

Mathematical Modeling of Chemical Processes

Mathematical Model (Eykhoff, 1974)

“a representation of the essential aspects of an existing system (or a system to be constructed) which represents knowledge of that system in a usable form”

Everything should be made as simple as possible, but no simpler.

General Modeling Principles

- The model equations are at best an approximation to the real process.
- *Adage*: “All models are wrong, but some are useful.”
- 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.
- Process modeling is both an art and a science. Creativity is required to make simplifying assumptions that result in an appropriate model.
- Dynamic models of chemical processes consist of ordinary differential equations (ODE) and/or partial differential equations (PDE), plus related algebraic equations.

Table 2.1. 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).

Table 2.1. (continued)

6. Introduce equilibrium relations and other algebraic equations (from thermodynamics, transport phenomena, chemical kinetics, equipment geometry, etc.).
7. Perform a degrees of freedom analysis (Section 2.3) 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.

Modeling Approaches

- Physical/chemical (fundamental, global)
 - Model structure by theoretical analysis
 - Material/energy balances
 - Heat, mass, and momentum transfer
 - Thermodynamics, chemical kinetics
 - Physical property relationships
 - Model complexity must be determined (assumptions)
 - Can be computationally expensive (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)

- Conservation Laws

Theoretical models of chemical processes are based on conservation laws.

Conservation of Mass

$$\left\{ \begin{array}{c} \text{rate of mass} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of mass} \\ \text{in} \end{array} \right\} - \left\{ \begin{array}{c} \text{rate of mass} \\ \text{out} \end{array} \right\} \quad (2-6)$$

Conservation of Component i

$$\left\{ \begin{array}{c} \text{rate of component i} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{c} \text{rate of component i} \\ \text{in} \end{array} \right\} - \left\{ \begin{array}{c} \text{rate of component i} \\ \text{out} \end{array} \right\} + \left\{ \begin{array}{c} \text{rate of component i} \\ \text{produced} \end{array} \right\} \quad (2-7)$$

Conservation of Energy

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

$$\left\{ \begin{array}{l} \text{rate of energy} \\ \text{accumulation} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of energy in} \\ \text{by convection} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of energy out} \\ \text{by convection} \end{array} \right\} \\ + \left\{ \begin{array}{l} \text{net rate of heat addition} \\ \text{to the system from} \\ \text{the surroundings} \end{array} \right\} + \left\{ \begin{array}{l} \text{net rate of work} \\ \text{performed on the system} \\ \text{by the surroundings} \end{array} \right\} \quad (2-8)$$

The total energy of a thermodynamic system, U_{tot} , is the sum of its internal energy, kinetic energy, and potential energy:

$$U_{tot} = U_{int} + U_{KE} + U_{PE} \quad (2-9)$$

- Black box (empirical)
 - 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

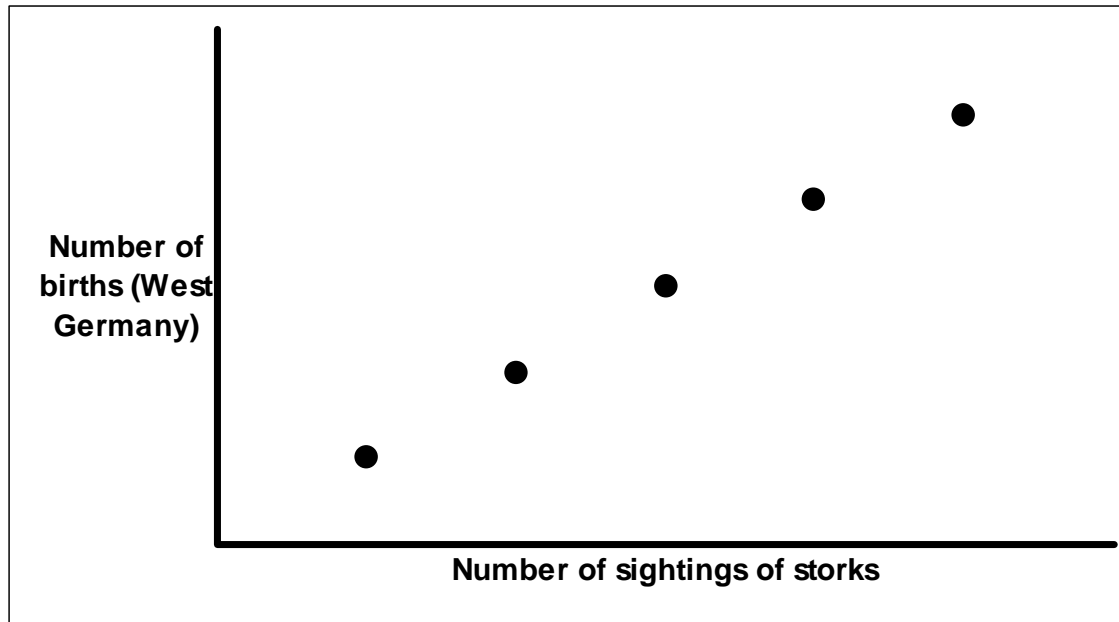
- linear regression

$$y = c_0 + c_1x + c_2x^2$$

- nonlinear regression

$$y = K(1 - e^{-t/\tau})$$

- 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

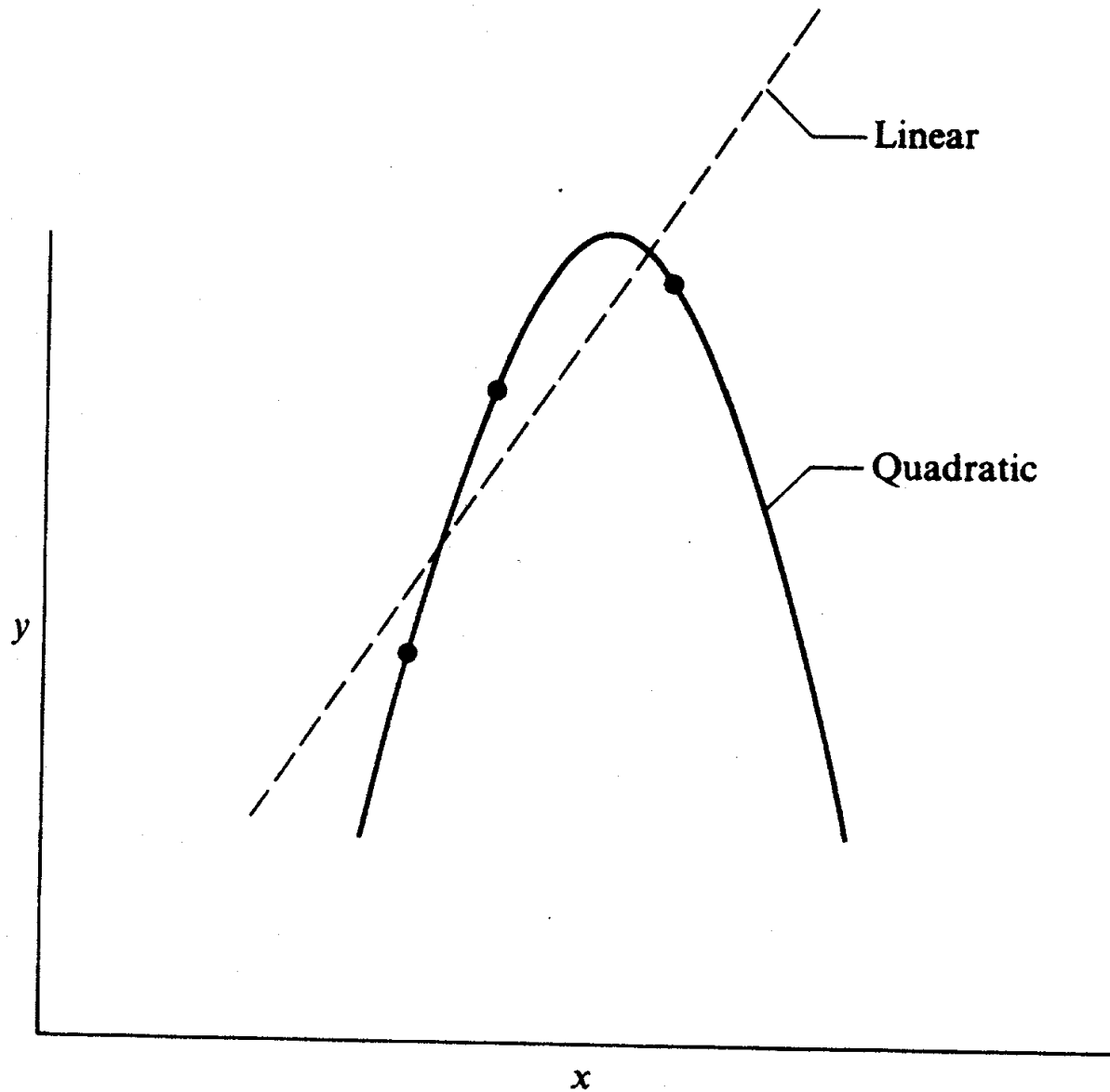
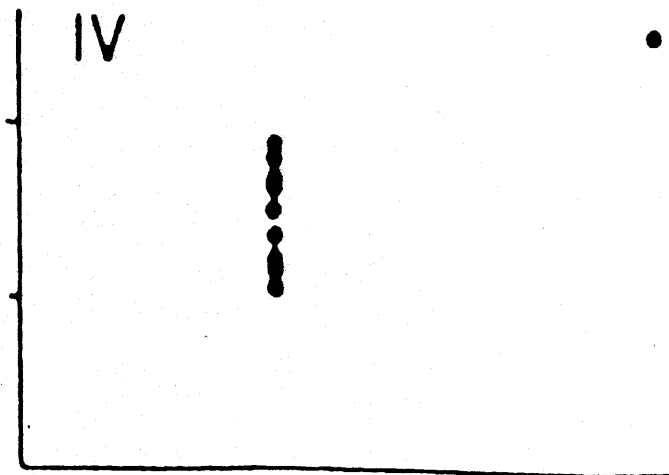
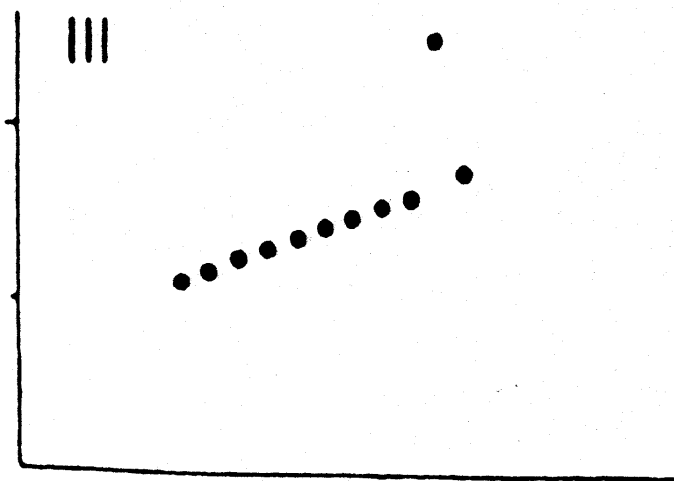
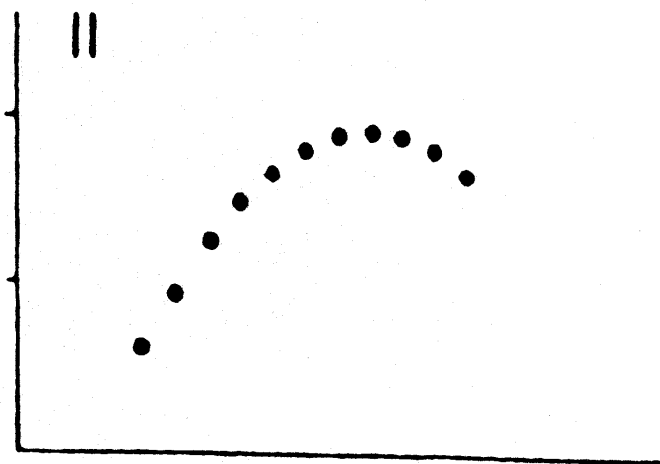
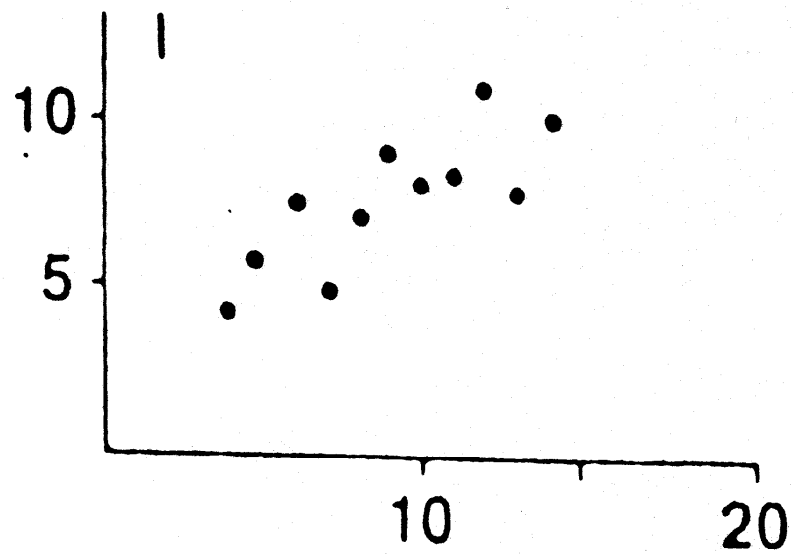


