

On the buffer index of a single weak monoprotic acid system

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Received 28 April 1995; revised 22 June 1995; accepted 7 July 1995

Abstract

Mathematical consideration of the course of titration of a weak acid with a strong base shows that buffer index versus pH curve, $\pi = f(\text{pH})$, should contain two minima and one maximum under certain conditions, which coincides with the three inflection points of the pH versus fraction titrated, $\text{pH} = f(T)$, curve. Ionic strength is assumed to be constant in this treatment, and the effect of dilution is neglected. The theory developed is applied to the acetic acid/sodium acetate and boric acid/sodium borate systems. The central maximum in the $\pi = f(\text{pH})$ does not coincide with the pK_a because of the self ionization equilibria of water. The end point inflection (when occurs) at which the slope of the $\text{pH} = f(T)$ curve is greater (minimum buffer capacity) precedes the equivalence point.

Keywords: Buffer index curve; Titration curve; Monoprotic acid

1. Introduction

The ability of a solution to resist attempts to change its pH is called the buffer capacity, the buffering effectiveness being expressed numerically as a buffer index (capacity) which is defined (Van Slyke, 1922) as the number of equivalents of strong base (eq liter^{-1}) needed to change the pH value by 1 unit

$$\pi = \frac{dC_B}{d\text{pH}} = -\frac{dC_A}{d\text{pH}} \quad (1)$$

Buffer solutions are used since the beginning of the century (Rideal, 1940), and buffer index calculations have been discussed in many studies since the publication in 1922 of the classical paper due to Van Slyke. In particular, a great deal of atten-

tion has been paid to this topic in textbooks. Though any aspect of buffer and titration theory has been treated in great detail by Ricci, 1952, the presentation of the matter in a more comprehensible form is still an open question, as indicated recently by Rilbe (Rilbe, 1993; Rilbe, 1994). Buffer solutions have value for natural (Dickson, 1993; Millero et al., 1993) and technical systems (Galster, 1991), and the approximate calculation of a buffer value is also of practical importance for the design of new buffer solutions.

This paper is devoted to the buffer index of a monoprotic acid system and is intended to occupy the middle ground between oversimplification and a rigorous and complete treatment which requires consideration of both dilution and ionic strength effects.

2. 2. Basic equations

Let us consider the strong base BOH added to a weak acid HA. It is assumed that the total volume of the solution remains constant throughout, that is, we suppose that the titrant is much more concentrated than the titrated solution. Using $[H^+]$ to represent total hydronium ion concentration, we have the usual equation

$$K_a = \frac{|H^+||A^-|}{|HA|} \quad (2)$$

A neutral salt is assumed to be present in sufficient amount to keep activity coefficient constants hence these coefficients are not explicitly included in Eqn. (1), and K_a is a concentration or stoichiometry (Rossotti, 1978) constant. These approximations are typically encountered in most analytical textbooks (Connors, 1982).

Suppose C_A moles of HA were originally dissolved in each liter of solution. Then a mass balance gives

$$C_A = |HA| + |A^-| \quad (3)$$

After addition of BOH, the electroneutrality rule must hold

$$|B^+| + |H^+| = |A^-| + |OH^-| \quad (4)$$

Taking into account that $C_B = |B^+|$, by combining Eqns. (2) and (3), on rearranging Eqn. (4), we get

$$C_B = \frac{C_A}{1 + \frac{K_a}{|H^+|}} - |H^+| + \frac{K_w}{|H^+|} \quad (5)$$

where K_w is the stoichiometric ion product of water

$$K_w = |H^+||OH^-| \quad (6)$$

By differentiating Eqn. (5) with respect to pH we obtain the buffer index

$$\begin{aligned} \pi &= \frac{dC_B}{dpH} = \frac{dC_B}{d|H^+|} \frac{d|H^+|}{dpH} \\ &= \ln 10 \left(\frac{C_A \frac{|H^+|}{K_a}}{\left(1 + \frac{|H^+|}{K_a}\right)^2} + |H^+| + |OH^-| \right) \end{aligned} \quad (7)$$

which has the dimension of concentration. It follows from Eqn. (7) that the total buffer index is equal to the sum of the buffer index of the individual species

$$\pi = \pi_{HA} + \pi_H + \pi_{OH} \quad (8)$$

The first term on the right of Eqn. (7) describes the behaviour of HA, whereas the second and third term describes the behaviour of the titrated medium. The buffer index is thus additively composed of two parts, that due to water $\pi_{H_2O} = \pi_H + \pi_{OH}$ being important at very low and very high pH values; it does not influence titration curves near the neutral point, but it does have around low and high pK_a values. Solutions of strong acids and bases behaves as buffers, though their pH values fall outside the usual range of interest in physiology and chemistry. Since π for a weak acid is both pH and concentration dependent, it can vary by several order of magnitude. Fig. 1 shows the theoretical buffer index curves for a fixed value of $C_A = 0.1$ and varying values of pK_a , calculated by use of Eqn. (7).

