

An Algebraic Derivation of Buffer Capacity

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Abstract Acid-base chemistry is becoming evermore infamous amongst new chemistry students—especially specialized topics such as buffers and their capacities. Currently, introductory chemistry students struggle to fully understand the formal definition of buffer capacity. In this manuscript, we algebraically derive a new and simple mathematical representation for buffer capacity from the Henderson-Hasselbalch equation. We find that three buffer capacity formulas evolve—each with a specific application depending on the concentration-ratio of weak acid or base to its corresponding conjugate.

Keywords: analytical chemistry, first-year undergraduate/general, high school/introductory chemistry, problem solving/decision making, acids-bases

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1. Introduction

A buffer is defined as a solution that resists changes in pH upon the addition of either a strong acid or base. [1] Buffer capacity is then defined as the amount of strong acid or base needed to change the pH of a one liter buffer solution by one unit. [2] Calculating buffer capacity, however, deems to be a daunting—and seemingly esoteric—task to new chemistry students. As of now, the current, formal definition of buffer capacity is as follows:

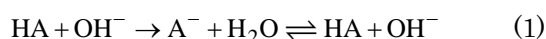
$$\frac{dn}{dpH} = 2.303([H_3O^+] + \frac{C_A K_a [H_3O^+]}{(K_a + [H_3O^+])^2} + [OH^-]),$$

where n is the number of equivalents added of either strong acid or base and C_A denotes the analytical concentration of acid. [3] Without context, the above formula is difficult to fully understand—and introductory chemistry students are likely to agree.

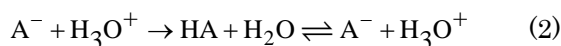
It is therefore the purpose of this work to derive a more comprehensible formula for the capacity of a buffer. The proposed methods are directed towards undergraduate courses in chemistry, but may deem applicable to Advanced Placement curricula. The major contributions in this article include our derivation of buffer capacity and the formulas that result. We base our method off of the Henderson-Hasselbalch representation for acid-base reactions.

2. Methods

All assertions in this section will be made regarding the following reactions:



and



where A^- denotes the conjugate base for some weak acid HA.

We begin by considering the relationship between pH and pOH. For the purposes of this article, we assume the general definition of

$$pH + pOH = 14. \quad (3)$$

Thus, if the pH of a solution decreases by some amount Δ , the pOH of that same solution will increase by that same amount Δ . On account of eq 3, we can generalize the buffer capacity definition to the following:

Definition 1 The *buffer capacity* of a solution is the amount (in mol) of strong acid or strong base that must be added to one liter of solution to change either the pH or pOH by one unit.

To begin the derivation, consider the Henderson-Hasselbalch representation for eqs 1 and 2:

$$pH = pK_a + \log \frac{[A^-]}{[HA]}, \quad (4)$$

where pK_a represents the acidic strength of HA. [4] Because pK_a is a constant value—one unique to HA—the only term in eq 4 that could cause a change in pH (or pOH)

by ± 1 unit must be $\log \frac{[A^-]}{[HA]}$. Let

$$\delta = \log \frac{[A^-]}{[HA]}, \quad (5)$$

then $pH = pK_a + \delta$.

Before proceeding, note the definitions below.

Definition 2 We title a buffer solution as an *imperfect buffer solution* whenever $[A^-] \neq [HA]$ and a *perfect buffer solution* whenever $[A^-] = [HA]$.

Definition 3 If the buffer capacity of a solution is being tested via strong base, we title the capacity as the *base-buffer capacity*. If instead the solution is being tested via strong acid, we title the capacity as the *acid-buffer capacity*.

We begin by considering the addition of a strong base to an imperfect buffer solution (eq 1). As shown in eqs 1 and 2, the stoichiometric ratio of HA:A⁻ is 1:1. Thus, if α mol of HA reacts completely with α mol of OH⁻, then α mol of A⁻ will be produced (and eventually settled to equilibrium). Let Δ denote some arbitrary change in δ after α mol of HA have reacted. Then,

$$\delta + \Delta = \log \frac{[A^-] + \alpha}{[HA] - \alpha}. \quad (6)$$

Let β_b denote the base-buffer capacity for eq 1.¹ Then, $\alpha = \beta_b$ and $\Delta = 1$ because bases attempt to increase pH. We then obtain the formula

