Developing a Straightforward Tuning Method for Weak Acid or Weak Base Neutralization Control System

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Abstract

Control of pH in chemical reactors is a challenging issue due to the complex chemistry and the highly nonlinear nature of the dynamic model. The authors focus on the case in which weak acid (or weak base) is fed to a continuous stirred-tank reactor (CSTR) and neutralized by another stream of strong base (or strong acid). We developed a procedure of finding controller parameters: (1) Instead of pH, this work uses [H+] as the controlled or process variable; (2) Steady-state balance equations are established for "non-reactants", which in turn allow one to calculate [H+] ([OH-]) in CSTR by introducing water product K_w, acid dissociation constant K_a (or base dissociation constant K_b), and equation of electrical neutrality; (3) First-order dynamic model for the response of [H+] ([OH-]) to a small change in base (or acid) stream flow rate is derived; (4) A schedule of tuning parameters for a proportional-integral (PI) controller is established for various steady states by using internal model control (IMC) method. Simulation results suggest that IMC tuning method yields satisfactory performance of the feedback PI control system in tracking [H+] setpoint.

INTRODUCTION

The regulation of pH is a commonly encountered issue in the chemical industry [1-7] and waste water treatment processes [8,9]. One main challenge encountered in the design of pH control system is the nonlinear nature of the pH control process. Other complicating factors include the hydration of weak acid (or weak base), the existence of buffering compounds, and the splitting of water into H+ and OH- [1,4-6,10-13]. As a result, it is very difficult to obtain the dynamic behavior based on mass balances on [H+] or [OH-], although some studies used the concept of "excess hydrogen" to overcome this problem under specific conditions [14]. Many researchers have explored a new approach to implement pH control based on the Wiener model (a dynamic linear element for mixing in series with a static nonlinearity or pH) [15]. Many publications adopt advanced control strategies such as fuzzy logic, neural network [5,10,16], model predictive control [5,17] and many other methods [1,7].

The objective of this work is to present a straightforward and simplistic approach to the design of a gain-scheduled proportion-integral (PI) controller based on the dynamic model parameters obtained at various steady-states or operating conditions. Instead of using the highly non-linear pH as the controlled variable used by most workers in this area, this work uses [H+] ([OH-]) as the controlled variable in a hypothetical fixed-volume continuous stirred-tank reactor (CSTR) having two inlet streams: (1) weak acid (or weak base) at a fixed concentration and a fixed inlet flow rate, and (2) strong base (or strong acid) at a fixed concentration but varying flow rates. Steady-state [H+] ([OH-]) for various strong base (or strong acid) flow rates is solved by using mass balance of "non-reactants" or "reaction invariants" under the condition of electrical neutrality. We then derived the transfer functions for the responses of nonreactants and [H+] ([OH-]) to varying base (or acid) flow rate (the "manipulated" variable). Dynamic model parameters for various steady-state conditions were calculated, followed by the calculation of tuning parameters for a critically-damped feedback PI controller by using internal model control (IMC) method. Finally, a schedule of tuning parameters for adaptive gain-scheduled PI controller is recommended for the range of pH from weakly acidic (or weakly basic) up to the equivalence point.

We will first offer detailed simulation for the neutralization of weak acid by strong base. It will then be shown that the equations for the neutralization of weak base by strong acid appear to be analogous to those of the weak acid-strong base case.

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• pH Control
• IMC Tuning Method
• pH dynamic model
• Acid Neutralization
NEUTRALIZATION OF WEAK ACID WITH STRONG BASE

Theory

Assume that a CSTR has a liquid volume of V [L] with two inlet streams: Stream 1 containing a weak acid (such as acetic acid denoted as HA) at a concentration of C1 [mol/L] entering the CSTR at a volumetric flow rate of F1 [L/min] and Stream 2 containing a strong base (such as sodium hydroxide NaOH) at a concentration of C2 [mol/L] entering the CSTR at a volumetric flow rate of F2 [L/min]. The product stream is withdrawn at a volumetric flow rate of F1 + F2 (Figure 1). In this system, the reacting species are H+ and OH− that react instantaneously to form water:

\[ H^+ + OH^- \rightleftharpoons H_2O, K_w \]  (1)

where \( K_w = [H^+] [OH^-] = 10^{-14} \) at 25°C. Other "non-reactants" or "reaction invarients" \[4,12,16,18-20\] are dissociated acid A− and undissociated HA as well as sodium ions, defined as

\[ \alpha = [A^-] + [HA] \]  (2)

and

\[ \beta = [Na^+] \]  (3)

HA is a mono-protic weak acid with dissociate constant \( K_a \),

\[ HA \rightleftharpoons H^+ + A^-; K_a \]  (4)

where \( K_a = \frac{[H^+][A^-]}{[HA]} \)  (5)

We may express [A−] in terms of \( \alpha \) and \( K_a \) by combining Eqs. 2 and 5:

\[ \alpha = \left( \frac{K_a + [H^+]}{K_a} \right) [A^-] \]  (6)

