

pH Simulator  
A Process Control Challenge Problem  
R. Russell Rhinehart 2018-11-12

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## 1. Introduction

$pH$  is a measure of acid (or base) activity, often termed acidity. A simple definition is that  $pH$  is the negative of the base-10 logarithm of the Hydrogen ion concentration.

$$pH = -\log_{10}([H^+])$$

The brackets around a chemical species denote the concentration of that species in moles per liter.

However, more rigorously  $pH$  is defined as

$$pH = -\log_{10}(\gamma[H^+]/[H^+]_0)$$

Here  $\gamma$  is the activity coefficient, and  $[H^+]_0$  is the reference state which is commonly taken to be 1 mol/liter. If the activity coefficient is nearly the ideal  $\gamma = 1$  value, then the two equations are identical. The ideal first is commonly used even though it appears dimensionally inconsistent with the nominal value of 1 substituted for the symbol  $[H^+]_0$ .

Water is neutral, with a nominal  $pH$  of 7. Acids have lower  $pH$  values typically in the 1 to 4 range, and bases (or caustics) have  $pH$  values in the 9 to 12 range.

The units on the Hydrogen ion concentration are moles per liter. For those who have forgotten: A mole is a measure of the quantity of material. One mole is equal to  $6.02214 \times 10^{23}$  number (Avogadro's Number) of molecules. Atomic weight, from the periodic table of elements [1], is the mass in grams of one mole of that atom. Sodium has an atomic weight of 22.989770 g/mol, which

means that  $6.02214 \times 10^{23}$  Na atoms weigh 22.989770 g. Chlorine has an atomic weight of 35.453 g/mol. The molecule of  $\text{NaCl}$ , table salt, has the molecular weight of the sum of atomic weights, 58.443 g/mole.

*Note: I've rounded the sum to reflect the implied uncertainty on the Cl atomic weight. So, how to relate molecular weight and composition? If you wanted to mix a 0.01 molar solution of table salt in water, weigh out 0.58443 grams of salt (1/100<sup>th</sup> of a mole), place it in a vessel, and top it off to the 1 liter mark with water.*

*Note: If you start with 1 L of water and add salt to it, there is a volume change of the liquid as the salt is added. Let's say that 1 mole of salt, 58.443 g is added to 1 L of water and the volume rises to 1.01 L. The final volume is not 1 L, and the concentration would be 1 mole per 1.01 L or 0.99 mol/L. Do not pre-measure water and reagent then mix them. "Top off" the reagent with water – add water to the reagent, so that the total volume is as desired.*

*Note: However, I don't know where to acquire pure salt, or pure water, and I don't have access to weigh scales that have 0.00001 accuracy, or a method to ensure that the mixture volume is exactly 1 liter. So, probably, if I attempted to make a 0.01 molar solution of salt using my best engineering lab techniques, it would be off-target by a few %. Uncertainty in industrial practice is ever higher. This realization of uncertainty will be part of my defense later to not consider the complication of activity coefficients or volume change upon mixing in the pH calculations. Uncertainties in industrial control do not warrant scientific rigor.*

Many commercially important chemical reactions depend on acidity. Stomach digestive fluids are quite acidic, which need to be tempered by bases from several organs prior to entering the intestines. Blood is slightly basic. The tissues that surround and contain those fluids are designed to resist their  $pH$  and contain them. Your health depends on keeping the fluids within  $pH$  bounds. Many refreshing drinks, lemonade and sodas, are acidic. Household cleaning fluids of bleach and ammonia have high  $pH$  values – they are basic (caustic). And, since water is about neutral, we don't want to discharge acids or bases and ruin the environment for the natural lifeforms in rivers or lakes, or underground geology. So,  $pH$  control is important, and ubiquitous.

It is also nonlinear. This means that the sensitivity of the  $pH$  response to the control action changes as the  $pH$  changes, and with  $pH$  control it can change by several orders of magnitude. Often, this is termed "highly nonlinear", contrasting the magnitude of the nonlinear aspects of many process control applications (flow rate, distillation, etc.) with only a 3:1, or so, gain change. Additionally  $pH$  control is nonstationary, meaning that the sensitivity changes in time as the chemistry of the inflowing material changes. Both its nonlinear and nonstationary character make  $pH$  control difficult.

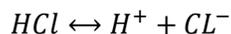
Because  $pH$  control is important, everywhere, and difficult, it has become a classic test case for control algorithms.

In my review of the literature, however, I find many researchers use clever approximations to simplify the  $pH$  calculation, and that researchers often use very simple  $pH$  process representations, all of which I think are too trivialized to represent a legitimate and credible test. Often, neither simulators nor lab-scale experiments are realistic models of commercial practice.

A small-scale process could still represent industrial practice, but play with toys cannot be considered as providing definitive guidance to the practice. Accordingly, I offer this approach to *pH* simulation, and to control as a benchmark challenge application for those who wish to explore *pH* control.

## 2. Representing the Reactions

In water, or an aqueous solution, an acid molecule releases a hydrogen ion. If Hydrochloric Acid, for example, the chemical reaction is simply indicated as



Often chemists include a water molecule to show that the  $H^+$  ion, a single atomic proton, is complexed as a hydronium ion.



I'll use the simpler representation.

In the molecule of *HCl* a Hydrogen atom and Chlorine atom are chemically combined. In this case, a simple but sufficient view is that the Chlorine atom grabs the electron of the Hydrogen atom. In water the electrically neutral *HCl* molecule can dissociate to a positively charged Hydrogen ion,  $H^+$  (missing its electron), and a negatively charged Chlorine ion,  $Cl^-$  (with an extra electron). Since the number of positive and negatively charged ions is identical, the solution is electrically neutral. The double headed arrow in the reaction equation indicates that the ions can recombine to make a neutral molecule. There is both a forward (left to right) and backward (right to left) reaction.

*Note: This is an elementary one-step view of the reaction. A rigorous kinetic model might include intermediate species or catalytic pathways. But, as I'll show uncertainties in many aspects do not justify greater rigor in a kinetic model.*

If you have a .01 molar solution of a monoprotic acid in water (0.01 mole of *HCl* per liter,  $[HCl] = .01$ ) and it all dissociates, and it is the only source of  $H^+$  ions, then the hydrogen ion concentration is .01 moles per liter,  $[H^+] = .01$ , and the *pH* is  $2 = -\log_{10}(.01)$ . That is the elementary concept, but, as I'll show, it is a bit more complicated by the natural dissociation of water.

The Chlorine atom has 17 protons in the nucleus and 17 electrons surrounding that. It also has electrically neutral neutrons in the nucleus with the number varying between *Cl* isotopes, but averaging about 18. The Hydrogen atom only has one proton and one electron. So, the  $H^+$  ion is actually just the tiny, extraordinarily tiny, one-proton nucleus. It is small, so it can both move fast and get into places. It is electron-hungry, so when it gets there, it wants to take an electron from another molecule, which initiates a chemical reaction.

In actuality, within the *HCl* molecule, the *H* atom does not totally give up the electron. The *H* and *Cl* atoms share the electron within the *HCl* molecule. But the *Cl* atom is greedier, and somewhat negatively charged, and the *H* atom is equivalently somewhat positively charged. A

better representation of the  $HCl$  molecule might be  $H^{\delta+}Cl^{\delta-}$ , where  $\delta$  indicates the partial electronic polarized state of the atoms. The charge attraction between the two atoms is the ionic bond, which keeps the molecule together. However, since all electrons are the same, and the  $Cl$  atom had 7 in its outer chemically active band, the particular electron from the Hydrogen gives 8 to the Chlorine, and all 8 are continuously juggled, shared, between the chemically bonded  $H$  and  $Cl$ .

Water molecules,  $H_2O$ , are similarly partially charged. The Oxygen atom grabs two electrons, one from each Hydrogen atom. Since each  $H$  atom is attached to the common  $O$  atom, a better representation of the structure of water is  $HOH$ , and acknowledging the polarized condition, a better representation would be  $H^{\delta+}O^{\delta-}H^{\delta+}$ . However, water is not a linear molecule. The two  $H^{\delta+}$  units are not 180 degrees apart, as implied by the line of type above, but are at about a 104.5 degree angle, a bit more open than a 90 degree right angle. The  $O$  atom at the apex of this triangle is partially negative charged, and the  $H$  atoms on the arms are partially positive charged.

When the acid dissociates, the released  $H^+$  ion attracts the  $O^{\delta-}$  of the surrounding water molecules. The  $H^+$  ion becomes surrounded with about 4 of  $O^{\delta-}$  segments. The  $H^+$  is in the center with the  $O^{\delta-}$  of about 4 water molecules surrounding it and the 8  $H^{\delta+}$  of the water molecules are pointing out. This is termed a solvated proton. It is not truly a single hydronium ion,  $H_3O^+$ , but a cluster perhaps represented as  $H(H_2O)_n^+$ . These spherical clusters of the oriented water have a positively charged surface, which attracts the  $O^{\delta-}$  of further surrounding water. But, wait a minute! All  $H^+$  protons are identical, and if an outer one was involved in a reaction, the water molecule that lost it would be happy to claim the inner  $H^+$  as its own. A solvated proton located here could cause a reaction over there.

There is more to the story. Pure water also partially dissociates.



Nominally, the  $H^+$  concentration of pure water is 0.0000001 moles per liter ( $[H^+] = 10^{-7}$ ). This makes the  $pH$  of pure water to be  $7 = -\log_{10}(10^{-7})$ . The water concentration is 55.5 moles per liter (an easy calculation from density and molecular weight). This means that only 1 of about 555,000,000 water molecules are dissociated.

