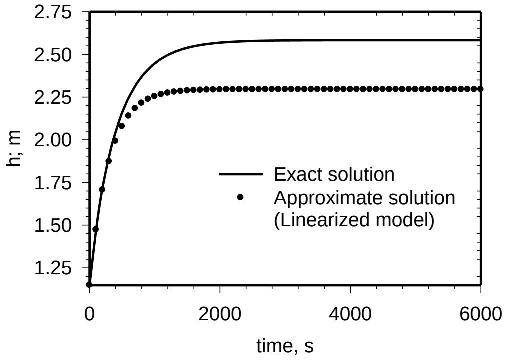
Solve (by substitution) to obtain:

$$\Rightarrow h(t) = 2.294 - 1.1462\mathrm{e}^{-0.00333t}$$

The **new steady-state** value of h can be found by setting(t=∞): $\bar{h} = 2.294$

Mathematical Modeling of Chemical Processes

Example 1: Liquid storage tank



"Comparison between exact solution and approximate solution resulted from linearized model"

Remarks.

- The linearized model gives the same results as the nonlinear one for time t < 400 s (6.67 min).
- The percent relative error in the new-steady state value resulted from linearized model is: $100 \times |2.294 - 2.583| / 2.583 = 11\%$

Mathematical Modeling of Chemical Processes

Example. Suppose that you would like to introduce a level controller to control the liquid height, h, by manipulating the outlet flow rate, *q*. What is the dynamic model required for such control task?.

Since *q* is manipulated variable, it must be now classified as input variable.

→ **Now, the input variables**: q_i , q

→**The output variables**: h

The degree of freedom must be **zero:**

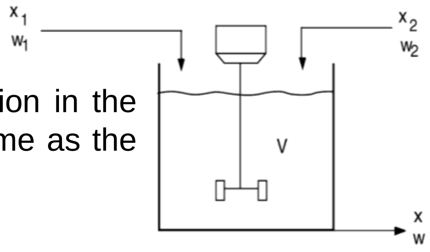
$$\mathbf{N_F = 0 = N_V - N_E = 1 - N_E \quad \Rightarrow \quad N_E = 1}$$

This means that dynamic model of this process with level controller must have only one dynamic equation which is the unsteady MB: $\frac{dh}{dt} = \frac{4}{\pi D^2} q_i - \frac{4}{\pi D^2} q$

Mathematical Modeling of Chemical Processes

Example 2: ***Blending Process;*** **see Topic I**

Assumptions:



- Perfect mixing: The composition in the tank is uniform and it is the same as the outlet composition.
- The liquid density , ρ, is constant everywhere.

An unsteady-state MB for the blending system:

$$\left\{\begin{matrix}\text{rate of accumulation}\\ \text{of mass in the tank}\end{matrix}\right\} = \left\{\begin{matrix}\text{rate of}\\ \text{mass in}\end{matrix}\right\} - \left\{\begin{matrix}\text{rate of}\\ \text{mass out}\end{matrix}\right\}$$

Mathematical Modeling of Chemical Processes

Example 2: ***Blending Process;* see Topic I**

- Apply **unsteady-state overall MB:**

$$\frac{d(V\rho)}{dt} = w_1 + w_2 - w$$

where w_1, w_2, and w are mass flow rates and V is liquid volume in the tank.

- Apply **unsteady-state component MB:**

$$\frac{d(V\rho x)}{dt} = w_1 x_1 + w_2 x_2 - wx$$

The corresponding steady-state model was derived **(topic I):**

$$0 = \bar{w}_1 + \bar{w}_2 - \bar{w}$$

$$0 = \bar{w}_1 \bar{x}_1 + \bar{w}_2 \bar{x}_2 - \bar{w}\bar{x}$$

Mathematical Modeling of Chemical Processes

For constant density (ρ **), unsteady equations** become:

$$\rho \frac{dV}{dt} = w_1 + w_2 - w$$

$$\frac{\rho d(Vx)}{dt} = w_1 x_1 + w_2 x_2 - wx$$

The above second equation can be simplified by expanding the accumulation term using the “chain rule” for differentiation of a product:

$$\rho \frac{d(Vx)}{dt} = \rho V \frac{dx}{dt} + \rho x \frac{dV}{dt}$$

Thus, component MB becomes:

$$\rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} = w_1 x_1 + w_2 x_2 - wx$$

Mathematical Modeling of Chemical Processes

Substitution of the overall mass balance for $\rho dV/dt$ in component mass balance gives:

$$\rho V\frac{dx}{dt}+x\left(w_1+w_2-w\right)=w_1x_1+w_2x_2-wx$$

After canceling common terms and rearranging the mass balance equations, a more convenient dynamic model form is obtained as follows:

$$\frac{dV}{dt}=\frac{1}{\rho}\left(w_1+w_2-w\right) \qquad \textbf{(Overall MB)}$$

$$\frac{dx}{dt}=\frac{w_1}{V\rho}\left(x_1-x\right)+\frac{w_2}{V\rho}\left(x_2-x\right) \qquad \textbf{(Component MB)}$$

➢ Note that this model is classified as: **1st-order nonlinear dynamic model**

Mathematical Modeling of Chemical Processes

Degree of Freedom Analysis: **$N_F = N_V - N_E$**

Parameters: ρ

N_V = 7 (w_1, w_2, w, V, x_1 , x_2, , x)
N_E = 2

N_F = 7-2 = 5 → 5 input variables should be specified.

Input variables : w_1, w_2, V, , x_1 , x_2

The output variables: w and x

➢Based on this classification the dynamic model is rewritten as:

$$w=w_1+w_2-\rho\frac{dV}{dt}$$

$$\frac{dx}{dt}=\frac{w_1}{V\rho}(x_1-x)+\frac{w_2}{V\rho}(x_2-x)$$

Mathematical Modeling of Chemical Processes

Example. A stirred-tank blending process with constant liquid holdup of 2 m^3 is used to blend two streams whose densities are both approximately 900 kg/m^3. The density does not change during the mixing.

