

Lecture Notes on Mathematical Modeling of Chemical Processes

General Modeling Principles

1. The model equations are at best an approximation to the real process.
2. 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.
3. Process modeling is both an art and a science. Creativity is required to make simplifying assumptions that result in an appropriate model.
4. Dynamic models of chemical processes consist of ordinary differential equations (ODE) and/or partial differential equations (PDE), plus related algebraic equations.

Physical Modeling Approaches

1. Thermodynamics, chemical kinetics (physical/chemical fundamental, global)
2. Model structure by theoretical analysis
3. Conservation Laws (Theoretical models of chemical processes are based on conservation laws.)
4. Heat, mass, and momentum transfer
5. Physical property relationships (viscosity, thermal conductivity, diffusivity)
6. Model complexity must be determined (assumptions, e. g. ideal gas)

Comment:

Can be computationally expensive (therefore, not real-time)
May be expensive/time-consuming to obtain
Good for extrapolation, scale-up
Does not require experimental data to obtain (data required for validation and fitting)

A Systematic Approach for Developing Dynamic Models

1. State the modeling objectives and the end use of the model. They determine the required levels of model detail and model accuracy.
2. Draw a schematic diagram of the process and label all process variables.
3. List all of the assumptions that are involved in developing the model. Try for parsimony; 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.
5. Write appropriate conservation equations (mass, component, energy, and so forth).

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.

Empirical (Black box)

- Large number of unknown parameters
- Can be obtained quickly (e.g., linear regression)
- Model structure is subjective
- Dangerous to extrapolate

Semi-empirical

- Compromise of first two approaches
- Model structure may be simpler
- Typically 2 to 10 physical parameters estimated (nonlinear regression)
- Good versatility, can be extrapolated
- Can be run in real-time
- linear regression
- nonlinear regression
- number of parameters affects accuracy of model, but confidence limits on the parameters fitted must be evaluated
- objective function for data fitting – minimize sum of squares of errors between data points and model predictions (use optimization code to fit parameters)
- nonlinear models such as neural nets are becoming popular (automatic modeling)

Uses of Mathematical Modeling

- to improve understanding of the process
- to optimize process design/operating conditions
- to design a control strategy for the process
- to train operating personnel

Conservation of Mass

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

Conservation of Component *i*

$$\left\{ \begin{array}{l} \text{rate of component } i \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of component } i \\ \text{in} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of component } i \\ \text{out} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of component } i \\ \text{produced} \end{array} \right\}$$

Conservation of Energy

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

$$\left\{ \begin{array}{l} \text{rate of energy} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of energy in} \\ \text{by convection} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of energy out} \\ \text{by convection} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of heat addition} \\ \text{to the system from} \\ \text{the surroundings} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of work} \\ \text{performed on the system} \\ \text{by the surroundings} \end{array} \right\}$$

Example 1: A Blending Process (discussed in Lecture I)

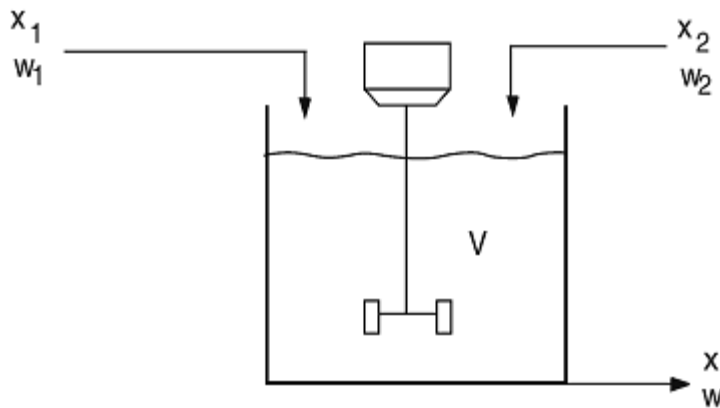


Figure 1. Stirred-tank blending process

An unsteady-state mass balance for the blending system:

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

that is

$$\frac{d(V\rho)}{dt} = w_1 + w_2 - w \quad 1$$

where w_1 , w_2 , and w are mass flow rates.