Electroneutrality requires that

\[ [Na^+] + [H^+] = [OH^-] + [A^-] \]  (7)

By substituting Eqs. 3 and 6 into Eq. 7 while recognizing \[ [OH^-] = K_w / [H^+] \], we have

\[ \beta + [H^+] = \frac{K_w}{[H^+]} + \frac{K_a}{K_a + [H^+] - \alpha} \]  (8)

which results in the cubic equation for \([H^+]\):

\[ [H^+]^3 + (\beta + K_a)[H^+]^2 + (\beta K_a - \alpha K_a) [H^+] - K_a K_w = 0 \]  (9)

With Eq. 9, we may solve for the concentration of hydrogen ions in the CSTR based on the concentrations of non-reactants along with \( K_a \) and \( K_w \). The rationale behind the use of concentrations of non-reactants has been discussed in the literature \[19\]. Basically, when dealing with issues of acid-base neutralization, it is very difficult to construct mass balances for \([H^+]\) or \([OH^-]\) due to the formation of \( H_2O \) as the neutralization product as well as dissociation of a weak acid, the extent of which in turn depends on the pH of the solution. In constrast, the concentrations of non-reactants \( \alpha \) and \( \beta \) undergo simple dilution in the CSTR. By using Eq. 9, \([H^+]\) can be solved, which in turn determines the values of \([A^-]\) and \([HA]\). Therefore, this approach of using the concentrations of non-reactants provides a convenient means to predict the steady-state condition as well as the dynamic responses in the transient state.

Although most published work uses highly nonlinear pH as the process variable, the derivation below uses \([H^+]\) as the process variable to remove one key nonlinearity in the acid neutralization process.

Steady-state Mass Balance for Non-reactants

Since HA and A− originally come from the feed of the acidic

Figure 1 Feedback control schematic diagram of weak acid neutralization by using feedback [H+] controller in a CSTR.
stream with inlet concentration of undissociated HA at C_{1,ss}:

\[ V \frac{d\alpha}{dt} = 0 = F_{1,ss}C_{1,ss} - (F_{1,ss} + F_{2,ss})\alpha \]  

(10)

Similarly, Na+ originally comes from the feed of the basic stream with inlet concentration of NaOH at C_{2,ss}:

\[ V \frac{d\beta}{dt} = 0 = F_{2,ss}C_{2,ss} - (F_{1,ss} + F_{2,ss})\beta \]  

(11)

where the subscript *ss* denotes initial steady-state condition. It is obvious from Eqs. 10 and 11 that

\[ \alpha = \frac{F_{1,ss}C_{1,ss}}{F_{1,ss} + F_{2,ss}} \]  

(12)

and

\[ \beta = \frac{F_{2,ss}C_{2,ss}}{F_{1,ss} + F_{2,ss}} \]  

(13)

Therefore, with the knowledge of flow rates and inlet concentrations of weak acid and strong base, we may solve for Eq. 9 may be regarded as the “titration equation” in terms of reactants.

Open-loop Transient-state Mass Balance for Non-reactants

For simplicity, it is assumed in the following derivation that the only operating condition that may vary with time is the flow rate of strong base F_2. This situation may be encountered when a weak acid with constant concentration C_{1,ss} is fed at a constant flow rate of F_1, while the strong base (with constant flow rate of F_2) may vary its flow rate in order to track the [H+] set point. In this situation, we may write transient-state equations

\[ V \frac{d\alpha}{dt} = F_{1,ss}C_{1,ss} - (F_{1,ss} + F_{2,ss})\alpha \]  

(14)

\[ V \frac{d\beta}{dt} = F_{2,ss}C_{2,ss} - (F_{1,ss} + F_{2,ss})\beta \]  

(15)

By subtracting Eq. 10 from Eq. 14, linearizing the non-linear function:

\[ \Delta F_2 \Delta \alpha = \Delta F_2 (-\alpha) = \frac{-\alpha}{(F_{1,ss} + F_{2,ss})(\tau_p s + 1)}\Delta F_2 \]  

(16)

where

\[ K_{p\alpha} = -\frac{\alpha}{F_{1,ss} + F_{2,ss}} \]  

(17)

Likewise, by subtracting Eq. 11 from Eq. 15 and following the similar procedure of linearization and Laplace transform, we have the following transfer function:

\[ \Delta \beta = \beta - \beta_n = \frac{C_{2,ss} - \beta_n}{(F_{1,ss} + F_{2,ss})(\tau_p s + 1)}\Delta F_2 \]  

(18)

where

\[ K_{p\beta} = \frac{C_{2,ss} - \beta_n}{F_{1,ss} + F_{2,ss}} \]  

(19)

**Open-loop Transient-State Response of [H+]**

The above derivations revealed that \Delta \alpha/\Delta F_2 and \Delta \beta/\Delta F_2 are both first-order transfer functions. If a small change in \Delta F_2 is made, the above equations will predict the transient-response of \Delta \alpha and \Delta \beta. If a small step change in \Delta F_2 with magnitude A is made, i.e.,

\[ \Delta F_2(s) = A \]  

