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Buffer Ridges, Equivalence Point Canyons and Dilution Ramps

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Part 1: Acid-Base Equilibrium

Chapter 1.2
Visualization of Buffer Capacity with 3-D Topos: Buffer Ridges, Equivalence Point Canyons and Dilution Ramps

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Abstract

The BufCap TOPOS software generates 3-D topographic surfaces for acid-base equilibrium studies that portray pH and buffer capacity behavior during titration and dilution procedures. This differs from the normal treatment of buffer capacity that follows pH as the independent variable. Topo surfaces are created by plotting computed pH and buffer capacity values above a composition grid with mL of NaOH as the \(x\)-axis and overall system dilution as the \(y\)-axis. What emerge are surface features that correspond to pH and buffer behaviors in aqueous solutions. Topo surfaces are created for pH, log buffer capacity and traditional linear buffer capacity (as a function of pH). Equivalence point breaks become pH cliffs and logarithmic buffer capacity canyons that grow shallower with dilution. Areas of high buffer capacity become rounded ridges. Dilution alone generates 45° ramps. Example systems include acetic acid, CH\(_3\)COOH (a weak monoprotic acid); hydrochloric acid, HCl (a strong acid); oxalic acid, HOOC\(\text{COOH}\) (a weak diprotic acid) and L-glutamic acid hydrochloride, C\(_5\)H\(_9\)NO\(_4\)
\(\text{·HCl}\) (a weak triprotic amino acid). The Supplementary files include a copy of the interactive BufCap TOPOS program as a downloadable Excel workbook. Its macro-enabled spreadsheets quickly generate surfaces for any mono-, di-, or triprotic acid. Only acid dissociation constants, \(K_a\) values, need be changed. Other materials include a PowerPoint lecture, materials/suggested laboratory activities for teaching with BufCap TOPOS, and derivation of new equations that permit the calculation of buffer capacities for titration/dilution composition grid points.
1.2.1 Introduction

Buffers have two characteristics: 1) the pH that they establish and stabilize, and 2) the capacity to maintain that pH against additions of strong acids or bases and dilution. These are analogous to the two characteristics of energy measurements: 1) temperature, and 2) heat. A system’s pH and temperature are intensive properties that are independent of sample size. A beaker full of water and a lake full of water can both exhibit the same pH and temperature but will undoubtedly differ greatly in their total buffer capacity and heat content. This is because buffer capacity and heat are extensive properties that depend on sample size. In practice, however, buffer capacity is converted to a “per liter” basis so that comparisons between systems can be made.

Buffer capacity is an important concept for students who need a comprehensive understanding of aqueous chemistry fundamentals – especially those majoring in chemistry, biochemistry and geochemistry. Buffers maintain the pH necessary for chemical analyses, physiological reactions and aquatic ecosystem health. As soon as a system’s buffer capacity is exceeded, no longer will its pH be stabilized. Frequently, buffer capacity is at the heart of a situation. For example, the IV fluids given to patients in respiratory distress boost the buffer capacity of the blood and prevent it from dropping too low. The pH
vulnerability of a freshwater lake hinges on its natural buffer capacity to counteract atmospheric deposition of sulfuric and nitric acids from acid rain. The accuracy of commercial buffers can be invalidated if the solution becomes too dilute.

Chapter 1.1 introduced 3-D surfaces (topos) for a system’s pH behavior during titrations and dilution. This chapter adds new 3-D surface topos for buffer capacity behavior. It offers expanded downloadable spreadsheet software that visually connects pH changes during a titration to the associated buffer capacity at each point. Beginning students can see the inter-relationship between a buffer’s two characteristics – the pH it establishes and its capacity to maintain it. At the same time, it can provide some new insights into buffer behavior for more advanced students. Instructors and students in upper-division or graduate-level analytical, biochemistry and aquatic chemistry courses will find it particularly useful.

1.2.2 Computational Approach

The quantitative expression of buffer capacity was introduced by Van Slyke in 1922. It addressed buffer capacity in a sample of a given volume with respect to the addition of strong base or strong acid. Since then, numerous papers have refined buffer capacity calculations. In 1954, Bates defined buffer capacity on the basis of the pH change when the volume of a sample was diluted by a factor of two. Olson graphically portrayed dilution conditions in a system where the buffer capacity of a sample was controlled by the contributions from the diluent water. Michlowski and Parczewski tracked the influence of dilution on buffer capacity when performing experimental procedures that changed sample volumes.