Usually, also, acids are not fully dissociated in water. A generic representation of an acid is



Here the symbol  $A$  could represent the Chloride part of Hydrochloric acid, or the Sulfuric, Acetic, Phosphoric, Citric, etc. part of those respective acids. If an acid totally dissociated then  $[HA]$ , the concentration of the molecule in water would be zero,  $[HA] = 0$ . If 0.001 moles of the acid were topped off with water to the 1 L mark, and it totally dissociated, then the  $[H^+]$  and  $[A^-]$  values from the acid would be  $[H^+] = [A^-] = 0.001$ . This is 4 orders of magnitude greater than the  $[H^+]$  concentration in neutral water. If the  $H^+$  contribution of the water is ignored, then the solution is  $pH = 3 = -\log_{10}(0.001)$ . However, not all acids fully dissociate. If one-fourth of the acid molecules dissociate in this 0.001 molar example, then the remaining  $[HA] = 0.00075$ , and

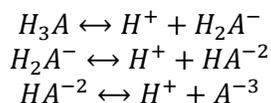
$[H^+] = [A^-] = 0.00025$ . In this case, still ignoring the relatively small effect of water, the same nominal acid concentration of 0.001 moles per liter results in a  $pH = 3.6 = -\log_{10}(0.00025)$ .

However, it is not that some of the  $HA$  molecules decide to dissociate and others decide to remain bonded. Each of them can be solvated by the water. But, when a solvated  $H^+$  and  $A^-$  “see” each other in the water, they are ionically attracted, and may recombine. Of course, every  $H^+$  is identical to any other, and every  $A^-$  is identical to any other, so the two original parts of the molecule may not be the ones that recombine. At equilibrium, the rate of  $HA$  molecules dissociating is equal to the rate of  $H^+$  and  $A^-$  ions that are recombining. At equilibrium the concentrations,  $[HA]$ ,  $[H^+]$ , and  $[A^-]$  remain constant. However, which atom is in which condition (ion or molecule) is continually shifting. This could be termed steady state, but it is a dynamic continually exchanging situation.

To help envision this dynamic steady state of equilibrium, imagine a room of 100 people and half of them, have a hand raised; then, randomly, one puts a hand down, and a random other raises a hand. If this continues there are always 100 people and always 50 hands in the air, but where the hands are randomly fluctuates. You probably have seen the noise on a TV set called “snow”, the continuous fluctuating black and white dots on the display that results from a lost signal. It is not a stationary pattern, but from one snapshot of the screen to another the number of dots is about the same. You may have flown over a large body of water and noticed the whitecaps on the surface, or looked across a lake and noticed the sparkles from reflected light. They continuously show and fade as the surface waves reflect sunlight from ever changing angles, but on average the same number of sparkles remain on the surface.

Similarly molecules are continually dissociating and recombining. To complicate it a bit more, the  $H^+$  from water is identical to the  $H^+$  from the acid. So, the recombining of water might be from an  $H^+$  from the acid, and the recombining of the acid might be from an  $H^+$  from the water.

One final reaction concept before the equations: Some acids have more than one  $H$  to release. A diprotic acid has two hydrogens to release. Sulfuric acid,  $H_2SO_4$ , is an example. And a triprotic acid can release three protons (hydrogen ions). Phosphoric acid,  $H_3PO_4$ , is an example. Generically a triprotic acid can be represented by  $H_3A$ , and the dissociation is considered to be sequential:



### 3. Equilibrium Relations

A mathematical relation between concentration of the  $H^+$  ions and amount of acids and bases in the solution is dependent on the reaction equilibrium relations. Here is the essence:

At equilibrium (the state of continual exchange, but with overall concentration values steady in time) the forward rate of a reaction (the number of molecules going toward the right per unit of time) is the same as the backward rate. Ideally, with concentration used to represent chemical activity, the generic reaction is



Simplistically, the forward part  $XY \rightarrow X^+ + Y^-$  has a rate that depends on the probability that an  $XY$  molecule exists, which is proportional to the concentration of  $XY$ ,  $r_f = k_f [XY]$ . And, it has a backward part  $XY \leftarrow X^+ + Y^-$  with a rate that depends on the chance that a  $X^+$  and a  $Y^-$  find each other in the solution, which is dependent on the product of concentrations,  $r_b = k_b [X^+] [Y^-]$ . At equilibrium the two rates are equal,  $r_f = r_b$ , and the ideal relation between all three concentrations is

$$\frac{k_f}{k_b} = K = \frac{[X^+] [Y^-]}{[XY]}$$

*Note: The rates of reaction, hence the equilibrium constant  $K$ , is temperature dependent. Not shown here, the temperature functionality is often adequately modeled by the Arrhenius relation,  $K(T) = k_0 e^{-E/RT}$ , and pressure can also have an impact.*

*Note: Ideally the probability of a molecule participating in a reaction is proportional to its concentration, but its propensity to react, its activity, also depends on its surrounding interactions. Rigorously, the reaction rate and equilibrium relations should use the activity of a molecule, which is usually modeled as the concentration times a factor (activity coefficient) related to its propensity to react. But, for this pH simulation study, the inclusion of activity coefficients makes a small contribution to either the realism or the control difficulty, and the magnitude of the adjustment to pH is small relative to the uncertainty of compositions within industrial practice. Activity coefficient relations are usually somewhat empirical, of many forms; and, I think, the attempt to include thermodynamic rigor of the electrolytes has more confusion than benefit in a simulator for pH control.*

*Note: All  $X^+$  elements are identical, regardless of their original origins. For example, a  $H^+$  ion donated from an acid is the same as any  $H^+$  released from a water molecule or any other acid. So, when calculating the concentration of any species, combine all of the sources.*

*Note: The science community refers to the  $K$ -values as “dissociation constants”, contrasting the engineering community label of “equilibrium constants”.*

For a monoprotic acid the equilibrium relation is

$$HA \leftrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+] [A^-]}{[HA]}$$

For water, the relation is the same

$$K = \frac{[H^+] [OH^-]}{[H_2O]}$$

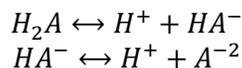
But, in this case,  $[H_2O]$  is about 555,000,000 times greater than the number of  $H^+$  or  $[OH^-]$  ions. If one out of 555,000,000 water atoms dissociate, “only” 554,999,999 remain. Accordingly, the concentration of  $H_2O$  can be considered independent of the reactions, constant at the nominal value. Then the water equilibrium is simply written as

$$K_w = [H^+][OH^-]$$

*Note: This representation of the equilibrium relation is termed the “ion product”.*

*Note: The nominal value for the ion product of water is  $K_w = 10^{-14}$ . But, it ranges from about  $10^{-15}$  (nearly ice) to about  $10^{-8}$  at high temperatures (and pressures). It is also dependent on the isotope of the molecules. At about 25 °C “light water”,  $H_2O$ , has a  $pK_w$  of 14, but at the same temperature “heavy water”,  $D_2O$ , has a  $pK$  of 14.95. Most pH control applications could use the nominal  $pK_w = 14$ , but if the applications are to high temperature boilers or to the nuclear industry, one should use better values. Further, the presence of ions changes the activity of ions and, even at 25 °C the  $pK_w$  value could be a point or so lower. So, in a simulation of normal temperatures  $pK_w = 13$  would also be reasonable.*

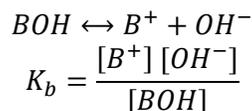
For a diprotic acid there is a sequence of dissociations



And an equilibrium relation for each

$$\begin{aligned} K_{a1} &= \frac{[H^+][HA^-]}{[H_2A]} \\ K_{a2} &= \frac{[H^+][A^{-2}]}{[HA^-]} \end{aligned}$$

A base has similar relations. For a simple, single hydroxyl (monovalent) base



Values of the equilibrium constants are properties of the particular acids, bases, and water (and their temperature). And, temperature-dependent  $K$  values are easily accessible in many references, such as the Handbook of Chemistry and Physics [2]. Some references give them as  $pK$  values, meaning  $pK = -\log_{10}(K)$ . The advantage is that  $pK$  values are in the convenient range of about 0 to 14. I’ll use the  $pK$  version.

By contrast, the concentrations and the particular components depend on the user’s choice of the mixture.

*Note: The terms “strong” and “weak” refer to the  $K$ -value, not the concentration. A strong acid or base fully dissociates, or nearly so. If 0.1 moles of a strong acid were in a 1 L solution, it would*

nearly fully dissociate to 0.1 moles of each ion type, and the pH would be 1. By contrast, a weak acid or base only partially dissociates. For example, if the same quantity, 0.1 moles, of a weak acid were in the solution, it would partially dissociate to perhaps 0.01 moles of each ion type (keeping 0.9 moles of the original acid molecules), and the pH would be 2. A strong acid with a concentration of 0.01 moles/L also has a pH of 2. So, pH is not a measure of the acid concentration, but it is a measure of the amount of the  $H^+$  ions released by the acid.

*Note: The terms “concentrated” and “dilute” refer to the nominal concentration of the material, based on the acid and base molecules, not the ion concentrations. For example, if 0.1 moles of a strong base were topped off with water to the 1 liter mark, and it fully dissociated, one would still say that the BOH concentration is 0.1 moles per liter, even if no BOH molecules remained undissociated in the solution.*

*Note: The lower is the pH, the higher is the  $[H^+]$  concentration, and the more reactive is the acid mixture. However, a fairly concentrated weak acid could have a pH of only 4 because most of the HA molecules are holding onto their  $H^+$  ions. Those HA molecules are able to release more  $H^+$  ions as the free ones in the solution are used. Such a mixture might have more reactive capacity than a dilute strong acid with a pH of 2, a lower pH. So, pH relates to immediate reactivity, not the total reactive capacity. Concentration relates to total reactive capacity, but not reactivity.*

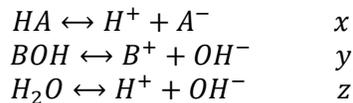
*Note: The term “buffering” means that the solution has reserve capacity that is released to keep the pH at a nominal level. For example, a .01 molar solution of a weak acid that is one tenth dissociated produces a 0.001 molar  $[H^+]$  with a pH = 3, and leaves the undissociated acid concentration as 0.009 molar. If 50% of those hydrogen ions are reacted, the  $[H^+]$  does not drop to 0.0005, with a pH = 3.3. Instead the reserve acid supplies more Hydrogen ions. If .0005 moles of the original 0.01 moles react, then there are 0.0095 moles of acid remaining, of which  $1/10^{th}$  dissociates to make  $[H^+] = 0.00095$  for which pH = 3.02. With normal instrumentation, this is measurably indistinct from pH = 3. Effectively, the solution acidity is unchanged. Buffer solutions effectively retain their pH even if a bit of acid or base is added.*

#### 4. Solving for pH – monoprotic acid and monovalent base

First, choose the nominal concentrations of your materials. If you are mixing in a continuous flow or fed-batch process (like a titration), this will likely require material balances. See Section 8.

