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Buffer index in the titration of a monoprotic acid with a strong base

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Summary

Buffer solutions are of great worth in analysis, in chemical and pharmaceutical research, in physiology and other fields of science and technology. On the other hand, buffer capacity is subject to precise algebraic treatment by using differential calculus. The location of the maximum and inflexion points in the buffer index against pH and in the volume of titrant added against pH plots for the titration of a weak monoprotic acid with a strong base, is the subject of consideration in this paper. In calculating buffer capacity in the titration of a weak acid with a strong base, an essential factor is the change in the volume resulting from dilution of the solution as titrant is added.

Introduction

As a matter of fact many chemical and biological processes are vitally dependent upon pH, in such a way that it is very important in laboratory work to be able to adjust the pH of a chemical system to a fixed value as well as to ensure that the pH will be maintained close to that value for the duration of a given experiment.

In this context, a solution containing a fairly large amount of an acid and its conjugate base is called an acid/base buffer solution system. Buffer solutions are of great value in analysis, chemical and pharmaceutical research, physiology and other fields of science and technology (King, 1965; Stumm and Morgan, 1981; Connors, 1985; Polster and Lachmann, 1989), because they allow the pH of a solution to be maintained with considerable accuracy at a nearly constant value, even on addition of small quantities of strong acids or bases or on dilution.

The ability of a solution to resist attempts to change its pH is called the buffer capacity (Van Slyke, 1922), which is defined by Eqn 1:

$$\beta = \frac{\mathrm{d}C_B}{\mathrm{dpH}} \tag{1}$$

where $\mathrm{d}C_B$ (and $\mathrm{d}C_A$) denotes the number of moles per liter of the strong base (or strong acid) added and is an expression of the rate at which the addition of strong base (strong acid) changes pH.

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In many analytical textbooks (Sucha and Kotrly, 1972; Hulanicki, 1987), it is shown that the final expression for the total buffer index of a mixture of a weak acid and its salt (i.e., HA/NaA) is equal to the sum of the buffer capacities of the individual systems

$$\beta = \beta_{H^+} + \beta_{OH^-} + \beta_{HA} \tag{2}$$

On the other hand, the buffer contribution with respect to pH of the β_{HA} term is shown by means of a bell-shaped curve with a maximum at pH = pK_a, the height of the maximum being dependent on the total concentration of the buffer solution, C_A

$$C_A = [HA] + [A^-] \tag{3}$$

While the expressions derived in such texts are correct if the solution volume is assumed to remain constant as the ratio of salt to acid varies, some different conclusions may be drawn if a titration process is being carried out. However, buffer capacity is subject to precise algebraic treatment using differential calculus. As a conclusion (Butcher and Fernando, 1966), it may be anticipated that in the calculation of buffer capacity during the titration of a weak acid with a strong base, an essential factor is the change in volume resulting from dilution of the solution as titrant is added.

In this paper, we discuss buffer capacity of HA/NaA systems primarily from a general and didactic point of view. This paper is of an expository type, and we do not claim completeness in our treatment. For a more comprehensive and advanced treatment of some topics to which this paper may serve as a useful introduction, the reader is referred to Butcher and Fernando (1966).

Theory

Basic algebra

If a weak acid HA of concentration C_A and initial volume V_0 is titrated with a strong base (i.e., NaOH) of concentration C_B and volume V, then at any moment during the titration the condition of electroneutrality must be fulfilled

$$[Na^+] + [H^+] = [A^-] + [OH^-] \tag{4}$$

Due to the volume increase in the course of the titration, we obtain

$$[Na^+] = C_B \frac{V}{V_0 + V} \tag{5}$$

$$[A^-] = C_A \frac{V_0}{V_0 + V} f_0 \tag{6}$$

f_j is the molar fraction of the species H_jA ($j = 0$, 1; for a monoprotic acid HA)

$$f_j = \frac{[H_jA]}{C_A} \quad (j = 0, 1) \tag{7}$$

Its derivative with respect to pH is given by (Asuero et al., 1986):

$$\frac{df_j}{dpH} = -\ln 10 f_j(j - \bar{n}) = -\ln 10 f_j(j - f_1) \tag{8}$$

so that for a monoprotic acid the formation function, $\bar{n} = \Sigma j f_j$, coincides with f_1.