Beginning in 1989, computer software to calculate buffer capacities became widely available. Ramette’s DOS-based program entitled “The Acid-Base Package” was featured as a Journal of Chemical Education Software item. A year later, Lambert created a Turbo-Pascal program BUFCALC. In 1998, Ramette updated his earlier program to the Windows 95 environment and renamed it “Buffers Plus”. Unfortunately, these comprehensive buffer calculation software packages are no longer available. At this writing, CurTiPot, a collection of
spreadsheet programs that do many of the same functions, is provided as a free download from I.G.R. Gutz.\(^{16}\)

This chapter introduces 3-D visualization of how buffer capacities change as the result of two very common procedures – titrations and dilutions.\(^{17}\) A composition grid is established with “mL of NaOH” on the \(x\)-axis (as for the titration of an acid sample) and overall dilution of the system (log \(C\)) on the \(y\)-axis. Plotted above this grid on the \(z\)-axis are the buffer capacities associated with each grid coordinate pair. The resulting 3-D surfaces depict how these two variables affect buffer capacity. BufCap TOPOS, Visual Basic software embedded in Excel spreadsheets, can be download as a Supplementary file. It can generate both pH and buffer capacity topos for any desired mono-, di- or triprotic acid system by supplying appropriate \(K_a\) values. The values for \(K_a\)s used in this chapter’s examples are taken from Martell and Smith’s Critical Stability Constants.\(^{18}\)

The buffer capacity calculations displayed here assume that the analyte is a 100 mL aliquot of acid. For the dilution axis, the acid analyte and NaOH titrant are assigned identical concentrations. This means that equivalence points always occur at 100-mL intervals.

For a monoprotic acid, the \(x\)-axis ranges in 5-mL steps from 0 to 200 mL, terminating 100 mL beyond the equivalence point. The \(y\)-axis is logarithmic and provides the initial concentration for both the analyte and titrant, \(C_a^0\) and \(C_b^0\). These values begin at 1.00 M and are reduced in 0.25 log-unit increments to a final concentration of 1.00 \(\times\) 10\(^{-9}\) M. For plots, the dilution axis is labeled “log \(C\)”, but in the equations below it appears as \(\gamma C_a^0\) where \(\gamma\) is the dilution factor. The two axes establish a composition grid with 41 \(\times\) 37 = 1517 points.

At each grid point, a polynomial equation is solved for the [H\(_3\)O\(^+\)] to 16 significant figures. The polynomial forms used for strong, monoprotic, diprotic and triprotic acids are widely available in the literature.\(^7\) The [H\(_3\)O\(^+\)] is simply converted to a pH value to create a pH titration topo surface. Computation of the associated buffer capacity is not so easily accomplished. A set of equations was derived for the volume of base added as a function of [H\(_3\)O\(^+\)] and the dilution factor (\(\gamma\)). Before dilution \(\gamma = 1.00\) and the molar concentrations of the acid analyte (\(C_a^0\)) and the base titrant (\(C_b^0\)) are both 1.00 M. Also in the expression are
\( K_w \) (water’s auto-dissociation constant), \( K_a \)s (acid dissociation constants), and \( V_a \) (the volume of acid to be titrated). For a monoprotic weak acid, the equation is:

\[
V'_b = V_a \left( \frac{K_w}{[H_2O^+]} + \left( \frac{K_a}{[H_2O^+]+K_a} \right) y C^o_a - \left[ H_3O^+ \right] \right) \left[ H_2O^+ \right] + y C^o_b - \frac{K_w}{[H_2O^+]} \]

(1.2-1)

Traditionally, buffer capacity, \( \beta \), is a measure of how many moles of acid or base can be added to 1.00 liter of buffer until the pH changes by one unit. Mathematically, it is usually expressed as a differential\(^4\) (eq 1.2-2):

\[
\beta = \frac{dC_b}{dpH} = \frac{dC_a}{dpH}
\]

(1.2-2)

where \( C_b \) and \( C_a \) are moles of acid or base per one liter of buffer. (Note that the \( C^0_a \) and \( C^0_b \) in eq 1.2-1 and other equations in this article refer to the initial concentrations of titrant and analyte, NOT the buffer capacity as defined in eq 1.1-2.)

To relate each point in the titration curve to its corresponding buffer capacity, eq 1.2-1 is differentiated with respect to \([H_3O^+]\) (eq 1.2-3)

\[
\frac{\partial V'_b}{\partial [H_3O^+]} = V_a \left( \frac{1}{[H_2O^+] + y C^o_b - \frac{K_w}{[H_2O^+]}} \right) \left[ -\frac{K_w}{[H_3O^+]^2} + \frac{K_a y C^o_a}{[H_2O^+] + K_a} \left( \frac{1}{\left[ H_3O^+ \right] + K_a} \right)^{-1} \right] \left( \frac{K_w}{[H_2O^+]^2} + \frac{K_a y C^o_b}{[H_2O^+] + K_a} \left( \frac{1}{\left[ H_3O^+ \right] + y C^o_a - \frac{K_w}{[H_2O^+]}} \right)^{-1} \right) \]

(1.2-3)

then modified via implicit differentiation (eq 1.2-4) to transform it with respect to pH.
The traditional definition of buffer capacity of a solution is presented on a “per liter” basis. To achieve this, the final expression must convert \( V_a \) to a 1-liter volume. The \( (1/V_a) \) first term in eq 1.2-5, accomplishes this. For example, because the BufCap TOPOS program uses a default value of 100 mL (0.100 L) as \( V_a \), the program multiplies the raw buffer capacity by \((1/0.100)\), or 10.0, to transform it to the 1.00-liter buffer capacity definition.