$$\delta + 1 = \log \frac{[A^-] + \beta_b}{[HA] - \beta_b}.$$

Identically,

$$10^{\delta+1} = \frac{[A^-] + \beta_b}{[HA] - \beta_b}.$$

Solving for β_b produces

$$\beta_b = \frac{10^{\delta+1}[HA] - [A^-]}{1 + 10^{\delta+1}}.$$

Substituting in δ (eq 5) and reformulating yields

$$\beta_b = \frac{10[HA] \times 10^{\log \frac{[A^-]}{[HA]} - [A^-]}}{1 + 10 \times 10^{\log \frac{[A^-]}{[HA]}}},$$

which simplifies to

$$\beta_b = \frac{9[A^-]}{1 + 10 \frac{[A^-]}{[HA]}}.$$

Finally, multiplying both the numerator and denominator by [HA] yields the imperfect base-buffer capacity formula

$$\beta_b = \frac{9[A^-][HA]}{10[A^-] + [HA]}. \quad (7)$$

In other words, the maximum amount of base (in mol) a one liter solution of HA/A⁻ buffer can withstand before experiencing a change in pH or pOH by one unit is given by eq 7.

In continuation, consider eq 2. Here a strong base is being added to the buffer solution. Let β_a denote the acid-buffer capacity for an imperfect buffer solution. To derive

a suitable formula for β_a , refer to eq 6. Because acids attempt to decrease pH, $\Delta = -1$. Moreover, because the addition of β_a mol of strong acid will decrease [A⁻] and increase [HA] by β_a (opposite to adding strong base), $\alpha = -\beta_a$. Thus, utilizing eq 6, we acquire the formula

$$\delta - 1 = \log \frac{[A^-] - \beta_a}{[HA] + \beta_a}.$$

Equivalently,

$$10^{\delta-1} = \frac{[A^-] - \beta_a}{[HA] + \beta_a}.$$

We find

$$\beta_a = \frac{[A^-] - 10^{\delta-1}[HA]}{1 + 10^{\delta-1}}.$$

Substituting in δ and reformulating yields

$$\beta_a = \frac{\frac{9}{10}[A^-]}{1 + \frac{1}{10} \frac{[A^-]}{[HA]}}.$$

Multiplying both the numerator and denominator by 10[HA] produces the imperfect acid-buffer capacity formula

$$\beta_a = \frac{9[A^-][HA]}{10[HA] + [A^-]}. \quad (8)$$

Comparing eqs 7 and 8, we find $\beta_b \neq \beta_a$ for all $\delta \neq 0$. This occurs because the buffer is imperfect. If [HA] > [A⁻], then we would expect $\beta_b > \beta_a$ because the buffer would have greater resistance to strong bases. If, however, the inverse were true, we would expect $\beta_b < \beta_a$ because the buffer would have greater resistance to strong acids.

We now consider a perfect buffer solution. Let β_p denote the buffer capacity for a perfect buffer. Because a perfect buffer implies [A⁻] = [HA], $\delta = 0$. We find, utilizing eqs 7 and 8, a perfect buffer's capacity—in terms of [HA]—to simply be

$$\beta_p = \frac{9}{11}[HA]. \quad (9)$$

Identically, in terms of [A⁻],

$$\beta_p = \frac{9}{11}[A^-]. \quad (10)$$

Eqs 9 and 10 yield a very trivial, yet quite surprising result. Both state that the maximum amount of strong acid or base that can be added to a perfect buffer solution, before a change of either one pH or pOH unit occurs, is simply the product of $\frac{9}{11}$ and the concentration of either HA or A⁻.

3. Limitations and Assumptions

Throughout this article we have assumed a simple buffer solution—that is, a buffer with only one weak acid

¹ For emphasis, β_b is the amount (in mol) of OH⁻ being added to eq 1 to change either the pH or pOH by one unit.

or base and its corresponding conjugate. If multiple weak acids or bases (and their corresponding conjugates) are present, the methods in this paper will not yield proper results. Further, we have assumed that polyprotic acids and bases do not introduce an additional level of acidity or basicity, respectively. Realistically, however, if the buffer capacity of a solution is being tested via a strong, polyprotic acid or base, it is likely the capacity will come out relatively low. This will occur because the additional level of acidity or basicity will cause a faster change in pH (or pOH) in comparison to a strong, monoprotic acid or base.

4. Implications and Conclusions

In this article, we introduced a new buffer capacity definition and derivation intended for entry-level chemistry courses. The derivation provides a more understandable notion on buffer capacity by utilizing one of the most fundamental equations in introductory acid-base chemistry: the Henderson-Hasselbalch equation. We believe this method will grant more intuition on buffer capacity than the current, formal definition—thus

allowing students to better understand from where their computational results evolve.

Notes

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