We assume that the ionic strength is left virtually unaltered by addition of the increment of base, so that variations in activity coefficient can be neglected.

By definition of β we have (Guenther, 1975)

$$\beta = \frac{d[Na^+]}{dpH} = C_B \frac{d}{dpH}\left(\frac{V}{V_0 + V}\right)$$

$$= C_B \frac{V_0}{(V_0 + V)^2} \frac{dV}{dpH} \tag{9}$$

The buffer value is inversely proportional to the slope of the titration curve and from Eqns 4 and 6 we have

$$\begin{aligned}\beta &= \frac{\mathrm{d}}{\mathrm{dpH}}([\mathrm{A}^-] + [\mathrm{OH}^-] - [\mathrm{H}^+]) \\ &= \frac{\mathrm{d}}{\mathrm{dpH}}\left(C_\mathrm{A}\frac{V_0}{V_0+V}f_0 - [\mathrm{H}^+] + [\mathrm{OH}^-]\right) \\ &= -\frac{C_\mathrm{A}V_0}{(V_0+V)^2}f_0\frac{\mathrm{d}V}{\mathrm{dpH}} \\ &\quad + \ln 10\left(\frac{C_\mathrm{A}V_0}{V_0+V}f_0f_1 + [\mathrm{H}^+] + [\mathrm{OH}^-]\right)\end{aligned} \tag{10}$$

By equating Eqns 9 and 10 the value of $\mathrm{d}V/\mathrm{dpH}$ may be extracted

$$\frac{\mathrm{d}V}{\mathrm{dpH}} = \ln 10\frac{(V_0+V)^2}{V_0} \times \left(\frac{[\mathrm{H}^+] + [\mathrm{OH}^-] + C_\mathrm{A}\frac{V_0}{V_0+V}f_0f_1}{C_\mathrm{A}f_0 + C_\mathrm{B}}\right) \tag{11}$$

which, on substitution into Eqn 9, gives for the buffer capacity the exact equation

$$\beta = \ln 10\frac{[\mathrm{H}^+] + [\mathrm{OH}^-] + C_\mathrm{A}\frac{V_0}{V_0+V}f_0f_1}{1 + \frac{C_\mathrm{A}}{C_\mathrm{B}}f_0} \tag{12}$$

As the equivalence point in the titration is reached when

$$C_\mathrm{A}V_0 = C_\mathrm{B}V_{\mathrm{p.eq.}} \tag{13}$$

taking into account the dilution parameter r

$$r = \frac{C_\mathrm{A}}{C_\mathrm{B}} \tag{14}$$

and the fraction titrated, T, which is defined as the ratio of the number of millimoles of base added as titrant to that of acid being titrated

$$T = \frac{C_\mathrm{B}V}{C_\mathrm{A}V_0} = \frac{V}{\frac{C_\mathrm{A}V_0}{C_\mathrm{B}}} = \frac{V}{V_{\mathrm{p.eq.}}} \tag{15}$$

we have for the ratio of the initial to actual volume

$$\frac{V_0}{V_0+V} = \frac{1}{1+\frac{V}{V_0}} = \frac{1}{1+\frac{V}{V_{\mathrm{p.eq.}}}\frac{V_{\mathrm{p.eq.}}}{V_0}} \tag{16}$$

and then, by combining Eqns 12–14 and 16, we obtain for the buffer capacity the final rigorous general description

$$\beta = \frac{\ln 10}{1+rf_0}\left([\mathrm{H}^+] + [\mathrm{OH}^-] + \frac{C_\mathrm{A}f_0f_1}{1+rT}\right) \tag{17}$$