Note that eq 1.2-5 does not include \( V_b \) as an independent variable through which to calculate \( \beta \). Instead, we use the value of \([H_3O^+]\) attached to a pair of grid-point coordinates, \( i.e., \ [H_3O^+] = f(V_b, y) \). The \( \beta \)s that emerge from this procedure are plotted as log \( \beta \) values above grid-points so that a wide range of magnitudes can be captured simultaneously in a single plot. (The complete set of \( V_b \) and \( \beta \) equations for strong, monoprotic, diprotic and triprotic acids are derived in a downloadable Supplementary file.)

The validity of all buffer capacity equations was checked using raw pH data to compute finite difference approximations to the differential expression, adjusted by 10 to match the 1.00-L definition (eq 1.2-6).

\[
\beta = \frac{10y}{V_a} \frac{\partial V'_b}{\partial \text{pH}} \approx \frac{10y}{V_a} \frac{\Delta V'_b}{\Delta \text{pH}}
\]  (1.2-6)

The two surfaces were essentially indistinguishable except at the initial and equivalence points where finite differences miss specific grid point values.
1.2.3 Titration Curves and Buffer Capacities

Often buffer capacity is discussed as part of explaining titration curves.\textsuperscript{19-22} It is logical to describe how a titration curve’s flat spots, its buffer plateaus, behave. Figure 1.2-1 shows the titration curve for 100 mL of 0.100 M acetic acid being titrated with 0.100 M NaOH. A traditional buffer plateau appears before the equivalence point whose level is centered around pH = p\(K_a\) = 4.757. Not often discussed is a second type of flat spot, identified here as pseudo-buffering\textsuperscript{2}, a situation where the chemical inertia of the system prevents pH from changing rapidly as titrant is added. This appears in Figure 1.2-1 following the equivalence point break. Once an excess of NaOH exists, further additions of NaOH titrant only slowly change the pH.

**Figure 1.2-1.** Traditional titration curve for 100 mL of 0.100 M acetic acid titrated with 0.100 M NaOH.

A plot of buffer capacity (\(\beta\)) vs. pH often accompanies buffer capacity discussions.\textsuperscript{22} Using pH, a logarithmic x-axis, differs from the “mL of NaOH”, the linear x-axis of a titration curve. Figure 1.2-2 Panel a illustrates one version of a \(\beta\) vs. pH plot for the acetic acid system. Acetic acid’s p\(K_a\) is 4.757, so \(\beta\) reaches a local maximum at pH = p\(K_a\) = 4.757. This plot also suggests that buffer capacity is essentially proportional to the concentration of buffer components. Note that the buffer capacity for the 0.1 M solution at the p\(K_a\) maximum is 0.0576 M/pH. It doubles to 0.115 M/pH when the solution strength is increased to 0.2 M, a factor of two higher. As will be seen later, this direct relationship between buffer
Buffer capacity and concentration eventually erodes under extensive dilution procedures.

![Traditional buffer capacity plots](image)

**Figure 1.2-2.** Traditional buffer capacity plots. a) buffer capacity, $\beta$, vs. pH for acetic acid ($pK_a = 4.757$) at 0.100 M (blue lower trace) and 0.200 M (red upper trace) concentrations; b) buffer capacity, $\beta$, as the derivative of a $C_b$ vs. pH curve for the 0.100 M acetic acid system.

In a second version of buffer capacity vs. pH, the $\beta$ curve is superimposed onto a $C_b$ vs. pH curve to illustrate that the derivative of the $C_b$ generates the buffer capacity profile. Figure 1.2-2b illustrates this arrangement for the 0.1 M acetic acid system. This representation is good at demonstrating that the maximum buffer capacity of acetic acid’s buffer plateau occurs when pH = $pK_a = 4.757$. Less obvious is that the minimum buffer capacity occurs at the equivalence point when pH = 8.728. Although the $C_b$ vs. pH trace is related to a titration curve (with the $x$- and $y$-axes interchanged), it does not permit the eye to associate the buffer capacity values point-for-point with the progress of a titration. Data for this plot are generated by stepping at regular increments of pH, not regular increments of volume of base added.

With the logarithmic pH scale used as the $x$-axis, it is impossible to see the relationship between $\beta$ and volume of base added. To view this relationship, both pH and $\beta$ must be plotted against “mL of NaOH” (Figure
1.2-3). A logarithmic $y$-axis is used to display both pH and $\beta$ traces together.