(a) Assume that the process has been operating for a long period of time with flow rates of w_1=500 kg/min and w_2=200 kg/min, and the feed composition(mass fraction) of x_1 = 0.4 and x_2 = 0.75. What is the steady state value of *x and w*?

Constant liquid holdup means: $\frac{dV}{dt} = 0$

$$w = w_1 + w_2 - \rho \frac{dV}{dt} \Rightarrow \overline{w} = \overline{w}_1 + \overline{w}_2 - 0$$

$$\overline{w} = 200 + 500 = 700\,\text{kg/min}$$

Mathematical Modeling of Chemical Processes

To find the steady-state outlet composition, x, set the time derivative equals to zero:

$$\frac{dx}{dt} = 0 = \frac{\overline{w}_1}{V\rho}(\overline{x}_1 - \overline{x}) + \frac{\overline{w}_2}{V\rho}(\overline{x}_2 - \overline{x})$$

Solve for $\overline{x}$ to have:

$$\overline{x} = \frac{\overline{w}_1\overline{x}_1 + \overline{w}_2\overline{x}_2}{\overline{w}_1 + \overline{w}_2} = \frac{\overline{w}_1\overline{x}_1 + \overline{w}_2\overline{x}_2}{w} = \frac{(500)(0.4) + (200)(0.75)}{500 + 200} = 0.5$$

Mathematical Modeling of Chemical Processes

(b) Suppose w_1 changes suddenly from 500 to 400 kg/min and remains at this new value, how is the response of the composition x(t), plot it ?

Overall MB: $w = w_1 + w_2 - \rho\frac{dV}{dt} \Rightarrow w = w_1 + w_2 - 0$

$$w = 200 + 400 = 600\,\text{kg/min}$$

Component MB:

$$\frac{dx}{dt} = \frac{w_1}{V\rho}(x_1 - x) + \frac{w_2}{V\rho}(x_2 - x)$$

The component MB equation can be rearranged as:

$\tau\frac{dx}{dt} + x = C$ where $\tau = \frac{V}{w/\rho} = \frac{2}{600/900} = 3\,\text{min}$

and $C = (w_1 x_1 + w_2 x_2)/w = 0.517$

(τ is space time or mean residence time)

Mathematical Modeling of Chemical Processes

Analytical solution:

$\tau\frac{dx}{dt} + x = C$ $\quad at\, t = 0:\ x = \bar{x}_{old} = 0.5$ “Old steady state”

$\int_{0.5}^{x}\frac{dx}{C - x} = \int_0^t \frac{dt}{\tau}$ Integrate to have: $x(t) = C - (C - 0.5)e^{-t/\tau}$

But $\tau = 3\,\text{min}$ and $C = 0.517$

$$\Rightarrow x(t) = 0.517 - 0.017e^{-t/3}$$

The **new steady-state** value of *x* can be found by:

- using steady-state model

$$\bar{x}_{new} = \frac{\bar{w}_1\bar{x}_1 + \bar{w}_2\bar{x}_2}{\bar{w}_1 + \bar{w}_2} = \frac{(400)(0.4) + (200)(0.75)}{400 + 200} = 0.517$$

- or setting (t=∞) in x(t) equation : $\bar{x}_{new} = 0.517$

Mathematical Modeling of Chemical Processes

(c) Repeat part (b) for the case where w_2 (instead of w_1) changes suddenly from 200 to 100 kg/min and remains at this new value, how is the response of the composition x(t), plot it?

$$\tau\frac{dx}{dt}+x=C \qquad at\, t=0:\ x=\bar{x}=0.5$$ “Old steady state”

$$w=w_1+w_2=100+500=600\,\text{kg/min}$$

Where $\tau=\dfrac{V}{w/\rho}=\dfrac{2}{600/900}=3\min$ **(Space time)**

and $C=(w_1x_1+w_2x_2)/w$

$$=(500\times0.4+100\times0.75)/600=0.458$$

Analytical solution: $x(t)=C-(C-0.5)e^{-t/3}$

$$=0.458+.042e^{-t/3}$$

$$\bar{x}_{new}=0.458$$

Mathematical Modeling of Chemical Processes

(d) Repeat part (c) for the case where x_1 changes suddenly from 0.4 to 0.6 and remains at this new value, how is the response of the composition x(t), plot it ?

$$\tau\frac{dx}{dt}+x=C \qquad at\, t=0:\ x=\bar{x}_{old}=0.5$$ “Old steady state”

$$w=w_1+w_2=100+500=600\,\text{kg/min}$$

Where $\tau=\dfrac{V}{w/\rho}=\dfrac{2}{600/900}=3\min$ **(Space time)**

and $C=(500\times0.6+100\times0.75)/600=0.625$

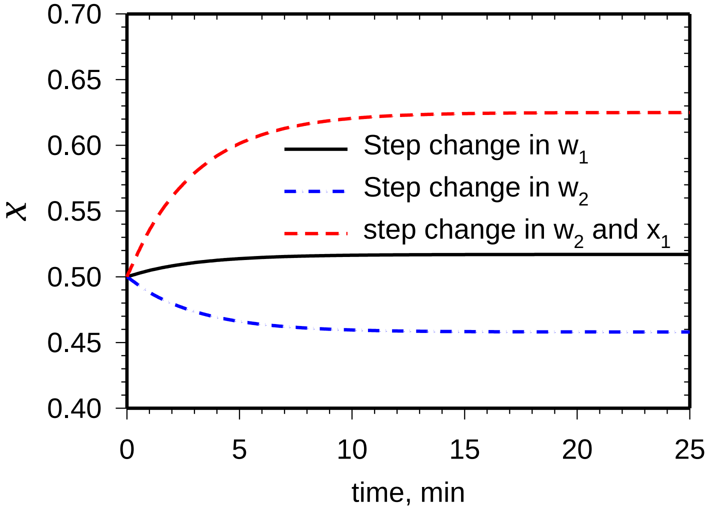
Analytical solution: $x(t)=C-(C-0.5)e^{-t/3}$

$$=0.625-.125e^{-t/3}$$

$$\bar{x}_{new}=0.625$$

Mathematical Modeling of Chemical Processes

Plot *x* versus *t* for different cases to see the dynamic response:



Mathematical Modeling of Chemical Processes

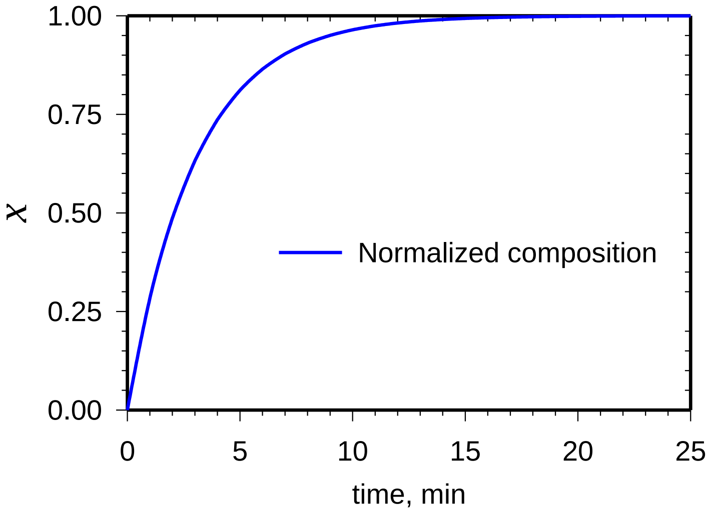
(e) For part (b) to (d), plot the normalized response $x_N(t)$ defined as:

$$X_N(t) = \frac{x(t) - x(0)}{x(\infty) - x(0)}$$

- part (b): $X_N(t) = \dfrac{0.517 - 0.017e^{-t/3} - 0.5}{0.517 - 0.5} = 1 - e^{-t/3}$
- part (c): $X_N(t) = \dfrac{0.458 + 0.042e^{-t/3} - 0.5}{0.458 - 0.5} = 1 - e^{-t/3}$
- part (d): $X_N(t) = \dfrac{0.625 - 0.125e^{-t/3} - 0.5}{0.625 - 0.5} = 1 - e^{-t/3}$

Mathematical Modeling of Chemical Processes

Plot $x_N(t)$ versus *t* for different cases to see the dynamic response:



Mathematical Modeling of Chemical Processes

Example. Suppose that you would like to introduce a level controller to control the liquid volume, *V*, by manipulating the outlet flow rate, *w* and composition controller to control x by manipulating w_2. How the dynamic model will be for such control tasks?.

Since ***w and w_2* are manipulated variables** they must be classified now **as input variables**. In addition, since **x and V are controlled variables** they must be classified as **output variables.** Moreover, the process dynamic model has **two equations**(**N_E =2**) thus we must have only **two output variables** to have **zero degree of freedom.**

Mathematical Modeling of Chemical Processes

The input variables: *:* x_1 , x_2 , w_1, w_2, w

Classification of 5 input variables:

Disturbances variables : x_1 , x_2 , w_1

Manipulated variables: *w and* w_2

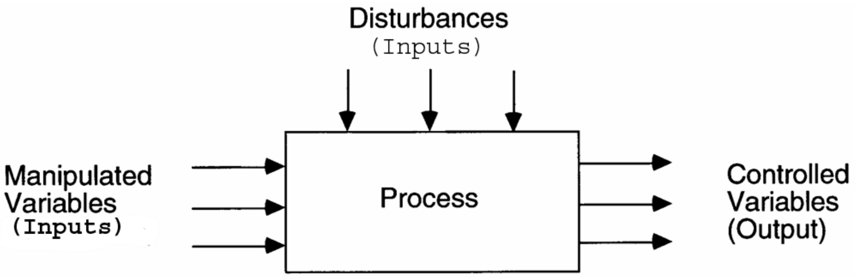
The output variables: V and x

Now the process dynamic model with controllers must be rewritten as:

$$\frac{dV}{dt} = w_1 + w_2 - w$$

$$\frac{dx}{dt} = \frac{w_1}{V\rho}(x_1 - x) + \frac{w_2}{V\rho}(x_2 - x)$$

Mathematical Modeling of Chemical Processes



MIMO: Multiple Input - Multiple Output

SISO: Single Input - Single Output

Mathematical Modeling of Chemical Processes

Example 3 : CSTR

A continuous stirred-tank reactor(CSTR) is used to produce a compound R in the liquid-phase elementary reaction A→ R. Feed enters the reactor at rate of q_i (L/s): the concentration of reactant in the feed is C_{A0} (mol A/L). The volume of the tanks content is V (L). The vessel may be considered perfectly mixed, so that the concentration of A in the product stream equals that in the tank. For this process the rate of consumption of A is $-r_A$ (mol A /s. L). All fluids (the feed, the tank content , and the product) may be taken to have the same density) ρ (g/L). The reaction takes place under isothermal conditions.

(a) Write the mathematical model to describe the variation of reactant concentration with time.