This is equivalent to dividing the buffer capacity into the sum of contributions, as shown in Eqn 2. In Eqn 17 there are two terms independent of the nature of the buffer used and corresponding to the concentrations of H^+ and OH^-. They determine the increase in buffer capacity in a strongly acidic region and in a strongly alkaline region, and confirm the buffering character of concentrated solutions of strong acids and bases

$$\beta_{\mathrm{H}^+} = \frac{\ln 10}{1+rf_0}[\mathrm{H}^+] \tag{18}$$

$$\beta_{\mathrm{OH}^-} = \frac{\ln 10}{1+rf_0}[\mathrm{OH}^-] \tag{19}$$

As the value of f_0, the molar fraction of the A^- species of the monoprotic acid, tends to unity as the alkalinity of the solution increases and becomes smaller as the concentration of hydrogen ion rises, the individual contributions of β_{H^+} and β_{OH^-} to the total buffer capacity are not strictly symmetrical with respect to a pH value equal to $\mathrm{p}K_\mathrm{w}/2$.

The buffer contribution of the HA/NaA system, β_{HA}, is given by

$$\beta_{\mathrm{HA}} = \frac{\ln 10}{1 + rf_0}\left(\frac{C_{\mathrm{A}} f_0 f_1}{1 + rT}\right) \tag{20}$$

However, it should be noted that in Eqns 17 and 20 the volume and the concentration of the solution being titrated are used directly (via r or T), so that the change in β during the titration of a weak acid with a strong base depends on the initial concentrations or the dilution of the solution during titration (Meites and Goldman, 1963).

Most buffers have pH values between 3 and 11 and total concentrations C_{A} between 0.01 and 0.1 mol l^{-1}; the buffer value is then virtually fixed by the third term of Eqn 17 (i.e., Eqn 20).

Nevertheless, on titration of a strong acid of initial concentration C_{H} and volume V_0 with a strong base of concentration C_{B}, the following equation may be similarly derived

$$\beta = \frac{\ln 10}{1 + R}([\mathrm{H}^+] + [\mathrm{OH}^-]) = \beta_{\mathrm{H}^+} + \beta_{\mathrm{OH}^-} \tag{21}$$

where

$$R = \frac{C_{\mathrm{H}}}{C_{\mathrm{B}}} \tag{22}$$

the β_{H^+} and β_{OH^-} terms in this case being symmetrical with respect to $\mathrm{p}K_{\mathrm{w}}/2$.

Solutions of strong acids or bases are used to adjust pH only in both extreme regions of the pH scale where high values of buffer capacity must be reached, alkali metal salts of strong acids being added to maintain constancy of ionic strength; pH values of such buffers fall outside the usual range of interest in physiology and chemistry.

When the titration of a mixture of strong and weak acids of total volume V_0 and concentrations C_{H} and C_{A}, respectively, is carried out by the addition of a strong base, an entirely analogous treatment leads to the following expression

$$\beta = \frac{\ln 10}{1 + R + rf_0}\left([\mathrm{H}^+] + [\mathrm{OH}^-] + \frac{C_{\mathrm{A}} f_0 f_1}{1 + R + rT}\right) \tag{23}$$

with T in this case being equal to

$$T = \frac{C_{\mathrm{B}}V - C_{\mathrm{H}}V_0}{C_{\mathrm{A}}V_0} \tag{24}$$

If $[\mathrm{H}^+]$ and $[\mathrm{OH}^-]$ can be disregarded compared with the concentration of the buffer constituents, i.e., if the concentration of hydrogen and hydroxide ions is low compared with the degree of dissociation, as occurs in moderately alkaline or acidic solutions, then the graph of the titration fraction vs pH (the titration curve) is identical with that of the degree of dissociation vs pH

$$f_0 = T \tag{25}$$

and then

$$\beta_{\mathrm{HA}} = \ln 10 \frac{C_{\mathrm{A}} f_1 f_0}{(1 + rf_0)^2} \tag{26}$$

Maximum buffer capacity of the β_{HA} curve

The slope of the plot of β vs pH may be found by differentiating Eqn 26 with respect to pH, and is given by

$$\frac{\mathrm{d}\beta_{\mathrm{HA}}}{\mathrm{dpH}} = -\ln^2 10 C_{\mathrm{A}} \frac{f_0(1 - f_0)((2 + r)f_0 - 1)}{(1 + rf_0)^3} \tag{27}$$

