Understanding, Deriving, and Computing Buffer Capacity†

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We dedicate this paper to the memory of aquatic chemist Werner Stumm and to all those who helped to lay the foundations of aqueous equilibrium chemistry.

In the past two years more than 600 papers have been published involving buffer capacity. It appears in varied disciplines, including analytical, environmental, geo-, and biochemistry, physiology, medicine, dentistry, and agriculture. The following indicates the range of topics in the recent literature: acid rain (*1*), pollution control (*2*), metal interactions in fish (*3*), cellular metabolism (*4*), drug solubility (*5*), muscle function (*6–7*), thyroid function (*8*), tooth decay (*9–11*), plant nutrient uptake (*12*), soil lime application (*13*), potentiometry (*14*), and corrosion in potable water systems (*15–16*). From these examples, it is clear that buffer capacity finds application throughout the sciences.

Despite this importance, a well-known environmental chemistry text omits the topic (*17*), and a volume on corrosion has limited coverage (*18*). Although *mass balance* and *charge balance* are covered in quantitative analysis textbooks (*19–21*), buffer capacity is treated minimally. Texts that treat equilibrium and buffer capacity more rigorously are often reserved for upper-level or specialty chemistry courses (*22–29*).

Donald Van Slyke's classic authoritative work (*30*) was published in 1922, several years after that of better known Henderson and Hasselbalch. Van Slyke's specialty was blood chemistry, where carbon dioxide equilibria dominate the acid–base chemistry. Since that time, attempts have been made to clarify the definition of buffer capacity (*31*) or provide an approach for its computation (*32*). Others have expanded Van Slyke's work, applying the concept of buffer capacity to various areas (*27, 29, 33–36*). Fortunately, the advent of spreadsheets has made short work of the lengthy, involved calculations required for effective use of buffer capacity (*1, 37–39*), and *JCE Software* itself has produced a software package that includes buffer capacity calculation (*40*).

Definition of pH

Understanding pH is a prerequisite for understanding buffer capacity. The term pH is formally defined by eq 1:

$$pH = -\log\{H^+\} = -\log\left(\frac{\gamma_{H^+} m_{H^+}}{m_{H^+}^{\circ}}\right) \qquad (1)$$

where $\{H^+\}$ represents the activity of hydrogen ion, γ_{H^+} represents the activity coefficient of the hydrogen ion, m_{H^+} represents the molality of the hydrogen ion in the solution being measured, and $m_{H^+}^{\circ}$ represents the standard state molality of the hydrogen ion, normally defined as unity. For reasons

beyond the scope of this article, the activity coefficient cannot be determined. In practice, pH is defined *operationally* in terms of a Nernstian relationship (eq 2) between an electrode's response (measured potential) in a solution of unknown pH and its response in a solution of known pH. In both cases, the potential is measured relative to a standard reference half-cell, for example Hg/Hg_2Cl_2 or $Ag/AgCl$ electrodes:

$$pH_{unk} = pH_{std} + \frac{F(E_{unk} - E_{std})}{(\ln 10)RT} \qquad (2)$$

where pH_{unk} is the calculated pH of the unknown solution; pH_{std} is the defined pH of the standard solution; E_{unk} is the measured potential of the unknown solution relative to the reference electrode; E_{std} is the measured potential of the standard solution; R is the universal gas constant (8.314 J mol^{-1} K^{-1}); and F is the Faraday constant, 96,485 C $(mol\ e)^{-1}$. In the United States, standard buffers of known pH are established by the National Institute of Standards and Technology (NIST), and NIST-traceable buffers are routinely used in American laboratories.