Mathematical Modeling of Chemical Processes

- **Total mass balance:**

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

$$\frac{d\rho V}{dt} = \rho q_i - \rho q$$

$$\frac{dV}{dt} = q_i - q \qquad \textbf{(1)}$$

- **Component A mole balance:**

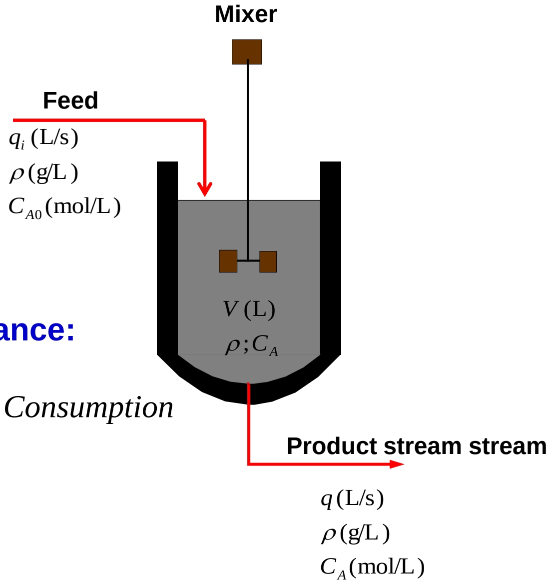
Accumulation =

In – Out + Generation - Consumption

$$In = \dot{N}_{A,in} = C_{A0} q_i$$

$$Out = \dot{N}_{A,out} = C_A q$$

$$Generation = 0$$



Mathematical Modeling of Chemical Processes

Example 3 : CSTR

$$Accumulation = \frac{dN_A}{dt} = \frac{dC_A V}{dt} = C_A \frac{dV}{dt} + V\frac{dC_A}{dt} = C_A(q_i - q) + V\frac{dC_A}{dt}$$

$$Consumption = -r_A V$$

$$\Rightarrow C_A(q_i - q) + V\frac{dC_A}{dt} = C_{A0}q_i - C_A q - (-r_A)V$$

$$\frac{dC_A}{dt} + \frac{q_i}{V}C_A = \frac{q_i}{V}C_{A0} - (-r_A)$$

Elementary reaction $\Rightarrow$ Reaction rate Eq. : $(-r_A) = kC_A$

$$\Rightarrow \frac{dC_A}{dt} + \frac{q_i}{V}C_A = \frac{q_i}{V}C_{A0} - kC_A$$

$$\tau = V/q_i$$

Or $\tau\frac{dC_A}{dt} + (1 + k\tau)C_A = C_{A0}$ **(2)**

Mathematical Modeling of Chemical Processes

(b) Do Degree of Freedom Analysis:

Parameters: ρ, k

N_V = 5 (C_{A0}, C_A, V, q_i, q)
N_E = 2

N_F = 5-2 = 3 → 3 input variables should be specified.
Input variables: q_i , C_{A0}, V
Output variables: C_A *and q*

→ **The dynamic model is:**

$$q = q_i - \frac{dV}{dt}$$

$$\tau\frac{dC_A}{dt} + (1 + k\tau)C_A = C_{A0}$$

Mathematical Modeling of Chemical Processes

(c) Find the steady-state concentration and conversion if the reaction rate constant is k=0.01 s^{-1}, the liquid volume is 250 L, the reactant feed concentration is 0.6 mol/L, and the feed flow rate is 0.4 L/s?.

$$\tau \frac{dC_A}{dt} = 0 \Rightarrow (1+k\tau)\bar{C}_A = C_{A0} \Rightarrow \bar{C}_A = \frac{C_{A0}}{(1+k\tau)}$$

$$\tau = \frac{V}{q_i} = \frac{250}{0.4} = 625\,\mathrm{s}$$

$$\Rightarrow \bar{C}_A = \frac{0.6}{(1+0.01\times 625)} = 0.083\,\frac{\mathrm{mol}}{\mathrm{L}}$$

The corresponding steady-state conversion is:

$$\bar{X}_A = \frac{C_{A0}-\bar{C}_A}{C_{A0}} = \frac{0.6-0.083}{0.6} = 0.86$$

Mathematical Modeling of Chemical Processes

(d) Suppose the feed flow rate changes suddenly from 0.4 to 0.8 L/s and remains at this new value, plot the response of concentration $C_A(t)$.

$$\tau \frac{dC_A}{dt} + (1+k\tau)C_A = C_{A0} \rightarrow \tau \frac{dC_A}{dt} = C_{A0} - (1+k\tau)C_A$$

$$\frac{dC_A}{C_{A0}-(1+k\tau)C_A} = \frac{dt}{\tau} \rightarrow \int_{\bar{C}_{A,old}}^{C_A} \frac{dC_A}{C_{A0}-(1+k\tau)C_A} = \int_0^t \frac{dt}{\tau}$$

$$\rightarrow -\frac{\ln\left[C_{A0}-(1+k\tau)C_A\right]_{\bar{C}_{A,old}}^{C_A}}{(1+k\tau)} = \frac{t}{\tau}$$

$$\rightarrow \ln\left[\frac{C_{A0}-(1+k\tau)C_A}{C_{A0}-(1+k\tau)\bar{C}_{A,old}}\right] = -\frac{(1+k\tau)t}{\tau}$$

$$\therefore C_A = \left(C_{A0} - \left[C_{A0}-(1+k\tau)\bar{C}_{A,old}\right]e^{-\frac{(1+k\tau)t}{\tau}}\right)\Big/(1+k\tau)$$

Mathematical Modeling of Chemical Processes

$$C_A(t)=\frac{C_{A0}-\left[C_{A0}-(1+k\tau)\overline{C}_{A,old}\right]e^{-\frac{(1+k\tau)t}{\tau}}}{(1+k\tau)}$$

$$\overline{C}_{A,\,old}=0.083\ \mathrm{mol/L}\ ;\tau=\frac{250}{0.8}=312.5\mathrm{s}\ ;\ k=0.01\ ;C_{A0}=0.6$$

$$C_A(t)=0.145-0.062e^{-0.0132t}$$

The new steady-state concentration (t→∞):

$$\overline{C}_{A,new}=C_A(t)=0.145-0.062e^{-0.0132(\infty)}=0.145\frac{\mathrm{mol}}{\mathrm{L}}$$

It can be found from the st. st. Eq.:

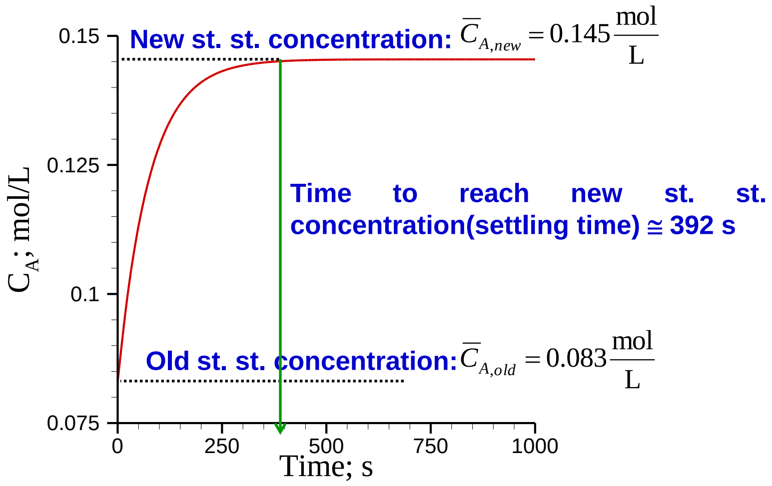
$$\overline{C}_{A,new}=\overline{C}_A=\frac{C_{A0}}{(1+k\tau)}=\frac{0.6}{(1+0.01\times312.5)}=0.145\frac{\mathrm{mol}}{\mathrm{L}}$$

And the new steady-state conversion is:

$$\overline{X}_{A,new}=\frac{C_{A0}-\overline{C}_{A,new}}{C_{A0}}=\frac{0.6-0.145}{0.6}=0.76$$

Mathematical Modeling of Chemical Processes

Example 3 : CSTR



New st. st. concentration: $\overline{C}_{A,new}=0.145\frac{\mathrm{mol}}{\mathrm{L}}$

Time to reach new st. st. concentration(settling time) ≅ 392 s

Old st. st. concentration: $\overline{C}_{A,old}=0.083\frac{\mathrm{mol}}{\mathrm{L}}$

Mathematical Modeling of Chemical Processes

(e) Suppose that you would like to introduce a level controller to control the liquid volume, *V*, by manipulating the outlet flow rate, *q*, and concentration controller to control C_A by manipulating q_i. How the dynamic model will be for such control tasks?.

Input variables: q_i, C_{A0}, q
Output variables: C_A *and V*

→ **The dynamic model of the controlled process is:**

$$\frac{dV}{dt} = q_i - q$$

$$\frac{dC_A}{dt} + \frac{(1+k\tau)}{\tau} C_A = \frac{C_{A0}}{\tau}$$

Where $\tau = V/q_i$ is the mean residence time.

Mathematical Modeling of Chemical Processes

Exercise.

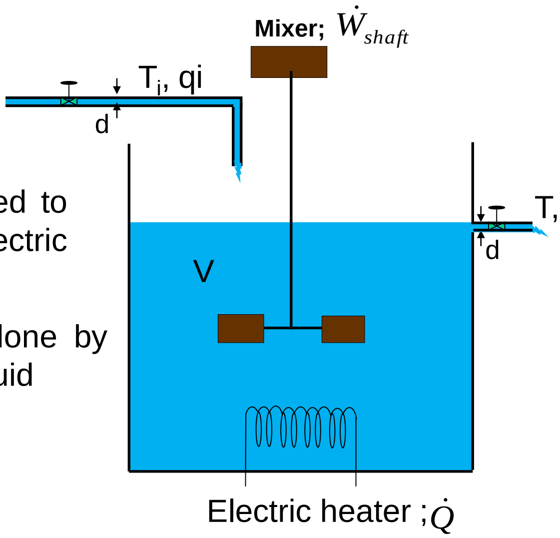
- Suppose feed concentration changes suddenly from 0.6 to 0.2 mol/L and remains at this new value and all other values are kept as in part (c). plot the response of concentration $C_A(t)$.

- Repeat the previous example if the reaction is non-elementary(2nd-order reaction): $-r_A=kC_A^2$ with k=0.1 L/(mol.s). Solve the original model, compare its results with the linearized one.

Mathematical Modeling of Chemical Processes

Example 4.

Stirred-tank heating process with constant holdup, *V*:



$\dot{Q}$: Heating rate added to the liquid by electric heater

$\dot{W}_{shaft}$: Rate of work done by mixer on the liquid

Mathematical Modeling of Chemical Processes

(a) Write the dynamic model to describe the temperature response, T(t):

Assumptions:

1. Perfect mixing; thus, the exit temperature *T* is also the temperature of the tank contents.
2. The liquid holdup, *V*, is constant because the inlet and outlet flow rates are equal.
3. The density, ρ, and heat capacities of the liquid are assumed to be constant. Thus, their temperature dependence is neglected.
4. Heat losses are negligible.
5. The net rate of shaft (mixer) work can be neglected because it is small compared to the rates of heat transfer and convection→ $\dot{W}_{shaft} \approx 0$

Mathematical Modeling of Chemical Processes

- **Total mass balance:**

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

$$\frac{d(\rho V)}{dt} = \rho q_i - \rho q$$

Constant liquid holdup(*V* is constant) $\rightarrow \frac{dV}{dt} = 0$

$$\therefore q = q_i \qquad \textbf{(1)}$$

- Here, **MEB is NOT applicable** since this process is neither adiabatic nor isothermal. **Energy balance** must be applied instead:

$$\frac{dE}{dt} = \dot{E}_{in} - \dot{E}_{out} + \dot{Q} + \dot{W}_{shaft} \qquad ; \ \dot{W}_{shaft} \approx 0 \ \ (\text{Assumption})$$

$$E = m(\hat{U} + \frac{u^2}{2} + gz)$$

Mathematical Modeling of Chemical Processes

$\hat{U}$: Specific internal energy of liquid in the system (tank)

u : Velocity of the system (liquid in tank)

z : Vertical position of the system

- **For flowing streams, another form of energy must be added which is the pressure energy:**

$$\dot{E}_{in} = \dot{m}_{in}(\hat{U} + p\hat{V} + \frac{u^2}{2} + gz)_{in} = \dot{m}_{in}(\hat{H} + \frac{u^2}{2} + gz)_{in}$$

$$\dot{E}_{out} = \dot{m}_{out}(\hat{U} + p\hat{V} + \frac{u^2}{2} + gz)_{out} = \dot{m}_{out}(\hat{H} + \frac{u^2}{2} + gz)_{out}$$