3. Buffer index versus titration curves

However, in potentiometric titrations, the pH is usually plotted against a parameter related to the amount of acid titrated, such as the titration fraction, T

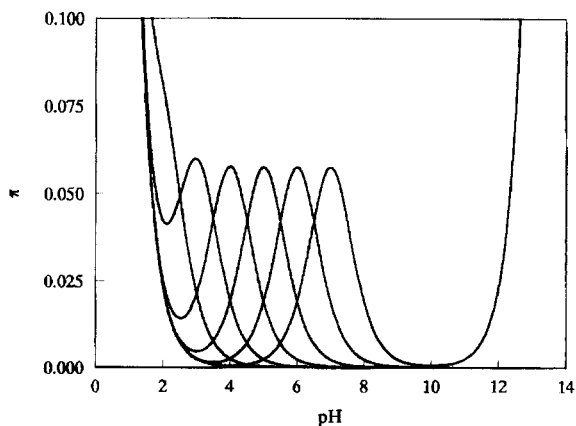


Fig. 1. Buffer index curves for a monoprotic acid with $C_A = 0.1$ M and pK_a values of 7, 6, 5, 4, 3, 2.431 and 2.

$$T = \frac{C_B}{C_A} \quad (9)$$

which has also been referred in the literature as a (Inczedy, 1976), θ (Butler, 1964), f (Meites, 1981), degree of titration π (Waser, 1967) and degree of advancement of neutralization x (Covington et al., 1978). This parameter is very appropriate since that takes single normalised values at each titration step, e.g. before titration, $T = 0$, at the half point titration, $T = 0.5$, and at the equivalence point, $T = 1$. Taking into account Eqns. (5) and (9) we get

$$T = \frac{C_B}{C_A} = \frac{1}{1 + \frac{|H^+|}{K_a}} - \frac{|H^+| - \frac{K_w}{|H^+|}}{C_A} \quad (10)$$

In those cases in which $|\text{OH}^-|$ and $|\text{H}^+|$ are negligible in comparison with C_A , the titration curve coincides with the dissociation curve, f_0 ; that is, the fraction molar of the unprotonated species A^-

$$f_0 = \frac{|\text{A}^-|}{C_A} = \frac{1}{1 + \frac{|H^+|}{K_a}} \quad (11)$$

The titration $\text{pH} = f(T)$ equation is monotonous, i.e. it has no maximum or minimum points. The slope of the titration curve $\text{pH} = f(T)$ or sharpness index indicates how strongly the sample resist a change of pH (González et al., 1990) and is positive throughout the whole titration; it never shifts sign, and is given by

$$\frac{d\text{pH}}{dT} = \frac{C_A}{dC_B} = \frac{C_A}{\pi} \quad (12)$$

Thus, the buffer index may be defined as the inverse slope of the titration curve provided the titrant is a strong acid or base and dilution effects are negligible. Plots of π versus pH may lead to conclude erroneously that π approaches ∞ at pH 0 (or 14), or that for a certain pH region, $\pi = 0$. This may readily avoided in plotting (Olson et al., 1977) $\log \pi$ against pH (Fig. 2).

By differentiation of Eqn. (12) with respect to pH we obtain

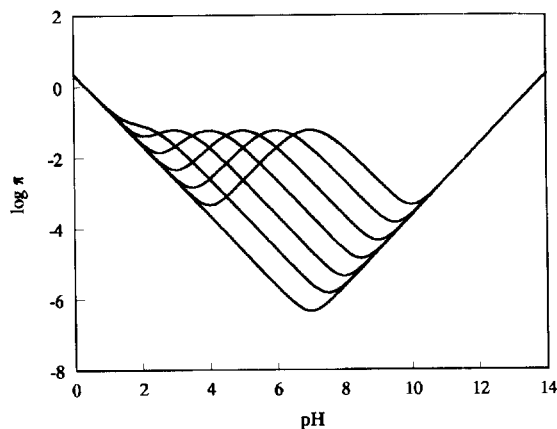


Fig. 2. Logarithm of the π versus pH curves with $C_A = 0.1$ and $\text{p}K_a$ values of 7, 6, 5, 4, 3 and 2.