**Figure 1.2-3.** The relationship between buffer capacity and a titration curve for 100 mL of 0.100 M acetic acid titrated with 0.100 M NaOH.

Half-way to the equivalence point (50.00 mL), the log $\beta$-curve shows a maximum value. The buffer capacity subsequently plunges to a minimum at the exact equivalence point, the place where pH changes most dramatically. With the traditional representation, no comparable visual feature appears at Figure 1.2-2’s equivalence point. On the other hand, the $\beta$ vs. pH curve better emphasizes the local maximum $\beta$ at pH $= p\mathcal{K}_a$, the half-equivalence point.

### 1.2.4 pH and Buffer Capacity Surfaces

A complete description of pH and buffer capacity behavior during acid-base titrations and dilution procedures can be visualized by 3-D topo surfaces above the $\nu_b$ vs. log $C$ composition grid. This is just an extension of literature plots that show multiple titrations at different concentrations. If many dilution slices, 37 in the present example, are stacked in the right manner, an overall “topo” trend surface is created. The complete 3-D pH topo surface for acetic acid appears as Figure 1.2-4. Each slice represents a 100-mL acid sample titrated with an NaOH solution of the same concentration.
Figure 1.2-4. The acetic acid pH topo surface. (Note: this is the same as Figure 1.1-2)

The right-hand edge of Figure 1.2-4 is the pH titration curve for 100 mL of 1.00 M acetic acid titrated with 1.00 M NaOH. As one moves left along the log $C$ axis, progressively more dilute conditions are encountered. Successive lines indicate repeating the titration with the initial concentration of both the acid and base adjusted identically. Thus, under the most dilute conditions (the surface’s left-hand edge), $1.00 \times 10^{-9}$ M CH$_3$COOH is being titrated with $1.00 \times 10^{-9}$ M NaOH.

Viewing the entire pH topo surface, one discerns a series of ramp, cliff and plateau features. Ramps are associated with grid regions where dilution alone dominates pH behavior. Cliffs occur at titration initial and equivalence points. Plateaus indicate situations in which pH is somewhat stable against addition of NaOH titrant or dilution, i.e., buffer zones and extreme dilution conditions. These surface features are discussed in detail in a Chapter 1.1.3

3-D topo surfaces can also be generated for associated buffer capacities. Figure 1.2-5 introduces one variety of buffer capacity surface. It is a linear buffer capacity surface that has extended the traditional buffer capacity vs. pH plot into a dilution dimension. Note, this surface is not plotted above a composition grid.
Instead, it uses a system parameter, pH, as one of the axes rather than the solution composition. Shown here for the first time is the buffer capacity vs. pH extended systematically in the dilution direction. To make the surface correspond to traditional buffer capacity plots, both the y- and z-axes are linear.

**Figure 1.2-5.** Linear buffer capacity topo for the acetic acid system of Figure 1.2-4.

Figure 1.2-5 shows two features of the buffer system: 1) the pH at which maximum buffer capacity occurs \((i.e., \text{pH} = pK_a)\), and, 2) the linear relationship between buffer capacity and concentration when plotted using pH as the x-axis. The top of the buffer ridge on this example is located at \(\text{pH} = 4.800\), the grid line closest to the half-equivalence point \((\text{pH} = pK_a = 4.757 \text{ for acetic acid})\). The maximum value observed is 0.572 mol/L for a 1.00 M buffer content and 0.286 mol/L for a 0.500 M buffer content, a 2:1 ratio as expected.

The linear buffer capacity surface shows two features of the buffer system: 1) the pH at which maximum buffer capacity occurs \((i.e., \text{pH} = pK_a)\), and, 2) the linear relationship between buffer capacity and concentration when plotted using pH as the x-axis. The top of the buffer ridge on this example is located at \(\text{pH} = 4.800\), the grid line closest to the half-equivalence point \((\text{pH} = pK_a = 4.757 \text{ for acetic acid})\). The maximum value observed is 0.572 mol/L for a 1.00 M buffer content and 0.286 mol/L for a 0.500 M buffer content, a 2:1 ratio as expected.

The linear β plot of Figure 1.2-5 does not have a strong feature for the equivalence point pH of 8.728. The equivalence point pH lands in a broad valley that lies between the buffer ridge and the NaOH wing. The β-curves of Figure 1.1-2a are the 0.100 M and 0.200 M slices of the linear buffer capacity surface above. The equivalence point pH is labeled at a position with no visible feature. The buffer capacity curve is practically flat between pHs of 7.000 and 10.500. If one were to use a logarithmic z-axis for the surface plot, the ridge crest would be visible but less sharp, and the equivalence point pH would be at the bottom of a V-shaped canyon.
The wings at the linear surface’s edges represent additions of concentrated NaOH or HCl that are necessary to achieve high or low pH values in the grid range. They are not related to the buffer component itself. Their buffer capacities are pseudo-buffering from the added NaOH or HCl.