FIGURE 2.7

Linear versus quadratic fit for three data points.



- *Development of Dynamic Models*
- *Illustrative Example: A Blending Process*

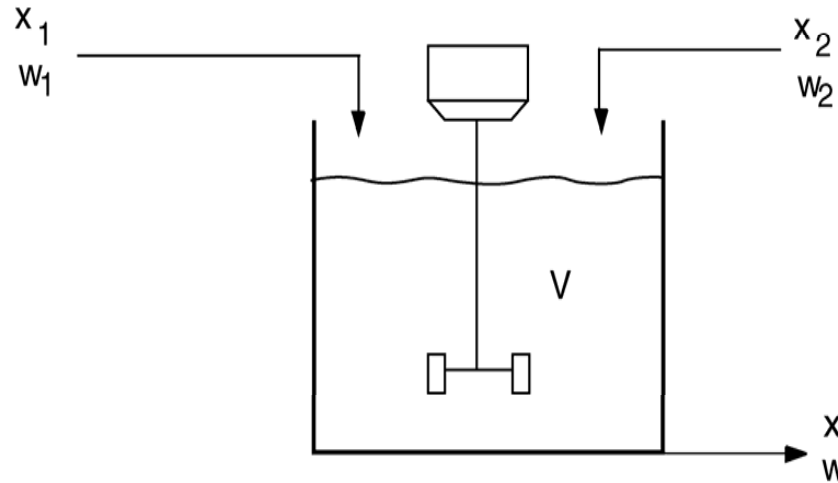


Figure 2.1. Stirred-tank blending process.

An unsteady-state mass balance for the blending system:

$$\left\{ \begin{array}{l} \text{rate of accumulation} \\ \text{of mass in the tank} \end{array} \right\} = \left\{ \begin{array}{l} \text{rate of} \\ \text{mass in} \end{array} \right\} - \left\{ \begin{array}{l} \text{rate of} \\ \text{mass out} \end{array} \right\} \quad (2-1)$$

or

$$\frac{d(V\rho)}{dt} = w_1 + w_2 - w \quad (2-2)$$

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

- **The unsteady-state component balance is:**

$$\frac{d(V\rho x)}{dt} = w_1 x_1 + w_2 x_2 - wx \quad (2-3)$$

The corresponding steady-state model was derived in Ch. 1 (cf. Eqs. 1-1 and 1-2).

$$0 = \bar{w}_1 + \bar{w}_2 - \bar{w} \quad (2-4)$$

$$0 = \bar{w}_1 \bar{x}_1 + \bar{w}_2 \bar{x}_2 - \bar{w} \bar{x} \quad (2-5)$$

The Blending Process Revisited

For constant ρ , Eqs. 2-2 and 2-3 become:

$$\rho \frac{dV}{dt} = w_1 + w_2 - w \quad (2-12)$$

$$\frac{\rho d(Vx)}{dt} = w_1 x_1 + w_2 x_2 - wx \quad (2-13)$$

Equation 2-13 can be simplified by expanding the accumulation term using the “chain rule” for differentiation of a product:

$$\rho \frac{d(Vx)}{dt} = \rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} \quad (2-14)$$

Substitution of (2-14) into (2-13) gives:

$$\rho V \frac{dx}{dt} + \rho x \frac{dV}{dt} = w_1 x_1 + w_2 x_2 - wx \quad (2-15)$$

Substitution of the mass balance in (2-12) for $\rho dV/dt$ in (2-15) gives:

$$\rho V \frac{dx}{dt} + x(w_1 + w_2 - w) = w_1 x_1 + w_2 x_2 - wx \quad (2-16)$$

After canceling common terms and rearranging (2-12) and (2-16), a more convenient model form is obtained:

$$\frac{dV}{dt} = \frac{1}{\rho} (w_1 + w_2 - w) \quad (2-17)$$

$$\frac{dx}{dt} = \frac{w_1}{V\rho} (x_1 - x) + \frac{w_2}{V\rho} (x_2 - x) \quad (2-18)$$