The unsteady-state component balance is:

$$\left\{ \begin{array}{l} \text{rate of component i} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of component i} \\ \text{in} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of component i} \\ \text{out} \end{array} \right\} + \left\{ \begin{array}{l} \text{rate of component i} \\ \text{produced} \end{array} \right\}$$

that is

$$\frac{d(V\rho x)}{dt} = w_1 x_1 + w_2 x_2 - wx \quad 2$$

The corresponding steady-state model was derived in Lecture I:

$$0 = \bar{w}_1 + \bar{w}_2 - \bar{w} \quad 3$$

$$0 = \bar{w}_1 \bar{x}_1 + \bar{w}_2 \bar{x}_2 - \bar{w} \bar{x} \quad 4$$

For constant ρ , Eqs. 1 and 2 become:

$$\rho \frac{dV}{dt} = w_1 + w_2 - w \quad 5$$

$$\rho \frac{d(Vx)}{dt} = w_1 x_1 + w_2 x_2 - wx \quad 6$$

Equation 6 can be simplified by expanding the accumulation term (left side) using the “chain rule” for differentiation of a product:

$$\rho \frac{d(Vx)}{dt} = \rho V \frac{d(x)}{dt} + \rho x \frac{d(V)}{dt} \quad 7$$

Substitution of 7 into 6 gives:

$$\rho V \frac{d(x)}{dt} + \rho x \frac{d(V)}{dt} = w_1 x_1 + w_2 x_2 - wx \quad 8$$

Substitution of the mass balance in 5 for $\rho dV / dt$ in 8 gives:

$$\rho V \frac{d(x)}{dt} + x(w_1 + w_2 - w) = w_1 x_1 + w_2 x_2 - wx \quad 9$$

After canceling common terms and rearranging 5 and 9, a more convenient model form is obtained:

$$\frac{dV}{dt} = \frac{1}{\rho} (w_1 + w_2 - w) \quad 10$$

$$\frac{dx}{dt} = \frac{w_1}{V\rho} (x_1 - x) + \frac{w_2}{V\rho} (x_2 - x) \quad 11$$

Rearrange Eq.6,

$$\rho V \frac{dx}{dt} + wx = w_1 x_1 + w_2 x_2 \quad 12$$

At steady state, Eq.6 becomes,

$$w^0 x^0 = w_1^0 x_1^0 + w_2^0 x_2^0 \quad 13$$

$$\rho V \frac{d(x^0 + \Delta x)}{dt} + w(x^0 + \Delta x) = x_1^0 (w_1^0 + \Delta w_1) + w_2^0 x_2^0 \quad 14$$

Subtract Eq.13 from Eq.14,

$$\rho V \frac{d(\Delta x)}{dt} + w(\Delta x) = x_1^0 (\Delta w_1) \quad 15$$

Similarly,

$$\rho V \frac{d(\Delta x)}{dt} + w(\Delta x) = x_2^0 (\Delta w_2) \quad 16$$

$$\rho V \frac{d(\Delta x)}{dt} + w(\Delta x) = w_1^0 (\Delta x_1) \quad 17$$

Let $x = \Delta x$, $w_1 = \Delta w_1$, $w_2 = \Delta w_2$ and $x_1 = \Delta x_1$,