Linear β topos also do not show how dilution-driven dissociation eventually breaks down the linear relationship between buffer capacity and buffer component concentration. The linear dilution scale compresses much interesting buffer behavior into the final grid interval. This detail only becomes visible by expanding this last interval via a logarithmic scale.

Building a buffer capacity surface above a titration/dilution composition grid, \((V_b, \log C)\), draws out additional buffer capacity information (Figure 1.2-6). This base arrangement exactly matches the pH topo of Figure 1.2-4 and allows the viewer to associate changes in pH with the corresponding buffer capacity behavior. A logarithmic buffer capacity axis, \(\log \beta\), can display values covering many orders of magnitude of dilution. The buffer capacity topo is viewed from a different angle than Figure 1.2-4 to promote inspection of as many surface features as possible.

**Figure 1.2-6.** Logarithmic buffer capacity surface for acetic acid above a titration/dilution composition grid.

For \(\log \beta\) surfaces, the back edge of the surface is the most concentrated \((\log C = 0, i.e., 1.00 \text{ M})\) slice for the topo. The most dilute conditions are at the
previous work with buffer capacity has only explored dilution to a minor extent\textsuperscript{11}, from a factor of two to slightly more than an order of magnitude. Figure 1.2-6 covers nine orders of dilution magnitude.

Logarithmic buffer capacity surface features fall into three general categories: ramps, ridges and canyons. Ramps are associated with pseudo-buffer situations where changes are mostly physical dilution processes rather than acid-base interactions.\textsuperscript{2} Ridges correspond to true buffer situations where the acid-to-base ratio plays a controlling role. Finally, canyons correspond to the equivalent point breaks and are the lowest buffer capacities observed during a titration slice.

Log buffer capacity features correlate to features seen on pH topo surfaces. During the course of a titration, the following buffer capacity behaviors will be seen: The “initial point cliff” on the pH topo manifests itself as the rapid rise to the “buffer ridge” on the buffer capacity topo. This makes logical sense. Wherever the pH is changing quickly, buffer capacities will be small. As pH stabilizes, buffer capacities will too. By the time a few 5.00-mL aliquots of NaOH are added to the starting solution, a reasonably stable buffer system exists. This develops into the broad “buffer ridge”. At the half-equivalence point, the buffer capacity increases to a maximum value on a rounded crest. The pH and buffer capacity are quite stable here. Near the equivalence point, the system’s pH and buffer capacity become highly sensitive to additions of more NaOH. At the exact equivalence point, the buffer capacity plunges to a local low in the bottom of the “equivalence point canyon”. For the 1.00 M slice of acetic acid, a drop of 3.566 log units occurs from the preceding buffer ridge maximum. Ultimately, the buffer capacity climbs to high values as excess NaOH dominates the system beyond the equivalence point. The pseudo-buffering slows pH and buffer capacity changes.

In the log $C$ direction, all slices slope downward toward the “pH 7 dilution ramp”. This occurs because buffer capacity is an extensive system property, proportional to concentration. At half-equivalence points on buffer capacity topos there are no flat spots extending in the dilution direction as in the buffer plateaus of the pH surfaces. The intensive pH property is dependent on the [base]/[acid] ratio, whereas the extensive buffer capacity is simply dependent on [acid]. Dilution does not initially alter the [base] to [acid] ratio on the pH topo, thus a plateau is established. But for the buffer capacity surface, dilution creates a ramp feature from the start; the concentration of the available acid form...
Buffer capacity decreases steadily. Eventually, depending on the buffer system’s $K_a$, dilution will begin to shift the [base]/[acid] ratio. The pH topo’s buffer plateau deteriorates and tilts toward $\text{pH} = 7$.

When dilution reaches about $10^{-6}$ M, the auto-dissociation of water provides almost equivalent amounts of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ as the buffering agent itself. Beyond $10^{-7}$ M, the $\text{H}_3\text{O}^+$ and $\text{OH}^-$ of water overwhelm what little buffering agents are present. Dilution no longer changes the buffer capacity because the diluent has nearly the same composition as the solution to which it is being added. Thus, beyond $10^{-6}$ M, the buffer capacity slices in the dilution direction become essentially flat.

The “pH 7 dilution ramp” slopes gently upwards in the $V_b$ direction, another instance in which the chemical inertia of the system is at play. Though the NaOH titrant being added is very dilute, it still slowly accumulates and raises the pH a slight amount. This results in corresponding higher buffer capacities, too.