Then consider a unit volume of 1 liter, a basis of 1 L. This might be a small portion of the 10,000 gal tank that you are dealing with, or 100 times more than your test tube sample. It is not necessary to have 1 L, but the 1 L concept simplifies the calculation, because the stoichiometric coefficients are the same as concentrations. The number of moles of each component in the volume is 1 times the concentration.

The three component reaction stoichiometry is



The reaction extent for each will be represented by  $x$ ,  $y$ , and  $z$ . These are the reaction moles in the forward direction. If the reaction is in the backward direction, the reaction extent will have a negative value. When acids and bases are added to water, the recombination of  $H^+$  and  $OH^-$  ions form water, the backward reaction dominates the water equation, and the value of  $z$  will be negative.

In this example  $a$  is the number of moles of acid in the 1 L sample, and  $b$  is that of the base. Here, the acid, water, and base provide  $x$ ,  $y$ , and  $z$  reaction moles, leaving  $a - x$  and  $b - y$  moles of the undissociated acid and base. The reaction set with after-equilibrium moles of each species indicated is

|        |                |
|--------|----------------|
| $HA$   | $(a - x)$      |
| $BOH$  | $(b - y)$      |
| $H_2O$ | $(\infty - z)$ |
| $H^+$  | $(x + z)$      |
| $A^-$  | $(x)$          |
| $B^+$  | $(y)$          |
| $OH^-$ | $(y + z)$      |

*Note: Really, there is not an infinite number of moles of water, but there is so much more than the  $z$  moles that dissociate that it can be considered unchanged in the reactions.*

*Note: This is termed an ICE table in chemistry. The initial I means initial concentration, C means change in concentration, and E means the after equilibrium concentration.*

The three equilibrium relations are then

$$K_a = \frac{(x + z)(x)}{(a - x)}$$

$$K_b = \frac{(y)(y + z)}{(b - y)}$$

$$K_w = (x + z)(y + z)$$

That represents three equations with three unknowns. Solution of those three equations will give values for  $x$ ,  $y$ , and  $z$ . Then  $(x + z)$  is the number of moles of  $H^+$  ions in the 1 liter basis, which is the  $[H^+]$ ; so the  $pH = -\log_{10}(x + z)$ . It would be easy to solve for  $x$ ,  $y$ , and  $z$  if the equation set was linear. But it is nonlinear. As a further problem, the robustness of the solution method can be very sensitive to trial initial values, and many classic approaches to root finding (like Newton's method) diverge when solving these relations.

Here, often diverse simplifications are chosen to simplify the solution. Although they may be valid for simple two or three component systems, they are not appropriate for more complex mixtures of several and multivalent species.

So, my solution [3] is to use interval halving with a trial  $pH$  value. With a guess of the  $pH$  value,  $pH_g$ , the definition of  $pH$  can be used to determine the Hydrogen ion concentration.  $(x + z)_g = [H^+]_g = 10^{-pH_g}$ . The water equilibrium relation then provides the consequential hydroxyl ion

concentration.  $(y + z)_c = [OH^-]_c = K_w/[H^+]_g = K_w 10^{+pH_g}$ . This leaves two linear relations for the two unknowns  $x$  and  $y$ , the consequence of the  $pH$  guess.

$$\begin{aligned}(a - x_c)K_a &= [H^+]_g(x_c) \\ (b - y_c)K_b &= (y_c)[OH^-]_c\end{aligned}$$

The subscript  $g$  means guess, and the subscript  $c$  means consequence.

*Note: In this case, the equations are wholly independent, as well as being linear in the unknowns.*

Each can be solved independently for  $x_c$  and  $y_c$ . Here

$$\begin{aligned}x_c &= \frac{aK_a}{K_a + [H^+]_g} \\ y_c &= \frac{bK_b}{K_b + [OH^-]_c}\end{aligned}$$

With  $y_c$  so calculated, the  $z_c$  response can be obtained from the  $[OH^-]_c$  consequence of the  $pH$  guess,  $z_c = [OH^-]_c - y_c$ . Finally, the response  $pH_c$  can be calculated as  $pH_c = -\log_{10}(x_c + z_c)$ . If the response  $pH$  is the same as the guess, you guessed at the right value. Probably the initial guess was not the right value, but probably the right value is between the  $pH$  extremes of -2 and 16. So, start with  $pH_g = 16$  and  $pH_g = -2$  and calculate the associated  $pH_c$  responses. Then use interval halving to search for the  $pH_g$  that is close enough to the root value that makes the  $pH_c = pH_g$ . Since  $pH$  measurements might have a 0.1 unit certainty, convergence on a change in  $pH_g$  of 0.01 is adequate. If the initial search range is 18, then interval halving will be within .01  $pH$  units or the true root after 16 trials (including the initial extremes).

This is a robust and computationally fast procedure. It presumes familiarity with two relatively simple numerical procedures (interval halving and solution to a system of linear equations).

When instructors feel that their audience might not have that numerical skill, they revert to one of many trivializations of the equations to simplify solution procedure.

## 5. Trivializations

Under the idealization that the monovalent (single hydroxyl) base and the monoprotic acid fully dissociate (that the back reaction in the equilibrium relation does not occur), then  $x = a$  and  $y = b$ . Further, if the components are pure in pure water at about 25 °C, and the water contributions to  $H^+$  ions can be ignored; then, if the acid is in excess,  $pH = -\log_{10}(a - b)$ . If the base is in excess,  $pH = 14 - \log_{10}(b - a)$ . This is reasonably true for HCl, the first dissociation of  $H_2SO_4$ , NaOH, KOH, the first dissociation  $Mg(OH)_2$ , and some other common compounds. But, it is not true in many more cases than those for which it could be a reasonable assumption.

If the acid and base are fully dissociated, but the ion production from water cannot be ignored, the water equilibrium then can be solved for the water dissociation extent using the quadratic

formula.  $z = [-(a + b) \pm \sqrt{(a + b)^2 - 4(ab - K_w)}]/2$ . Using the "+" root,  $pH = -\log_{10}(a + z)$ . The "-" root would imply that  $|z| > (a + b)$ , which not physically realizable.

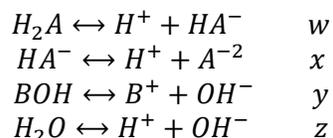
Alternately, the definition of  $pH$  can be inverted to determine the  $[H^+]$ . If the acid is fully dissociated then  $(a + z) = 10^{-pH}$ . If the water is in equilibrium, and the base is fully dissociated, then then  $(b + z) = K_w 10^{+pH}$ . Subtracting these two relations eliminates the  $z$  term.  $a - b = 10^{-pH} - K_w 10^{+pH}$ . This strong component trivialization is often used to calculate  $pH$  given concentrations of strong, monovalent acids and bases. As written, it is a nonlinear root-finding exercise. But it can be multiplied by  $10^{-pH}$ , solved by the quadratic formula to obtain  $pH = \log_{10} \left\{ 5 \left[ (a - b) \pm \sqrt{(a - b)^2 + 4K_w} \right] \right\}$ . If  $a \leq b$  use the "+" root. If  $a > b$  use the "-" root.

With a further idealization that the water dissociation is inconsequential in providing  $H^+$  ions, if the acid is in excess, then the  $[H^+] = a - b$ , and then  $pH = -\log_{10}(a - b)$ . Alternately this can be derived considering that  $K_w = 0$ . However, if  $b > a$  this approach cannot be taken.

I find this ideally strong acid/base assumption is often chosen by investigators. Although it simplifies the calculation, I believe it is generally indefensible. It does not extend to multi-valent ions, common-ion salts, multi-component solutions (such as dissolved  $CO_2$  which becomes carbonates), or the reality of acids and base partial dissociation.

## 6. Solving for pH – diprotic acid and monovalent base

This is a very similar procedure as in Section 4. First, choose the concentrations of your materials, and consider a unit volume of 1 liter. Then, the number of moles of each component in the basis volume has the same numerical value as the concentration. In the following three-component example  $a$  is the number of moles of acid, and  $b$  is that of the base. Here, the diprotic acid, water, and base provide  $w$ ,  $x$ ,  $y$ , and  $z$  reaction moles. The reaction set is



The after-equilibrium moles of each species indicated is

|          |                |
|----------|----------------|
| $H_2A$   | $(a - w)$      |
| $HA^-$   | $(w - x)$      |
| $BOH$    | $(b - y)$      |
| $H_2O$   | $(\infty - z)$ |
| $H^+$    | $(w + x + z)$  |
| $A^{-2}$ | $(x)$          |
| $B^+$    | $(y)$          |
| $OH^-$   | $(y + z)$      |

The four equilibrium relations are then

$$K_{a1} = \frac{(w + x + z)(w - x)}{(a - w)}$$

$$K_{a2} = \frac{(w + x + z)(x)}{(w - x)}$$

$$K_b = \frac{(y)(y + z)}{(b - y)}$$

$$K_w = (w + x + z)(y + z)$$

Now, there are four nonlinear equations with four unknowns. Again, my solution [3] is to use interval halving with a trial  $pH$  value. With a guess of the  $pH$  value,  $pH_g$ , the  $(w + x + z)_g = [H^+]_g = 10^{-pH_g}$ . The water equilibrium relation then provides the consequential hydroxyl ion concentration  $(y + z)_c = [OH^-]_c = K_w/[H^+]_g = K_w 10^{+pH_g}$ . This leaves three linear relations for the three unknown  $w$ ,  $x$ , and  $y$ , responses to the  $pH$  guess.

$$(a - w_c)K_{a1} = [H^+]_g(w_c - x_c)$$

$$(w_c - x_c)K_{a2} = [H^+]_g(x_c)$$

$$(b - y_c)K_b = (y_c)[OH^-]_c$$

*Note: The first two equations both contain the same two unknowns,  $w_c$  and  $x_c$ . This simple set of equations can be rearranged to isolate each variable, and then solved independently.*

$$x_c = a \frac{K_{a1}K_{a2}}{([H^+]_g^2 + K_{a1}(K_{a2} + [H^+]_g))}$$

$$w_c = a \left[ 1 - \frac{[H^+]_g^2}{([H^+]_g^2 + K_{a1}(K_{a2} + [H^+]_g))} \right]$$

$$y_c = \frac{bK_b}{K_b + [OH^-]_c}$$

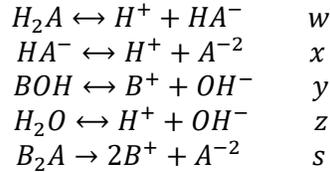
*Note: However, the sets of interactive relations increase with triprotic acids and trivalent bases. It may be more convenient to use a generic procedure for solving a system of linear equations, such as Gaussian Elimination, as presented in [3].*

With  $y_c$  so calculated, the  $z_c$  response can be obtained from the  $[OH^-]_c$  consequence of the  $pH$  guess,  $z_c = [OH^-]_c - y_c$ . Finally, the response  $pH_c$  can be calculated as  $pH_c = -\log_{10}(w_c + x_c + z_c)$ . If the response  $pH$  is the same as the guess, you guessed at the right value. Start with  $pH_g = 14$  and  $pH_g = 0$  and calculate the associated responses. Then use interval halving to search for the  $pH_g$  that is close enough to the value that makes the  $pH_c = pH_g$ . Again, starting with the -2 and 16 extremes, interval halving will be within 0.0022  $pH$  units of the root in 15 trials (13 intervals and 2 initial extremes).