$$\rho V \frac{dx}{dt} + wx = x_1^0 w_1 \quad 18$$

$$\rho V \frac{dx}{dt} + wx = x_2^0 w_2 \quad 19$$

$$\rho V \frac{dx}{dt} + wx = w_1^0 x_1 \quad 20$$

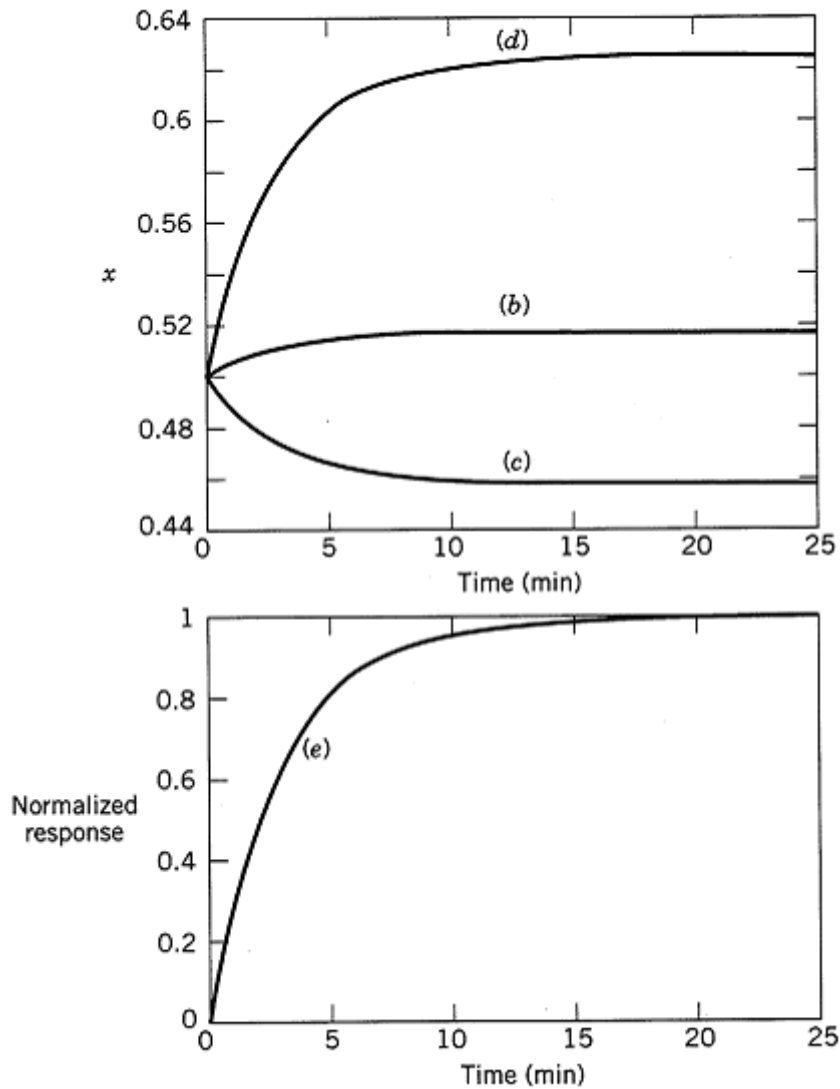
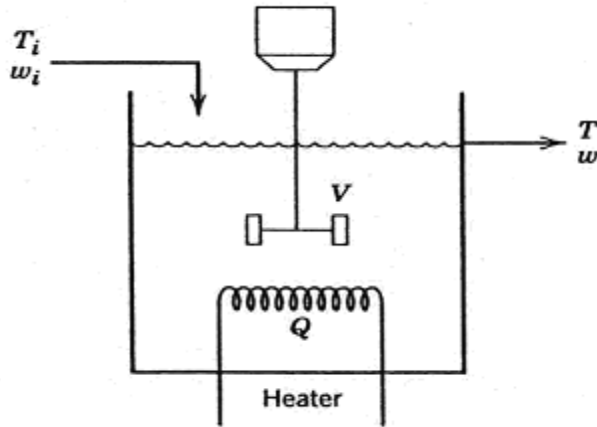


Figure 2. Exit composition responses of a stirred-tank blending process to step changes in:
 (b) flow rate w_1
 (c) flow rate w_2
 (d) inlet composition x_1

(e) Normalized response for parts (b)-(d).

Example 2: Stirred-Tank Heating Process with constant holdup, V



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 and heat capacity C of the liquid are assumed to be constant. Thus, their temperature dependence is neglected.
4. Heat losses are negligible.

In addition, for the processes and examples considered in this course, it is appropriate to make two assumptions:

1. Changes in potential energy and kinetic energy can be neglected because they are small in comparison with changes in internal energy.
2. The net rate of work can be neglected because it is small compared to the rates of heat transfer and convection.

For these reasonable assumptions, the energy balance

$$\left\{ \begin{array}{l} \text{rate of energy} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of energy in} \\ \text{by convection} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of energy out} \\ \text{by convection} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of heat addition} \\ \text{to the system from} \\ \text{the surroundings} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of work} \\ \text{performed on the system} \\ \text{by the surroundings} \end{array} \right\}$$

that is

$$\frac{dU_{\text{int}}}{dt} = -\Delta(w\hat{H}) + Q \quad 21$$

where

U_{int} = the internal energy of the system

\hat{H} = enthalpy per unit mass

w = mass flow rate

Q = rate of heat transfer to the system

Δ = denotes the difference between outlet and inlet conditions of the flowing streams; therefore

$-\Delta(w\hat{H})$ = rate of enthalpy of the inlet stream(s)-the enthalpy of the outlet stream(s)

Model Development

The definition of the enthalpy of a pure substance,

$$H = U_{\text{int}} + pV \quad 22$$

Therefore, for a pure liquid at low or moderate pressures, the internal energy is approximately equal to the enthalpy, $U_{\text{int}} \approx H$, and H depends only on temperature.

