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In the Classroom

Buffer Calculations Deceive and Obscure[1]

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The pH of a buffer, calculated by the method given in introductory texts, is so dramatically inaccurate that it is dangerous. If the calculation is to be taught, then it must use either conditional constants or (for more advanced students) activity coefficients.

It would be better not to teach the calculation at all, but to concentrate on the qualitative description of buffers, buffering, and buffer capacity.

Buffer capacity is a useful concept that is rendered useless by the way it is presented in introductory texts.

Introduction

When I have asked them what they want their students to learn, understanding buffers was near the top of the priority list for every department that requires its students to take a year

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[1] Contribution from the American Chemical Society Task Force on the General Chemistry Curriculum

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of chemistry. Still the texts for their courses show that it is a qualitative understanding that they need, not the ability to perform even simple calculations.

This is fortunate, because the simplistic calculations in our texts give dangerously incorrect answers.

Consider the case of biologists who have learned how to use the Henderson–Hasselbach equation and then use this knowledge in designing an experiment buffering human blood. They find that warm healthy human blood has a pH of 7.4. Looking up the pK_2 for phosphoric acid [1] they find it to be 7.184 at blood temperature. They insert this into the equation, find that a ratio of 1.65 is needed between the concentrations of HPO_4^{2-} and $H_2PO_4^-$,and they make up an appropriate solution. Actually the pH 7.06 (calculated from National Bureau of Standards data [2]), an error of 0.34 pH units or a factor of 2 in the activity of H^+. If this ruins the work, or if erroneous results are published as a result of our incorrect teaching, will we be sued for malpractice? If somebody dies, will the heirs sue us?

The usual practice in introductory texts is to quote the thermodynamic constant, which is properly defined as the ratio of activities

$$K_a(\text{thermodynamic}) = a_{H+}\, a_{\text{conjugate base}} / a_{\text{conjugate acid}} \tag{1}$$

and then to use concentrations instead of activities. If we insist on doing this, then we are morally obligated to point out that the resulting pH deserves only one decimal at best and may be in error by as much as 0.5 pH unit. Some examples of this are shown in Table 1 where the calculated pH is compared to the experimental pH shown in the Handbook of Chemistry and Physics. If this approach is taught, then exam questions should be set asking whether the method is appropriate for a particular buffer system and the accuracy that is needed. It is unlikely that teachers will do this.

How Should the Calculations be Taught (if at all)?

We have several possible solutions to the problem. The easiest is to pretend there is no problem and go on teaching the same lies that we were taught. So long as the students never use the algorithm for any practical purpose, the only harm will be to have wasted their time.

TABLE 1. Errors in pH from the Usual Textbook Calculation

Reagent	half-neutralised using	pH expt [7]	pH calc	Error
THAM*	HCl	8.14	8.07	0.07
KHPhthalate	HCl	2.92	2.94	0.02
KHPhthalate	NaOH	5.08	5.38	0.30
KH_2PO_4	NaOH	6.89	7.20	0.31

*Tris(hydroxymethyl)aminomethane

The most difficult approach is to teach students to use activity coefficients. Few teachers will do this in an introductory course, and even fewer will do it twice. A realistic solution recognises that the concentration $[H^+]$ cannot be measured, but the activity can be measured as 10^{-pH}. The concentrations of acid and base are usually known in real situations, but their activity is not. These strictures are solved for real solutions by using the “practical” or “mixed” or “Bronsted” definition of K_a [3, 4] for solutions with the ionic strength of the buffer being considered:

$$K_a \text{ (practical)} = a_{H+} [X^-] / [HX] \tag{2}$$

$$= 10^{-pH}[X^-] / [HX] \tag{3}$$

or more generally, since the acid is not necessarily electrically neutral,

$$K_a \text{ (practical)} = a_{H+}[\text{base}] / [\text{acid}] \tag{4}$$

$$= 10^{-pH}[\text{base}] / [\text{acid}] \tag{5}$$

Students must then be given the practical K_a for the ionic strength of the buffer. Values of these for the more common acids are given by Hawkes [3]. An exhaustive compilation is given in Smith and Martell [4] but they give conditional constants,

$$K_a(\text{conditional}) = [H^+][\text{base}]/[\text{acid}]$$

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TABLE 2. *PH from Different Definitions of K_a using the Henderson-Hasselback Equation, pH = pK_a + log([base]/[acid])*

	Standard Buffer[a]	half-neutralized KH_2PO_4[b]
By pK_a (thermodynamic[c]) using concentrations instead of activities	7.74	7.20
By pK_a (conditional[d]) using pH = –log[H^+] instead of –log a_{H^+}	7.29	6.70
By pK_a (practical[e])	7.38	6.81
Experimental	7.41	6.82

[a] 0.008665 M KH_2PO_4 and 0.03032 M Na_2HPO_4
[b] 0.1 M KH_2PO_4 half-neutralized with 0.1 M NaOH
[c] K_a (thermodynamic) = $a_{H^+}a_{base}/a_{acid}$
[d] K_a (conditional) = [H^+][base]/[acid] (at a specified ionic strength)
[e] K_a (practical) = a_{H^+}[base]/[acid]

which must be converted to the practical constants: the authors give the necessary correction factor in their introduction. If it is inappropriate to teach students to calculate ionic strength, exercises can be written to include such words as "...value of K_a is 2.34×10^{-5} in the presence of this many ions." Students are, thus, notified that the concentration of ions affects the calculation, and they realize that in the real world they should consult a chemist who can make the necessary allowance for them.