(20)

We may find the time-domain response equations for \Delta \alpha and \Delta \beta from any published Laplace transform table:

\[ \Delta \alpha(t) = A K_{p\alpha} \left(1 - \exp\left(-\frac{t}{\tau_p}\right)\right) \]  

(22)

\[ \Delta \beta(t) = A K_{p\beta} \left(1 - \exp\left(-\frac{t}{\tau_p}\right)\right) \]  

(23)

By applying Eq. 9, we may predict the transient response of [H+] in the following manner: First, we may write a steady-state equation for Eq. 9 and solve for steady-state [H+]_{ss}:

\[ [H^+]_{ss} = \beta_{ss}C_{2,ss} - (\alpha_{ss} - \alpha) \]  

(24)

Second, Eq. 24 may be subtracted from Eq. 9 to yield the linearized result:

\[ \Delta [H^+] = \Delta \alpha - \Delta \beta \]  

(26)

where

\[ Q = \Delta \beta_{ss} + 2 \beta_{ss} \Delta [H^+]_{ss}\Delta \beta - K_{s}[H^+]_{ss}\Delta \alpha \]  

(27)

Finally, by combining Eqs. 12, 13, 16-20, and 22-26, we may obtain the transient-state response function for [H^+] in terms of \Delta F_2 and initial steady-state or operating conditions of F_{1,ss}, F_{2,ss}, C_{1,ss}, and C_{2,ss}. Since [H^+] is a linear combination of \Delta \alpha and \Delta \beta, both of which being first-order models, we expect the resultant transfer function to be first-order model as well:

\[ \Delta [H^+] = \frac{K_{p\alpha}\Delta F_2}{(\tau_p s + 1)} \]  

(29)

\[ \Delta [H^+] = \frac{K_{p\beta}\Delta F_2}{(\tau_p s + 1)} \]  

(30)
where the magnitude of step change in $\Delta F_2$ is $A$, and the process gain $K_p$ can be found from the calculated results (Eq. 26):

$$K_p = \frac{\Delta[H^+](t \rightarrow \infty)}{A}$$  

(Eq. 31)

Or, we may combine Eqs. 16-19 and 26-28 to yield the analytical expression for $K_p$:

$$K_p = -\left(\left[H^+\right]K_{p1} + K_{p2} + K_p[H^+]\right)K_{p3} - K_p[H^+], K_p$$  

(Eq. 32)

### Prediction of the Performance of A Closed-loop Feedback PI Controller

Assuming that the process is controlled by a feedback controller with $[H^+]$ as the controlled (or process) variable and base flow rate $F_2$ as the manipulated variable, we may describe the block diagram of the closed-loop control system in Figure 2. It is also assumed that a proportional-integral (PI) controller is used to adjust the base stream flow rate $\Delta F_2$ according to error $\epsilon$ and the transfer function $G_c$ for the controller:

$$G_c = \frac{\Delta F_c}{\epsilon} = K_c\left(1 + \frac{1}{\tau_s s}\right)$$  

(Eq. 33)

where $K_c$ = Proportional Gain of the PI controller

$\tau_s$ = Integral Time of the PI controller

$\epsilon = error = [H^+]_{sp} - [H^+]$ = $\Delta[H^+], [H^+]_{sp} - \Delta[H^+]$

The subscript $sp$ denotes setpoint. From Eq. 29, we may define the neutralization process model $G_p$ as

$$G_p = \frac{\Delta[H^+]}{\Delta F_2} = \frac{K_p[s + K_p]}{\tau_s s + 1}$$  

(Eq. 34)

With the process model $G_p$ defined, we may derive the transfer function for the closed-loop setpoint tracking $\Delta[H^+]_{sp}/\Delta[H^+]_{wp}$ under the assumption that both sensor and actuator respond instantaneously to their respective inputs ($G_s = 1, G_a = 1$) [21]

$$\frac{\Delta[H^+]}{\Delta[H^+]_{wp}} = \frac{G_c G_p}{1 + G_c G_p}$$  

(Eq. 35)

$$\frac{\Delta[H^+]}{\Delta[H^+]_{or}} = \frac{\tau_s s + 1}{\tau_s s^2 + 2\zeta\tau_s s + 1}$$  

(Eq. 36)

Therefore, if a step change in $\Delta[H^+]_{wp}$ with magnitude $B$ is made, as shown below

$$\Delta[H^+]_{wp}(\epsilon) = \frac{B}{s}$$  

(Eq. 39)

the resultant response of $\Delta[H^+]$ would be a combination of the response of a second-order process to an impulse input with magnitude of $(B \tau_s)$ plus that of a second-order process to a step input of magnitude $B$:

$$\Delta[H^+] = \frac{\tau_s s + 2\zeta\tau_s s + 1}{\tau_s s^2 + 2\zeta\tau_s s + 1} \frac{\Delta[H^+]_{wp}}{s} + \frac{1}{\tau_s s^2 + 2\zeta\tau_s s + 1} \frac{\Delta[H^+]_{or}}{s}$$  

