Myths about pH and pH Control

T. K. GUSTAFSSON and
K. V. WALLER

Process Control Laboratory
Department of Chemical Engineering
Åbo Akademi
20500 Åbo, Finland

INTRODUCTION

pH is a difficult and confusing concept. It is often mistakenly treated as a quantity of the same nature as mass and energy, for which conservation balances can be written. This approach can lead to serious errors, and a number of misconceptions, discussed below, are caused by this often unconscious assumption.

In the following discussion pH will be defined as

$$pH = -\log[H^+] \tag{1}$$

where $[H^+]$ denotes hydrogen ion concentration divided by mol/L.

It is irrevelant for the discussion whether pH is defined by means of concentration, as in Eq. 1, by means of activities, or by means of the signal given by a device for measuring pH.

CALCULATING AVERAGE pH VALUES

In the literature there has been much discussion and much confusion concerning the concept "average pH." Part of the confusion has been caused by the fact that the concept has not been defined. As a consequence, the average pH of some solutions is taken to mean the pH obtained after mixing the solutions.

In an article with the title "Avoid Errors in Averaging pH Values" it is suggested that for mixing equal volumes (or flow rates) the average pH is given by

$$p[H]_{av} = -\log\left[\frac{1}{n}\sum_{i=1}^{n}[H^+]_i\right] \tag{2}$$

This is suggested as a correction of the reportedly not uncommon procedure of simply averaging the pH values.

Both calculation methods—Eq. 2 and averaging—are generally wrong. For example, if a strong base with, say, pH = 12 is diluted tenfold by pure water of pH = 7, then pH is decreased by one unit to pH = 11. Eq. (2) on the other hand predicts the pH to be only slightly above 7:

$$p[H]_{av} = -\log\left[\frac{1}{10}(9\cdot 10^{-7} + 10^{-12})\right] \approx 7.05$$

In connection with a subsequent article (Gumtz and Gray, 1981) in the same journal, the purpose of which was to correct the article mentioned above, there is a comment, obviously by the editor, that Eq. 2 "applies only to mixtures of acids." Unfortunately, this statement is also misleading. If a strong acid with pH = 4 is diluted by pure water, the final pH is not independent of the presence of a weak acid (buffer) in the system.

More information is needed, in particular, information about the chemistry of the system, i.e., about the chemical reactions taking place in the mixture. This means that the pH of a mixture cannot generally be calculated by some averaging of the individual pH values. Or more generally: the pH of a mixture cannot generally be calculated if nothing more than the pH values (and the mixing proportions) of the individual solutions are known.

As stated, the chemistry of the system has to be known for a calculation of pH. This does not mean, however, that one has to know explicity what species are contained in the mixture. It is enough if the titration curves of the individual solutions are known, as illustrated by Gustafsson (1982; see also comment by Rudziński, 1984, and Gustafsson, 1984a).

CALCULATING pH FROM A DILUTED PROCESS STREAM

The reverse calculation, i.e., the calculation of the pH of one of the solutions in a mixture, if the pH of the other(s) and of the mixture are known, is also generally impossible if nothing but the pH values are known. Thus, if a solution is diluted by water before pH is measured, it is in the general case impossible to calculate from the measured pH what the pH was before dilution.

If the titration curve of a solution, diluted or undiluted, is known and constant, the effect of dilution by a solution of known composition (e.g., pure water) can be calculated. If, however, the titration curve is unknown, perhaps because of varying buffer concentrations, the effect of the dilution is unknown within certain bounds.

This means that in a feedback control system in which a small part of the process stream is diluted before pH is measured, the feedback is generally based on an incorrect estimation of pH in the process stream. Such systems are reported to be used in industrial practice.

DAMPING OSCILLATIONS IN pH

It is quite common that systems for continuous control of pH oscillate for various short or long periods of time. The reason for this is easy to understand: The form of the titration curve determines the process gain, and for slightly buffered solutions the S-shaped titration curve means that the process gain can vary much in the pH range of the control. If in a feedback system the controller gain is set low enough to insure stability around, e.g., the neutral point, then the controller can be very inefficient far from the neutral point, and recovery from large upsets can be extremely slow. A fixed-gain controller that is efficient for large upsets can then sometimes cause continuous cycling around the neutral point because the controller gain is too high for stability in that region.

Even if the delicate balance in fixed controller settings is found, thus ensuring a nonoscillatory response as fast as possible, the system is still very sensitive to changes in the slope of the titration curve. This means that a decrease in buffer concentrations easily brings about continuous oscillations.