From the laws of thermodynamics, a differential change in temperature, dT , produces a corresponding change in the internal energy per unit mass, $d\hat{U}_{\text{int}}$,

$$d\hat{U}_{\text{int}} = d\hat{H} = CdT \quad 23$$

where C is the constant pressure heat capacity (assumed to be constant). The total internal energy of the liquid in the tank is:

$$U_{\text{int}} = \rho V \hat{U}_{\text{int}} \quad 24$$

An expression for the rate of internal energy accumulation can be derived from Eqs.14 and 15:

$$\frac{dU_{\text{int}}}{dt} = \rho VC \frac{dT}{dt} \quad 25$$

Note that this term appears in the general energy balance of Eq.21.

Suppose that the liquid in the tank is at a temperature T and has an enthalpy, \hat{H} . Integrating Eq.14 from a reference temperature T_{ref} to T gives,

$$\hat{H} - \hat{H}_{\text{ref}} = C(T - T_{\text{ref}}) \quad 26$$

where \hat{H}_{ref} is the value of \hat{H} at T_{ref} . Without loss of generality, we assume that $\hat{H}_{ref} = 0$. Thus, Eq.26 can be written as:

$$\hat{H} = C(T - T_{ref}) \quad 27$$

For the inlet stream

$$\hat{H}_i = C(T_i - T_{ref}) \quad 28$$

Substituting Eq.27 and 28 into the convection term of Eq.21 gives:

$$-\Delta(wH) = w[C(T_i - T_{ref})] - w[C(T - T_{ref})] \quad 29$$

Finally, substitution of Eq.25 and 29 into 21

$$\rho VC \frac{dT}{dt} = wC(T_i - T) + Q \quad 30$$

Rearrange Eq.30,

$$\rho VC \frac{dT_{out}}{dt} + w_{in} CT_{out} = w_{in} CT_{in} + Q_{in} \quad 31$$

At steady state,

$$wCT_{out}^0 = w_{in} CT_{in}^0 + Q_{in}^0 \quad 32$$

Let

$$\begin{aligned} T_{out} &= T_{out}^0 + \Delta T_{out} \\ T_{in} &= T_{in}^0 \\ Q_{in} &= Q_{in}^0 + \Delta Q_{in} \end{aligned} \quad 33$$

$$\rho VC \frac{d(T_{out}^0 + \Delta T_{out})}{dt} + w_{in} C(T_{out}^0 + \Delta T_{out}) = w_{in} CT_{in}^0 + Q_{in}^0 + \Delta Q_{in} \quad 34$$

Subtract Eq.32 from Eq.34

$$\rho VC \frac{d\Delta T_{out}}{dt} + w_{in} C\Delta T_{out} = \Delta Q_{in} \quad 35$$

Let

$$\begin{aligned}
 T_{out} &= T_{out}^0 + \Delta T_{out} \\
 T_{in} &= T_{in}^0 + \Delta T_{in} \\
 Q_{in} &= Q_{in}^0
 \end{aligned}
 \tag{36}$$

$$\rho V C \frac{d(T_{out}^0 + \Delta T_{out})}{dt} + w_{in} C (T_{out}^0 + \Delta T_{out}) = w_{in} C (T_{in}^0 + \Delta T_{in}) + Q_{in}^0
 \tag{37}$$

Subtract Eq.232 from Eq.37

$$\rho V C \frac{d\Delta T_{out}}{dt} + w_{in} C \Delta T_{out} = w_{in} C \Delta T_{in}
 \tag{38}$$

Rearrange Eqs.35 and 38

$$\frac{\rho V}{w_{in}} \frac{d\Delta T_{out}}{dt} + \Delta T_{out} = \frac{1}{w_{in}} \Delta Q_{in}
 \tag{39}$$

$$\frac{\rho V}{w_{in}} \frac{d\Delta T_{out}}{dt} + \Delta T_{out} = \Delta T_{in}
 \tag{40}$$