$$\frac{d^2\text{pH}}{dT^2} = -\frac{1}{\pi} \left(\frac{d\pi}{d\text{pH}} \right) \left(\frac{d\text{pH}}{dT} \right)^2 \quad (13)$$

As $d\text{pH}/dT \neq 0$, $d^2\text{pH}/dT^2 = 0$ requires that $d\pi/d\text{pH} = 0$, and in this way, to each inflection point in the titration $\text{pH} = f(T)$ curve corresponds a minimum or maximum value in the buffer index $\pi = f(\text{pH})$ curve of the HA/A^- system.

The relative error for the titration of a weak acid with a strong base will be

$$\Delta T = T - 1 = \frac{|\text{OH}^-| - |\text{H}^+|}{C_A} - f_1 \quad (14)$$

where f_1 is the molar fraction of the undissociated form HA ($f_0 + f_1 = 1$)

$$f_1 = \frac{\frac{|H^+|}{K_a}}{1 + \frac{|H^+|}{K_a}} \quad (15)$$

The titration error may be calculated from Eqn. (14) provided that the concentration of acid C_A , the acidity constant K_a of the titrated acid, and the pH at the end point of the titration are known.

4. Maximum and minima in the buffer index versus pH curve

The buffer index $\pi = f(\text{pH})$ curve of a monoprotic acid system has, in general, a central

maximum (indicated as c in the following), and two minima, one in the acid side, and the other in the alkaline one (indicated as a and b, respectively, in the course of the paper), unless K_a (pK_a) is either too small (large) or too large (small).

4.1. The complete description

Differentiation of Eqn. (7) gives the slope of the graph of π as a function of pH

$$\frac{d\pi}{dpH} = \ln^2 10 \left[\frac{C_A \frac{|H^+|}{K_a} \left(\frac{|H^+|}{K_a} - 1 \right)}{\left(1 + \frac{|H^+|}{K_a} \right)^3} - |H^+| + |OH^-| \right] \quad (16)$$

Fig. 3 shows a family of theoretical $d\pi/dpH$ against pH curves for varying values of pK_a . Values of $d\pi/dpH = 0$ will locate the position of the maximum and minima in the π versus pH curve. However, in order to make the treatment more convenient we introduce the auxiliary variable x

$$x = \frac{|H^+|}{K_a} \quad (17)$$

$d\pi/dpH = 0$ then requires

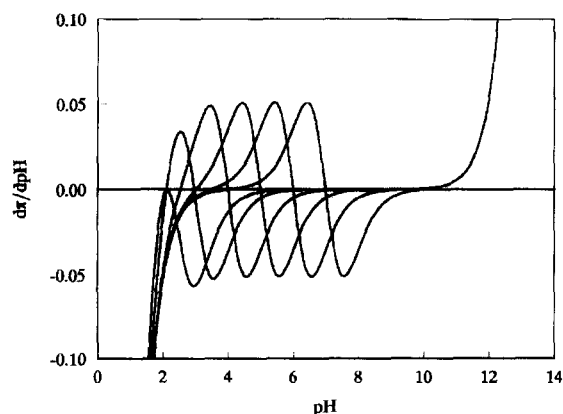


Fig. 3. Derivative π versus pH curves with $C_A = 0.1$ and pK_a values of 7, 6, 5, 4, 3 and 2.431.

$$x'^5 + 3x'^4 - \left(\frac{C_A}{K_a} - 3 + \frac{K_b}{K_a} \right) x'^3 + \left(\frac{C_A}{K_a} + 1 - 3 \frac{K_b}{K_a} \right) x'^2 - 3 \frac{K_b}{K_a} x' - \frac{K_b}{K_a} = 0 \quad (18)$$

x' being the value of x which satisfy the condition met, and K_b is the basicity constant of A^- , the conjugate base of the acid HA ($K_b = |HA| |OH^-| / |A^-|$). Note that the acidity constant and the basicity constant of a same acid/base pair hold

$$K_w = K_a K_b \quad (19)$$

Equation (18) may be solved for various values of r

$$r = \frac{C_A}{K_a} \quad (20)$$

and K_a , i.e. by applying the Newton-Raphson (Valkó and Vajda, 1989) method.