Values of $\mathrm{d}\beta_{\mathrm{HA}}/\mathrm{dpH} = 0$ will locate singular points in the graph of β_{HA} vs pH. Apart from the trivial solutions $f_0 = 0$, or $f_0 = 1$, which correspond to limiting values to which the graph tends asymptotically to zero, we have

$$f_0' = \frac{1}{2 + r} \tag{28}$$

and then

$$f_1' = 1 - f_0' = \frac{1 + r}{2 + r} \tag{29}$$

TABLE 1

Effect of dilution on the point of maximum buffer capacity

r	$\mathrm{p}K_a - \mathrm{pH}'$	f'_0
0	0	0.500
0.05	0.021	0.488
0.1	0.041	0.476
0.2	0.079	0.455
0.4	0.146	0.417
0.5	0.176	0.400
1.0	0.301	0.333
1.5	0.398	0.286
2.0	0.477	0.250

The hydrogen ion concentration at such a stationary point (maximum) is given by

$$[\mathrm{H}'] = K_a \frac{f'_1}{f'_0} = K_a(1+r) \tag{30}$$

By substituting the values of f_0 and f_1 given by Eqns 28 and 29 into Eqn 26, we obtain

$$\beta'_{\mathrm{HA}} + \frac{\ln 10}{4} \frac{C_{\mathrm{A}}}{1+r} \tag{31}$$

The maximum buffer capacity in the titration of a weak monoprotic acid with a strong base proceeds at pH values

$$\mathrm{pH}' = \mathrm{p}K_a - \log(1+r) \tag{32}$$

lower than the value of $\mathrm{p}K_a$, when one takes into account the dilution effect (Table 1). Only in the particular case in which dilution is ignored ($r = 0$; coulometric titrations) does pH′ coincide with the $\mathrm{p}K_a$ value of the HA/NaA system.

The β_{HA} vs pH curve given by Eqn 26, however, is symmetric with respect to the pH′ point. In effect, making (charges being omitted for simplicity in the following)

$$y = \frac{[\mathrm{H}]}{[\mathrm{H}']} \tag{33}$$

we obtain

$$\Delta\mathrm{pH}^* = \mathrm{pH}' - \mathrm{pH} = \log y \tag{34}$$

and taking into account Eqn 30 we have

$$[\mathrm{H}] = (1+r)K_a y \tag{35}$$

which, substituted into Eqn 26 leads to

$$\beta_{\mathrm{HA}} = \frac{\ln 10 C_{\mathrm{A}}}{1+r} \frac{1}{2 + \left(\dfrac{1}{y} + y\right)} \tag{36}$$

which may be expressed in an equivalent hyperbolic cosine relationship

$$\beta_{\mathrm{HA}} = \frac{\ln 10 C_{\mathrm{A}}}{1+r} \frac{1}{2(1+\cosh(\ln 10 \Delta\mathrm{pH}^*))} \tag{37}$$

which is symmetrical with respect to the pH′ values as $\cosh x = \cosh(-x)$.

Inflexion points in the β_{HA} vs pH curve

Differentiation of Eqn 25 with respect to pH gives

$$\frac{\mathrm{d}^2\beta}{\mathrm{dpH}} = -\ln^3 10 \frac{C_{\mathrm{A}} f_0 f_1}{(1+rf_0)^4} [(1-2f_0)[(2+r)f_0 - 1] + f_0(1-f_0)(2+r)] \cdot [(1+rf_0) - 3rf_0(1-f_0)[(2+r)f_0 - 1]] \tag{38}$$

which, on rearrangement, leads to

$$\frac{\mathrm{d}^2\beta}{\mathrm{d(pH)}^2} = \ln^3 10 \frac{C_{\mathrm{A}} f_0 f_1}{(1+rf_0)^4} \times [(r^2+6r+6)f_0^2 - (4r+6)f_0 + 1] \tag{39}$$

In this way, by substituting the values of f_0' and f_1' given by Eqns 28 and 29, respectively, into eqn 39, we obtain

$$\left|\frac{d^2\beta}{dpH}\right|_{pH=pH'} = -\ln^3 10 \frac{C_A}{8(1+r)} < 0 \tag{40}$$

the condition $d\beta/dpH = 0$ consequently leading to a maximum in the buffer index as previously indicated.