(Eq. 40)

The Impulse Component and the step component have the following well-established time-domain response equations:

**Impulse component**

$$\text{for } \zeta < 1; \Delta[H^+]_{impulse}(t) = \text{B} \frac{\tau_s s + 2\zeta\tau_s s + 1}{\tau_s s^2 + 2\zeta\tau_s s + 1} \frac{\Delta[H^+]_{wp}}{s}$$  

(Eq. 41)

$$\text{for } \zeta = 1; \Delta[H^+]_{impulse}(t) = \text{B} \frac{s}{\tau_s s^2 + 2\zeta\tau_s s + 1} \frac{\Delta[H^+]_{wp}}{s}$$  

(Eq. 42)

$$\text{for } \zeta > 1; \Delta[H^+]_{impulse}(t) = \text{B} \frac{s}{\tau_s s^2 + 2\zeta\tau_s s + 1} \frac{\Delta[H^+]_{wp}}{s}$$  

(Eq. 43)

**Figure 2** Feedback control block diagram for the acid neutralization process. Here $G_c$ = controller transfer function, $G_s$ = process model, $\epsilon$ = error, and $G_a$ (actuator) = $G_s$ (sensor) = 1 for this simulation.
Neutralization of Weak Acid by Strong Base

Assume that a CSTR has a liquid volume of $V$ [L] with two inlet streams: Stream 1 containing mono-basic weak base (such as ammonia NH$_3$, denoted as B) at a concentration of $C_1$ [mol/L] entering the CSTR at a volumetric flow rate of $F_1$ [mol/min] and Stream 2 containing strong acid (such as hydrogen chloride HCl) at a concentration of $C_2$ entering the CSTR at a volumetric flow rate of $F_2$. The product stream is withdrawn at a volumetric flow rate of $F_1 + F_2$. In this system, the reacting species are H$^+$ and OH$^-$ that react to form water:

$$H^+ + OH^- \rightleftharpoons H_2O, K_w$$  \hspace{1cm} (49)

where $K_w = [H^+][OH^-] = 10^{-14}$ at 25°C. Other "non-reactants" are conjugated acid BH and unreacted base B as well as chloride ions. Define

$$\alpha = \left[ BH^+ \right] + [B]$$  \hspace{1cm} (50)

and

$$\beta = \left[ Cl^- \right]$$  \hspace{1cm} (51)

Since B is a mono-basic weak base with dissociate constant $K_b$,

$$B + H_2O \rightleftharpoons BH^+ + OH^-, K_b$$  \hspace{1cm} (52)

where

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$  \hspace{1cm} (53)

We may express [BH$^+$] in terms of $\alpha$ and $K_b$ by combining Eqs. 50 and 53:

$$\alpha = \frac{K_b + [OH^-]}{K_w} [BH^+]$$  \hspace{1cm} (54)

Electroneutrality requires that

$$[Cl^-] + [OH^-] = [H^+] + [BH^+]$$  \hspace{1cm} (55)

By substituting Eqs. 51 and 54 into Eq. 55 while recognizing $[H^+] = K_w / [OH^-]$ we have

$$\beta + [OH^-] = \frac{K_w}{K_b} + \frac{K_b}{K_w} \alpha$$  \hspace{1cm} (56)

which results in the final cubic equation of [OH$^-$]:

$$[OH^-]^3 + (\beta + K_b)[OH^-]^2 + (\beta K_w - K_b \alpha) [OH^-] - K_b K_w = 0$$  \hspace{1cm} (57)

If Eqs. 1-9 are compared with Eqs. 49-57, it is interesting to find that analogous equations are obtained. Due to this analogy, the equations from the weak acid-strong base case can be applied to the weak base-strong acid case with the variables replaced according to Table 1.

RESULTS AND DISCUSSIONS

Neutralization of Weak Base with Strong Acid

Assume that a CSTR has a liquid volume of $V$ [L] with two inlet streams: Stream 1 containing mono-basic weak base (such as ammonia NH$_3$, denoted as B) at a concentration of $C_1$ [mol/L] entering the CSTR at a volumetric flow rate of $F_1$ [mol/min] and Stream 2 containing strong acid (such as hydrogen chloride HCl) at a concentration of $C_2$ entering the CSTR at a volumetric flow rate of $F_2$. The product stream is withdrawn at a volumetric flow rate of $F_1 + F_2$. In this system, the reacting species are H$^+$ and OH$^-$ that react to form water:

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If Eqs. 1-9 are compared with Eqs. 49-57, it is interesting to find that analogous equations are obtained. Due to this analogy, the equations from the weak acid-strong base case can be applied to the weak base-strong acid case with the variables replaced according to Table 1.
Weak acid neutralized by strong base (Eqs. 1-48)

- $F_1$: Inlet flow rate of weak acid stream
- $C_1$: Inlet concentration of weak acid [HA]
- $F_2$: Inlet flow rate of strong base
- $C_2$: Inlet concentration of strong base [NaOH]

Weak base neutralized by strong acid (Eqs. 49-57 and more)