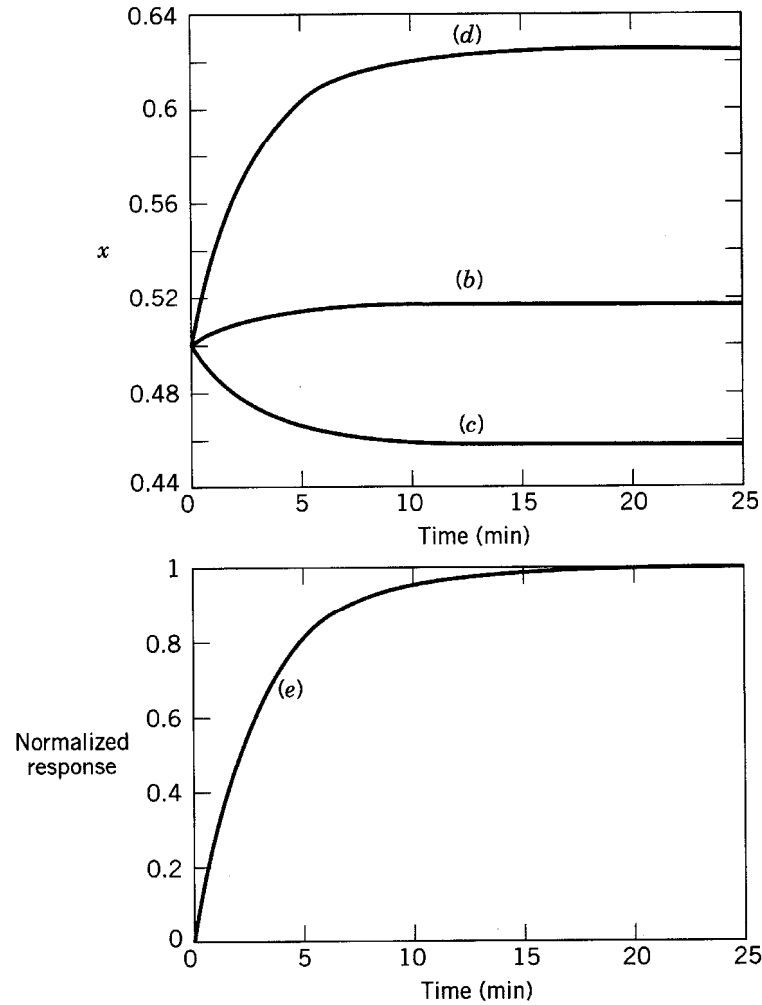


Figure 2.2 Exit composition responses of a stirred-tank blending process to step changes in:

- (b) flow rate w_1
- (c) flow rate w_2
- (d) flow rate w_2 and inlet composition x_1
- (e) Normalized response for parts (b)–(d).

Stirred-Tank Heating Process

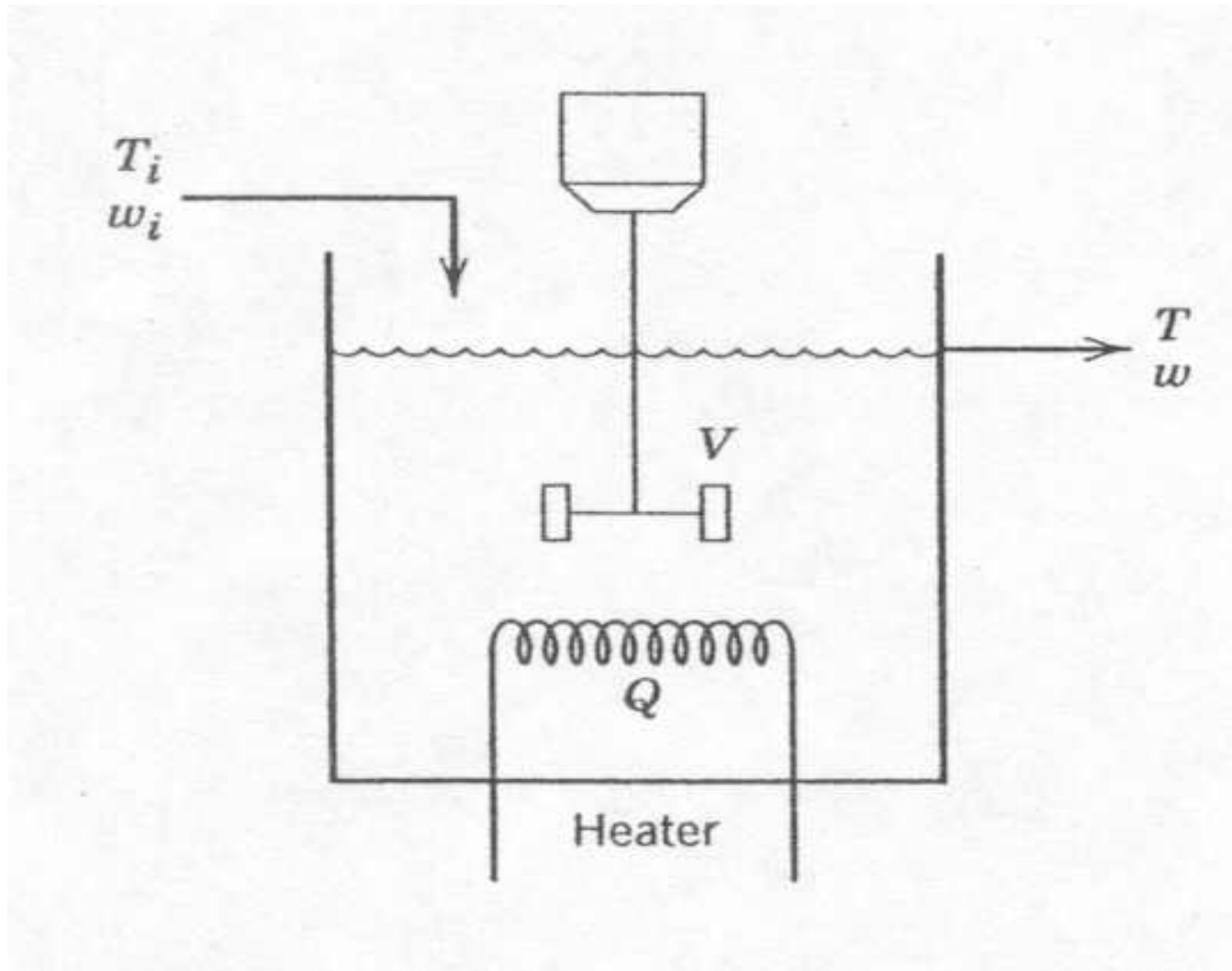


Figure 2.3 Stirred-tank heating process with constant holdup, V .