The superiority of this approach is shown in Table 2, where only the practical constant gives correct answers within the uncertainty of literature values of K_a.

The base hydrolysis constant K_b is an unnecessary complication. If K_a(practical) is specified for NH_4^+ then K_b for NH_3 need never be discussed; it merely adds unnecessarily to the concepts a student must master. If it is used, then some practical definition must be found that gives correct answers from experimental data, and such a definition eludes me. Alternatively, it may be used merely as an ordinal indicator of the relative strengths of bases without attempting to use it for calculation.

But Do They Then Understand About Buffers?

Buffer calculations are almost the least valuable aspect of buffers that we might teach. My examinations of texts that depend on a year of chemistry have not found a real situation in which the calculation would be useful. Calculations do not provide any insight into the nature or usefulness of buffers except to a tiny group of mathophilic students, which may have included many of us. The overwhelming majority of students will learn the algorithm for the calculation while obtaining no insight into the function that a buffer serves, why it works, why it must involve a conjugate acid-base pair, why the acid and the base must be present in about equal proportions, or how the pH is related to the strength or concentration of the acid or base. These qualitative concepts must be approached by a qualitative treatment of the acid-base equilibrium. This is a harder task than teaching how to plug numbers into formulae. It is also more difficult to test.

The following objectives are seldom tested in national tests or in the end-of-chapter questions in textbooks but are of greater importance than many that are.

1. Be able to decide which of several solutions is a buffer from a description of the effect of adding each of them to another solution containing acid or base.
2. Be able to decide whether a solution is a buffer from a listing of its solutes.
3. Be able to predict the effect on the solutes of adding a buffer to an unbufferred solution, given the names or formulae of the solutes.
4. Be able to decide which of several possible buffer solutions, all with the same pH, will be the most effective buffer, by considering the concentrations of their solutes or the ratio of concentrations of the conjugate acid and base.
5. Be able to explain or to correct the explanation of why the constituents of a buffer must be a conjugate acid/base pair.

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6. Be able to write the equations for the reactions that result from adding base or acid to a given buffer.
7. Be able to explain or to correct explanations of how a buffer works.

Buffer Capacity

Buffer capacity is a useful concept that is rendered useless by the way it is presented in introductory texts. It is usually incorrectly defined as the number of moles of strong acid or base that must be added per liter to change the pH by one. This seems to be a mathophobic interpretation of the correct [5] definition:

$$\text{Buffer Capacity} = \frac{d\left(\text{moles added per liter}\right)}{d\,\text{pH}} \tag{6}$$

For students who know no calculus, this is better written as

$$\text{Buffer Capacity} = \frac{\delta\ \text{moles strong acid or base added per liter}}{\delta\ \text{pH}} \tag{7}$$

Most students will need to be reminded that δ implies a small quantity.

This is not the same as the usual definition in introductory texts because pH is not even approximately linear over a range of one pH unit. The reason it is used is evident when it comes to calculating the buffer capacity. The incorrect definition is easy to calculate, whereas the true definition needs some mathematical ability.

So why not use the easy one? Because it denies the student the use of what they have learned. Any buffer worth the name will be near enough linear over the range of pH that it is expected to buffer, so even mathophobic students will be able, from the correct definition, to answer the practical questions, “How much strong acid or base may be added to the buffer, before it changes pH by 0.2?” or “What must the capacity be, if the addition of 0.01 mol must not change the pH by more than 0.005?”

Still, the calculation of the true buffer capacity from concentration requires a formula for which few students will understand the derivation. The calculus derivation of the buffer capacity/concentration relation is given in texts such as Laitinen [6].

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Mathophilic noncalculus students could derive it, if they are told that the limit of $\ln(1 + \delta)$ is δ. But most will need to be told that when the buffer consists of an acid and its conjugate base, the buffer capacity is given by

$$\text{buffer capacity} = (\ln 10) / (1/[\text{acid}] + 1/[\text{base}]) \qquad (8)$$

We naturally dislike magic formulae, but it is worth mastering our distaste to ensure that what we are teaching is worth learning.

The following objectives on buffer capacity are useful and easily testable:

1. Be able to calculate the buffer capacity needed to limit the change of pH to a specified maximum for addition of a specified amount of strong acid or base (using equation 7).
2. Given the buffer capacity of a solution, be able to calculate the change in pH for a given addition of H^+ or OH^- or be able to calculate the maximum H^+ or OH^- that can be added before there is a specified change in pH (using equation 7).
3. Given the concentrations of the acid and its conjugate base in a buffer, be able to calculate the buffer capacity (using equation 8).
4. Be able to design a buffer with a given buffer capacity (using equation 8).
5. Given the concentrations of acid and base and the values of K_a for two buffers, be able to decide from qualitative reasoning which has the higher buffer capacity, in unambiguous cases.

If these objectives were met in introductory courses, more manufacturers would give buffer capacities on the labels of the buffers they sell. Graduates of the course would then be able to use buffers more intelligently.

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