Letting $d^2\beta/d(pH)^2 = 0$ we have

$$(r^2+6r+6)f_0''^2 - (4r+6)f_0'' + 1 = 0 \tag{41}$$

Solving this quadratic equation, we obtain for f_0'' the two values

$$(f_0'')_{(I)} = \frac{r(2+\sqrt{3})+3+\sqrt{3}}{r^2+6r+6} \tag{42}$$

$$(f_0'')_{(II)} = \frac{r(2-\sqrt{3})+3-\sqrt{3}}{r^2+6r+6} \tag{43}$$

and then, the corresponding values of f_1'' are given by

$$(f_1'')_{(I)} = \frac{r^2+r(4-\sqrt{3})+3-\sqrt{3}}{r^2+6r+6} \tag{44}$$

$$(f_1'')_{(II)} = \frac{r^2+r(4+\sqrt{3})+3+\sqrt{3}}{r^2+6r+6} \tag{45}$$

By substituting the values of f_0 and f_1 at the inflexion points into the acidity constant expression we obtain two hydrogen ion concentration values

$$[H'']_{(I)} = K_a \frac{r^2+r(4-3\sqrt{3})+3-\sqrt{3}}{r(2+\sqrt{3})+3+\sqrt{3}} \tag{46}$$

$$[H'']_{(II)} = K_a \frac{r^2+r(4+\sqrt{3})+3+\sqrt{3}}{r(2-\sqrt{3})+3-\sqrt{3}} \tag{47}$$

and making

$$\alpha = 3 \mp \sqrt{3} \tag{48}$$

we have

$$[H''] = K_a(2 \mp \sqrt{3})\frac{(r+\alpha)(r+1)}{(r+\alpha)}$$

$$= K_a(2 \mp \sqrt{3})(r+1) \tag{49}$$

and then, taking into account Eqn 30, we obtain finally

$$pH'' = pH' - \log(2 \mp \sqrt{3}) = pH' \pm 0.5719 \tag{50}$$

The inflexion points are symmetrically disposed about the point of maximum buffer capacity, pH′. The same conclusion may be drawn by substituting the value of f_0'' as a function of K_a and $[H'']$

$$f_0'' = \frac{K_a}{K_a + [H'']} \tag{51}$$

into Eqn 41 and taking into account Eqn 30

$$[H'']^2 - 4[H'][H''] + [H']^2 = 0 \tag{52}$$

which leads (as before) to

$$\frac{[H'']}{[H']} = 2 \pm \sqrt{3} \tag{53}$$

The buffer capacity at the inflexion points may be evaluated either by substituting the values of f_0'' and f_1'' (given by Eqns 42, 44 and 43, 45, respectively) into Eqn 26, or by substituting the value of $[H'']$ given by Eqn 49 into

$$\beta_{HA} = \ln 10 C_A \frac{K_a[H]}{(K_a(1+r)+[H])^2} \tag{54}$$

an expression easily derived from Eqn 26, which in both cases leads to

$$\beta''_{HA} = \frac{\ln 10 C_A}{6(1+r)} \tag{55}$$

and then, the following identity is satisfied

$$\frac{\beta'_{HA}}{\beta''_{HA}} = \frac{3}{2} \tag{56}$$

Singular points in the dV / dpH vs pH curve

Although the maximum buffer capacity is not reached at a pH value equal to the pK_a, no special problems are encountered in the evaluation of the acidity constant of a moderately weak acid by potentiometry, based on the location of the singular point of the V vs pH curve.