## 7. Solving for pH – in more complicated systems

The procedure is the same. But, the system might have common ion salts, and the linear equations might not have as convenient rearrangement for a hand solution as above. However, even with a more complicated chemical system, with a guess of the  $pH$  and the  $[OH^-]_c$  consequence, the remaining equations are linear in the unknowns, and any linear equation solver algorithm will find the unique solution.

If common ion salts of the diprotic acid and monovalent titrant are included, the reaction set is



Note that salts are considered to be fully dissociated and in solution (not as precipitates).

The after-equilibrium moles of each species indicated is

|          |                |
|----------|----------------|
| $H_2A$   | $(a - w)$      |
| $HA^-$   | $(w - x)$      |
| $BOH$    | $(b - y)$      |
| $H_2O$   | $(\infty - z)$ |
| $H^+$    | $(w + x + z)$  |
| $A^{-2}$ | $(x + s)$      |
| $B^+$    | $(y + 2s)$     |
| $OH^-$   | $(y + z)$      |

The four equilibrium relations are then

$$\begin{aligned}
 K_{a1} &= \frac{(w + x + z)(w - x)}{(a - w)} \\
 K_{a2} &= \frac{(w + x + z)(x + s)}{(w - x)} \\
 K_b &= \frac{(y + 2s)(y + z)}{(b - y)} \\
 K_w &= (w + x + z)(y + z)
 \end{aligned}$$

Again, there are four nonlinear equations with four unknowns, and my solution [3] is to use interval halving with a trial  $pH$  value.

This procedure was benchmarked on a wide range of test cases with data from both laboratory titration experiments and commercial software [3].

Salt precipitates that have a common metal or acid ion create a nonlinear complication. This approach considers that all salts are totally dissociated, and do not precipitate.

Similarly, products of the neutralization reactions may produce a gas that exceeds its solubility in water (recall vinegar and baking soda volcanoes), which is not considered here.

Equilibrium constants are temperature dependent, and often also depend on pressure and other electrolytes that confound solvation by water. The approach here just uses nominal  $pK$  values. But certainly, one can perturb all givens (concentrations,  $pK$  values. I chose to just perturb the water  $pKW$  and  $pH$  sensor calibration error to generate alternate realizations of the resulting  $pH$ .

## 8. Calculating Concentrations for a Process Control Simulator

Material balances are fairly simple. What flows in, minus what flows out, is what accumulates.

$$In - Out = Accumulation$$

The acronym is IOA.

In a reaction system, one could include the internal generation (and depletion) in the balance. But, even though the dissociation and recombination reactions generate ions, and perhaps salts, since the reaction species are invariant (a Sulfate or Sodium component is the same whether it is in a compound or as an ion), only the nominal inflowing components (water, acids, bases, salts) need to be considered. More completely, this balance will often be  $I - O + G - D = A$ , with the acronym IOGDA, or more simply IOGA, a pronounceable Greek-sounding pretend letter.

We will first consider a well-mixed, continuous flow through, constant level tank, often termed a CSTR (continuous stirred tank reactor). Alternate acronyms are CFSTR (continuous flow stirred tank reactor) or CST (continuous stirred tank). A CST is considered to be perfectly and instantly mixed. As soon as a drop of something enters, it is considered to be instantly, completely, and uniformly dispersed throughout the liquid volume. The tank contents change in time, but are considered to be spatially uniform. In Section 9, this idealization will be relaxed to represent a nonideal mixer using dead zones.

We will also consider that there are no density changes or volume changes from the mixing. Like the use of activity coefficients, I find that this complication does not add to the realism of the simulator or the control investigation benefits, and the “improvement” by such scientific rigor is lost within industrial uncertainty of technical grade composition or material metering.

Typically, flow rates and concentrations are used to quantify the rate that material flows in or out, but the  $I - O = A$  equation above represents mass quantity not mass rate. If mass is measured in grams, then the I-O=A water balance on a vessel is:

$$\rho F_{in,t} \Delta t - \rho F_{out,t} \Delta t = m_{t+\Delta t} - m_t$$

Here  $m_t$  is the mass of water at the current time and  $\Delta t$  represents a small time interval.  $F_{in}$  and  $F_{out}$  represent the inflow and out flow during  $\Delta t$ , which is small enough to consider the flow rates constant during the small interval.  $m_{t+\Delta t}$  is the mass after a time interval of  $\Delta t$ . Dividing by  $\Delta t$ ,

and recognizing that in the limit of very small  $\Delta t$ ,  $(m_{t+\Delta t} - m_t)/\Delta t$  is the calculus differential  $\frac{dm}{dt}$ ; and assuming that density is constant and dividing by  $\rho$ , the mass balance becomes

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

*Note: Some people derive this by using a volume basis, but volume is not conserved, mass is.*

*Note: Some people derive this by using a rate balance, but I believe fewer errors are made if one uses mass in the I-O=A relation, not mass rate.*

If the level in the tank is unchanged, then  $\frac{dV}{dt} = 0$ , and the equation becomes  $F_{out} = F_{in}$ , which is the common basis for an ideal CSTR. If the process is a laboratory titration with titrant added to a sample, or an industrial tank batch being neutralized, then  $F_{out} = 0$ , and the equation becomes  $\frac{dV}{dt} = F_{in}$ .

The material balance for any component, such as an acid  $H_2A$ , is similarly derived from the I-O=A basis. Using the symbol  $n$  to represent moles of the component as a measure of mass in the vessel:

$$c_{in,t}F_{in,t}\Delta t - c_{out,t}F_{out,t}\Delta t = n_{t+\Delta t} - n_t = V_{t+\Delta t}c_{t+\Delta t} - V_t c_t$$

Dividing by  $\Delta t$ , and recognizing that in the limit of very small  $\Delta t$ , the numerical difference becomes the calculus differential

$$\frac{d(Vc)}{dt} = c_{in}F_{in} - c_{out}F_{out}$$

If volume is a constant (if  $F_{in} = F_{out}$ ) then this component mass balance becomes the familiar

$$V \frac{dc}{dt} = c_{in}F_{in} - c_{out}F_{out}$$

But, if volume changes such as in a titration, or when a process tank is batch processed, or in the process of filling, or when under active level control, then  $V$  is not a constant over time and the chain rule yields

$$V \frac{dc}{dt} + c \frac{dV}{dt} = c_{in}F_{in} - c_{out}F_{out}$$

If a closed batch, such as a titration, then  $F_{out} = 0$ , and with constant density, and with continuous inflow  $\frac{dV}{dt} = F_{in}$ , and with an initial volume  $V_0$ , the differential equation representing component concentration becomes

$$(V_0 + F_{in}t) \frac{dc}{dt} = (c_{in} - c)F_{in}$$

*Note: Although the initial consideration was for a diprotic acid  $H_2A$ , the inflowing and in-tank component could be an acid or a base of any number of protons or hydroxyls.*

*Note: The equations describing how component concentration changes in time are presented as differential equations. However, a simulator will use a numerical method to approximate a solution. I typically choose Euler's Explicit Method, and replace the differential with a forward finite difference, because it is simple, and (as long as the time interval is small relative to process time-constants) fully adequate.*

This model seems to consider that the acid or base does not dissociate or react, but retains its nominal concentration. However, the inflowing material is partly dissociated, as is the initial tank contents. It might seem that one needs to perform a mass balance on each species, on  $H^+$  from all of its sources, on  $OH^-$  from all of its sources, all of the  $HA^-$  sources, and  $A^{-2}$  sources, etc. Fortunately, tracking the reaction invariant species, the  $A$  of the acid or the  $B$  of the base, for instance, also accounts for the concentration of  $H^+$  or  $OH^-$  units whether dissociated or undissociated. So, just do a mass balance on each nominal molecular species – water, acid, base, and salt.

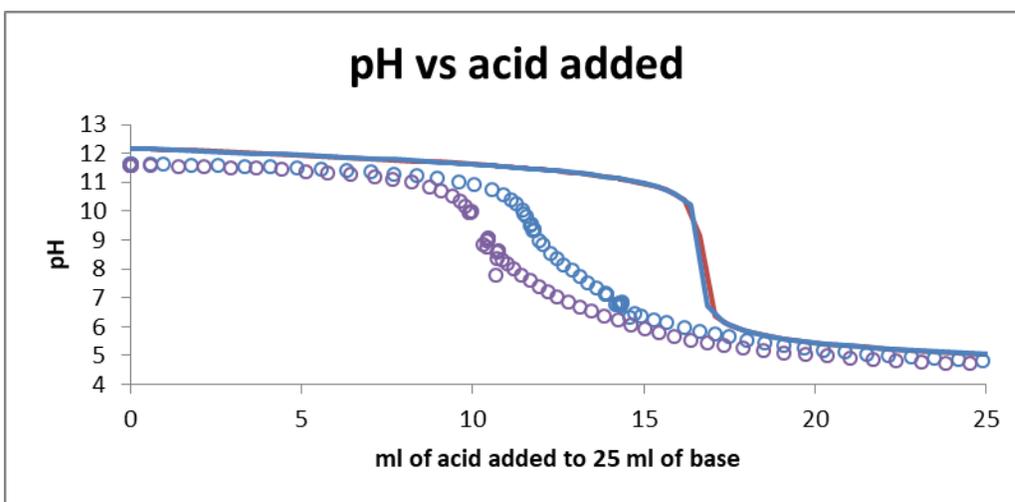
The material balances describe how species concentrations change in time. Normally, reaction equilibrium is much faster than the time scale for flow rates to change volumes or nominal concentrations, so once material balances provide concentrations, the thermodynamic equilibrium calculations of Sections 4, 6, or 7 will provide extents of dissociation and  $pH$ .