Stirred-Tank Heating Process (cont'd.)

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

For the processes and examples considered in this book, 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 in Eq. 2-8 can be written as

$$\frac{dU_{\text{int}}}{dt} = -\Delta(wH) + Q \quad (2-10)$$

U_{int} = the internal energy of
the system

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

$-\Delta(wH)$ = rate of enthalpy of the inlet
stream(s) - the enthalpy
of the outlet stream(s)

Model Development - I

For a pure liquid at low or moderate pressures, the internal energy is approximately equal to the enthalpy, $U_{int} \approx H$, and H depends only on temperature. Consequently, in the subsequent development, we assume that $U_{int} = H$ and $\hat{U}_{int} = \hat{H}$ where the caret (^) means per unit mass. As shown in Appendix B, a differential change in temperature, dT , produces a corresponding change in the internal energy per unit mass, $d\hat{U}_{int}$,

$$d\hat{U}_{int} = d\hat{H} = CdT \quad (2-29)$$

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

$$U_{int} = \rho V \hat{U}_{int} \quad (2-30)$$

Model Development - II

An expression for the rate of internal energy accumulation can be derived from Eqs. (2-29) and (2-30):

$$\frac{dU_{\text{int}}}{dt} = \rho V C \frac{dT}{dt} \quad (2-31)$$

Note that this term appears in the general energy balance of Eq. 2-10.

Suppose that the liquid in the tank is at a temperature T and has an enthalpy, \hat{H} . Integrating Eq. 2-29 from a reference temperature T_{ref} to T gives,

$$\hat{H} - \hat{H}_{\text{ref}} = C(T - T_{\text{ref}}) \quad (2-32)$$

where \hat{H}_{ref} is the value of \hat{H} at T_{ref} . Without loss of generality, we assume that $\hat{H}_{\text{ref}} = 0$ (see Appendix B). Thus, (2-32) can be written as:

$$\hat{H} = C(T - T_{\text{ref}}) \quad (2-33)$$

Model Development - III

For the inlet stream

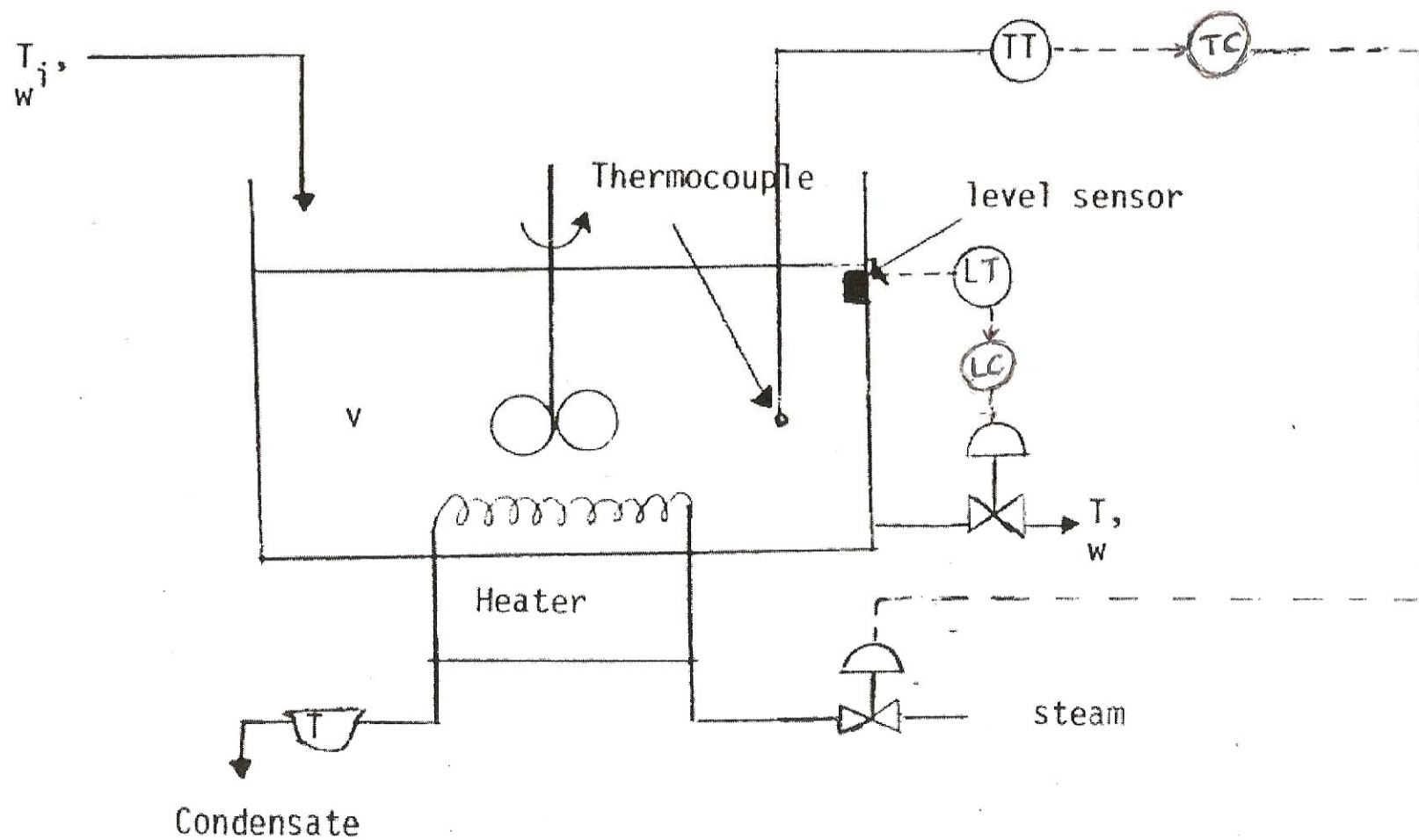
$$\hat{H}_i = C(T_i - T_{ref}) \quad (2-34)$$