For comparative purposes, it is useful to look at pH and buffer capacity surfaces for a strong acid like HCl. Figure 1.2-7a displays HCl’s pH topo. Panels b and c hold the log buffer capacity topo and the linear buffer capacity surfaces, respectively. The log buffer capacity topo has a deep equivalence point canyon. The linear $\beta$ surface shows no equivalence point feature; it simply has HCl and NaOH wings at either edge. There is no real buffering in this system, just pseudo-buffering created by chemical inertia of the HCl and NaOH.

**Figure 1.2-7.** Topo surfaces for hydrochloric acid, HCl. a) pH; b) log $\beta$; c) $\beta$ vs. pH.
1.2.5 Effect of \( pK_a \) and Dilution on Buffer Capacity

The size of the initial point cliff on a pH topo varies with the \( pK_a \) of the acid – the higher the \( pK_a \), the more dramatic the initial point cliff. The higher the \( pK_a \), the more dramatic the rise to its buffer ridge crest, too (Figure 1.2-8).

Shown are buffer capacity traces for three acids as 0.100 M solutions of each are titrated with 0.100 M NaOH. HCl, a strong acid with a \( pK_a \) of -6, has no rise to a buffer ridge. Its maximum buffer capacity is at the initial point before systematically declining to the equivalence point. HCl exhibits pseudo-buffering.

The dashed line is acetic acid with a \( pK_a \) of 4.757. About an order of magnitude rise is seen between the initial buffer capacity and the maximal value at 50 mL. The dotted line is phenol, a very weak acid with \( pK_a = 9.996 \). The rise to the buffer ridge crest is about four orders of magnitude. Its buffer pH of 9.996 is much higher than its starting pH of 4.989.

![Figure 1.2-8. The effect of \( pK_a \) on log buffer capacity curves of three 0.100 M acids: HCl (solid blue line); acetic acid (dashed red line); phenol (dotted black line)](image)

Notice that pre-equivalence point capacities at the half-equivalence point are practically identical for both weak acids, acetic acid and phenol. While acetic acid and phenol differ greatly in strength and buffer pHs, once a buffer has formed, their buffer capacity traces are indistinguishable. They have the same ability to consume added NaOH while maintaining the current pH value. The difference is that acetic acid maintains pH near its \( pK_a \) of 4.757 while phenol
maintains pH around its $pK_a$ of 9.998. Acid is acid. One molecule of any acid will consume one OH\(^-\) ion.

The depth of the equivalence point canyon depends on the size of the equivalence point break, which is a function of an acid’s $pK_a$. The HCl buffer capacity runs above the weak acid traces until about 60 mL. HCl’s buffer capacity canyon then plunges to -6.094, far below that of either weak acid. Beyond the equivalence point, the traces for all three systems are superimposed as pseudo-buffering from excess NaOH dominates in all three cases.

The initial rise in buffer capacity disappears with dilution. Figure 1.2-9 shows comparative plots for three acids - hydrochloric, formic and acetic - at successive 100-fold dilutions. At higher concentrations weak acids display differing amounts of capacity according to their strength. In the upper group at 0.100 M, acetic acid displays the lowest initial buffer capacity since it is the weakest. It experiences the greatest jump between its initial pH (2.379) and its optimal buffered pH (4.757). The bigger the pH jump, the lower the initial buffer capacity. Formic acid undergoes a smaller jump, 1.875 to 3.745. HCl exhibits no rise.

![Figure 1.2-9](image)

**Figure 1.2-9.** Effect of dilution on the buffer capacity curve for three acids at 0.100 M, 0.00100 M and 0.0000100 M.

Dilution to 1.00 x $10^{-3}$ M causes both formic and acetic acids to dissociate further. Formic acid dissociates sufficiently to also exhibit pseudo-buffering; no buffer ridge is present. When diluted to 1.00 x $10^{-5}$ M, both weak acid buffer capacity curves coincide with HCl. Sufficient dissociation from dilution makes the three buffer capacities essentially pseudo-buffer equivalents.
1.2.6 Polyprotic Systems

Buffer capacity topos for polyprotic species can display multiple buffer ridges and equivalence point canyons. The equivalence point canyon depths vary with the size of associated equivalence point breaks from the pH surface. Unless pre- and post-equivalence point pHs differ by about three orders of magnitude, only a shallow canyon appears on the log buffer capacity surface.

Figure 1.2-10 holds topo surfaces for diprotic oxalic acid. Oxalic acid’s $pK_a$s are 1.27 and 4.266. The pH topo (Figure 1.2-10a) shows two equivalence point cliffs. The log buffer capacity topo (Figure 1.2-10b) displays two buffer capacity canyons. There is no initial rise on either the pH or buffer capacity topo due to the low $pK_{a1}$. It overlaps with the HCl wing as seen in the flare-out of its right edge (instead of rounding downwards). The first equivalence point canyon has modest depth, bottoming out at -0.890 log units, because $pK_{a1}$ and $pK_{a2}$ differ by just three orders of magnitude. The second equivalence point canyon is more substantial, hitting a much lower -3.963, because the pH changes by eight orders of magnitude. With the $pK_{a1}$ so small, the linear buffer capacity surface (Figure 1.2-10c) has the HCl wing interfering with the first buffer ridge. Cleanly separated buffer peaks on this style of plot always extend to the same height. Note that the combined $pK_{a1}$ + HCl wing is taller than the $pK_{a2}$ isolated peak.