From Eqns 4–6, we obtain

$$C_B\frac{V}{V_0+V}+[\mathrm{H}]=[\mathrm{OH}]+C_A\frac{V_0}{V_0+V}f_0 \qquad (57)$$

and then the following expression may readily be derived

$$(C_A f_0+C_B)\frac{V_0}{V_0+V}=C_B+[\mathrm{H}]-[\mathrm{OH}] \qquad (58)$$

which, combined with Eqn 11, yields

$$\frac{\mathrm{d}V}{\mathrm{dpH}}=\ln 10\frac{(V_0+V)([\mathrm{H}]+[\mathrm{OH}])+V_0C_A f_1 f_0}{C_B+[\mathrm{H}]-[\mathrm{OH}]} \qquad (59)$$

In moderately acidic or basic medium, the hydrogen and hydroxide ion concentration may be neglected with respect to the other basic or acidic species, and then

$$\frac{\mathrm{d}V}{\mathrm{dpH}}=\ln 10\frac{V_0C_A f_1 f_0}{C_B}=\ln 10V_0 r f_1 f_0 \qquad (60)$$

The first and second derivatives of dV/dpH vs pH are respectively given by

$$\frac{\mathrm{d}^2V}{\mathrm{d(pH)}^2}=-\ln^2 10V_0 r f_0 f_1(f_0-f_1) \qquad (61)$$

and

$$\frac{\mathrm{d}^3V}{\mathrm{d(pH)}^3}=\ln^3 10V_0 r f_0 f_1(f_1^2-4f_1f_0+f_0^2) \qquad (62)$$

Examination of Eqn 61 reveals that

$$(f_0=f_1)_{V''=0} \qquad (63)$$

which implies

$$(\mathrm{pH})_{V''=0}=\mathrm{p}K_a \qquad (64)$$

This point is a maximum, since $\mathrm{d}^3V/\mathrm{d(pH)}^3$ at this point is negative and equals $-1.5260V_0r$.

The inflexion points in the graph of dV/dpH vs pH may be calculated from the condition $\mathrm{d}^3V/\mathrm{d(pH)}^3=0$ which leads to

$$(f_1''^2-4f_1''f_0''+f_0''^2)_{V'''}=0 \qquad (65)$$

Replacing f_1'' by $1-f_0''$ and operating, we have

$$(6f_0''^2-6f_0''+1)_{V'''}=0 \qquad (66)$$

which coincides with the expression, Eqn 41, when $r=0$, and then, Eqn 49 ($r=0$) is also applicable in this case

$$\frac{[\mathrm{H}'']_{V'''}}{[\mathrm{H}']_{V''}}=2\pm\sqrt{3} \qquad (67)$$

Advances in instrumentation enable the automatic recording during an acid-base titration not only of pH, but also of the rate of change of pH with change in titre (Covington et al., 1978).

Variation of the buffer capacity with change in the salt / acid ratio

In order to locate the maximum value in the curve which describes the variation of buffer capacity with the proportion of salt to acid, we must derive Eqn 26 against f_0

$$\frac{\mathrm{d}\beta}{\mathrm{d}f_0}=\frac{\ln 10}{(1+rf_0)^3}[1-(r+2)f_0] \qquad (68)$$

TABLE 2

Effect of dilution on the maximum and inflexion point in the graph of β_{HA} against f_0

r	f_0'	f_0''
1.0	0.333	1.000
1.1	0.323	0.938
1.2	0.313	0.885
1.3	0.303	0.839
1.4	0.294	0.798
1.5	0.286	0.762
2.0	0.250	0.625

The condition for maximum is given by $d\beta/df_0 = 0$, and then, again

$$f_0' = \frac{1}{r+2} \tag{69}$$

On the other hand, by straightforward differentiation of Eqn 68, we obtain

$$\frac{d^2\beta}{df_0^2} = \frac{\ln 10 C_A}{(1+rf_0)^4}[2r+1-rf_0(r+2)] \tag{70}$$

$d^2\beta/df_0^2 = 0$ requires

$$f_0'' = \frac{2r+1}{r(2+r)} \tag{71}$$

Since Eqn 71 is single-valued, there is only one inflexion point, which lacks physical significance only in those cases in which $r > 1$ (Table 2). Values of r lower than the unity lead to no physically meaningful f_0'' values (i.e., $f_0'' > 1$).

