# Mathematical Modeling of Chemical Processes

- The rationale for dynamic process models
- Dynamic models of representative processes

# The rationale for dynamic process models

***Roles of dynamic models***

- to improve understanding of the process
- to train plant operating personnel
- to develop control strategies
- to optimize process operating conditions.

***Model classification (according to modeling approaches)***

(a) Theoretical models: using the principles of chemistry, physics and biology

(b) Empirical models: fitting experimental data

(c) Semi-empirical models: combination of (a) and (b)

# 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.

# 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

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

## Conservation of Component i

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

$$- \left\{\begin{matrix}\text{rate of component i}\\ \text{out}\end{matrix}\right\} + \left\{\begin{matrix}\text{rate of component i}\\ \text{produced}\end{matrix}\right\} \quad \text{(2-7)}$$

# •*Development of Dynamic Models*

## •*Illustrative Example: A Blending Process*

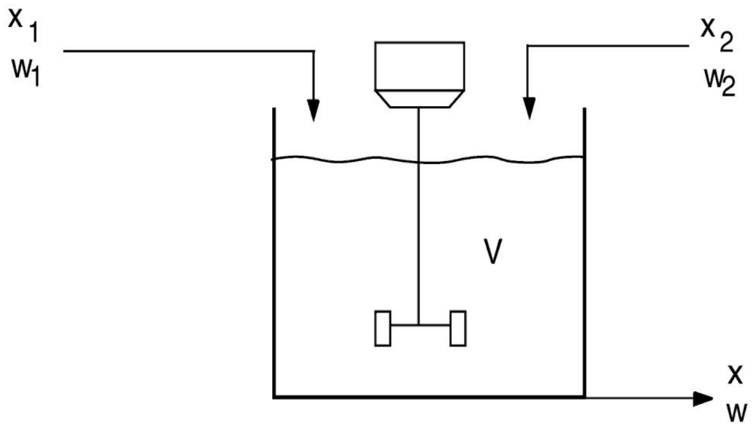


Figure 2.1. Stirred-tank blending process.

**An unsteady-state mass balance for the blending system:**

$$\begin{Bmatrix}\text{rate of accumulation} \\ \text{of mass in the tank}\end{Bmatrix} = \begin{Bmatrix}\text{rate of} \\ \text{mass in}\end{Bmatrix} - \begin{Bmatrix}\text{rate of} \\ \text{mass out}\end{Bmatrix} \qquad (2\text{-}1)$$

or

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

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

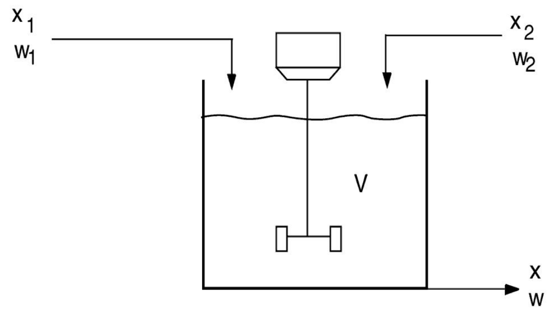


Figure 2.1. Stirred-tank blending process.

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

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

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

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

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

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

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

For constant $\rho$, Eqs. 2-2 and 2-3 become:

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

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

Equation 2-13 can be simplified :

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

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

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

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

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

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

$$\boxed{\begin{aligned} \frac{dV}{dt} &= \frac{1}{\rho}(w_1 + w_2 - w) && (2\text{-}17) \\ \frac{dx}{dt} &= \frac{w_1}{V\rho}(x_1 - x) + \frac{w_2}{V\rho}(x_2 - x) && (2\text{-}18) \end{aligned}}$$

Example 2.1

(1) Constant liquid holdup, $V$=2m³
(2) Density is approximately constant $\rho = 900 kg/m^3$

Questions:

(a) Assume that the process is operated in steady state for a long time, with $w_1$=500kg/min, $w_2$=200kg/min, $x_1$=0.4, and $x_2$=0.75. What is the steady-state value of x?

(b) Suppose that w1 changes suddenly from the 500kg/min to 400 kg/min. Determine an expression for *x(t)*.

(c) Repeat part (b) for the case where $w_2$ (instead of $w_1$) changes suddenly from 200 to 100 kg/min and remain there.