Example 3 Surge Tank

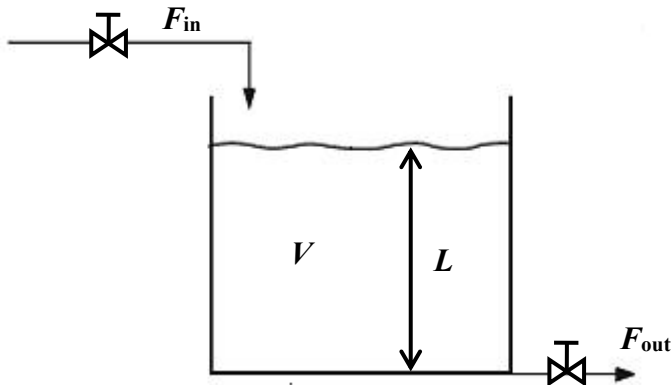


Figure 4. Surge Tank

Mass balance (assume constant density),

$$\frac{dV}{dt} = F_{in} - F_{out}
 \tag{41}$$

Use the knowledge you learned from the Unit Operation of Chemical Engineering, in the laminar flow region,

$$F_{out} = C'_v L \quad 42$$

where C'_v is the flow parameter

also,

$$\frac{dV}{dt} = A \frac{dL}{dt} \quad 43$$

where A is the cross section of the tank.
therefore,

$$A \frac{dL}{dt} + C'_v L = F_{in} \quad 44$$

From mass balance,

$$F_{in} = F_{out} \quad 45$$

At steady state,

$$F_{in}^0 = F_{out}^0 = C'_v L^0 \quad 46$$

$$A \frac{d(L^0 + \Delta L)}{dt} + C'_v (L^0 + \Delta L) = (F_{in}^0 + \Delta F_{in}) \quad 47$$

$$A \frac{d\Delta L}{dt} + C'_v \Delta L = \Delta F_{in} \quad 48$$

Rearrange,

$$\frac{A}{C'_v} \frac{d\Delta L}{dt} + \Delta L = \frac{1}{C'_v} \Delta F_{in} \quad 49$$

Similarly,

$$\frac{A}{C'_v} \frac{d\Delta L}{dt} + \Delta L = \frac{-1}{C'_v} \Delta F_{out} \quad 50$$

Combine

$$\frac{A}{C'_v} \frac{d\Delta L}{dt} + \Delta L = \frac{1}{C'_v} (\Delta F_{in} - \Delta F_{out}) \quad 51$$

When flow is large, it becomes turbulent, then,

$$F_{out} = C_v \sqrt{L} \quad 52$$

Let K be the slope of the tangent of the F - L curve at the set point,

$$K = \left. \frac{dF_{out}}{dL} \right|_{L=L^0} = \left. \frac{d(C_v \sqrt{L})}{dL} \right|_{L=L^0} = \frac{C_v}{2\sqrt{L^0}} \quad 53$$

therefore,

$$\Delta F_{out} = \frac{C_v}{2\sqrt{L^0}} \Delta L \quad 54$$

$$\begin{aligned} F_{out} &= F_{out}^0 + \Delta F_{out} \\ &= F_{out}^0 + \frac{C_v}{2\sqrt{L^0}} \Delta L \end{aligned} \quad 55$$

Substitute back to the mass balance equation,

$$\frac{dV}{dt} = A \frac{dL}{dt} = F_{in} - F_{out}^0 - \frac{C_v}{2\sqrt{L^0}} \Delta L \quad 56$$

and

$$A \frac{d(L^0 + \Delta L)}{dt} = (F_{in}^0 + \Delta F_{in}) - F_{out}^0 - \frac{C_v}{2\sqrt{L^0}} \Delta L \quad 57$$

therefore

$$A \frac{d\Delta L}{dt} = \Delta F_{in} - \frac{C_v}{2\sqrt{L^0}} \Delta L \quad 58$$

After rearrange,

$$\frac{A}{C_v / 2\sqrt{L^0}} \frac{d\Delta L}{dt} + \Delta L = \frac{1}{C_v / 2\sqrt{L^0}} \Delta F_{in} \quad 59$$

General form of the first order system

Let $y = T_{out}$ and $x = T_{in}$, omit Δ for simplicity,

$$\tau \frac{dy}{dt} + y = Kx \quad 60$$

where τ is called the time constant, K is the gain, y is the output variable, and x is the input variable.