It is also possible to directly measure the proton molar concentration, represented as $[H^+]$. This is done by the calibrating electrodes through titrations of strong acid and strong base (e.g., $HClO_4$ and $NaOH$) at constant ionic strength[1] in a strong electrolyte (depending on the application, usually KNO_3, $NaCl$, $LiClO_4$ or $NaClO_4$) and while sparging with a minimally soluble unreactive gas (e.g., Ar) to keep out CO_2. To prevent evaporative loss, the gas is presaturated with water vapor. Proton concentrations are often used in kinetic studies where it is desirable to accurately quantitate all species in molar concentrations. Equilibrium constants are expressed in molar concentrations rather than activities, but they are valid only for a specific ionic strength and medium, for example, 0.50 M $NaClO_4$. Other than seawater, natural and potable waters tend to have low ionic strength; thus, this approach is limited in applicability even though it is always valid. Activity-based equilibrium constants are generally measured using an inert strong electrolyte to control ionic strength. After determination of the molar-concentration-based values, a plot of K against μ is used to extrapolate to zero ionic strength (infinite dilution).

In common usage, a pH meter estimates $\{H^+\}$. As solutions become more dilute and ionic strength approaches zero, the activity coefficients for all ions approach unity; that is,

$$\lim_{\mu \to 0} \gamma = 1$$

Unit activity coefficients are routinely assumed since $\gamma \approx 1$ for $\mu < 0.005$ M. Nevertheless, this remains an assumption; a particular situation may demand ionic strength corrections. By assuming unit activity coefficients, we can interchange molalities, molarities, and activities and dispense with activity

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coefficients in subsequent equations. However, we must not forget that activity coefficients are always implicitly present.

Definition of Buffer Capacity[2]

For an aqueous solution, the *buffer capacity* is defined in terms of the concentration of acid or base that must be added to influence pH. The formal definition of the buffer capacity, $\mathscr{B}$, is given by eq 3:

$$\mathscr{B} = dC_b/d(pH) = -dC_a/d(pH) \tag{3}$$

where C_b represents the concentration (normality) of added base and C_a represents the concentration of added acid. Van Slyke expressed the definition in this form because he was most interested in deducing $\Delta[CO_2]$ or $\Delta[HCO_3^-]$ for a $\Delta(pH)$ that he could measure. We retain this form for historical reasons and because it simplifies the mathematics.

Buffer capacity is always positive; every solution resists pH change according to Le Châtelier's principle. Because pH goes down upon the addition of acid, a minus sign is required when considering acid. Buffer capacity is a continuous and nonlinear function; therefore, it is a derivative. For a given value of pH, it makes no difference whether we think in terms of a differential change in pH resulting from an infinitesimal addition of acid versus an infinitesimal addition of base (other than the sign of the differential).

The buffer capacity can be resolved into a series of terms, with one term for each active component.

$$\mathscr{B} = \mathscr{B}_{OH^-} + \mathscr{B}_{H^+} + \Sigma\mathscr{B}_i \text{(all weak acids and bases)} \tag{4}$$

For convenience, the first two terms ($\mathscr{B}_{OH^-} + \mathscr{B}_{H^+}$) are often combined and referred to as the buffer capacity of water, $\mathscr{B}_w$. However, $\mathscr{B}_{OH^-}$ and $\mathscr{B}_{H^+}$ increase upon the respective addition of strong Arrhenius bases and acids. $\mathscr{B}_w$ should not be associated with K_w and does not stem only from the auto-ionization of water.

An *n*-protic acid and its conjugate bases make a contribution to the overall buffer capacity that is expressible as the following equivalent statements (eqs 5–7):

$$\mathscr{B}_{H_nX} = [X]_T \times \frac{d}{d(pH)}\left[\sum_{i=1}^{i=n-1}(n-1)f_{H_iX^{n-}}\right] \tag{5}$$

$$\mathscr{B}_{H_nX} = [X]_T \times \frac{d}{d(pH)}\left[f_{X^{n-}}\left(n + \sum_{i=1}^{i=n-1}(n-1)\beta_i[H^+]^i\right)\right] \tag{6}$$

$$\mathscr{B}_{H_nX} = (-\ln 10)[H^+][X]_T \times \frac{d}{d[H^+]}\left[f_{X^{n-}}\left(n + \sum_{i=1}^{i=n-1}(n-1)\beta_i[H^+]^i\right)\right] \tag{7}$$

where the *i*th cumulative protonation constant $\beta_i = [H_iA^{i-q}]/([H^+]^i[A^{q-}])$, and the fraction of X^{n-}, $f_{X^{n-}} = 1/(1 + \Sigma_{i=1}^{i=n}\beta_i[H^+]^i)$. Application of these equations follows.