- $\alpha$: $[A^-] + [HA]$ [$BH^+] + [B]$ 
- $\beta$: $[Na^+]$ [$Cl^-$]
- $[H^+]$ or $[OH^-]$ $[H^+]$ $[OH^-]$
- $pH$ or $pOH$ $pH$ $pOH$

Acid or base dissociation constant $K_a$ ($= 1.8 \times 10^{-5}$ for acetic acid in water)

Water product $K_w$

<table>
<thead>
<tr>
<th>Table 1: Table of analogy between the weak acid-strong base case and the weak base-strong acid case.</th>
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</thead>
<tbody>
<tr>
<td>Weak acid neutralized by strong base (Eqs. 1-48)</td>
</tr>
<tr>
<td>$F_1$</td>
</tr>
<tr>
<td>$C_1$</td>
</tr>
<tr>
<td>$F_2$</td>
</tr>
<tr>
<td>$C_2$</td>
</tr>
</tbody>
</table>

| $\alpha$ | $[A^-] + [HA]$ | $[BH^+] + [B]$ |
| $\beta$ | $[Na^+]$ | $[Cl^-]$ |
| $[H^+]$ or $[OH^-]$ | $[H^+]$ | $[OH^-]$ |
| $pH$ or $pOH$ | $pH$ | $pOH$ |

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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>$K_a$</td>
</tr>
<tr>
<td>$1.8 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$F_{2,ss}$ (L/min)</th>
<th>$\alpha_{ss}$ (mol/L)</th>
<th>$\beta_{ss}$ (mol/L)</th>
<th>$[H^+]_{ss}$ (mol/L)</th>
<th>$pH_{ss}$</th>
<th>$K_{p1}$</th>
<th>$K_{p2}$</th>
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</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0667</td>
<td>0.0333</td>
<td>$1.80 \times 10^{-5}$</td>
<td>4.75</td>
<td>-0.0222</td>
<td>0.0222</td>
</tr>
<tr>
<td>1.4</td>
<td>0.0588</td>
<td>0.0412</td>
<td>$7.71 \times 10^{-6}$</td>
<td>5.11</td>
<td>-0.0173</td>
<td>0.0173</td>
</tr>
<tr>
<td>1.8</td>
<td>0.0526</td>
<td>0.0474</td>
<td>$2.00 \times 10^{-6}$</td>
<td>5.70</td>
<td>-0.0139</td>
<td>0.0139</td>
</tr>
</tbody>
</table>

**Figure 3** Titration curve for 0.1 M acetic acid neutralized by 0.1 M NaOH. The flow rate of the acid is fixed at 2 L/min, and that of the base ranges from 0.5 between 2.5 L/min. The CSTR has a constant volume of 10 L.

**Open-loop Transient Response:** By using Eqs. 22, 23, and 26, the dynamic responses of $\Delta \alpha$, $\Delta \beta$, $\Delta [H^+]$ and $[H^+] = [H^+]_{ss} + \Delta [H^+]$ are calculated and presented in Figures 4-6. With the calculated $\Delta [H^+](t \rightarrow \infty)$, the $K_p$ values can be calculated from Eqs. 31 or 32. Then the ultimate $[H^+]_{ss}$ can be calculated as $[H^+]_{new} = ([H^+]_{ss} + \Delta [H^+](t \rightarrow \infty))$. The results are summarized in Table 4. It is evident that the process gain $K_p$ depends on initial steady state, which is characteristic of non-linear models. It is also shown that the change of pH is more pronounced as the initial steady-state base flow rate $F_{2,ss}$ is increased.

**Closed-loop Response Using Feedback PI Controller:** By choosing a reasonable closed-loop time constant $\tau_c = 3$ min, the IMC tuning rule (Eqs. 47 and 48) would recommend the tuning parameters for each initial steady-state, as summarized in Table 5.

To predict the performance of a PI controller at different initial steady states, we choose the size of setpoint change $\Delta$ corresponding to the expected ultimate changed $([H^+]_{sp} = [H^+]_{new} - [H^+]_{ss})$ for each range of base flow rate change ($F_2$: 1.0 $\rightarrow$ 1.1, 1.4 $\rightarrow$ 1.5, or 1.8 $\rightarrow$ 1.9 L/min). We designed a Visual Basic procedure to calculate $\Delta [H^+]$ as well as $[H^+]$ versus $t$, according to the resultant $\zeta$ value in Eqs. 37-46. The simulation is done for each initial steady state using four sets of controller tuning parameters with the
Figure 4 Simulated response of $[\text{H}^+]$ to the change in the base flow rate from 1.0 to 1.1 L/min.

Figure 5 Simulated response of $[\text{H}^+]$ to the change in the base flow rate from 1.4 to 1.5 L/min.

Figure 6 Simulated response of $[\text{H}^+]$ to the change in the base flow rate from 1.8 to 1.9 L/min.
first one derived from IMC tuning rule and the other three having \( K_c \) or \( \tau_I \) changed from the original IMC settings. The results are summarized in Table 6 and Figures 7-12.