Time constant $\tau = \text{Resister } R \times \text{Capacity } C$

$$\text{Heat Resister } R = \frac{\Delta T}{q} = \frac{1}{F_{in} C} = \frac{\Delta T}{F_{in} \Delta U}$$

$$\text{Flow Resister } R = \frac{\Delta L}{F_{out}} = \frac{2\sqrt{L_0}}{C_v}$$

$$\text{Heat Capacity } C = \frac{\Delta U}{\Delta T_{out}}$$

$$\text{Flow Capacity } C = \frac{\Delta V}{\Delta L}$$

Let $x = u = 1$ (step input), $y(t) = K \left(1 - e^{-\frac{t}{\tau}} \right)_{t=\tau} = 0.632$.

Figure 5. Step response of a first order system

Example 4. Modeling Surge Tank Using State Space Techniques

Recall Eqs.5, 6 and 52 assume constant density,

$$\frac{dV}{dt} = F_1(t) + F_2(t) - F(t)$$

$$\frac{d(V(t)x(t))}{dt} = F_1(t)x_1(t) + F_2(t)x_2(t) - F(t)x(t) \quad 6$$

$$F(t) = C_v \sqrt{L(t)} = C_v \sqrt{L(t)} \quad 52$$

At steady state,

$$F_1^0(t) + F_2^0(t) - F^0(t) = 0 \quad 63$$

$$F_1^0(t)x_1(t) + F_2^0(t)x_2(t) - F(t)^0 x(t) = 0 \quad 64$$

$$F^0(t) = C_v \sqrt{\frac{V^0}{A}} \quad 65$$

Assume small deviations about this point, let,

$$F_1(t) = F_1^0 + \mu_1(t) \quad 66$$

$$F_2(t) = F_2^0 + \mu_2(t) \quad 67$$

$$V(t) = V^0 + \xi_1(t) \quad 68$$

$$x(t) = x^0 + \xi_2(t) \quad 69$$

Also recall the linearization procedure

$$K = \left. \frac{dF}{dL} \right|_{L=L^0} = \left. \frac{d(C_v \sqrt{L})}{dL} \right|_{L=L^0} = \frac{C_v}{2\sqrt{L^0}} \quad 53$$

Similarly,

$$K = \left. \frac{dF}{dV} \right|_{V=V^0} = \left. \frac{d(C_v \sqrt{V/A})}{dV} \right|_{V=V^0} = \frac{C_v}{2\sqrt{AV^0}} \quad 70$$

$$\Delta F = \frac{C_v}{2\sqrt{AV^0}} \Delta V = \frac{C_v}{2\sqrt{AV^0}} \xi_1(t) \quad 71$$

$$\frac{F^0}{V^0} = \frac{C_v \sqrt{\frac{V^0}{A}}}{V^0} = \frac{C_v}{\sqrt{AV^0}} \quad 72$$

$$F = F^0 + \frac{1}{2} \frac{F^0}{V^0} \xi_1(t) \quad 73$$

Substitute Eqs.66, 67, 68, 69 and 73 back to Eqs.5 and 6 and subtract Eqs.63 and 64,

$$\frac{d\xi_1}{dt} = \mu_1 + \mu_2 - \frac{1}{2} \frac{F^0}{V^0} \xi_1 \quad 70$$

$$V^0 \frac{d\xi_2}{dt} + x^0 \frac{d\xi_1}{dt} = x_1 \mu_1 + x_2 \mu_2 - \frac{1}{2} x^0 \frac{F^0}{V^0} \xi_1 - F^0 \xi_2 \quad 71$$

Subtract Eq.70 from 71,

$$V^0 \frac{d\xi_2}{dt} + x^0 (\mu_1 + \mu_2) = x_1 \mu_1 + x_2 \mu_2 - F^0 \xi_2 \quad 72$$