Monoprotic Weak Acid and Its Conjugate Base

First consider the case of a monoprotic weak acid, such as acetic acid and its conjugate base (e.g., the sodium salt).

mass balance: $\qquad [X]_T = [HX] + [X^-] \tag{8}$

charge balance: $\quad [H^+] + [Na^+] = [OH^-] + [X^-] \tag{9}$

It is possible to make the substitution $[Na^+] = C_b$, the concentration of base that must have been added. In addition, we substitute $[OH^-] = K_w/[H^+]$, and solve for C_b.

$$C_b = K_w/[H^+] - [H^+] + [X^-] \tag{10}$$

To express eq 10 in terms of $[X]_T$, we must use the mass balance (eq 9) and the acid dissociation constant, $K_a = [H^+][X^-]/[HX]$. The ratio of total concentration of all forms of X to that of X^-, which also represents the reciprocal of the fraction of X^-, is given by eq 11. Subsequent substitution into eq 10 gives eq 12, which simplifies to eq 13.

$$\frac{[X]_T}{[X^-]} = 1 + \frac{[H^+]}{K_a} \tag{11}$$

$$C_b = \frac{K_w}{[H^+]} - [H^+] + \frac{[X]_T}{1 + \frac{[H^+]}{K_a}} \tag{12}$$

$$C_b = \frac{K_w}{[H^+]} - [H^+] + [X]_T \times \frac{K_a}{K_a + [H^+]} \tag{13}$$

At this point, we differentiate with respect to $[H^+]$:

$$\frac{dC_b}{d[H^+]} = -\frac{K_w}{[H^+]^2} - 1 + [X]_T \times \frac{(-K_a)(1)}{(K_a + [H^+])^2} \tag{14}$$

Since $d[H^+]/d(pH) = -\ln 10\,[H^+]$, we apply the chain rule for composite functions to obtain the final result:

$$\mathscr{B} = \frac{dC_b}{d(pH)} = \ln 10\left(\frac{K_w}{[H^+]} + [H^+] + [X]_T \times \frac{K_a[H^+]}{(K_a + [H^+])^2}\right) \tag{15}$$

Equation 15 shows three distinct components of $\mathscr{B}$. The hydroxide and hydrogen terms can be expressed as $\mathscr{B}_w$, and the weak electrolyte term as $\mathscr{B}_{buffer}$. Figure 1 shows the buffer capacity plot for acetic acid. The logic applies likewise to a weak base, for example, NH_3. In this case the mass balance is given by $[B]_T = [B] + [HB^+]$, and C_a (instead of C_b) is used to write the charge balance: $[H^+] + [HB^+] = C_a + [OH^-]$. Nonetheless, the final result obtained for $\mathscr{B}$ is the same.

Diprotic Weak Acid and Its Conjugate Bases

The buffering of natural and potable waters and biophysiological solutions is influenced by dissolved carbon dioxide, carbonic acid,[3] hydrogen carbonate, and carbonate. As a result, the buffer capacity expression for the diprotic acid, CO_2, has been derived elsewhere. Only the final results will be stated here.

$$\mathscr{B}_{CO_2} = (\ln 10)[H^+][CO_2]_T \times \frac{\beta_1 + 4\beta_2[H^+] + \beta_1\beta_2[H^+]^2}{(1 + \beta_1[H^+] + \beta_2[H^+]^2)^2} \tag{16}$$

$$\mathcal{B}_{CO_2} = (\ln 10) K_{a_1} [H^+][CO_2]_T \times \frac{K_{a_1} K_{a_2} + 4 K_{a_2} [H^+] + [H^+]^2}{\left(K_{a_1} K_{a_2} + K_{a_1} [H^+] + [H^+]^2\right)^2} \quad (17)$$

We note that the same equations apply to all diprotic acids and bases, even zwitterions (e.g., glycine), for which the initial charge balance equations are different. We leave these derivations as exercises.