**Figure 1.2-10.** Topo surfaces for diprotic oxalic acid. a) pH; b) log buffer capacity; c) linear buffer capacity vs. pH.
Figure 1.2-11 shows superimposed buffer capacity slices for 1 M solutions of oxalic acid and 8-hydroxyquinoline (8HQ). The $pK_a$ values for 8HQ are 4.94 and 9.82. The higher $pK_a$ for 8HQ leads to a more pronounced initial rise. The small difference between its $pK_a$ and the pseudo-buffering pH reduces the second equivalence point canyon depth. Between the canyons of polyprotic systems are buffer ridges, all of similar height. Maximum log capacity on most weak acid buffer ridges is near -0.240. Both buffer ridges for 8HQ show a maximum of ~-0.240. Oxalic acid’s first ridge maximum is slightly higher than usual because its $pK_a$ is small and overlaps with a contribution from the HCL wing.

**Figure 1.2-11.** Buffer capacity curves for the 1.00 M slice of oxalic acid (solid blue line) and 8-hydroxquinoline (dotted black line). The dashed red line indicates typical maximum log buffer capacity of -0.240 for weak acid protons.

Example topos for a triprotic system, L-glutamic acid hydrochloride (L-Glu), are in Figure 1.2-12. The only new features seen with the L-Glu surface are those associated with a third equivalence point. The $K_a$ values are $6.92 \times 10^{-3}$, $5.0 \times 10^{-5}$ and $1.10 \times 10^{-10}$ with corresponding $pK_a$ values of 2.160, 4.30 and 9.96, respectively. The pH topo (Panel a) exhibits three equivalence point cliffs and three buffer plateaus. The first equivalence point cliff is small because $pK_{a1}$ is fairly strong (less than 3) and much of the acid starts already dissociated. The logarithmic buffer capacity surface (Panel b) reveals a shallow first equivalence point canyon because the difference between successive $pK_a$ is only 2.14. The second equivalence point canyon’s depth is the deepest of the three as $pK_{a2}$ and $pK_{a3}$ are 5.531 log units apart. The third equivalence point canyon is intermediate in depth because $pK_{a3}$ differs from the titrant pH of 14 by 4.04 log units. The linear buffer capacity surface for L-Glu (Panel c) shows a first buffer ridge with elevated saddles to both sides. The low $pK_{a1}$ value causes the first high
saddle because it overlaps a tiny bit with the HCl pseudo-buffering wing. The second high saddle is due to the close spacing of the first two $pK_a$s that only differ by 2.14 log units as pointed out above. For complete separation of a buffer ridge, a spacing of 3 or more is needed.

**Figure 1.2-12.** Topo surfaces for L-glutamic acid. a) pH; b) log buffer capacity, c) linear buffer capacity vs. pH.

### 1.2.7 Extent and Depth of the Equivalence Point Canyon

The extent of the equivalence point canyon in the dilution direction is a combination of two factors: 1) the size of the equivalence point break; and 2) the closeness of the equivalence point pH to 7.0. Because the buffer capacity is the inverse derivative at any grid point location, the larger the equivalence point break, the more dramatic the changes in buffer capacity. If a break is small, the equivalence point canyon will be shallow and less extensive in length. When an equivalence point break happens far away from pH 7.0, the pre- or post-equivalence point ramp (pseudo-buffering) overwhelms it at an earlier dilution volume.

The first equivalence point canyon for L-Glu in Figure 1.2-12 is short because its pH of 3.234 is well below 7.0. It is associated with a small equivalence point cliff since $pK_{a1}$ and $pK_{a2}$ differ by less than 3. The second equivalence point canyon for L-Glu extends over 5.5 orders of dilution magnitude. The equivalence point pH of 7.130 is very close to 7.000 so the essentially ends only when it reaches the pH 7 dilution ramp. L-Glu’s third equivalence point canyon at 300 mL is shallow because $pK_{a3}$ and the post-equivalence plateau pH differ by only three
orders of magnitude. The third equivalence point pH (11.672) is well away from 7.0, so its canyon merges into the post-equivalence point ramp early on.