$\hat{V}$: Specific volume of the liquid

p : Pressure

Mathematical Modeling of Chemical Processes

$$\frac{d\left(m(\hat{U}+u^2/2+gz)\right)}{dt}=\dot{m}_{in}(\hat{H}+\frac{u^2}{2}+gz)_{in}-\dot{m}_{out}(\hat{H}+\frac{u^2}{2}+gz)_{out}+\dot{Q}$$

$$\frac{d\left(\rho V(\hat{U}+u^2/2+gz)\right)}{dt}=\rho q(\hat{H}+\frac{u^2}{2}+gz)_{in}-\rho q(\hat{H}+\frac{u^2}{2}+gz)_{out}+\dot{Q}$$

Constant liquid holdup (V is constant) and constant density:

$$\tau\frac{d\left((\hat{U}+u^2/2+gz)\right)}{dt}=(\hat{H}+\frac{u^2}{2}+gz)_{in}-(\hat{H}+\frac{u^2}{2}+gz)_{out}+\frac{\dot{Q}}{\rho q}$$

Where τ is the space time: $\tau=\frac{V}{q}$

Mathematical Modeling of Chemical Processes

$$\frac{d\left(\hat{U}+u^2/2+gz\right)}{dt}=\frac{d\hat{U}}{dt}+\frac{du^2/2}{dt}+g\frac{dz}{dt}$$

Since **the tank is not moving**: $\frac{d\,u^2/2}{dt}=\frac{dz}{dt}=0$

$$\Rightarrow\frac{d\left(\hat{U}+u^2/2+gz\right)}{dt}=\frac{d\hat{U}}{dt}$$

$$\tau\frac{d\hat{U}}{dt}=(\hat{H}_{in}-\hat{H}_{out})+\frac{u_{in}^2-u_{out}^2}{2}+g(z_{in}-z_{out})+\frac{\dot{Q}}{\rho q}$$

But the **cross-section area of the inlet pipe is the same as that of the outlet one**: $\rightarrow u_{out}=u_{in}$

$$\tau\frac{d\hat{U}}{dt}=(\hat{H}_{in}-\hat{H}_{out})+g(z_{in}-z_{out})+\frac{\dot{Q}}{\rho q}$$

Mathematical Modeling of Chemical Processes

Assume that the **vertical distance between inlet ad outlet streams is negligible**: $\rightarrow z_{out} \approx z_{in}$

Finally, the unsteady energy balance becomes:

$$\tau \frac{d\hat{U}}{dt} = (\hat{H}_{in} - \hat{H}_{out}) + \frac{\dot{Q}}{\rho q}$$

We know from thermodynamics:

$$\frac{d\hat{U}}{dT} = C_v \Rightarrow d\hat{U} = C_v dT$$

C_v :Constant volume heat capacity

$$\frac{d\hat{H}}{dT} = C_p \Rightarrow \int_{\hat{H}_{ref}}^{\hat{H}} d\hat{H} = \int_{T_{ref}}^{T} C_p dT$$

C_p : Constant pressure heat capacity

Mathematical Modeling of Chemical Processes

One of the assumption is that **heat capacities of the liquid are assumed to be constant.** Thus, their temperature dependence is neglected:

$$\Rightarrow \int_{\hat{H}_{ref}}^{\hat{H}} d\hat{H} = C_p \int_{T_{ref}}^{T} dT \Rightarrow \hat{H} = \hat{H}_{ref} + C_p\left(T - T_{ref}\right)$$

$$\hat{H}_{in} = \hat{H}_{ref} + C_p\left(T_i - T_{ref}\right)$$

$$\hat{H}_{out} = \hat{H}_{ref} + C_p\left(T - T_{ref}\right)$$

Then, the unsteady energy balance in terms of inlet and outlet temperature becomes:

$$\tau C_v \frac{dT}{dt} = C_p T_i - C_p T + \frac{\dot{Q}}{\rho q}$$

Note that for liquids: $C_p \approx C_v = C$

Thus, the final energy balance is: $\tau \frac{dT}{dt} = T_i - T + \frac{\dot{Q}}{C\rho q}$ **(2)**

Mathematical Modeling of Chemical Processes

(b) Perform Degree Of Freedom analysis:

Parameters: *ρ, V, C*

N_V = 5 ($\dot{Q}, T_i, q_i, T, q$)
N_E = 2

N_F = 5-2 = 3 → 3 input variables should be specified.

Input variables: $\dot{Q},\ T_i,\ q_i$

Output variables: $T,\ q$

→ **The dynamic model is:**

$$q = q_i$$

$$\tau \frac{dT}{dt} = T_i - T + \frac{\dot{Q}}{C\rho q}$$

Mathematical Modeling of Chemical Processes

(c) Assume that the process has been operating for a long period of time with flow rate of q_i=10 m^3/hr, heating rate of $\dot{Q} = 4.98\times10^8$ cal/hr and inlet temperature of 40 °C. In addition, the liquid density is 1000 kg/m^3 and liquid heat capacity is 1 cal/g.°C, and the liquid volume in the tank is 20 m^3. What is the steady-state temperature inside the tank?

$$q = q_i = 10\,\frac{m^3}{hr}$$

$$\tau \frac{dT}{dt} = 0 = \overline{T}_i - \overline{T} + \frac{\overline{\dot{Q}}}{C\rho q} \Rightarrow \overline{T} = \overline{T}_i + \frac{\overline{\dot{Q}}}{C\rho q}$$

$$\overline{T}_i = 40\ ^{\circ}\mathrm{C}\ ;\ C = 1000\ \mathrm{cal/kg.^{\circ}C}\ ;\ \rho = 1000\ \mathrm{kg/m^3}\ ;$$

$$\overline{\dot{Q}} = 4.98\times10^8\ \mathrm{cal/hr}$$

$$\overline{T} = 40 + \frac{4.98\times10^8}{1000\times1000\times10} = 89.8\ ^{\circ}\mathrm{C}$$