Triprotic Weak Acid and Its Conjugate Bases

This derivation is more complicated and some level of detail is instructive.

mass balance: $[X]_T = [X^{3-}] + [HX^{2-}] + [H_2X^-] + [H_3X]$ (18)

charge balance: $C_b = K_w/[H^+] - [H^+] + 3[X^{3-}] + 2[HX^{2-}] + [H_2X^-]$ (19)

Limiting ourselves to the contribution of the weak electrolyte system alone (i.e., excluding $\mathcal{B}_w$), we use the equilibrium expressions and execute similar mathematical operations:

$$dC_b(H_3X)/d[H^+] = [X]_T S/D \quad (20)$$

where $S = (1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3)(2\beta_1 + 2\beta_2[H^+]) - (3 + 2\beta_1[H^+] + \beta_2[H^+]^2)(\beta_1 + 2\beta_2[H^+] + 3\beta_3[H^+]^2)$ and $D = (1 + \beta_1[H^+] + \beta_2[H^+]^2 + \beta_3[H^+]^3)^2$. Multiplication of eq 20 by $(-\ln 10)[H^+]$ produces the following result for the buffer capacity contribution of this weak electrolyte system:

$$\mathcal{B}_{H_3X} = (\ln 10)[H^+][X]_T N/D \quad (21)$$

where $N = \beta_1 + 4\beta_2[H^+] + (\beta_1\beta_2 + 9\beta_3)[H^+]^2 + 4\beta_1\beta_3[H^+]^3 + \beta_2\beta_3[H^+]^4$. The function is plotted for phosphoric acid in Figure 2.

Hydrolysis Reactions

Many metal cations, for example Al(III), are Lewis acids, reacting with water to produce hydrogen ions. They can precipitate as insoluble hydroxides and oxides; accordingly, it is necessary to ensure that solubility products have not been exceeded by the ion products. In this case, cumulative *hydrolysis* constants, rather than protonation constants are used.

mass balance: $[Al^{III}]_T = [Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3] + [Al(OH)_4^-]$ (22)

charge balance: $[Al(OH)_4^-] + [OH^-] = C_b + [H^+] + [Al(OH)_2^+] + 2[AlOH^{2+}] + 3[Al^{3+}]$ (23)

We leave it to readers and their advanced students to show that

$$\mathcal{B}_{Al(III)} = (\ln 10)[Al^{III}]_T [H^+] N/D \quad (24)$$

where $N = \beta_{h_1}[H^+]^6 + 4\beta_{h_2}[H^+]^5 + (9\beta_{h_3} + \beta_{h_1}\beta_{h_2})[H^+]^4 + (16\beta_{h_4} + 4\beta_{h_1}\beta_{h_3})[H^+]^3 + (9\beta_{h_1}\beta_{h_4} + \beta_{h_2}\beta_{h_3})[H^+]^2 + 4\beta_{h_2}\beta_{h_4}[H^+] + \beta_{h_3}\beta_{h_4}$ and $D = ([H^+]^4 + \beta_{h_1}[H^+]^3 + \beta_{h_2}[H^+]^2 + \beta_{h_3}[H^+] + \beta_{h_4})^2$.

Computation and Numerical Approximation

Computing the buffer capacity equations is easily accomplished with any commercial spreadsheet, and a text (*20*) exists on spreadsheet use. The analytic solutions have been the primary focus of this discussion; however, extremely com-
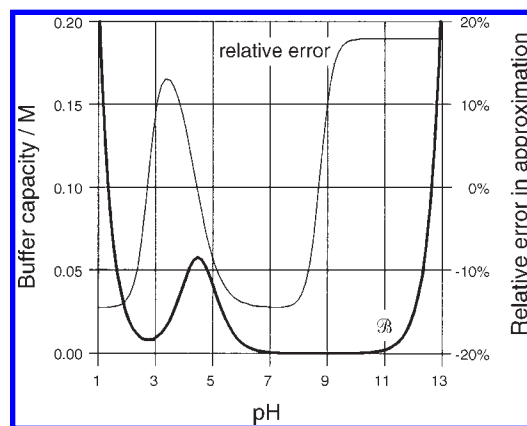