(d) Repeat part (c ) for the case where $x_1$ suddenly changes from 0.4 to 0.6.

(e) For parts (b) through (d), plot the normalized response $x_N(t)$;

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

Chapter 2

Example 2.1

(1) Constant liquid holdup, $V$=2m$^3$

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Questions:

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Solution:

$$\boxed{\begin{aligned}&\overline{w}_1\overline{x}_1 + \overline{w}_2\overline{x}_2 = \overline{w}\overline{x}\\ &\overline{x} = \frac{\overline{w}_1\overline{x}_1 + \overline{w}_2\overline{x}_2}{\overline{w}} = \frac{500\times 0.4+200\times 0.75}{500+200} = 0.5\end{aligned}}$$

Example 2.1

(b) Suppose that w1 changes suddenly from the 500kg/min to 400 kg/min. Determine an expression for *x(t)*.

Solution:

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

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

$$\Rightarrow$$

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

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

$$\boxed{\tau\frac{dx}{dt} + x = c^* \qquad \tau = \frac{v\rho}{w_1 + w_2} \qquad c^* = \frac{w_1 x_1 + w_2 x_2}{w_1 + w_2}}$$

$$\boxed{\tau\frac{dx}{dt} + x = c^*}$$

$$\boxed{x(t) = x(0)e^{-t/\tau} + c^*(1 - e^{-t/\tau})}$$

Example 2.1

For case b, $\tau = \dfrac{v\rho}{w_1 + w_2}$

$$= \frac{2\text{m}^3 \times 900 kg/m^3}{400 kg/\min + 200 kg/\min}$$

$$= 3\min$$

$$c^* = \frac{w_1 x_1 + w_2 x_2}{w_1 + w_2}$$

$$= \frac{400 kg/\min \times 0.4 + 200 kg/\min \times 0.75}{600 kg/\min}$$

$$= 0.517$$

$$\boxed{x(t) = 0.5 e^{-t/3} + 0.517(1 - e^{-t/3})}$$

Example 2.1

(c) Repeat part (b) for the case where $w_2$ (instead of $w_1$) changes suddenly from 200 to 100 kg/min and remain there.

For case c,

$$\tau = \frac{v\rho}{w_1 + w_2}$$

$$= \frac{2\mathrm{m}^3 \times 900 kg/m^3}{500 kg/\min + 100 kg/\min}$$

$$= 3\min$$

$$c^* = \frac{w_1 x_1 + w_2 x_2}{w_1 + w_2}$$

$$= \frac{500 kg/\min \times 0.4 + 100 kg/\min \times 0.75}{600 kg/\min}$$

$$= 0.458$$

$$\boxed{x(t) = 0.5 e^{-t/3} + 0.458(1 - e^{-t/3})}$$

Example 2.1

(d) Repeat part (c ) for the case where $x_1$ suddenly changes from 0.4 to 0.6.

For case d,
$$\tau = \frac{v\rho}{w_1 + w_2}$$

$$= \frac{2\text{m}^3 \times 900 kg/m^3}{500 kg/\min + 100 kg/\min}$$

$$= 3\min$$

$$c^* = \frac{w_1 x_1 + w_2 x_2}{w_1 + w_2}$$

$$= \frac{500 kg/\min \times 0.6 + 100 kg/\min \times 0.75}{600 kg/\min}$$

$$= 0.625$$

$$\boxed{x(t) = 0.5 e^{-t/3} + 0.625(1 - e^{-t/3})}$$

Example 2.1

(e) For parts (b) through (d), plot the normalized response $x_N(t)$:

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

Solution:

$$\boxed{x(t) = x(0)e^{-t/\tau} + c^*(1 - e^{-t/\tau})}$$

$$\boxed{x(\infty) = x(0)e^{-\infty/\tau} + c^*(1 - e^{-\infty/\tau}) = c^*}$$

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

$$= \frac{x(0)e^{-t/\tau} + c^*(1 - e^{-t/\tau}) - x(0)}{c^* - x(0)}$$

$$= \frac{c^*(1 - e^{-t/\tau}) - x(0)(1 - e^{-t/\tau})}{c^* - x(0)}$$

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

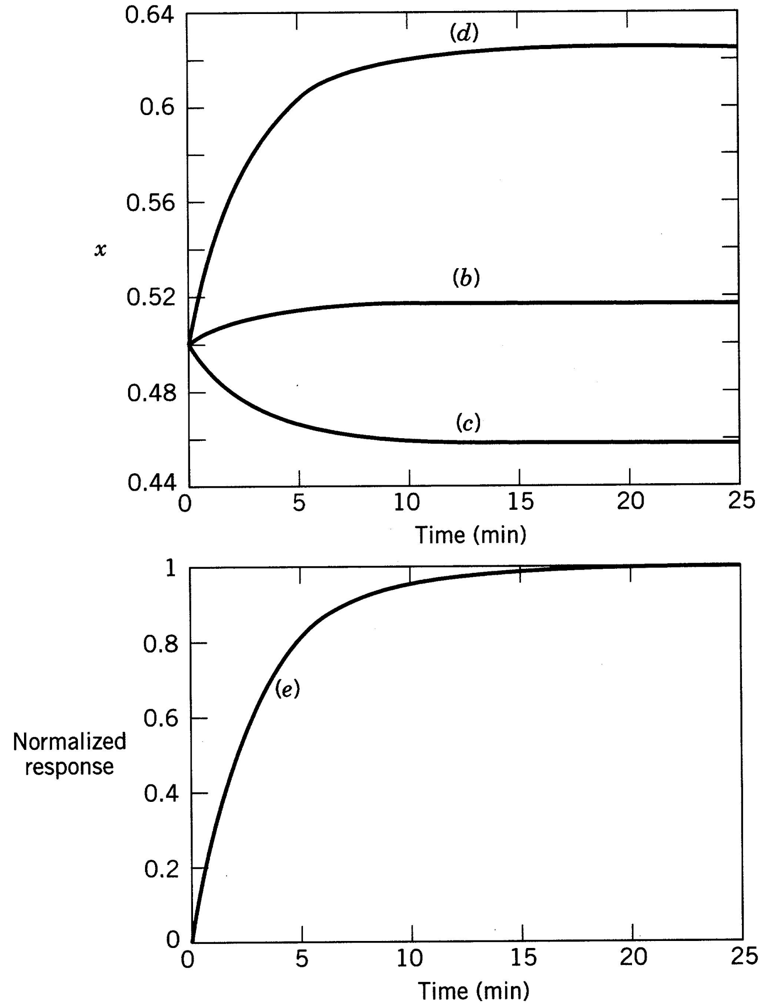



**Figure 2.2** Exit composition responses of a stirred-tank blending process to step changes in:
(b) flow rate $w_1$
(c) flow rate $w_2$
(d) flow rate $w_2$ and inlet composition $x_1$
(e) Normalized response for parts (b)–(d).

# Stirred-Tank Heating Process

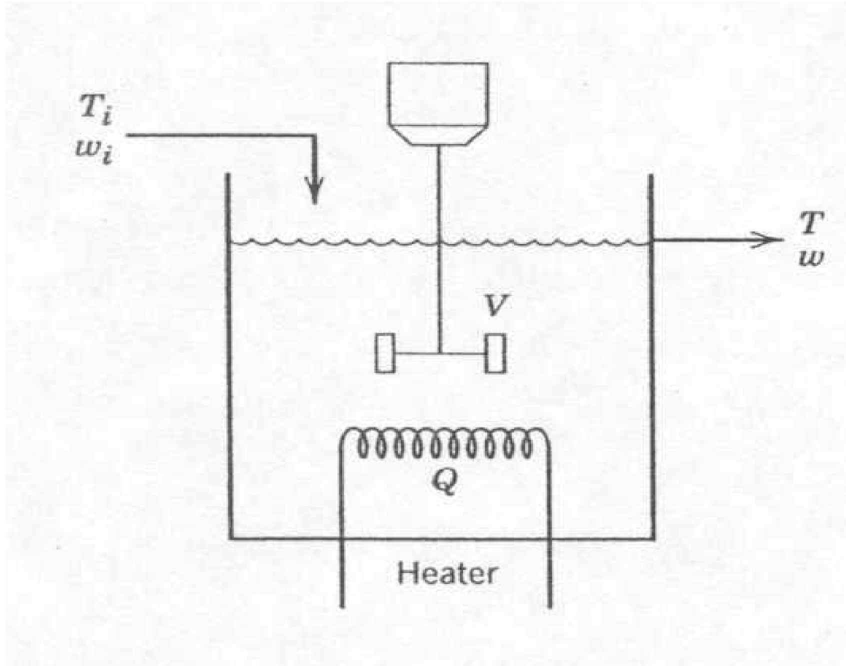



**Figure 2.3** Stirred-tank heating process with constant holdup, *V*.

Assumptions:

1. Perfect mixing
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.
4. Heat losses are negligible.

# Conservation of Energy

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

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

$$+\left\{\begin{matrix}\textbf{net rate of heat addition}\\ \textbf{to the system from}\\ \textbf{the surroundings}\end{matrix}\right\} + \left\{\begin{matrix}\textbf{net rate of work}\\ \textbf{performed on the system}\\ \textbf{by the surroundings}\end{matrix}\right\} \qquad \textbf{(2-8)}$$

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

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

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

$$\frac{dU_{\text{int}}}{dt} = -\Delta\left(w\hat{H}\right) + Q \qquad (2\text{-}10)$$

$U_{\text{int}}$ = the internal energy of the system

$\hat{H}$ = enthalpy per unit mass

$w$ = mass flow rate

$Q$ = rate of heat transfer to the system

$\Delta$ = denotes the difference between outlet and inlet conditions of the flowing streams; therefore

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

# Model Development - I

$$\frac{dU_{\text{int}}}{dt} = -\Delta\left(w\widehat{H}\right) + Q \qquad (2\text{-}10)$$

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

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

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

# Model Development - II

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

$$\frac{dU_{\text{int}}}{dt} = \rho VC \frac{dT}{dt} \tag{2-31}$$

$$\frac{dU_{\text{int}}}{dt} = -\Delta\left(w\hat{H}\right) + Q \tag{2-10}$$

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

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

# Steam-heated Stirred-Tank

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

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

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

subtract (2) from (1)

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

divide by $wC$

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

Chapter 2

# Define deviation variables (from set point)

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

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

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

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

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

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

Suppose u = 1 (unit step response)

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

# Example 1:

$$T_i = 40^\circ C, \ \overline{T} = 90^\circ C, \ T_i' = 0^\circ C$$

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

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

$$\Delta H_v = 600 \ \ cal/g$$

$$C = 1 \ \ cal/g^\circ C$$

$$w = 10^4 \ kg/hr$$

$$\rho = 10^3 \ kg/m^3$$

$$V = 20 \ m^3$$

$$\rho V = 2 \times 10^4 kg$$

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

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

dynamic model

$$y = T - \overline{T}$$
$$u = w_s - \overline{w}_s$$

*t*=0 double $w_s$

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

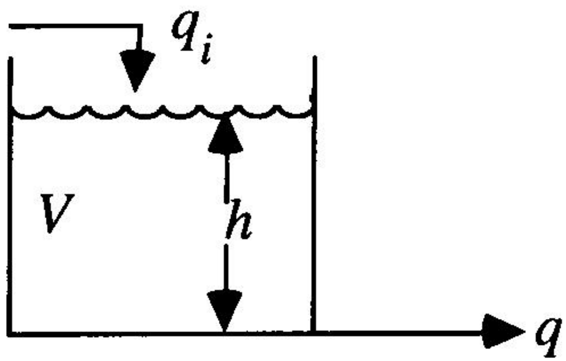
$$u = +0.83\times 10^6 \text{ g/hr}$$

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

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

final $$T = y_{ss} + \overline{T} = 50 + 90 = 140^o C$$

# Liquid storage system




$q_i$ and $q$ are volumetric flow rates

Mass balance equation:

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

$R_v$

Mass balance equation:

(1)If $q$ is constant ( q is kept at a constant value by a pump)

(2) If $q$ is dependant on $h$

If $$\mathrm{q} = \frac{1}{\mathrm{R_v}}\mathrm{h}$$ $R_v$: line resistance

$$A\frac{dh}{dt} = q_i - \frac{1}{R_v}h \qquad (2\text{-}57)$$

linear ODE

If:

$$q = C_v^* \sqrt{\frac{P - P_a}{\rho}}$$

$$P = P_a + \frac{\rho g}{g_c} h$$

$P_a$ :ambient pressure

$$A\frac{dh}{dt} = q_i - C_v^* \sqrt{\frac{g}{g_C} h} = q_i - C_v \sqrt{h} \qquad (2\text{-}61)$$

nonlinear ODE