Now with $F(t) - F^0$ and $x(t) - x^0$ as output, we get the model

$$\begin{aligned} \dot{\underline{x}} &= \begin{bmatrix} \dot{\xi}_1 \\ \dot{\xi}_2 \end{bmatrix} \\ \underline{P} &= \begin{bmatrix} -\frac{F^0}{2V^0} & 0 \\ 0 & -\frac{F^0}{V^0} \end{bmatrix} \\ \underline{x} &= \begin{bmatrix} \xi_1 \\ \xi_2 \end{bmatrix} \\ \underline{B} &= \begin{bmatrix} 1 & 1 \\ \frac{x_1 - x^0}{V^0} & \frac{x_2 - x^0}{V^0} \end{bmatrix} \\ \underline{u} &= \begin{bmatrix} \mu_1 \\ \mu_2 \end{bmatrix} = \begin{bmatrix} F_1 - F_1^0 \\ F_2 - F_2^0 \end{bmatrix} \\ \underline{C} &= \begin{bmatrix} F - F^0 \\ x - x^0 \end{bmatrix} \\ \underline{L} &= \begin{bmatrix} \frac{F^0}{2V^0} & 0 \\ 0 & 1 \end{bmatrix} \end{aligned}$$

Example 5. Tanks in series

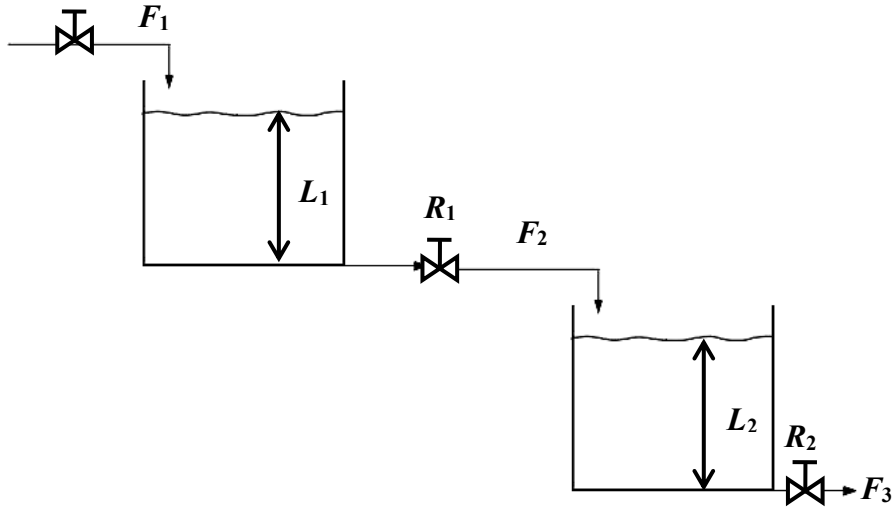


Figure 6. Tanks in series

Mass balance,

$$A_1 \frac{dL_1}{dt} = F_1 - F_2 \quad 73$$

$$F_2 = \frac{L_1}{R_1} \quad 74$$

$$A_2 \frac{dL_2}{dt} = F_2 - F_3 \quad 75$$

$$F_3 = \frac{L_2}{R_2} \quad 76$$

where A_1, A_2 are the capacity of tank 1 and tank 2,
 R_1, R_2 are the resistor of tank 1 and tank 2,
 assume they are all linear.

$$A_1 \frac{dL_1}{dt} + \frac{L_1}{R_1} = F_1 \quad 77$$

$$A_2 \frac{dL_2}{dt} + \frac{L_2}{R_2} = \frac{L_1}{R_1} \quad 78$$

$$L_1 = R_1 A_2 \frac{dL_2}{dt} + \frac{R_1}{R_2} L_2 \quad 79$$

differentiate

$$\frac{dL_1}{dt} = R_1 A_2 \frac{d^2 L_2}{dt^2} + \frac{R_1}{R_2} \frac{dL_2}{dt} \quad 80$$

$$A_1 R_1 A_2 R_2 \frac{d^2 L_2}{dt^2} + (A_1 R_1 + A_2 R_2) \frac{dL_2}{dt} + L_2 = R_2 F_1 \quad 81$$

let $T_1 = A_1 R_1$ and $T_2 = A_2 R_2$,

$$T_1 T_2 \frac{d^2 L_2}{dt^2} + (T_1 + T_2) \frac{dL_2}{dt} + L_2 = R_2 F_1 \quad 82$$

This is a second order system.