Figure 1. Buffer capacity (left ordinate) for the acetic acid/acetate + water system is calculated using eq 15. $[HOAc]_T = [HOAc] + [OAc^-] = 0.10$ M and $pK_a = 4.50$. A relative maximum occurs at pH = pK_a = 4.50. If we approximate $\mathcal{B}$ using $\Delta(pH) = 0.14$ in eq 26, an error is introduced. The relative error, $(\mathcal{B}_{approx} - \mathcal{B})/\mathcal{B}$, is also shown (right ordinate). $\mathcal{B}_w$ is not shown explicitly.
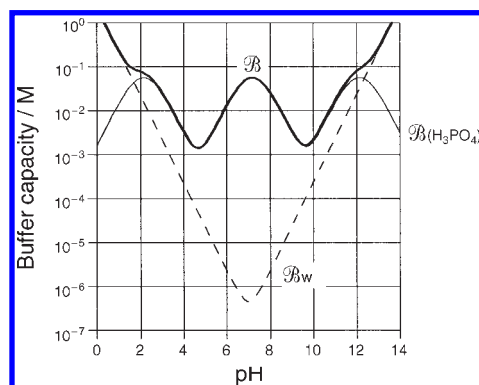

Figure 2. Buffer capacity for the phosphate system is calculated using eq 21. $[PO_4]_T = 0.10$ M, $pK_{a_1} = 2.15$, $pK_{a_2} = 7.20$, $pK_{a_3} = 12.15$; $\log \beta_1 = 12.15$, $\log \beta_2 = 19.35$, and $\log \beta_3 = 21.50$. Contributions of H^+ and OH^- are shown as $\mathcal{B}_w$. Contribution of the phosphate system is $\mathcal{B}_{(H_3PO_4)}$. $\mathcal{B} = \mathcal{B}_{(H_3PO_4)} + \mathcal{B}_w$. Local maxima occur where the pH reaches a pK_a.

plicated cases may be approximated with reasonable accuracy. Equilibrium constants generally have at least 1–5% uncertainty. Accordingly, even the analytic solutions are limited by experimental error. We recall the definition of buffer capacity as a derivative:

$$\mathcal{B} = \frac{dC_b}{d(pH)} = \lim_{\Delta pH \to 0} \frac{\Delta C_b}{\Delta(pH)} \quad (25)$$

As a continuous function, $\mathcal{B}$ can be subjected to linear approximation. The exactness obtained depends on how closely $\Delta(pH)$ approaches $d(pH)$. For $0.01 \leq \Delta(pH) \leq 0.1$, the speciation changes are often (but not always) small enough. Values chosen for $\Delta(pH)$ are best limited to ≥ 0.001; otherwise, too many computations may be required. Buffer capacity is always positive. However, choice of C_a or C_b is arbitrary, and C is evaluated over the entire pH domain. Thus, negative numbers correspond to changing from adding acid to adding base or vice versa. For this reason, the absolute value

is required for the approximation:

$$\mathcal{B}_{\text{approx}} = \left| \frac{C_b(\text{pH}_2) - C_b(\text{pH}_1)}{\text{pH}_2 - \text{pH}_1} \right| \qquad (26)$$

Note that $\Delta(\text{pH}) = 1.0$, the value used in Chiriac and Balea's interpretation of the IUPAC definition (31), poorly approximates the analytic solution. Figure 1 includes a plot that illustrates the relative error in the acetic acid buffer capacity curve when eq 26 is used for $\Delta(\text{pH}) = 0.14$. The relative error in the approximation reaches a maximum of about 20%, but the approximation itself can fall below the analytic solution by 10% as shown. The error can be reduced by choosing a smaller value for $\Delta(\text{pH})$, but at the cost of increasing the number of computations.