From Figures 7 and 8, it is found that all four sets of tuning parameters provide satisfactory patterns of response for the initial steady state \( F_{2,ss} \) of 1.0 L/min or [H⁺]\(_{ss}\) of 1.80 x 10\(^{-5}\) mol/L. The response pattern using IMC tuning rule with \( \tau_C = 3 \) minutes offers almost critically-damped response (\( \zeta \sim 1 \)). Its response time is about the same as that of other three sets of controller settings without showing any extent of overshooting. Of course, we may make \( |K_c| \) somewhat greater than 30900 by choosing a more aggressive closed-loop time constant \( \tau_c \) (say 1 or 2 min.) to allow some extent of overshooting.

**Near Equivalence Point:** Question may arise if one wishes to move pH further toward equivalence point. Using our approach, the process gain \( K_p \) (Eq. 31) can also be calculated from two adjacent points on the titration curve as pH is approaching the equivalence point (Table 7). The value of \( K_p \) would be small (due to small \( \Delta [H^+] \) near equivalence point), which would result in large \( K_c \) required theoretically as shown in Table 7. The required proportional gain \( K_c \) is -8.950 x 10\(^{-4}\) (for a critically damped feedback control with \( \tau_c = 3 \) min) whose absolute value is only somewhat greater than those in the weakly acidic range (Table 6).

**Gain Scheduled PI Controller:** The above calculations reveal that a feedback PI controller for regulating [H⁺] by manipulating the flow rate of strong base requires different proportional gains and integral times as operating condition varies. Many modern-day control algorithms offer one form of adaptive control that would automatically change tuning parameters to suit a wider range of operating conditions. One such widely used algorithm is the gain-scheduled PI controller. This type of PI controller allows the users to build a schedule of tuning parameters at several operating conditions. As the operating condition changes, the algorithm would use linear interpolation or extrapolation to find the appropriate \( K_c \) and \( \tau_I \) for any operating conditions. Alternatively, the algorithm can simply pick the control parameters corresponding to the operating condition at the lower end of the appropriate range. Based on this work, we may build a schedule as summarized in Table 8 by assuming closed-loop time constant \( \tau_c \) of 3 min. The resultant pattern of closed-loop feedback control would be critically damped, which would have the advantage of avoiding overshooting near the equivalence point.

From Tables 5-8, it is found that the value of process gain \( K_p \) and the required proportional gain \( K_c \) of the PI controller still vary somewhat with operating condition, which is typical of nonlinear process models. However, the extent of variation of \( K_c \) is considered mild as compared with that reported in literature when pH is used as the controlled variable. Our work uses [H⁺] instead of pH as the controlled (or process variable) which

### Table 4: 1st-order model parameters for transient response of [H⁺] at various initial steady states.

<table>
<thead>
<tr>
<th>( F_{2,ss} ) (L/min)</th>
<th>( F_{2,new} )</th>
<th>( \Delta F_2 )</th>
<th>( \tau_p ) (min)</th>
<th>( \Delta[H^+] ) ( t\rightarrow\infty )</th>
<th>( [H^+]_{ss} ) ( new )</th>
<th>( pH_{ss} ) ( new )</th>
<th>( K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.1</td>
<td>0.1</td>
<td>3.33</td>
<td>-3.59 x 10(^{-4})</td>
<td>1.44x10(^{-5})</td>
<td>4.84</td>
<td>-3.59x10(^{-5})</td>
</tr>
<tr>
<td>1.4</td>
<td>1.5</td>
<td>0.1</td>
<td>2.94</td>
<td>-1.84 x 10(^{-4})</td>
<td>5.87x10(^{-6})</td>
<td>5.23</td>
<td>-1.84x10(^{-5})</td>
</tr>
<tr>
<td>1.8</td>
<td>1.9</td>
<td>0.1</td>
<td>2.63</td>
<td>-1.11 x 10(^{-4})</td>
<td>8.89x10(^{-7})</td>
<td>6.05</td>
<td>-1.11x10(^{-5})</td>
</tr>
</tbody>
</table>

### Table 5: Tuning parameters for a PI controller by IMC method.

<table>
<thead>
<tr>
<th>Initial Steady</th>
<th>( F_{2,ss} ) (L/min)</th>
<th>( K_p )</th>
<th>( \tau_p ) (mins)</th>
<th>IMC Tuning</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_p )</td>
<td>( \tau_p ) (arbitrally chosen)</td>
<td>( K_c )</td>
<td>( \tau_I ) (min)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>-3.59 x 10(^{-5})</td>
<td>3.33</td>
<td>3</td>
<td>-30900</td>
<td>3.33</td>
</tr>
<tr>
<td>1.4</td>
<td>-1.84 x 10(^{-5})</td>
<td>2.94</td>
<td>3</td>
<td>-53300</td>
<td>2.94</td>
</tr>
<tr>
<td>1.8</td>
<td>-1.11 x 10(^{-5})</td>
<td>2.63</td>
<td>3</td>
<td>-79000</td>
<td>2.63</td>
</tr>
</tbody>
</table>

### Table 6: Net 2nd-order model parameters for a feedback PI control system. The italized bold numbers are based on IMC tuning method.

