Teaching Buffering by Comparing Observed and Expected Hydrogen and Hydroxide Ion Change

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Introduction

Buffering is an easily-understood example of chemical homeostasis, and is commonly included in freshman biology courses. However, the common definition of buffers as molecules that "control changes in pH when acid or base are added" can lead students to try to judge a

buffer's effect by watching changes in pH. This will lead to incorrect conclusions in many cases. The essence of buffering is that addition of some amount of hydrogen ions or hydroxide ions results in a much smaller increase in concentration of "free" hydrogen or hydroxide ions. This suggests that a good test for the presence of buffering would be to compare the observed increase in hydrogen or hydroxide ion with the increase expected *if there were no buffering*.

For example, say that we add 2 mL of 0.1 N HCl to 40 mL of distilled water. If the only effect is dilution in the water, we would expect that the concentration of hydrogen ions would start out at 1×10^{-7} M, and after addition of the acid it would increase by:

normality of acid x added acid volume in liters/final solution volume in liters

or

$$0.1 \times 0.002/0.042 = 0.0048 \text{ M} = 4.8 \times 10^{-3} \text{ M}.$$

To the extent that the increase in hydrogen ion concentration in less than this, the solution shows buffering against acid. For example, addition of 2 mL of this acid to a 0.01 M solution of both HPO_4^{-2} and $H_2PO_4^{-1}$ only decreases the pH from 7.20 to 6.75, a hydrogen ion increase of 1.16×10^{-7} M, which is only 0.0024% of the expected increase in hydrogen ions.

The same argument holds for addition of base, but here we must use hydroxide concentrations instead. If we add 2 mL of 0.1 M NaOH to distilled water, the expected increase in hydroxide ions is 4.8×10^{-3} M, as seen above. This would raise the pH of the water to 11.8. However, if we add the 2 mL of base to a 0.01 M solution of both HPO_4^{-2} and $H_2PO_4^{-1}$, the pH increases only to 7.65. To compute the hydroxide ion increase, we would reason as follows:

initial pH = 7.20; initial pOH = 6.80

initial $[OH^-] = 10^{-6.80} = 1.58 \times 10^{-7}$ (computed using pOH, not pH)

final pH = 7.65; final pOH = 6.35

final $[OH^-] = 10^{-6.35} = 4.47 \times 10^{-7}$

change = final $[OH^-]$ - initial $[OH^-]$ =

$4.47 \times 10^{-7} - 1.58 \times 10^{-7} = 2.89 \times 10^{-7}$ M

This change is about 0.006% of the change expected if there were no buffering.

This suggests that a sensitive method for distinguishing between solutions that buffer against acid, against base, and against both would be to compare the observed increase in hydroxide or hydrogen ions with the increase expected if there were no buffering. This method is used in the following exercise to compare four "mystery solutions": distilled water, a solution containing $H_2PO_4^{-1}$ only, a solution containing HPO_4^{-2} only, and a solution containing both $H_2PO_4^{-1}$ and HPO_4^{-2}. By showing dramatic differences between the solutions, this comparison reinforces the point that a solution may buffer against acid, against base, against both, or against neither. By challenging the students to determine which solution is which, it also has an engaging element of detective work.

Procedures

This exercise asks you to distinguish between four "mystery solutions": distilled water, a solution containing $H_2PO_4^{-1}$ only, a solution containing HPO_4^{-2} only, and a solution containing both $H_2PO_4^{-1}$ and HPO_4^{-2}. The solutions are labeled A, B, C, and D, but not necessarily in that order.

1. Place 40 mL of solution A in a beaker. Record the pH in Table 1.
2. Add 2 mL of 0.1 N HCl. Record the pH after mixing in Table 1.
7. Rinse out the beaker and get a new 40 mL sample of the solution. Record the pH in Table 2.
8. Add 2 mL of 0.1 N NaOH. Record the pH after mixing in Table 2.
5. Repeat steps 1-4 with solutions B, C, and D.
6. For each solution, compute the observed increase in H^+ and OH^- by filling in the Table 1 and Table 2. Conversion factors appear below:

$$pH = -\log([H^+])$$

$$pOH = -\log([OH^-])$$

$$pOH = 14 - pH$$

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

$$[OH^-] = 10^{(-pOH)}$$

Table 1. Changes after addition of 2 mL of acid to each solution.

Solution	pH before Acid	pH after Acid	$[H^+]$ before Acid (M)	$[H^+]$ after Acid (M)	$[H^+]$ Change Due to Acid
A	_____	_____	_____	_____	_____
B	_____	_____	_____	_____	_____
C	_____	_____	_____	_____	_____
D	_____	_____	_____	_____	_____

Table 2. Changes after addition of 2 mL of base to each solution.

Solution	pH before Base	pH after Base	[OH⁻] before Base (M)	[OH⁻] after Base (M)	[OH⁻] Change Due to Base
A	_____	_____	_____	_____	_____
B	_____	_____	_____	_____	_____
C	_____	_____	_____	_____	_____
D	_____	_____	_____	_____	_____

7. If there were no buffering in these solutions, the expected increase in hydrogen ion (after acid) or hyroxide ion (after base) would be 0.0048 M. Fill in Table 3 below with the percentage of this expected increase and your conclusions about whether solutions A, B, C, or D buffer against acids, bases, both acids and bases, or neither acids nor bases. Finally, in the last column of Table 3, designate each solution as distilled water, $H_2PO_4^{-1}$ only, HPO_4^{-2} only, or both $H_2PO_4^{-1}$ and HPO_4^{-2}.