Buffer Capacity Extrema

Buffer capacity functions usually reach relative maxima at $\text{pH} = \text{p}K_a$ for an individual deprotonation reaction. However, when $\text{p}K_a < 3$ or >11, the maxima begin to converge and a single relative maximum is eventually formed. One relative minimum usually occurs at the intersection of the contribution of the most protonated acid form and the hydrogen ion contribution. Another relative minimum usually occurs at the intersection of the contribution of the most deprotonated alkaline form and the hydroxide ion contribution. One of these is usually, but not always, the absolute minimum. However, it is possible for a species to have $\text{p}K_a$ values suitably far away from 7 that the minimum between two forms coincides with the minimum of the water contribution. The function always has an absolute minimum, but there are no absolute maxima. The buffer capacity function is strictly decreasing for $\text{pH} < 0$, since $d\mathcal{B}_{H^+}/d(\text{pH}) = -2(\ln 10)[H^+]$. It is strictly increasing for $\text{pH} > 14$, since $d\mathcal{B}_{OH^-}/d(\text{pH}) = 2(\ln 10)K_w/[H^+]$. As a practical limitation, buffer capacity is limited to solubilities, for example 50% w/w NaOH (ca. 19 M OH^-) or 98% w/w H_2SO_4 (ca. 19 M H^+). However, neither of these represents a typical aqueous solution and the activity of the water is not unity.

The explicit analytic functions for buffer capacity are continuous functions and are continuously differentiable; therefore, the first derivative test may be used to locate critical points and thus possible relative minima and maxima. For example, a monoprotic acid and its conjugate base have $\mathcal{B}'$ given by

$$\mathcal{B}' = 2(\ln 10)K_a[X]_T[H^+]([H^+] - K_a)/([H^+] + K_a) \quad (27)$$

Because $\mathcal{B}'$ changes sign about $\text{p}K_a$, a relative extremum must occur at the critical point $(\text{p}K_a, \mathcal{B})$; in this case, it is a relative maximum.

Applications

Suppose the concentration of the titrant is much larger than the concentration of the species being titrated, that is, $C_{\text{titrant}} \gg C_{\text{titrated}}$. The slope of the titration curve, $d(\text{pH})/dV$, is ca. $1/\mathcal{B}$. Buffer capacity is a guide to titration. This occurs, for example, if 1.0 mL of 5.0 mM $CH_3CO_2H(aq)$ is titrated with 2.0 M NaOH(aq); such a method is used in the determination of stability constants. Plots of buffer capacity

can be used to find regions of maximal buffering when a mixture of species is present and to estimate the overall amount of acid or base that may be added without changing solution pH. Such a need is common in aqueous studies and can be encountered in many disciplines.

Notes

1. Ionic strength is defined as $\mu = \frac{1}{2}\Sigma c_i z_i^2$ for all i, where c_i represents the concentration of an ion i and z_i represents its charge (+1, -2, etc.).

2. The terms *buffer capacity*, *buffer intensity*, and *buffer index* are often used interchangeably. In general, analytical chemists have favored the first, geochemists the second, and engineers the third. In this paper, we will use the term *buffer capacity*. We do not make the distinction made by Chiriac and Balea between buffer capacity and buffer index (*14*). We feel this distinction is the result of the ambiguous semantics of the IUPAC definition. IUPAC did not specify a derivative explicitly, but rather described a change in molar concentration of strong acid or base relative to 1 pH unit. We interpret this usage is to mean a change in molarity per pH unit and thereby to represent the derivative conventionally thought of as buffer capacity. Certainly, Chiriac and Balea are correct in asserting that the normality of added base or acid to cause a pH shift of ±1 is not equal to the derivative, because the buffer capacity function is nonlinear over such a large interval of the pH domain.

3. Although carbonic acid is a real species, it is often excluded from expressions because it behaves identically to carbon dioxide in terms of overall acidity. Reference *19* has an excellent discussion of this matter.

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