<table>
<thead>
<tr>
<th>( F_{2,ss} ) (L/min)</th>
<th>( [H^+]_{ss} ) (mol/L)</th>
<th>( B = \Delta[H^+]_{ss} ) (mol/L)</th>
<th>( K_c )</th>
<th>( \tau ) (min)</th>
<th>Closed-loop 2nd-order parameters</th>
<th>Plots of [H⁺] or pH vs. t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \zeta )</td>
<td>( \tau_s )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.80x10(^{-5})</td>
<td>-3.59 x 10(^{-4})</td>
<td>-30900</td>
<td>3.33</td>
<td>3.16</td>
<td>1.00</td>
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<td>2.00</td>
<td>3.05</td>
<td>0.785</td>
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<td>0.555</td>
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<td>1.00</td>
<td>3.05</td>
<td>0.621</td>
</tr>
<tr>
<td>1.4</td>
<td>7.71x10(^{-5})</td>
<td>-1.84 x 10(^{-4})</td>
<td>-53300</td>
<td>2.94</td>
<td>2.97</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-20000</td>
<td>2.00</td>
<td>4.00</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>1.00</td>
<td>2.83</td>
<td>0.658</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>-10000</td>
<td>1.00</td>
<td>4.00</td>
<td>0.805</td>
</tr>
<tr>
<td>1.8</td>
<td>2.00x10(^{-6})</td>
<td>-1.11 x 10(^{-6})</td>
<td>-79000</td>
<td>2.63</td>
<td>2.81</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-20000</td>
<td>2.00</td>
<td>4.87</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-20000</td>
<td>1.00</td>
<td>3.44</td>
<td>0.800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-10000</td>
<td>1.00</td>
<td>4.87</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Figure 7 Simulated response of $[H^+]$ to the step change of the set point by manipulating the base (0.1 M NaOH) feed rate for $F_{2,ss} = 1.0$ L/min.

Figure 8 Simulated pH responses to the step change of the set point by manipulating the base (0.1 M NaOH) feed rate for $F_{2,ss} = 1.0$ L/min.

Figure 9 Simulated response of $[H^+]$ to the step change of the set point by manipulating the base (0.1 M NaOH) feed rate for $F_{2,ss} = 1.4$ L/min.
Figure 10 Simulated pH responses to the step change of the set point by manipulating the base (0.1 M NaOH) feed rate for $F_{2,ss} = 1.4 \text{ L/min}$.

Figure 11 Simulated response of $[H^+]$ to the step change of the set point by manipulating the base (0.1 M NaOH) feed rate for $F_{2,ss} = 1.8 \text{ L/min}$.

Figure 12 Simulated pH responses to the step change of the set point by manipulating the base (0.1 M NaOH) feed rate for $F_{2,ss} = 1.8 \text{ L/min}$.
Central

applied to the case of neutralization of NH₃ with HCl by replacing the axis is base flow rate, then K is simply the slope or ∆[H⁺]/Δ (base flow rate) on this titration curve. Finally, the tuning parameters would be obtained by the procedure outlined in this work with the knowledge of flowrates of the streams and the volume of CSTR.

Neutralization of Weak Base by Strong Acid

Due to the analogy between the weak acid-strong base case and the weak base-strong acid case, we may easily “map” the results from the former case to the latter case with variables in the second column of Table 1 replaced by those in the third column. Incidentally, the base dissociation constant of NH₃ (Kₐ = 1.8 X 10⁻⁵), which is the same as the acid dissociation constant of acetic acid (Kₐ = 1.8 x 10⁻⁵). Therefore, Figures 3-12 may be applied to the case of neutralization of NH₃ with HCl by replacing variables according to Table 1.

We are currently conducting experimental work using a mini CSTR with automatic monitoring and control system to verify the model and the tuning procedure developed in this work. The Internet-based control system using LabVIEW hardware and software, as well as experimental results, will be reported in our subsequent work. Also, we are analyzing the process dynamics of using strong acid to neutralize weak base, as well as acid-base neutralization with any type titration curve.

CONCLUSIONS

Our work may be summarized as follows:

(1) A procedure of calculating steady-state conditions for the process of weak acid neutralization by strong base in a CSTR is established by using mass balance on nonreactants under the condition of electrical neutrality with known acid-dissociation constant and water product.

(2) Gains and time constant for the first-order dynamic models of nonreactants and [H⁺] around various steady states (created at various base flow rates) can be calculated based on the transient-state response models developed in this work.

(3) The performance of a feedback control system by using a PI controller can be predicted. The tuning parameters for a gain-scheduled PI controller can be computed from IMC tuning rule by using the dynamic model parameters obtained in this work. The schedule of tuning parameters for critically damped feedback control is applicable in the weakly acidic range as well as near the equivalence point without causing overshooting of pH.