Substituting (2-33) and (2-34) into the convection term of (2-10) gives:

$$-\Delta(w\hat{H}) = w[C(T_i - T_{ref})] - w[C(T - T_{ref})] \quad (2-35)$$

Finally, substitution of (2-31) and (2-35) into (2-10)

$$V\rho C \frac{dT}{dt} = wC(T_i - T) + Q \quad (2-36)$$



steam-heating: $Q = w_s \Delta H_v$

$$V \rho C \frac{dT}{dt} = wC(T_i - T) + w_s \Delta H_v \quad (1)$$

$$0 = wC(T_i - \bar{T}) + \bar{w}_s \Delta H_v \quad (2)$$

subtract (2) from (1)

$$V \rho C \frac{dT}{dt} = wC(\bar{T} - T) + (w_s - \bar{w}_s) \Delta H_v$$

divide by wC

$$\frac{V \rho}{w} \frac{dT}{dt} = \bar{T} - T + \frac{\Delta H_v}{wC} (w_s - \bar{w}_s)$$

Define deviation variables (from set point)

$$y = T - \bar{T} \quad \bar{T} \text{ is desired operating point}$$

$$u = w_s - \bar{w}_s \quad \bar{w}_s(\bar{T}) \text{ from steady state}$$

$$\frac{\rho V}{w} \frac{dy}{dt} = -y + \frac{\Delta H_v}{wC} u \quad \text{note that } \frac{\Delta H_v}{wC} = K_p \text{ and } \frac{\rho V}{w} = \tau_1$$

$$\text{note when } \frac{dy}{dt} = 0 \quad y = K_p u$$

$$\tau_1 \frac{dy}{dt} = -y + K_p u$$

General linear ordinary differential equation solution: sum of exponential(s)

Suppose $u = 1$ (unit step response)

$$y(t) = K_p \left(1 - e^{-\frac{t}{\tau_1}} \right)$$

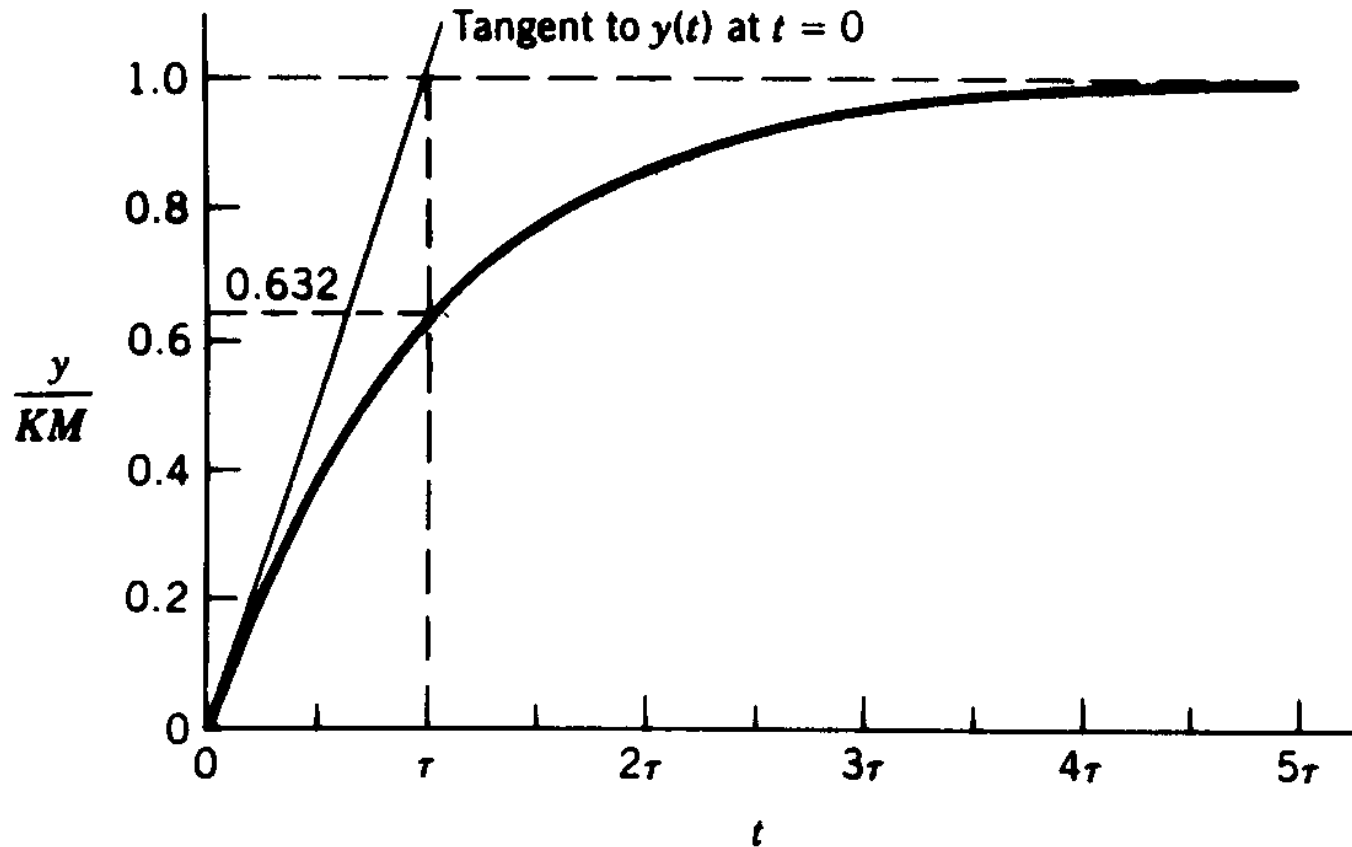


Figure 7.2. Step response of a first-order system and graphical constructions used to estimate the time constant, τ .