## 9. Reality in Simulations

This is the fun part:

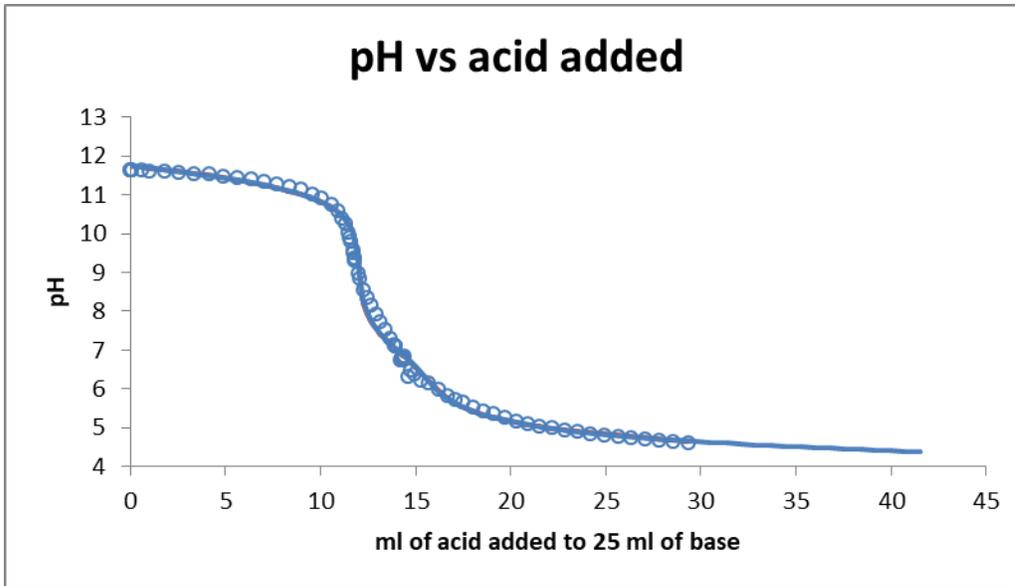
*Concentration uncertainty in lab:* If you wish to mix up a 0.1 N solution of NaOH, you would weigh out 3.999711 g of NaOH and top it off to the 1 L mark with water. But your scales might only be accurate to 0.001 g, which is a 0.025% error, and the volume may be uncertain by a similar amount. Propagation of uncertainty would indicate a 0.05% uncertainty in the concentration. But, wait! What is the purity of your NaOH? The jar might indicate 99.5%. So what you weigh may also contain  $Na_2CO_3$  or  $Ca(OH)_2$  as impurity. Further, your jar of NaOH pellets will probably have been opened many times, each time admitting moisture and  $CO_2$  from the air. Since solid NaOH is deliquescent, as you are weighing it, it is also actively absorbing moisture from the air. (A day later, a dropped NaOH pellet will absorb so much moisture that it will become a puddle of concentrated caustic.) Since it is basic it reacts with the  $CO_2$  in the air. So, what did you actually add to the water? And what is water? Fish breathe because  $O_2$  is dissolved in it.  $CO_2$  also dissolves in water and becomes carbonic acid. So, the water you used to make the NaOH solution also contains  $H_2CO_3$  which partly neutralizes the NaOH you added. The point is that, regardless of the concept of preparing a 0.1 N solution of NaOH in water, A) the concentration is not 0.1 N and B) the composition has more than those two components. If a researcher is wishing to use a simulation to reveal how wonderful one's controller is, one cannot pretend to be able to exactly know the composition of any fluid in a simulation. The simulator should add a random error to the nominal desired composition to convert it to the true value used by the simulator. Further the simulator should include additional components, not just the nominal ones.

This graph is from a senior-level chemical engineering lab experiment. The students made a 0.01 molar  $\text{Ca}(\text{OH})_2$  solution in water and titrated 25 ml of it with a 0.03 molar acetic acid solution. The water was reverse-osmosis water, and the acid and base materials were normal laboratory reagent grade. The two separate traces reveal independent titrations with independently formulated solutions. Note that the neutral points (at  $\text{pH} = 7$ ), were at titrant volumes of about 12 and 14 ml. The separation in the replicate traces, and the contrast with the expected 16.7 ml of the monoprotic acid to neutralize the divalent base are indications of composition variation in normal laboratory practice. The solid line is the ideally calculated  $\text{pH}$ . Note that it has a steep slope at  $\text{pH} = 7$ , and shows 16.7 ml for neutralization.



The non-steep slope of the data in the near-neutral region could be from  $\text{CO}_2$  dissolved in the water.

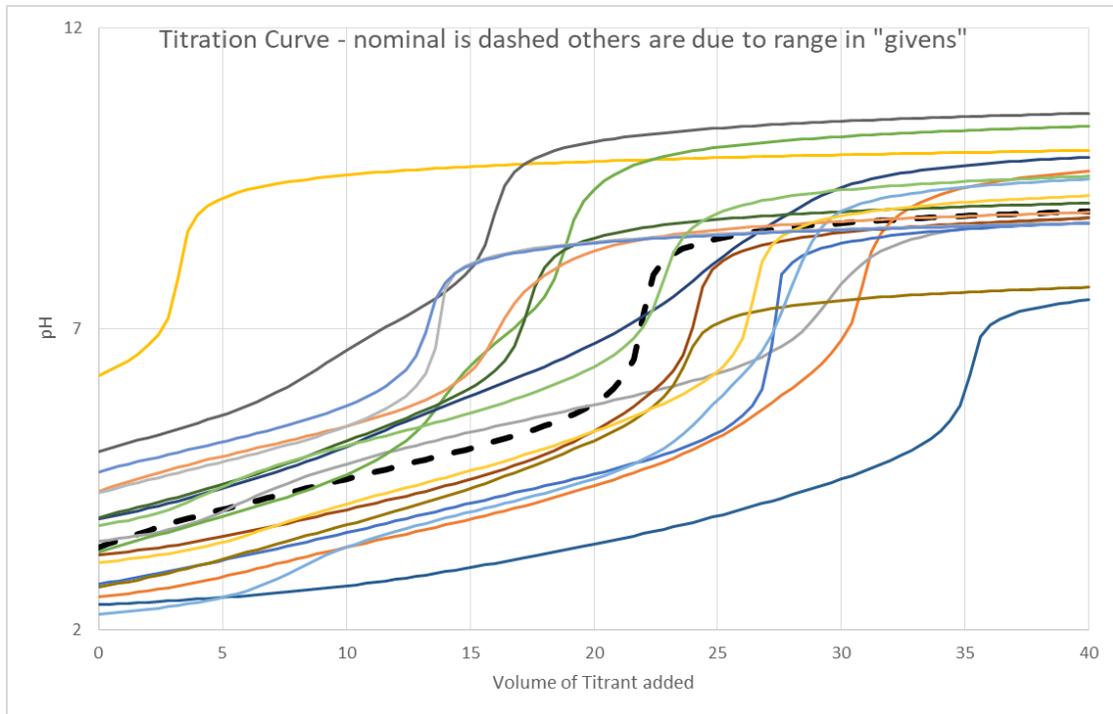
Letting an optimizer choose acid, base and dissolved  $\text{CO}_2$  concentrations; a best fit to the upper of the two titrations indicates a caustic concentration of 0.0095 molar, an acid concentration of 0.029 molar, and a dissolved  $\text{CO}_2$  concentration of 0.005 moles/liter. The optimizer also adjusted the water, base, and acid equilibrium constants from the book-values. Adjusting all values partly accounts for other impurities that were in the materials, experimental temperature effects on equilibrium constants, and the attempt to model the data jointly (not each trace individually). I used Akaho's approach to estimate normal deviations (a maximum likelihood concept, as opposed to vertical least squares) and a simple heuristic cyclic direct search as the optimizer [4, 5]. The graph is below.



Even with the flexibility of the model to adjust concentrations and coefficients, and to include  $\text{CO}_2$ , the model does not capture the entire functionality of the data. The model is still steeper in the  $pH = 9$  range than the data, which indicates the model is missing some impurity, or several that were present in the acid, base, or water. The bottom line is that the above replicate graphs and the best fit model to one titration, reflect normal engineering laboratory practice. Undoubtedly laboratories with best scientific precision would result in more consistent data. But, industrial practice is even coarser.

*Concentration of industrial caustic:* Industrial  $pH$  control of an acidic mixture does not use 0.01 N NaOH. It uses 40 wt% caustic (technical grade NaOH concentrate in water). Or perhaps technical grade solid lime. But, these also have batch-to-batch composition variation and a plethora of impurities, some active, some not. Like the lab sample preparation, there is composition uncertainty about industrial grade reagents. But, the uncertainty is even greater in industrial practice than laboratory practice. Again the simulator should add a random error to the nominal composition, should include additional components, and should reflect control application practice of 40% caustic. One might think that the concentration of the caustic is irrelevant, if one is in a continuum or double precision frame of mind, but that is not so. Read on.

Here is a graph of titration curves with inflow composition perturbations about the nominal that might represent industrial wastewater as upstream processing discharges would affect composition, and electrolyte interactions and temperature might affect  $pK$  values. (Consider your household wastewater as pickle-jar vinegar and bleach cleaners are separately flushed down the drain.) The thick dashed curve is the nominal titration curve, and the others represent realizations.