A detailed analysis of equivalence point canyons on the logarithmic surfaces for all acids (hydrochloric, acetic, oxalic and l-glutamic) are summarized in Table 1.2-1. $\Delta p_{H_{pp}}$ is the difference in pH, 50 mL before and 50 mL after the equivalence point. $\Delta p_{H_{7.00}}$ is the offset between the equivalence point pH and 7.00. Canyon length is expressed as the closest grid point value at which there is still a visible depression on the topo. Finally, the depth of the canyon is the difference between the log $\beta$ of the ridge maximum at the half-equivalence point and the log $\beta$ at the bottom of the canyon. Note that for diprotic acid topos, the surface extends to 400 mL, far beyond the last equivalence point. This was done to force exact equivalence point volumes to land on grid values.

**Table 1.2-1.** Equivalence Point Canyon Parameters for logarithmic buffer capacity topos (in log units).

<table>
<thead>
<tr>
<th>Equivalence Point</th>
<th>Magnitude of break: $\Delta p_{H_{pp}} \pm 50$ mL of equivalence point</th>
<th>$\Delta p_{H_{7.00}}$: Offset of equivalence point pH from 7.00</th>
<th>Canyon length (in log dilution units)</th>
<th>Depth of canyon $(\text{ridge}<em>{\text{max}} - \text{canyon}</em>{\text{min}})$ at 1.0 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>13.297 – 0.477 = 12.820</td>
<td>7.000 – 6.998 = 0.002</td>
<td>5.50</td>
<td>-0.064 – (-6.034) = 5.970</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>13.297 – 4.757 = 8.540</td>
<td>9.228 -7.000 =2.228</td>
<td>5.50</td>
<td>-0.240 – (-3.806) = 3.566</td>
</tr>
<tr>
<td>Oxalic acid 1st</td>
<td>4.268 – 1.376 = 2.892</td>
<td>7.000 – 2.790 = 4.210</td>
<td>2.25</td>
<td>-0.164 – (-0.840) = 0.676</td>
</tr>
</tbody>
</table>
1.2.8 Conclusions

This paper extends use of three-dimensional trend surfaces (topos) to visualize buffer capacity behavior in aqueous acid-base equilibria systems. A novel aspect is the link between buffer capacity and titration curves. This required the derivation of new equations to make it possible. Traditional plots of buffer capacity vs. pH have logarithmic spaced data, not linear-spaced volumes like a titration. By tying the buffer capacity to the linear progress of the titration, a more realistic view for the dynamics of buffer capacity change is provided. Traditional buffer capacity plots have been expanded into analogous three-dimensional topo surfaces so that the relationship between the two representations can more easily be seen.

Buffer capacity topo surfaces provide an effective method of illustrating properties of buffer behavior:

- The maximum buffer capacity of a system essentially depends on the concentration of the buffer agent, not its specific identity;

- The maximum buffer capacity of each proton in a polyprotic system is essentially the same; and

- The extent to which buffering breaks down near an equivalence point is dependent on both the closeness of its $pK_a$ to pH 7 and the magnitude of the break.
While BufCap TOPOS could be used in a first-year collegiate course, an understanding of its fine points belongs more in junior- and graduate-level courses in analytical chemistry, biochemistry or geochemistry. The speed and ease with which new systems can be visualized makes this a powerful tool for simulation studies. Because BufCap TOPOS is a series of MicroSoft Excel macros, no new software need be purchased. With its speed and ease of use, it can even be exploited for “on-the-fly” calculations by an instructor during a classroom session.

1.2.9 Supplementary Files

Four supplementary files accompany this chapter:

1. The free down-loadable BufCap TOPOS software as a Microsoft Excel workbook.

2. A set of PowerPoint slides on how to teach the BufCap TOPOS software in lecture settings or as a stand-alone tutorial.

3. A Microsoft Word document containing teaching objectives with suggested worksheet activities (homework problems, pre-lab exercises, recitation section examples or peer-led team discussion material) and coordinated laboratory experiments.

4. Detailed mathematical derivations of the expressions used to generate the log buffer capacity topo surfaces as a function of volume of NaOH added ($V_b$) and overall system dilution ($\log C$).

The BufCap TOPOS software contains tabs for monoprotic, diprotic and triprotic acids to be titrated by NaOH. Each worksheet is populated with the weak acid examples presented in this paper. To generate buffer capacity surfaces for any other acid, the user needs only to supply new $K_a$s. An additional workbook tab includes an extensive table of $K_a$s that can be cut-and-pasted for easy program use. By examining several sample surfaces, anyone should be able to predict trends in buffer capacities without resorting to detailed calculations.
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We thank the Department of Chemistry and Biochemistry at the University of Montana for a graduate teaching assistantship that supported early phases of this research. Dr. Patrick MacCarthy from the Colorado School of Mines helped develop the topo trend surface approach in aqueous equilibrium settings. Daniel Berry’s assistance as an undergraduate researcher helped perform experimental verifications of computed results.

REFERENCES