(4) Due to the analogy between the case of weak acid neutralized by strong base and that of weak base neutralized by strong acid, the dynamic models and tuning rule developed for the former can be applied to the latter with variables replaced according to Table 1 of this work.

In this work, we successfully developed a procedure of predicting the dynamics of neutralization process of weak acid (with strong base) and weak base (with strong acid). This model allows the user to further tune a feedback PI controller based on well established theories. The results from this work can be easily incorporated in the curriculum of undergraduate process control class.

ACKNOWLEDGMENT

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NOMENCLATURE

A The magnitude of step change in F₂, L/min
B Molar concentration of dissociated acetate ions, mol/L
C Molar concentration of weak base NH₃, mol/L

Table 7: PI Controller Settings for τ = 3 min near equivalence point by IMC method that would yield critically-damped response (with ζ = 1).  

<table>
<thead>
<tr>
<th>Base Flow Rate F₂,ss (L/min)</th>
<th>Steady-state [H⁺], mol/L</th>
<th>Steady-state pH</th>
<th>Kₑ (Δ[H⁺]/ΔF₂)</th>
<th>τₑ (min)</th>
<th>Kₑ</th>
<th>τₑ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.92</td>
<td>7.50 x 10⁻⁵</td>
<td>6.13</td>
<td>-9.42 x 10⁻⁶</td>
<td>2.53</td>
<td>-8.95 x 10³</td>
<td>2.53</td>
</tr>
<tr>
<td>1.99</td>
<td>9.05 x 10⁻⁴</td>
<td>7.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8: Gain-scheduled PI Controller Settings for τ = 3 min by IMC Method for critically-damped feedback control.

<table>
<thead>
<tr>
<th>[H⁺]*,ss (mol/L)</th>
<th>Kₑ</th>
<th>τₑ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80 x 10⁻⁵</td>
<td>-30900</td>
<td>3.33</td>
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</tr>
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<td>2.00 x 10⁻⁴</td>
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<td>2.63</td>
</tr>
<tr>
<td>7.50 x 10⁻⁷</td>
<td>-89500</td>
<td>2.53</td>
</tr>
</tbody>
</table>

greatly reduces the extent of non-linearity in the control system.

This work is based on the system with well known chemistry whose titration curve (Figure 3 and Eq. 9). If one would use our approach to tackle system with unknown chemistry, the first step would be to conduct acid-base titration experiments in the laboratory to produce titration curves, followed by converting pH scale to [H⁺] scale. Then, the practical Kₑ value may be easily calculated from Eq. 31 for various points on the titration curve where the horizontal axis may be easily converted from (base/acid volume ratio) to (base/acid flow rate ratio), or even base flow rate for a given acid flow rate. Note that if the horizontal axis is base flow rate, then Kₑ is simply the slope or ∆[H⁺]/Δ (base flow rate) on this titration curve. Incidentally, the base dissociation constant of NH₃ (Kₑ = 1.8 X 10⁻⁵), which is the same as the acid dissociation constant of acetic acid (Kₐ = 1.8 x 10⁻⁵). Therefore, Figures 3-12 may be applied to the case of neutralization of NH₃ with HCl by replacing variables according to Table 1.

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3. The performance of a feedback control system by using a PI controller can be predicted. The tuning parameters for a gain-scheduled PI controller can be computed from IMC tuning rule by using the dynamic model parameters obtained in this work. The schedule of tuning parameters for critically damped feedback control is applicable in the weakly acidic range as well as near the equivalence point without causing overshooting of pH.

4. Due to the analogy between the case of weak acid neutralized by strong base and that of weak base neutralized by strong acid, the dynamic models and tuning rule developed for the former can be applied to the latter with variables replaced according to Table 1 of this work.

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Table 7: PI Controller Settings for τ ≈ 3 min near equivalence point by IMC method that would yield critically-damped response (with ζ = 1).

<table>
<thead>
<tr>
<th>Base Flow Rate F₂,ss (L/min)</th>
<th>Steady-state [H⁺], mol/L</th>
<th>Steady-state pH</th>
<th>Kₑ (Δ[H⁺]/ΔF₂)</th>
<th>τₑ (min)</th>
<th>Kₑ</th>
<th>τₑ (min)</th>
</tr>
</thead>
<tbody>
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<td>7.50 x 10⁻⁵</td>
<td>6.13</td>
<td>-9.42 x 10⁻⁶</td>
<td>2.53</td>
<td>-8.95 x 10³</td>
<td>2.53</td>
</tr>
<tr>
<td>1.99</td>
<td>9.05 x 10⁻⁴</td>
<td>7.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8: Gain-scheduled PI Controller Settings for τ = 3 min by IMC Method for critically-damped feedback control.

<table>
<thead>
<tr>
<th>[H⁺]*,ss (mol/L)</th>
<th>Kₑ</th>
<th>τₑ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80 x 10⁻⁵</td>
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<td>2.63</td>
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<tr>
<td>7.50 x 10⁻⁷</td>
<td>-89500</td>
<td>2.53</td>
</tr>
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REFERENCES


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