Mathematical Modeling of Chemical Processes

(d) Suppose that the heating rate increases to double its old value and remains at this new value, plot the time response of temperature deviation about its old steady-state value?

$$\dot{Q} = 2\times 4.98\times 10^{8} = 9.96\times 10^{8}\ \text{cal/hr}$$

(Step change in heating rate)

$$\tau = \frac{V}{q} = \frac{20}{10} = 2\,\text{hr}$$

Remark. In process dynamic and control, it is common to use the deviation of variables about their corresponding steady state(set point). This can be obtained by subtracting the steady state equations from the corresponding dynamic equation

Mathematical Modeling of Chemical Processes

$$\text{Dynamic Eq.:}\quad \tau\frac{dT}{dt} = T_i - T + \frac{\dot{Q}}{C\rho q} \qquad (1)$$

$$\text{St.St.Eq.:}\quad \tau\frac{d\bar{T}}{dt} = 0 = \bar{T}_i - \bar{T} + \frac{\bar{\dot{Q}}}{C\rho q} \qquad (2)$$

Subtract Eq. 2 from Eq. 1:

$$\Rightarrow \tau\frac{d\left(T-\bar{T}\right)}{dt} = \left(T_i - \bar{T}_i\right) - \left(T - \bar{T}\right) + \frac{\left(\dot{Q} - \bar{\dot{Q}}\right)}{C\rho q}$$

Let: $y = T - \bar{T}\ ;\ y_i = T_i - \bar{T}_i\ ;\ u = \dot{Q} - \bar{\dot{Q}}\ ; K = \dfrac{1}{\rho q C}$

$$\Rightarrow \tau\frac{dy}{dt} = y_i - y + Ku$$

$$at\ t = 0\ \text{(old desired st.st.)}:\ y = \bar{T} - \bar{T} = 0$$

Mathematical Modeling of Chemical Processes

In this part of example, the inlet temperature remains constant: $T_i = \bar{T}_i = 40\,^{o}\mathrm{C} \Rightarrow \quad y_i = T_i - \bar{T}_i = 0$

$$\Rightarrow \tau \frac{dy}{dt} = -y + Ku \quad at\ t = 0:\ y = 0$$

Analytical solution: $y = Ku\left(1 - e^{\frac{-t}{\tau}}\right)$

$$K = \frac{1}{C\rho q} = \frac{1}{1000 \times 1000 \times 10} = 1 \times 10^{-7}\ ^{o}\mathrm{C.hr/cal}$$

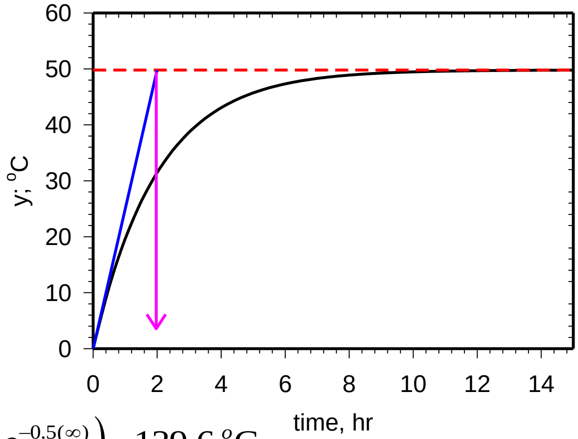
$$u = \dot{Q} - \bar{\dot{Q}} = 9.96 \times 10^{8} - 4.98 \times 10^{8} = 4.98 \times 10^{8}\ \mathrm{cal/hr}$$

$$Ku = 49.8\,^{o}\mathrm{C}$$

$$\therefore y = 49.8\left(1 - e^{-0.5t}\right)$$

$$or \quad y = T - \bar{T} = 49.8\left(1 - e^{-0.5t}\right) \Rightarrow T = 89.8 + 49.8\left(1 - e^{-0.5t}\right)$$

Mathematical Modeling of Chemical Processes



$$\bar{T}_{new} = 89.8 + 49.8\left(1 - e^{-0.5(\infty)}\right) = 139.6\,^{o}\mathrm{C}$$

Useful information: the space time can be estimated by drawing the tangent line at t=0 (the blue line in the plot above) .

Mathematical Modeling of Chemical Processes

(e) Suppose that now you turned off the electric heater, how long does it take for temperature to return from its new value (139.6) ^oC to the original steady-state value(89.8 ^oC) ?

Now: $\dot{Q}=0 \Rightarrow u=0-\overline{\dot{Q}}=-4.98\times10^{8}$

$$K=1\times10^{-7}\ {}^{o}\text{C.hr/cal}$$

$$Ku=-49.8\,{}^{o}\text{C}$$

$$\Rightarrow \tau\frac{dy}{dt}=-y-49.8 \quad at\ t=0:\ y=49.8$$

Analytical solution: : $y=99.6e^{-t/\tau}-49.8$

Thus, the time required for liquid temperature to return back to its original st. st. value is:

$$\rightarrow\ y=0\Rightarrow 0=99.6e^{-t/2}-49.8\Rightarrow t=1.386\,\text{hr}$$

Mathematical Modeling of Chemical Processes

Example 5. Biological Reactions

- Biological reactions that involve micro-organisms and enzyme catalysts are pervasive and play a crucial role in the natural world.
- Without such *bioreactions*, plant and animal life, as we know it, simply could not exist.
- Bioreactions also provide the basis for production of a wide variety of pharmaceuticals and healthcare and food products.
- Important industrial processes that involve bioreactions include fermentation and wastewater treatment.
- Chemical engineers are heavily involved with biochemical and biomedical processes.