Now, "common sense" has led to the following solution: a damping vessel is placed after the oscillating control system so as to average-out the oscillations. Such an arrangement is shown in Figure 1. However, one should be careful with common sense—it often goes wrong in complicated systems. And the concept of pH, as simple as it may seem, is sufficiently complex to make common sense go astray. Figure 2 illustrates how.

Figure 2 is a recording from an experiment illustrated in Figure 1. It is seen that the measured pH of the damping tank moves so as to become completely outside the range of the measured oscillations in the first tank. The dotted line shows the measured pH used for feedback, denoted pH_m in Figure 1. The full line is pH_a, which denotes the pH measured in the damping vessel. The system is weakly buffered and the set point is pH = 9. For $t < 1$ min a steady state without control is shown. At $t = 1$ min a step disturbance is introduced and the conventional PID controller is connected. At $t = 4$ min the controller gain is increased, resulting in stationary oscillations.

The fact that the final pH of a storage tank placed downstream may be far from the setpoint of the oscillating control system has been pointed out previously, e.g., in a paper by Trevathan (1979). It needs to be repeated, however, since recommendations to place a damping vessel downstream appear every now and then in the literature; a recent example is Rys (1984).

The fact that the pH of the damping vessel is completely outside the range of the measured oscillations may be astonishing at first. The explanation is that the actual pH oscillates with significantly larger amplitude than the measured pH, the difference being caused by the dynamics of the pH electrode. The pH of the damping vessel cannot, of course, be outside the range of the actual oscillations.

The results shown in Figure 2 are by no means obtained under exceptional laboratory conditions, such as extremely fast oscillations. The pH electrodes used were standard commercial ones and the oscillations have a period of 45 s. The latter value can be compared to that illustrated by Rys (1984) where the period of oscillation is 30 s.

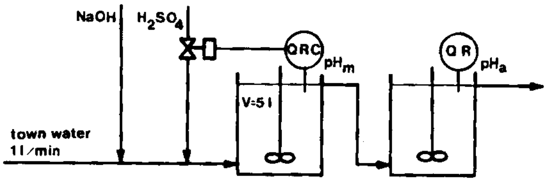

Figure 1. Setup for experimental averaging of pH.

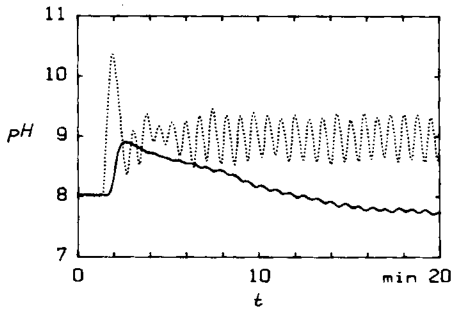

Figure 2. pH_m -------- and pH_a ——— of experiment with system shown in Figure 1.

CONTINUOUS CONTROL BY FEEDFORWARD FROM pH

For continuous control of pH, it can be dangerous to use feedforward from a measurement of pH in the feed. One reason is that pH generally is a nonlinear function of the reagent added, and if the correct nonlinear relation is not used in the controller, overcompensation (or undercompensation) occurs. An illustration is given by Waller and Gustafsson (1983).

More important, however, may be the fact that a change of pH in the feed to a continuous pH control system does not alone tell in which direction the reagent flow added should be changed. If, for example, an alkaline feed is neutralized by acid, an increase in the pH of the feed can mean that less acid should be added, not more as one might believe at first thought.

The explanation is that the buffering capacity of the incoming liquid can change, and a change in pH can be a consequence of a change in buffering, not only a consequence of a change in base content. The situation is common in practice, e.g., in wastewater treatment, where a change between feeds often brings about a change in both base (or acid) and buffer content at the same time. A clear illustration is given in Figure 3, which shows experimental data from an adaptive pH control system (Gustafsson, 1985).

At the times denoted by the three vertical dotted lines, it is seen that the reagent added (lower diagram) is changed in a direction which is opposite to what would be expected at first. A slight increase in pH at time $t = 0.21$ h is accompanied by a considerable decrease in acid added. At $t = 1.25$ h a slight decrease in pH corresponds with a slight increase in acid added, and at time $t = 2.92$ h a large increase in pH is accompanied by a slight decrease in acid added.

It is also seen that the other changes in feed pH are followed by changes in reagent flow in the "natural" direction. However, here also large changes in pH can result in small changes in reagent flow, and vice versa.

Thus, feedforward control from measured feed pH cannot generally be used unless one knows more about the properties of the feed than just its pH.