Only in those cases in which $r = 0$ is the β vs f_0 curve symmetrical. In effect, making

$$f_0 = f_0' + p = \frac{1}{2+r} + p \tag{72}$$

we have

$$\beta_{HA} = \ln 10 \frac{[1+(2+r)p][1+r-(2+r)p]}{[2(1+r)+r(2+r)p]^2} \tag{73}$$

and then, when $r = 0$, it follows that

$$\beta_{HA} = \frac{\ln 10 C_A}{4}(1+2p)(1-2p) \tag{74}$$

On the other hand, from Eqn 26, taking into account that $f_1 = 1 - f_0$, the following quadratic equation in f_0 is derived

$$(1+r^2\beta^*)f_0^2 + (2r\beta^* - 1)f_0 + \beta^* = 0 \tag{75}$$

where

$$\beta^* = \frac{\beta_{HA}}{\ln 10 C_A} \tag{76}$$

The roots of Eqn 75 give the f_0 values for which the same value of β_{HA} is obtained

$$f_0 = \frac{0.5 - r\beta^* \pm \sqrt{0.25 - \beta^*(1+r)}}{1+r^2\beta^*} \tag{77}$$

the ratio of salt to acid consequently being given by

$$\frac{f_0}{f_1} = \frac{0.5 - r\beta^* \pm \sqrt{0.25 - \beta^*(1+r)}}{0.5 + r\beta^*(1+r) \mp \sqrt{0.25 - \beta^*(1+r)}} \tag{78}$$

In those cases in which dilution is neglected $(r = 0)$, Eqn 78 leads to

$$\frac{f_0}{f_1} = \frac{0.5 \pm \sqrt{0.25 - \beta^*}}{0.5 \mp \sqrt{0.25 - \beta^*}} \tag{79}$$

It should be borne in mind that the maximum attainable value for the buffer index is given by Eqn 31

$$\beta^* = \frac{1}{4(1+r)} = 0.25 \quad (r = 0) \tag{80}$$

Conclusion

An essential factor in calculation buffer capacity in the titration of a weak acid with a strong base is the change in volume resulting from dilution of the solution as titrant is added. When dilution is taken into account in the algebraic treatment of buffer capacity, a number of different conclusions regarding the location of the maximum and inflexion points in the buffer index vs pH curve may be drawn.

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References

Asuero, A.G., Jimenez-Trillo, J.L. and Navas, M.J., Mathematical treatment of absorbance versus pH graphs of polybasic acids. *Talanta,* 33 (1986) 929–934.

Butcher, J. and Fernando, Q., Use of a digital computer in equilibrium calculations: the effects of dilution and ionic strength of the buffer index and sharpness index in the titration of a monoprotic acid with a strong base. *Anal. Chim. Acta,* 36 (1966) 65–76.

Connors, K.A., *A Textbook of Pharmaceutical Analysis,* 3th Edn, Wiley, New York, 1985.

Covington, A.K., Robinson, R.A. and Sarbar, M., Determination of carbonate in the presence of hydroxide. Part 1. Analysis of first-derivative potentiometric curves. *Anal. Chim. Acta,* 100 (1978) 367–374.

Guenther, W.B., *Chemical Equilibrium, An Introduction to the Life and Physical Sciences,* Plenum, New York, 1975.

Hulanicki, A., *Reactions of Acids and Bases in Analytical Chemistry,* Ellis Horwood, Chichester, 1987.

King, E.J., *Acid-Base Equilibria,* Pergamon, New York, 1965.

Meites, L. and Goldman, J.A., Theory of titration curves. The location of inflection points on acid-base and related curves. *Anal. Chim. Acta,* 29 (1963) 472–479.

Polster, J. and Lachmann, H., *Spectrometric Titration,* VCH, New York, 1989.

Stumm, W. and Morgan, J.J., *Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters,* 2nd Edn, Wiley, New York, 1981.

Sucha, L. and Kotrly, St., *Solution Equilibria in Analytical Chemistry,* Van Nostrand Reinhold, London, 1972.

Van Slyke, D.D., On the measurement of buffer values and on the relationship of buffer value to the dissociation constant of the buffer and the concentration and reaction of the buffer solution. *J. Biol. Chem.,* 52 (1922) 525–570.