Mathematical Modeling of Chemical Processes

Example 5. Biological Reactions

- Typically, they are performed in a batch or fed-batch reactor.
- *Fed-batch* is a synonym for *semi-batch*.
- Fed-batch reactors are widely used in the pharmaceutical and other process industries.
- Bioreactions:

$$\text{substrate} \xrightarrow{\text{cells}} \text{more cells} + \text{products}$$

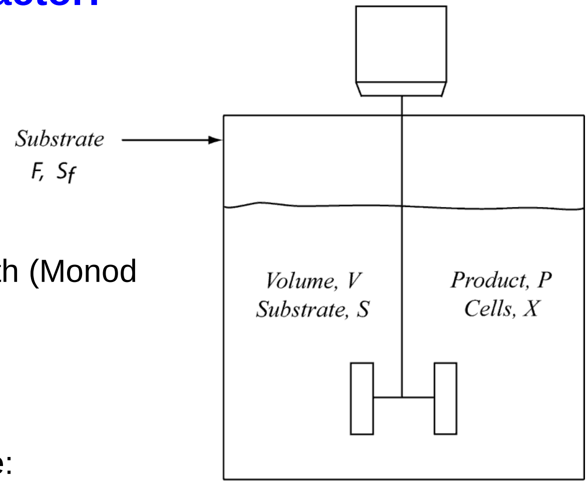
- Yield Coefficients:

$$Y_{X/S} = \frac{\text{mass of new cells formed}}{\text{mass of substrate consumed to form new cells}}$$

$$Y_{P/S} = \frac{\text{mass of product formed}}{\text{mass of substrate consumed to form product}}$$

Mathematical Modeling of Chemical Processes

Fed-Batch Bioreactor:



- The rate of cell growth (Monod Equation):

$$r_g = \mu X$$

- Specific Growth Rate:

$$\mu = \mu_{\max} \frac{S}{K_s + S}$$

Mathematical Modeling of Chemical Processes

- **Modeling Assumptions**

1. The exponential cell growth stage is of interest.
2. The fed-batch reactor is perfectly mixed.
3. Heat effects are small so that isothermal reactor operation can be assumed.
4. The liquid density is constant.
5. The *broth* in the bioreactor consists of liquid plus solid material, the mass of cells. This heterogeneous mixture can be approximated as a homogenous liquid.
6. The rate of cell growth r_g is given by the Monod equation.

Mathematical Modeling of Chemical Processes

7. The rate of product formation per unit volume r_p can be expressed as:

$$r_p = Y_{P/X} r_g$$

where the *product yield coefficient* $Y_{P/X}$ is defined as:

$$Y_{P/X} = \frac{\textit{mass of product formed}}{\textit{mass of new cells formed}}$$

8. The feed stream is sterile and thus contains no cells.

Mathematical Modeling of Chemical Processes

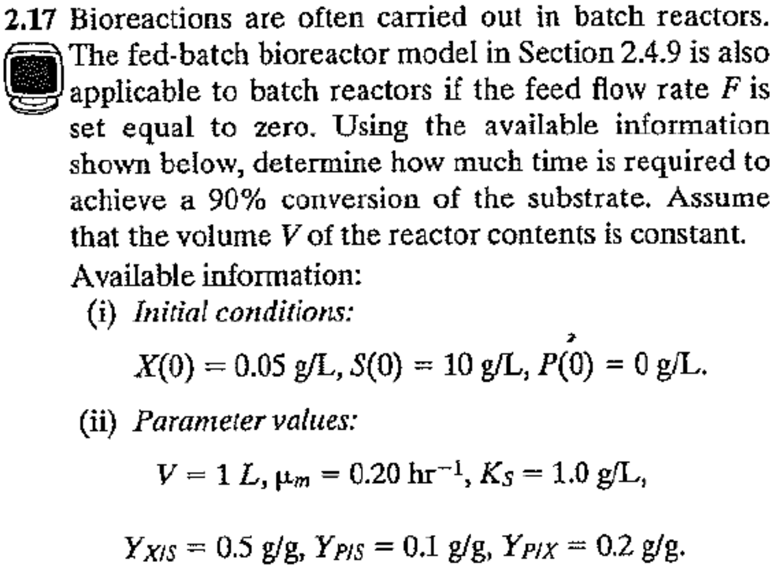
- **General Form of Each Balance:**

$$\{Rate\ of\ \ accumulation\} = \{rate\ in\} + \{rate\ of\ \ formation\}$$

- **Individual Component Balances:**
  - **Cells:** $\dfrac{d(XV)}{dt} = V\,r_g$
  - **Product:** $\dfrac{d(PV)}{dt} = Vr_p$
  - **Substrate:** $\dfrac{d(SV)}{dt} = F\,S_f - \dfrac{1}{Y_{X/S}} V\,r_g - \dfrac{1}{Y_{P/S}} V\,r_P$
  - **Overall Mass Balance:** $\dfrac{d(V)}{dt} = F$

Exercise. Solve problem 2.17 in your textbook

Mathematical Modeling of Chemical Processes



2.17 Bioreactions are often carried out in batch reactors. The fed-batch bioreactor model in Section 2.4.9 is also applicable to batch reactors if the feed flow rate F is set equal to zero. Using the available information shown below, determine how much time is required to achieve a 90% conversion of the substrate. Assume that the volume V of the reactor contents is constant.

Available information:

(i) *Initial conditions:*

$$X(0) = 0.05\text{ g/L},\ S(0) = 10\text{ g/L},\ P(0) = 0\text{ g/L}.$$

(ii) *Parameter values:*

$$V = 1\ L,\ \mu_m = 0.20\text{ hr}^{-1},\ K_S = 1.0\text{ g/L},$$

$$Y_{X/S} = 0.5\text{ g/g},\ Y_{P/S} = 0.1\text{ g/g},\ Y_{P/X} = 0.2\text{ g/g}.$$