*Note: One of the 19 random realizations indicates that a titrant volume of about 2.5 ml will neutralize the water, and another indicates that about 36 ml is required. Here the range of neutralizing caustic flow rates has about a 15:1 range, which exceeds standard industrial flow metering devices. With greater number of realizations, the range is higher. And, compounded with inlet flow rate changes in the acidic mixture to be neutralized, the required caustic range is even higher. A 30:1 range of required caustic flow rate is not unusual. Accordingly, large tanks are used to temper upstream composition effects, so that the blended in-tank material does not exceed reagent metering precision. And high and low flow range valves or pumps may be used in parallel to meet the low flow precision and high flow capacity. Alternately, especially when the waste is mainly unbuffered strong acids, the waste stream may run through a series of tanks, with the pH progressively adjusted toward neutrality.*

*Note: At neutrality the slope of these curves, the sensitivity of pH to titrant volume, which is the process gain, ranges from about 0.2 to 2. With more realizations, representing what comes over time to be neutralized, the gain at neutrality could have a 50:1 change. This makes control difficult. Again, industrial practice uses large mixers or a sequence of mixers and progressive neutralization to temper the composition excursions.*

*Note: When neutralization is the control objective, or pH control to a target needed for product specification or reaction control, and the control keeps pH near to the pH target, it is not the gain change over the full range of a particular titration curve that is important. It is the variation in gain in the vicinity of the pH set point. However, I find that researchers often consider the gain change over the full range of a nominal titration curve to reveal the nonlinearity. That is a valid view if a batch is being taken from an initial pH to a final one, in distinct stages, and in that case, the experimental or simulation should be for batch neutralization. However, for CST processes, the more important gain aspect is that of the time variation of pH sensitivity at neutrality.*

*Discharge or hold:* At neutrality the  $pH$  is that of water, nominally 7 (but it ranges from about 7.5 at the ice point to about 4 at 500 °C). Nominally, acids and bases are neutralized when the  $pH = 7$ , and discharge is often permitted when  $6 < pH < 9$ . The range depends on your locale and its local natural conditions. If an acidic wastewater is being neutralized prior to discharge to the environment, or to a biological treatment pond, and the  $pH$  is outside of the permissible range, then discharge needs to be stopped. This requires a tank or other sort of inventory capacity to hold the accumulating liquid until  $pH$  can be adjusted within limits. Then discharge can continue.

Your simulator should stop effluent flow when out of specification. However, accumulation must have a limit of the tank capacity, and when full, it must discharge some of the off-spec material. The quantity and  $pH$  violation of the material is a key measure of controller performance.

*Neutrality is not the equivalence point:* The equivalence point means that the number of  $H^+$  ions that could be released by the acid is identical to the number of  $OH^-$  ions provided by the base. It means stoichiometric equivalence. If the acid and base are both monovalent this means that the product of volume and concentration are equivalent.  $V_A[A] = V_B[B]$ . But, if either has a  $pK$  value in the near neutral range, then it is holding onto some of its ions, and at equivalence the  $pH$  will not be neutral. If neutralized, there could be excess base or acid capacity, and when discharged and diluted, those ions could be released shifting the  $pH$ .

*Discrimination ability of metering:* Your controller might be using double precision variables in its calculation. It might have a truncation error of any variable of  $10^{-10}$  parts. As a concept, the final element can have an infinite number of positions, a continuum of positions, between fully open or closed, but with the double precision calculation, it could only have  $10^{+10}$  possible values. However, in a control system, the current-generating device that sends the signal out of the controller might be a 12-bit device with only 4096 possible states, but effectively between the nominal 4-20 mA range, only 3,300 possible values. The i/p device might only be able to output 1,000 different P-values within the nominal 3-15 psig range. If the valve were not limited by sticktion, this would mean that there are only 1,000 possible flow rates between closed and fully open. The 1,000 possible flow values might represent best industrial practice. Then, if a nominal required flow rate is 10 L/min, and the valve is sized to provide double that as a maximum flow rate, then at the nominal flow rate of 10 L/m the smallest incremental change is .02 L/min. If the caustic is 10 normal and neutralizing 1,000 L/min of 0.1 N acid, then at neutrality the smallest incremental change in base concentration causes a 0.00011 error in acid or base excess, which is roughly a 4 to 10  $pH$  error. Don't think that your control system can implement what your computer can calculate. At least, simulate a discrimination of  $1/1000^{\text{th}}$  of what would be the ample flow rate range.

*Flow rate uncertainty:* if one knew the flow rate of an incoming acid, as well as the composition of inflowing acid and composition of the titrant to neutralize it, one could calculate the flow rate of the titrant needed to neutralize the acid. But, since the flow meter on a process line might have a 5% to 10% calibration error and noise on the measurement, the flow rate might easily have a 10%, or greater, uncertainty. One cannot know the true flow rate value of a process. If a researcher is wishing to use a simulation to reveal how wonderful the controller is, one cannot pretend to be able to know the flow rate in a simulation. The simulator should add bias and noise to convert the true flow rate to the measurement that would misdirect an ideal control calculation.

*Dynamics in metering:* The control concept is that the controller changes the flow rate of titrant. But, if a controller decides to instantly and totally shut off flow rate how does it do it? It cannot, as you cannot instantly and totally shut off a spigot. You need to turn the handle about 5 turns before the inner orifice is closed and flow stops. Even then, water in the spigot drips out 'til the exit line is empty. Conventionally, a controller sends an electrical signal to an i-to-p (i/p, current to pneumatic) device, which admits or exhausts air to a pneumatic line coupled to a volume in the valve actuator. As the air pressure rises or falls, the force on a flexible diaphragm in the actuator presses against a spring to make the inner orifice begin to open or close. The air pressure cannot instantly change. Typically, the valve opens or closes in a first-order manner with about a 1 second time-constant. If the final element is a variable speed pump, it might have a similar lag. Don't pretend that your controller can instantly change the flow rate. If process time-constants are on the order of ten seconds or less, include the final element lag in the simulation.

*Complexity of industrial inflows and process fluid:* Everything is in wastewater. It ranges from the weak acids in kitchen and lavatory waste to the strong acids and base discharges from periodic ion exchange resin regeneration, and hundreds of other sorts of sources. The sources intermittently discharge, so that the process streams can have substantial time-variation in both total acid content and the weak-strong nature of the acids. Cooling tower water has carbonates, and pollen, and algae, and all of the anti-corrosion, anti-biotic and *pH* control chemicals that are imaginable. Cooling tower or other process water might start fairly clean, but as it recycles to the evaporators, it progressively acquires and concentrates new components. Lemonade concentrate, tomato juice, and many such food products are made from natural materials with batch-to-batch variation, and they need to have acidity controlled prior to packaging. The bottom line is that *pH* control is not applied to simple, two-component systems. Your simulator should A) include a rich assortment of components, B) that change composition substantially in time, and C) the composition (both components and concentrations) of the simulator cannot be known by the controller.

*Measurement lags, noise, and error:* The *pH* sensor necessarily has a lag as the  $H^+$  ion concentration within the detector equilibrates with that in the process fluid on the other side of the glass membrane. The simulator might calculate the instantaneous process fluid *pH*, but the measurement will have a lag of about a 1 sec time-constant. Further, if fluid mixing were ideal, then at steady state the  $H^+$  ion concentration at the sensor would be constant, but the reality of mixing is that mixing is not ideal, and  $H^+$ -rich and  $H^+$ -diminished packets of fluid randomly pass by the sensor, causing *pH* measurement variation. The noise should be based on perturbing the  $H^+$  ion concentration, but often simulators add noise to the *pH* measurement. Composition variation may have little impact on *pH* near the 3 or 11 values, but it could have a substantial impact near neutrality, unless there are buffering agents with *pK* values in the 6.5 to 7.5 range. Adding noise to the *pH* measurement is better than nothing, but adding  $H^+$  ion concentration variation to the sensor is better. Finally, when *pH* sensors are in working order, they have a calibration bias. Often they are in the beginning of a failure mode. So, if the sensor is reporting *pH* = 7, making everyone happy, the *pH* might actually be 6. It is not unusual to install three *pH* sensors and use the middle value of the three (a procedure termed voting) as the signal to the controller.

*Dead zones in mixing:* A mixer cannot instantaneously blend all of the fluid contents with the fluid that flows in to it. There are zones of concentration which might be layers or rings. Further, there are baffles that break the mixing vortex, with dead zones behind the baffles. There are dead zones

in tank ridges and sample and drain ports. One simple approach to modeling a nonideal CST is to consider a single dead zone volume that has continual material exchange with the ideally mixed contents. The dead zone might be in several places or it might be several levels that progressively exchange material. Regardless, the simple nonideal concept is to have one dead zone of a smallish volume  $v$  relative to the overall volume  $V$ , and the main active volume of the CST as  $v_a = V - v_{dz}$ . The dead zone and the main mixing zones are both considered CSTs with a flow exchange between them. If they are of constant volume, the material balances for each component become

$$v_a \frac{dc_a}{dt} = c_{in}F_{in} - c_aF_{out} + (c_{dz} - c_a)F_{exchange}$$

$$v_{dz} \frac{dc_{dz}}{dt} = (c_a - c_{dz})F_{exchange}$$

My simulator considers that the dead zone volume is constant, but that the active volume will change with liquid inventory. Accordingly (with constant density)

$$\frac{dv_a}{dt} = F_{in} + F_{caustic} - F_{out} + F_{exchange} - F_{exchange}$$

$$v_a \frac{dc_a}{dt} + c_a \frac{dv_a}{dt} = c_{in}F_{in} - c_aF_{out} + (c_{dz} - c_a)F_{exchange}$$

$$v_{dz} \frac{dc_{dz}}{dt} = (c_a - c_{dz})F_{exchange}$$

Which reduce to

$$\frac{dv_a}{dt} = F_{in} + F_{caustic} - F_{out}$$

$$v_a \frac{dc_a}{dt} = c_{in}F_{in} + c_{dz}F_{exchange} - c_a(F_{in} + F_{caustic} + F_{exchange})$$

$$v_{dz} \frac{dc_{dz}}{dt} = (c_a - c_{dz})F_{exchange}$$

Numerically, with the Euler's Explicit method these become a rectangle rule of integration for the volume

$$v_{a,new} = v_{a,old} + \Delta t(F_{in} + F_{caustic} - F_{out})$$

And classic ARMA(1,1) models for the concentrations.

$$c_{a,new} = (1 - \lambda_a)c_{a,old} + \lambda_a(c_{in}F_{in} + c_{dz,old}F_{exchange})/(F_{in} + F_{caustic} + F_{exchange})$$

$$c_{dz,new} = (1 - \lambda_{dz})c_{dz,old} + \lambda_{dz}c_{a,old}$$

Here

$$\lambda_a = 1 - e^{-\Delta t(F_{in} + F_{caustic} + F_{exchange})/v_a}$$

$$\lambda_{dz} = 1 - e^{-\Delta t(F_{exchange})/v_{dz}}$$

*Controller Model(s) cannot be the same as the simulator:* Whatever you decide for your model of the real world, it is wrong. You cannot know the truth about Nature. So, don't use a controller model that is exactly the same as the model of the process simulator. Be sure that there is functional mismatch and coefficient mismatch.