Note: Solutions without buffering often do not yield 100% of the expected change (they may be as low as 1-10% of the expected). However, solutions that are buffered show *much* less change than this.

Table 3. Percent of the expected [H⁺] or [OH⁻] increase in each solution.

Sol.	Percent Acid	Percent Base	Buffers Acid (Y/N)	Buffers Base (Y/N)	Solution Contents
A	_____	_____	_____	_____	_____
B	_____	_____	_____	_____	_____
C	_____	_____	_____	_____	_____
D	_____	_____	_____	_____	_____

Prep Notes

A team of four students can be assigned to one pH meter. While two students do the acid titrations, two can do the base titrations. Since only one 2 mL addition of acid and base has to be done, it can be made with a 5 mL pipet rather than a buret.

Solutions A, B, C, and D might be assigned as follows:

A 0.01 M NaH_2PO_4

B A 1:1 mixture of 0.02 M NaH_2PO_4 and 0.02 M Na_2HPO_4 . When mixed, the combined solution will have 0.01 M of both salts.

C Distilled water

D 0.01 M Na_2HPO_4

The students may need coaching in how to compute logs and antilogs using their calculators. This could be complicated for the instructor if they have a diversity of calculators that do or do not use reverse Polish notation.

Sample Results

The following results were achieved with a Fisher Accumet analog pH meter (model 140) calibrated with a pH 7 buffer. The distilled water was taken from a carboy in our prep room, so it probably had equilibrium amounts of CO_2 dissolved in it. This would lower its pH to about 5.5, but we have no explanation for the even lower pHs seen below. The acidic pH of the $H_2PO_4^{-1}$ and the basic pH of the HPO_4^{-2} are expected.

Table 4. Sample results after addition of 2 mL of 0.1 N acid to each solution.

Solution	pH before Acid	pH after Acid	$[H^+]$ before Acid (M)	$[H^+]$ after Acid (M)	$[H^+]$ Change due to Acid
DH_2O	4.70	3.10	2.00×10^{-5}	7.94×10^{-4}	7.74×10^{-4}
$H_2PO_4^{-1}$	4.78	3.25	1.70×10^{-5}	5.62×10^{-4}	5.45×10^{-4}
HPO_4^{-2}	8.48	6.75	3.31×10^{-9}	1.78×10^{-7}	1.75×10^{-7}
Both	6.70	6.35	2.00×10^{-7}	4.47×10^{-7}	2.47×10^{-7}

Table 5. Sample results after addition of 2 mL of 0.1 N base to each solution.

Solution	pH before Base	pH after Base	$[OH^-]$ before Base (M)	$[OH^-]$ after Base (M)	$[OH^-]$ Change due to Base
DH_2O	4.50	10.10	3.16×10^{-10}	1.26×10^{-4}	1.26×10^{-4}
$H_2PO_4^{-1}$	4.70	6.70	5.01×10^{-10}	5.01×10^{-8}	4.96×10^{-8}
HPO_4^{-2}	8.32	10.32	2.09×10^{-6}	2.09×10^{-4}	2.07×10^{-4}
Both	6.65	7.15	4.47×10^{-8}	1.41×10^{-7}	9.66×10^{-8}

Table 6. Percent of expected [H^+] or [OH^-] increase in each solution, sample   results.

Sol.	Percent Acid	Percent Base	Buffers Acid (Y/N)	Buffers Base (Y/N)
DH_2O	16.13	2.62	no	no
$H_2PO_4^{-1}$	11.36	0.0013	no	yes
HPO_4^{-2}	0.0036	4.31	yes	no
Both	0.0051	0.0020	yes	yes

The results above make two points about the usefulness of the expected change method being proposed here.

First, it is very difficult to judge buffering capacity by pH changes alone. For example, in Table 4, the pH of distilled water, known to have no capacity to buffer acid, decreased 1.6 pH units when acid was added to it. The pH of the solution of HPO_4^{-2} (known to buffer against acids) decreased even more (1.73 pH units). Why would the student conclude that HPO_4^{-2} buffers against acids but distilled water does not? Likewise, in Table 5, addition of base caused the pH of the $H_2PO_4^{-1}$ solution (which supposedly buffers against bases) to rise from 4.70 to 6.70, 2 pH units. The rise in pH of the HPO_4^{-2} solution (which cannot buffer against base) was exactly the same amount, from 8.32 to 10.32. Again, why would the student believe that these two solutions have different buffering against base?

The second point is that the expected change method clearly differentiates between what may seem like the confusing cases above. In Table 4, we can see that the increase in hydrogen ions due to the addition of acid is much smaller in the HPO_4^{-2} solution and the $HPO_4^{-2} + H_2PO_4^{-1}$ solution than in the others, and in Table 5 the increases in hydroxide ion due to addition of base are smaller in the $H_2PO_4^{-1}$ solution and the $HPO_4^{-2} + H_2PO_4^{-1}$ solution. This is made even clearer in Table 6, where the percent of expected increase clearly differentiates between the cases where buffering occurs and the cases where it does not.

Summary

To summarize, this exercise:
a)   Allows students to use the pH meter for an actual investigation, rather than merely to measure the pH of some unknown solution;
b)   Emphasizes relationships among pH, pOH, hydrogen ion concentration, and hydroxide ion concentration;
c)   Allows students to explore buffering without trying to judge pH changes directly;
d)   Produces dramatic differences between solutions in which there is or is not buffering;
e)   Makes it clear that a solution can buffer against base while not buffering against acid or *vice versa*;
f)   Gives students practice at rejecting some hypotheses and accepting others, thus building a foundation for future work.