CONCLUSIONS

A close look at the literature on pH and pH control has revealed a number of common misconceptions. In practice it may well be that parts or components of the system are blamed for bad functioning of pH control systems instead of fundamental errors of reasoning.

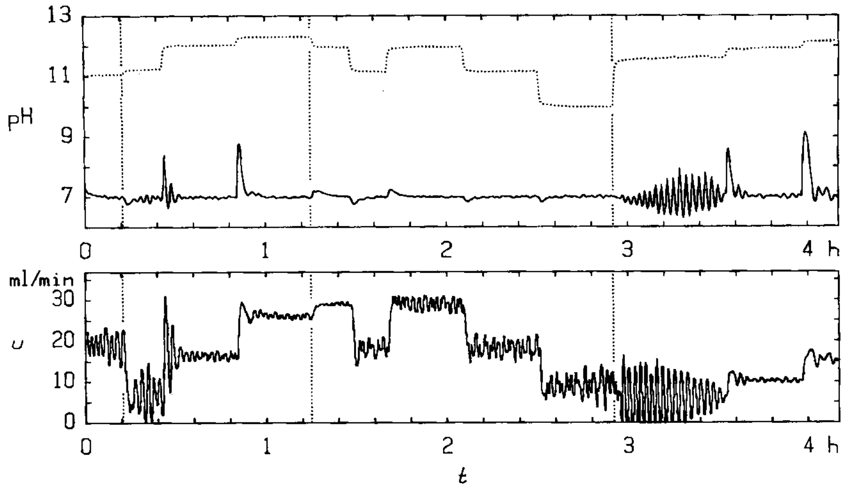

Figure 3. Experimental recording of adaptive pH control system. Top: measured pH of the feed ------ and measured control pH ———. Bottom: control signal, i.e., the reagent flow in mL/min of sulfuric acid solution.

Some common myths about pH and pH control have been discussed. It has been shown that:

- The pH of a mixture cannot be calculated by some averaging procedure from the individual pH values.
- More generally, the pH of a mixture cannot be calculated if nothing more than the individual pH values is known.
- In a feedback control system in which a small part of the process stream is diluted before pH is measured, the feedback is generally based on an incorrect estimation of the pH.
- If a damping vessel is placed after an oscillating pH control system, the pH of the damping vessel need not take a value within the range of the measured oscillations.
- It is quite possible that in a continuous pH control system with alkaline feed the acid flow used for control should be decreased in order to compensate for an increase in the pH of the feed (and vice versa for an acidic feed).
- More generally, for disturbances in the pH of the feed, it is questionable whether feedforward from a measurement of only the pH value of the feed can be used for control.

An extensive treatment of continuous control of pH, with special emphasis on the difficult situation of continuously changing buffering, is given elsewhere (Gustafsson and Waller, 1983, Gustafsson, 1984b, 1985).

LITERATURE CITED

Gumtz, G. D., and D. M. Gray, "A Closer Look at pH Estimates," *Chem. Eng.*, 88 (13), 111 (1981).

Gustafsson, T. K., "Calculation of the pH Value of Solutions—An Illustration of the Use of Chemical Reaction Invariants," *Chem. Eng. Sci.*, 37, 1,419 (1982).

———, "Reply to K. J. Rudziński," *Chem. Eng. Sci.*, 39, 198 (1984a).

———, "An Experimental Study of a Class of Algorithms for Adaptive pH Control," *Chem. Eng. Sci.*, 40, 827 (1985).

———, "A Study of Modeling and Control of pH in Fast Acid-Base Reaction Processes Based on Chemical Reaction Invariance," Report 84–4, Process Control Lab., Åbo Akademi, Finland (1984b).

Gustafsson, T. K., and K. V. Waller, "Dynamic Modeling and Reaction Invariant Control of pH," *Chem. Eng. Sci.*, 38, 389 (1983).

Rudziński, K. J., "Calculation of the pH Value of a Mixture of Solutions—A Supplement," *Chem. Eng. Sci.*, 39, 196 (1984).

Rys, R. A., "Advanced Control Methods," *Chem. Eng.*, 91 (17) 151 (1984).

Trevathan, V. L., "Characteristics of pH Control," *Proc. Workshop on Industrial Process Control*, AIChE (1979).

Waller, K. V., and T. K. Gustafsson, "Fundamental Properties of Continuous pH Control," *ISA Trans.*, 22 (1), 25 (1983).

Manuscript received Nov. 27, 1984, and revision received Mar. 18, 1985.