*Scientific Precision:* This monograph, along with most of the engineering literature, does not include activity coefficients, volume change upon mixing, detailed reaction pathways, or similar aspects of scientific rigor. If the objective is a process control simulator, the many uncertainties in a model about the real process (just in compositions and flow rates) far exceed any attempted improvement that could be added by thermodynamic or reaction kinetic rigor. So, don't view the opportunity of adding a bit of rigor as a way to claim you are adding value to the literature.

## 10. Evaluating Controller Performance

There are several aspects that need to be considered when evaluating controllers. One is the design of the tests, and the other is the criteria used for comparison. First, test design:

### *Test Design*

Test the controller for regulatory control, not set point changes. *pH* control rarely would have set point changes. Optimum conditions for reactions, regulatory specifications, product acidity requirements, etc. do not change in time. The major aspect of control is the regulatory response to keep *pH* on target as the environment or disturbances require. So, don't demonstrate the quality of your controller on set point changes, or tune it based on response to set point changes. Use regulatory measures of goodness for tuning and evaluation. For instance assess magnitude and duration of *pH* upsets as unmeasured disturbances affect the process, as opposed to overshoot or settling time response to set point changes.

Design environmental upsets to mimic what Nature would use to taunt the controller. Sources of waste water turn on and off, independently of each other, and in-line mixing of collection lines upstream of the neutralization process smears the on-off of acids and bases to a lag-like trend at the neutralization tank. In natural material processing, such as maintaining acidity of tomato juice or lemon concentrate, batch to batch sources contain varying levels of acidity that need to be adjusted in-process. At any time the concentration of materials in the process might be zero to double of the nominal values, and each component will be independent of the others.

Include noise, calibration drift, and digital discretization to any measurement that might go to the controller. No measurement is perfect. There are many sources of noise (mechanical vibrations, electronic interference, flow turbulence, mixing imperfection). Noise is an independent perturbation at each sampling. Calibration is never perfect, and has long term changing drift. And although the concept for numbers is that they represent a continuum of values, digitization discretizes them to perhaps only 1,000 values within the nominal range.

So, run the controller in the regulatory mode on enough realizations of inflow conditions and transitions to represent the entire population of possibilities. I've been using 100 runs of 1,000-

minute simulation times with new influent conditions on the hour. With 16 randomized changes each of the 100 runs, this is 16,000 randomized events in the controller assessment.

#### *Assessment Metrics on Process Data*

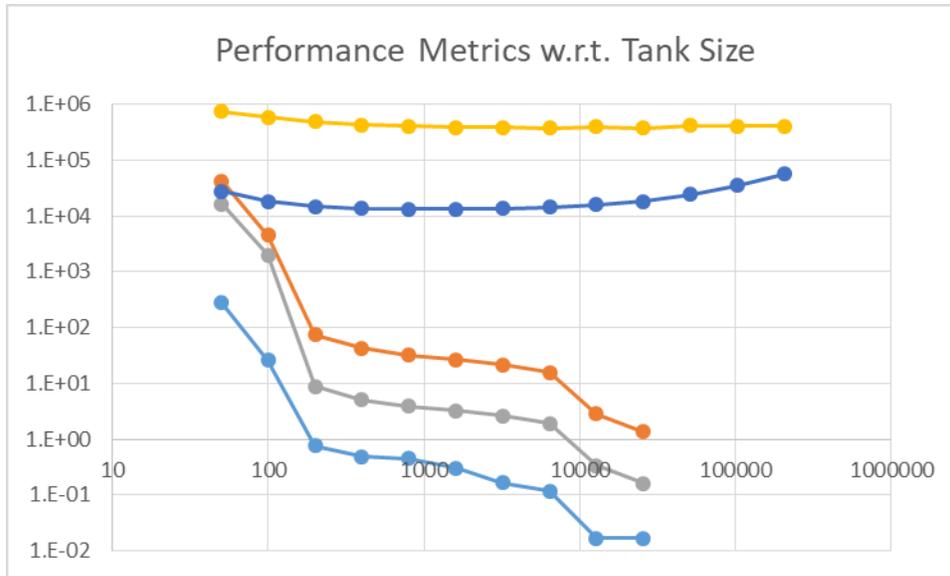
Traditional key regulatory control metrics might be ISE or the duration of *pH* excursions beyond upper and lower limits. Certainly, CV measures of closeness to *pH* set point, such as integral of the error (IE) or integral of the squared error (ISE) as the process influences change composition and flow rate, could be used as measures of goodness of control. A perfect controller would instantly exactly match the caustic addition to match the needs of the influent as it is diluted, and ISE would have a value of zero.

But, any controller that keeps the *pH* or the discharged material within specification over the range of influent variations (composition, temperature, flow rate) and other environmental effects (calibration error, delivery discrimination, measurement noise) is as good as one that is perfect. If there are no discharge violations, considering that functionality, an ISE of 0 does not beat an ISE of 500. The key controller performance metrics would be the quantity of discharge that exceeds the specifications and the magnitude of *pH* violation. I use quantity of material times its *pH* violation. Other metrics would be the frequency or duration of time in the proximity of needing to discharge off-spec material.

Certainly, classic CV metrics such as ISE are not wrong to assess, but these remain secondary to discharge violations in a real setting. Similarly, an often overlooked control objective is the desire to minimize changes to the manipulated variables, so you might also consider calculating travel (the sum of absolute value of changes to the MV) or energy (the sum of the squared value of changes to the MV). As an MV metric I decided to count the time that the discharge solenoid changes from open to closed, representing wear and shock to the processes.

So, for evaluating your controller, run the simulator for a long enough period of time to test it for regulatory control for a comprehensive (complete) range of influent conditions and environmental effects, and enough time at all conditions to be able to assess performance.

The performance of a controller is strongly dependent on the choice of tank size. Here is a graph of several performance metrics w.r.t. tank capacity (Liters) on a log-log scale. Traces from the top down represent the number of times the solenoid changes from open to closed, ISE, the cumulative volume of discharge in violation, that volume times the *pH* violation, and the cumulative time duration of any discharge violations.



The curves that stop at a tank size of about 25,000 L have zero values for higher tank sizes (no discharge events) which cannot be plotted on a log scale. Each data point represents the cumulative of 100 runs, each with 1,000 simulated minutes and 16 randomized influent changes (hourly) in each run.

#### *Assessment Metrics on Economics*

This aspect, fundamental to business, industry, society, or whatever political-economic organization is managing the process is usually wholly ignored by the research community. You do not buy the fanciest high-tech car. You buy the one that best balances function and desires with initial cost and annual costs. Industry uses the same values. A very large tank permits accumulation of out of spec material and gives the controller time to get an excursion neutralized. This could eliminate the penalty associated with discharging out-of-range material, but the larger tank costs more. The penalty for out-of-range discharge could be its upset to the process unit waste treatment facility, recycle of material, down-graded product, or it might be associated with a fine for discharge. In any case the magnitude and probability of a penalty is proportional to the quantity,  $Q$ , and magnitude,  $e$ , of discharge violations.  $\text{Penalty} = c \sum Q_i e_i$ .

The initial installed cost of a tank is roughly proportional to the tank capacity to the 6/10<sup>th</sup> power, and subsequent annual maintenance and depreciation is proportional to that. So, one could consider that the lifetime cost of the tank is proportional to the tank capacity to the 6/10<sup>th</sup> power.  $\text{Annual cost} \cong c(V)^{0.6}$ .

As a for instance, if one tank costs \$100,000 over a process life, and results in zero discharge events, and another smaller tank has a \$50,000 cost and results in a lifetime discharge penalty of \$1,000, then, effectively it costs \$51,000 and is the better decision. One could choose a large tank size and, using traditional CV metrics, demonstrate that control is perfect. But that ignores the whole context of the situation.

In any particular application case, the factors for the costs are situation dependent, but since they remain proportional to  $\sum Q_i e_i$  and to  $(V)^{0.6}$  one could compare controllers by graphing  $\sum Q_i e_i$

w.r.t  $(V)^{0.6}$  for a wide range of tank capacity,  $V$ , choices. In a Pareto Optimal manner, the better controller would be the one with non-dominated values.

Here is a graph of that for a more- and less-aggressive controller. The tank capacities range from 50 L (least expensive, but wholly inadequate) to 204,800 L (13 doublings larger). The smaller tank is in the upper left of the two curves, and markers represent a doubling of the size. The horizontal axis is proportional to volume to the 0.6 power, which represents lifetime cost of the tank. The vertical axis is the 4<sup>th</sup> root of the  $\sum Q_i e_i$  penalty, representing the economic undesirability of the system. I chose to use the 4<sup>th</sup> root for visual presentation. Doing so preserves the relative position of the dashed and solid curves. Often the log scale is used to compress very large data, but since some of the values are zero, I chose the 4<sup>th</sup> root. The two curves represent the same controller but tuned differently. Controller 1 is the solid curve, and the dashed curve represents the same controller with half the gain. Note that the solid curve dominates the dashed curve (for any volume, the marker on the solid curve is better or equal to the marker on the dashed curve). The axes are not cost, but represent scaled cost. Scaling by whatever is the appropriate factor to translate size or magnitude of violation to a cost will not change the relative position of the data.