Example 1:

$$T_i = 40^\circ\text{C}, \bar{T} = 90^\circ\text{C}, T'_i = 0^\circ\text{C}$$

$$\text{s.s. balance: } wC(\bar{T} - T_i) = \bar{w}_s \Delta H_v$$

$$\bar{w}_s = 0.83 \times 10^6 \text{ g/hr}$$

$$\Delta H_v = 600 \text{ cal/g}$$

$$C = 1 \text{ cal/g}^\circ\text{C}$$

$$w = 10^4 \text{ kg/hr}$$

$$\rho = 10^3 \text{ kg/m}^3$$

$$V = 20 \text{ m}^3$$

$$\rho V = 2 \times 10^4 \text{ kg}$$

$$\tau = \frac{\rho V}{w} = \frac{2 \times 10^4 \text{ kg}}{10^4 \text{ kg/hr}} = 2 \text{ hr}$$

$$2 \frac{dy}{dt} = -y + 6 \times 10^{-5} u$$

dynamic model

$$y = T - \bar{T}$$

$$u = w_s - \bar{w}_s$$

Step 1: $t=0$ double w_s

$$T(0) = \bar{T} \quad y(0) = 0$$

$$u = +0.83 \times 10^6 \text{ g/hr}$$

$$2 \frac{dy}{dt} = -y + 50$$

$$y = 50(1 - e^{-0.5t})$$

$$\text{final } T = y_{ss} + \bar{T} = 50 + 90 = 140^\circ\text{C}$$

Step 2: maintain $T = 140^\circ\text{C} / 24 \text{ hr}$

Step 3: then set $u = 0, w_s = 833 \text{ kg/hr}$

$$2 \frac{dy}{dt} = -y + 6 \times 10^{-5} u, \quad y(0) = 50$$

Solve for $u = 0$

$$y = 50e^{-0.5t} \quad \begin{matrix} t \rightarrow \infty \\ y \rightarrow 0 \end{matrix} \quad (\text{self-regulating, but slow})$$

how long to reach $y = 0.5$?

Step 4: How can we speed up the return from 140°C to 90°C?

$$w_s = 0 \text{ vs. } w_s = 0.83 \times 10^6 \text{ g/hr}$$

$$\text{at s.s } w_s = 0$$

$$y \rightarrow -50^\circ\text{C} \quad T \rightarrow 40^\circ\text{C}$$

Process Dynamics

Process control is inherently concerned with unsteady state behavior (i.e., "transient response", "process dynamics")

Stirred tank heater: assume a "lag" between heating element temperature T_e , and process fluid temp, T .

heat transfer limitation = $h_e A(T_e - T)$

Energy balances

Tank:
$$wCT_i + h_e A(T_e - T) - wCT = mC \frac{dT}{dt}$$

Chest:
$$Q - h_e A(T_e - T) = m_e C_e \frac{dT_e}{dt}$$

At s.s.
$$\frac{dT}{dt} = 0, \frac{dT_e}{dt} = 0$$

Specify $Q \rightarrow$ calc. T, T_e

2 first order equations \Rightarrow 1 second order equation in T

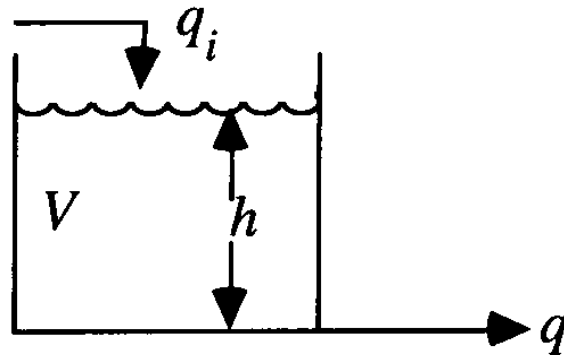
Relate T to Q (T_e is an intermediate variable)

$$y = T - \bar{T} \quad u = Q - \bar{Q} \quad T_i \text{ fixed}$$

$$\frac{m m_e C_e}{w h_e A_e} \frac{d^2 y}{dt^2} + \left(\frac{m_e C_e}{h_e A_e} + \frac{m_e C_e}{w C} + \frac{m}{w} \right) \frac{dy}{dt} + y = \frac{1}{w C} u$$

Note $C_e \rightarrow 0$ yields 1st order ODE (simpler model)

Fig. 2.2



$$q = \frac{1}{R_v} h$$

R_v : line resistance

$$A \frac{dh}{dt} = q_i - \frac{1}{R_v} h \quad P = p + \rho gh \quad (2-57)$$

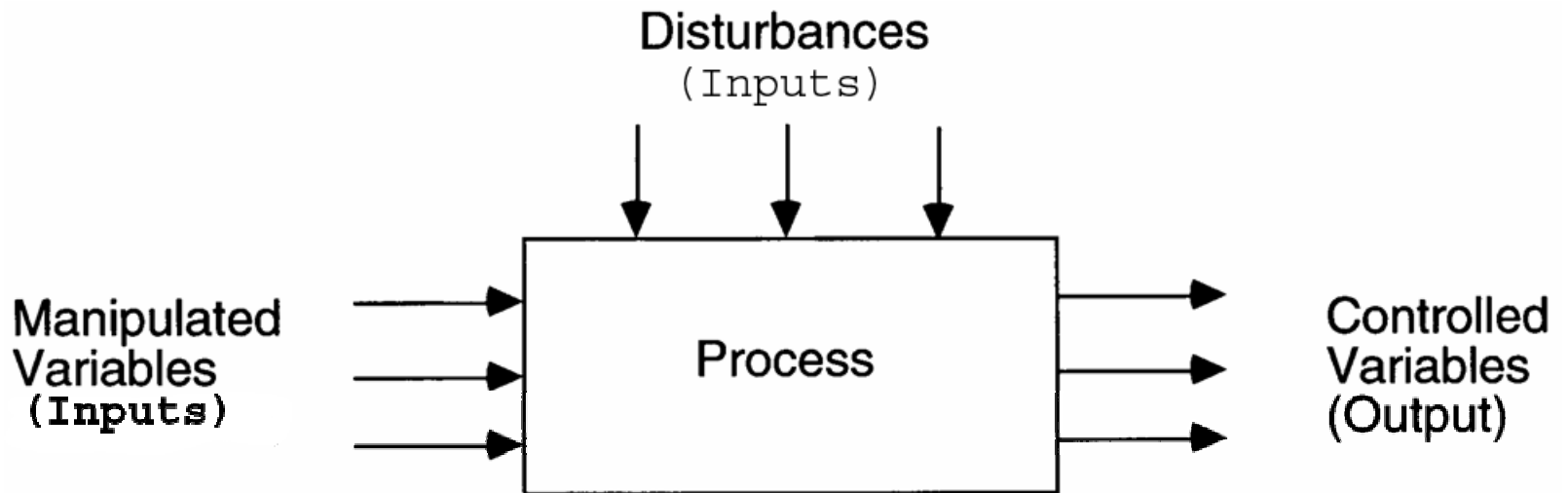
linear ODE

If $q = C_v^* \sqrt{P - P_a}$ $P = p + \rho gh$
 P_a : ambient pressure

$$A \frac{dh}{dt} = q_i - C_v^* \sqrt{\rho gh} = q_i - C_v \sqrt{h} \quad (2-61)$$

nonlinear ODE

Chapter 2



MIMO: Multiple Input - Multiple Output

SISO: Single Input - Single Output

Table 2.2. Degrees of Freedom Analysis

1. List all 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.

Degrees of Freedom Analysis for the Stirred-Tank Model:

3 parameters: V, ρ, C

4 variables: T, T_i, w, Q

1 equation: Eq. 2-36

Thus the degrees of freedom are $N_F = 4 - 1 = 3$. The process variables are classified as:

1 output variable: T

3 input variables: T_i, w, Q

For temperature control purposes, it is reasonable to classify the three inputs as:

2 disturbance variables: T_i, w

1 manipulated variable: Q

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.**

Bioreactions

- Are typically 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:**



- **Yield Coefficients:**

$$Y_{X/S} = \frac{\text{mass of new cells formed}}{\text{mass of substrate consumed to form new cells}} \quad (2-91)$$

$$Y_{P/S} = \frac{\text{mass of product formed}}{\text{mass of substrate consumed to form product}} \quad (2-92)$$

Fed-Batch Bioreactor

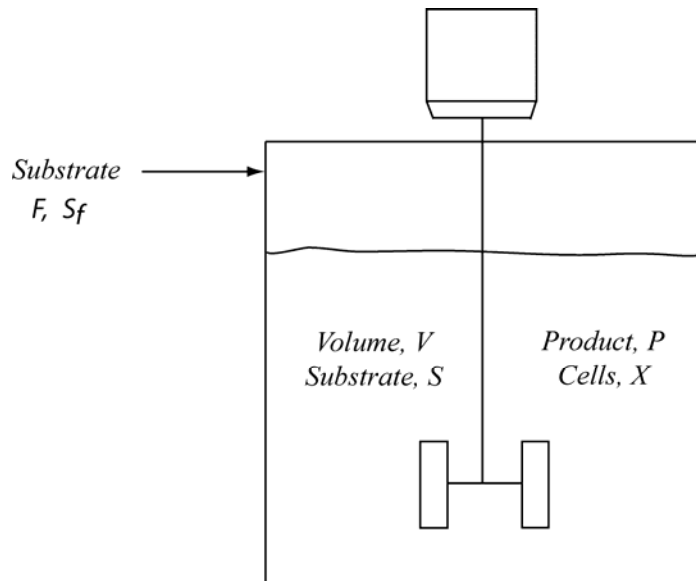


Figure 2.11. Fed-batch reactor for a bioreaction.

Monod Equation

$$r_g = \mu X \quad (2-93)$$

Specific Growth Rate

$$\mu = \mu_{\max} \frac{S}{K_s + S} \quad (2-94)$$

- 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 heterogenous mixture can be approximated as a homogenous liquid.
 6. The rate of cell growth r_g is given by the Monod equation in (2-93) and (2-94).

- Modeling Assumptions (continued)
7. The rate of product formation per unit volume r_p can be expressed as

$$r_p = Y_{P/X} r_g \quad (2-95)$$

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

$$Y_{P/X} = \frac{\text{mass of product formed}}{\text{mass of new cells formed}} \quad (2-96)$$

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

- General Form of Each Balance

$$\{\text{Rate of accumulation}\} = \{\text{rate in}\} + \{\text{rate of formation}\} \quad (2-97)$$

- Individual Component Balances

- **Cells:**
$$\frac{d(XV)}{dt} = V r_g \quad (2-98)$$

- **Product:**
$$\frac{d(PV)}{dt} = V r_p \quad (2-99)$$

- **Substrate:**
$$\frac{d(SV)}{dt} = F S_f - \frac{1}{Y_{X/S}} V r_g - \frac{1}{Y_{P/S}} V r_p \quad (2-100)$$

- Overall Mass Balance

- **Mass:**

$$\frac{d(V)}{dt} = F \quad (2-101)$$

Chapter 2

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