Owners of some application may decide that no discharge events are permissible, while those of another may choose that a different balance of operating cost and penalty is best. As a researcher, we can speculate about which is which. But regardless, the controller of the solid curve beats that of the dashed curve: For any lifetime cost (lower axis) the one controller has lower penalty cost than the other.

As a final practical issue, consider ranking of controllers w.r.t complexity, modeling effort, tuning and setup, and cost of measurements needed. Many “better mousetraps” never become accepted by the customer because they are too confusing, difficult to use, etc. Just because a PhD candidate devises a glorious integration of the latest fashions in academic research literature, which leads to publication acceptance and earning of a PhD, does not mean that it will have any practice acceptance. You make purchase decisions all the time. Apply the same criteria that you use in your personal life to assess the desirability, and customer acceptance, of your controller.

### *Control Dos and Don'ts*

Do not use set point changes as tests. Use regulatory control.

Do not design the one (or few regulatory) tests to match what your controller is good at doing. Design challenges that represent the whole confluence range that Nature might provide.

Do not pretend that your controller can know the properties of the inflowing or reagent material, or the mixer volume, or the calibration error on any measurement device. Be sure to have reasonable model mismatch between controller and simulator. You cannot know the truth about Nature.

Do not use diluted reagent to demonstrate how your controller might be the world's solution. It would be good to use lab-like concentrations to compare your simulation to lab-scale experiments. But, don't pretend that study provides a credible message to the practice community.

Don't pretend that your experiment is comprised of *HCl*, *NaOH*, and water, just because you (and many others) chose to use those materials for experimental demonstration. There are impurities in each reagent, there are salts and dissolved gases in the water, and any exposure of the caustic to air permits it to absorb both humidity and  $CO_2$ . Except for precisely controlled science preparation protocol experiments, you probably have such confounding effects. My lab-scale experiments seem to have carbonic acid from dissolved  $CO_2$ , at concentrations in the 0.005 molar range, which provides a substantial buffering at its second dissociation  $pK_a$  of about 6.7.

Include a start-up period. Control does not start with a fully under-control process. For wastewater, I start inflow to the neutralization tank, then when there is adequate volume (about 1/5<sup>th</sup> of the tank capacity), I start the neutralizing reagent. When the tank is about 40% full, and  $pH$  is within limits, I permit the out flow to keep it at about that level. Otherwise material accumulates in the tank. The 40% level set point provides a volume for mixing to temper concentration changes, and 60% capacity to accumulate material if needed.

Include the level changes due to stopping the outflow when  $pH$  is out of specification. Just because you were taught how to model ideal CST reactors in class does not mean that volume remains constant.

In my simulator, the run time is about 2-shifts duration (1,000 minutes). It starts with a partially filled tank and inflow of the nominal composition as set by the user. When the in-tank material is within  $pH$  limits and over 40% full, discharge begins. Periodically, the composition and flow rate are randomly changed to values within a 2:0 range of the initial, and the  $pK_w$  value within a reasonable range of 14. There are 100 trials to provide 100 realizations of the randomized upsets, which seems enough to have replicate consistency. The sensors all have a disturbance and noise.

## 11. Simulator Description

The file “pH Process Simulator 2018-11-12.xlsm” provides the code to perform the calculations. It uses Visual Basic for Applications (VBA) as the macro (programming code). You’ll probably need to click on the “Enable Macros” button when you open the file.

Enter nominal influent properties (concentrations and  $pK$  values) in the green highlighted cells in the upper left of the worksheet, and the process tank volume in Cell(1,13). In the upper left conditions, b3 is the concentration of the titrating reagent, but the process uses a 5 mol/L concentration of the caustic. The program simulates the controlled pH process as well as providing the titration curves of the inflowing process fluid. Because the process neutralization and titration only use caustic, you need to choose the concentrations of the other compounds to make an acidic mixture.

The symbol a1 means the first diprotic acid, and a2 the second diprotic acid. The symbol a3 represents the third, monoprotic, acid. Similarly, b1 and b2 represent the first and second divalent bases, and b3 is the monovalent base used for titration or neutralization. The symbols sa1b1 and sa2b2 are salts of acid 1 and base 1 and of acid2 and base 2.

When you press the “Titrator” button, the code provides the titration curve of the a1, a2, a3, b1, b2, sa1b1, and sa2b2 sample in the volume of Cell(11,3) with the titrant b3 concentration of Cell(8,3). Note: b3 is not in the sample to be titrated. The titration code calculates the acid equivalents of the mixture to be titrated then specifies a base reagent volume three times the equivalent volume. It then adds the base in 100 increments to reveal the titration curve on the graph titled “Influent Titration”.

The code is written in VBA. If you want to translate it to your preferred computing environment, you can open the VBA editor to read the code. Press ALT-F11 (on my keyboard it is FN-ALT-F11) or use the “DEVELOPER” menu item then the “Visual Basic” icon. I provide a primer on VBA, which you can access on my web site, [www.r3eda.com](http://www.r3eda.com). Click on the “ABOUT” menu item, then “Software”, which provides a link to download my 8-page introduction to programming in VBA.

The button “Process Simulation” starts the process, using a very primitive controller. You can add your own to the code, or translate the simulator to your preferred environment. The Main subroutine initializes the process then sequences between Events, Process, Measurement, Control, Evaluate, and Data\_Out subroutines. The tank is initialized being 20% full of the un-neutralized a1, a2, a3, b1, b2, sa1b1, sa2b2 mixture that you specify on the work sheet. The calculations start with that state, and an inflow of 100 L/min of the same material. The process is simulated for a period of 1,000 minutes, with a 1 minute time discretization for process updating and control. With a tank volume of 10,000 L which is 40% full, the time-constant is about  $.4 * 10,000 / 100 = 40$  minutes, which is 40 times greater than the  $\Delta t$  of the numerical simulation. If you choose much smaller tank sizes you will need a smaller time discretization for the process. A rule of thumb is that the discretization should be 5 to 10 times smaller than the time-constant.

The Events subroutine periodically changes the inflow composition and flow rate and lags the concentrations and flow rate to the new values. Also, to mimic the effect of temperature, electrolytes, and organics in the material on the  $pK$  values, the water ion product,  $pK_w$ , is also

randomly perturbed about the 12 to 15 range. Presently, the subroutine is set to make changes each simulated hour, and lag with a 10 min time-constant. The changes are randomly chosen to be zero to twice of the nominal values you chose. It is possible that a random perturbation could lead to an inflowing  $pH$  that is above the discharge limit, so randomization is repeated until the inflowing  $pH$  is below 9.

The Process subroutine then uses material balances to adjust the volume and compositions in both the active and dead zones using the inflow acidic mixture and caustic and outflow values. After calculating the new composition in the active zone, Process calls the  $pH\_Calculator$  subroutine to determine the  $pH$  of the active zone. The Process subroutine starts with taking the targets for the caustic inflow and the discharge out flow and lags those to the target values to simulate the dynamics of the final flow elements.

The subroutine Measurement adds noise and calibration drift to the measurable items of influent flow rate, caustic flow rate, and  $pH$ . This simulates reality. You cannot know the truth about Nature, only what the fallible sensors report. It does not lag the sensor data. In reality sensors and final elements have a lag of a few seconds, which is effectively instantaneous on the process time scale.

Now the subroutine Control can choose both the caustic inflow and discharge outflow rates. My subroutine uses very simple heuristic logic, expressed as conditionals. For the caustic inflow rate: If the  $pH$  is above 7, turn off the caustic addition. If a little below 7 use a little caustic flow rate, and if a lot below 7 use a high caustic rate. The caustic rate is actually calculated as a ratio of the inflowing rate. Certainly the same logic could be expressed in many other rule formats (fuzzy, logistic equations, etc.). Or, it could be PID based or model based. You make it yours.

In addition to  $pH$ , tank volume needs to be controlled, and discharge is only permitted when the  $pH$  is within the range of 6 to 9. The discharge rule seeks to keep the tank about 40% full and only discharge if the contents are within the permissible  $pH$  range. Initially, the tank is acidic and 20% full, so the out flow is kept at zero until both volume and  $pH$  are within range. If the volume is greater than 40% full and  $pH$  is out of range the outflow is kept at zero until the contents are neutralized. The discharge flow rate is smoothly lagged to a target. One cannot instantly discharge all excess material. The nominal 40% volume target provides two features: 1) a large volume for mixing dilution to temper inflow pulses and changes, and 2) capacity to accumulate off-specification material until it can be neutralized. However, if the tank is full, and  $pH$  is not within range, then out-of-specification material must be released (the tank overflows). In this case, minimal material is released, just to match the inflowing material volume, not to attempt to return the tank to 40% full. To minimize any discharge events the tank has two valves, an on-off solenoid valve and a flow control valve. If the  $pH$  is out of range the solenoid permits an immediate shut off, otherwise it is open and a flow control valve adjusts the discharge outflow rate.

Now the Evaluate subroutine can calculate goodness metrics. I count the number of times the exit solenoid is closed, the time duration of discharge events, and sum the volume of material discharged and a  $pH$ -violation-weighted volume. I also sum the squared  $pH$  deviation from set point to calculate the ISE.

The Data\_Out subroutine writes the data to the worksheet. The graph "Effluent pH and Caustic Flow Rate" reveals the main CV and MV trends in time, and the graph "Tank Volume and Flow Conditions" show volume, inflow rate, and outflow rate. After each 1,000-minute run, the goodness of control metrics are written in Rows 3-6 of Column 13.

The 1,000-minute simulation has  $1000/60=16$  random influent changes, startup and 16 disturbances. This is not enough realizations of influent conditions to be statistically confident in the assessment metrics. So, the Main subroutine actually runs 100 trials of the 1,000-min simulation, which reveals the impact of 1,600 realizations. Rows 3-6 of Column 14 sum the goodness of control metrics over all trials, and provide a more consistent assessment of controller performance.

Yes, feel free to change the program to better suit your application: Change the range of influents that could be used for a testing basis (concentrations and pK values). Change sampling interval and events, and impact of sampling interval.

## 12. References

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