In an analogous manner, the condition $d\pi/dpH = 0$ with

$$y = \frac{K_a}{|H^+|} \quad (21)$$

leads to

$$y'^5 + 3y'^4 - \left(\frac{C_A}{K_b} - 3 + \frac{K_a}{K_b} \right) y'^3 + \left(\frac{C_A}{K_b} + 1 - 3 \frac{K_a}{K_b} \right) y'^2 - 3 \frac{K_a}{K_b} y' - \frac{K_a}{K_b} = 0 \quad (22)$$

which may be solved for different values of K_a and s

$$s = \frac{C_A}{K_b} = \frac{C_A K_a}{K_w} \quad (23)$$

4.2. The symmetrical (complete) description

The condition for the complete buffer index curve to be symmetrical is given by $r = s$, $K_a = K_b = \sqrt{K_w}$ ($pK_a = pK_w/2$). Then, from Eqn. (22) we get

$$(y' - 1)(y'^4 + 4y'^3 + (6 - s)y'^2 + 4y' + 1) = 0 \quad (24)$$

The root $y'_c = 1$ correspond to the central maximum, c, in the $\pi = f(pH)$ curve, and Eqn. (7) gives

Table 1

Distance (in pH units) from the central maximum (pK_a) to the acid or alkaline minimum for the symmetrical (complete) condition case

$r = s$	$\log x'_a = -\log y'_b$, $pK_a - pH'_a = pH'_b - pK_a$	$r = s \log$	$x'_a = -\log y'_b$, $pK_a - pH'_a = pH'_b - pK_a$
10^7	3.4997	50	0.6871
10^5	2.4972	27	0.4550
10^3	1.4711	24	0.3977
100	0.8961	16	0

* Theoretical data in Tables were rounded off to 0.0001 for the sake of comparison in spite of that this number of significant digits could not be obtained in any real situation

$$|\pi_{\max}|_{pH=pK_w/2} = \ln 10 C_A \left(\frac{1}{4} + \frac{2\sqrt{K_w}}{C_A} \right) \\ = \ln 10 \left(\frac{C_A}{4} + 2\sqrt{K_w} \right) \quad (25)$$

The two lateral minima in this case are equidistant in pH from $pK_w/2$, and are given by the roots of the four degree equation shown in the second parenthesis of Eqn. (24), which may be factored to

$$\left(y'^2 + \frac{1}{y'^2} \right) + 4 \left(y' + \frac{1}{y'} \right) + 6 - s = 0 \quad (26)$$

and making

$$Y' = y' + \frac{1}{y'} \quad (27)$$

we get the following second degree equation

$$Y'^2 + 4Y' + 4 - s = 0 \quad (28)$$

which leads to

$$|y'|_{a,b} = \sqrt{\frac{s}{4} - 1} \pm \sqrt{\left(\sqrt{\frac{s}{4} - 1} \right)^2 - 1} \quad (29)$$

and so in order for Eqn. (29) to have a proper root

$$s = \frac{C_A}{K_b} \geq 16 \quad (30)$$

When s takes the limiting value of 16, the two minima merge simultaneously with the maximum at $pH = pK_a = pK_w/2$. The location of the pH axis of the minima for various values of s (r) when $pK_a = pK_w/2$ are given in Table 1. The maximum in π occurring at $H^+ = \sqrt{K_w}$ can vanish only if C_A becomes zero, leaving the $\pi_{H2O} = \pi_H + \pi_{OH}$ curve.

4.3. The acid side approximation: pH' calculations at the acid minimum and central maximum

Calculations involving Eqns. (18) and (22) are cumbersome and involves the application of numerical methods; i.e. iterative techniques which may present convergence problems. It is highly desirable to introduce approximations which make more tractable the problem.

Thus, for $K_a > \sqrt{K_w}$ ($pK_a < pK_w/2$) we may neglect $|\text{OH}^-|$ relative to $|H^+|$, and then Eqns. (7) and (16), taking into account Eqns. (17) and (20) leads to

$$\pi = \ln 10 \left(\frac{C_A x}{(1+x)^2} + x K_a \right) \\ = \ln 10 C_A x \left(\frac{1}{(1+x)^2} + \frac{1}{r} \right) \quad (31)$$

$$\frac{d\pi}{dpH} = \ln^2 10 \left(\frac{C_A x (x-1)}{(1+x)^3} - |H^+| \right) \\ = \ln^2 10 C_A x \left(\frac{x-1}{(1+x)^3} - \frac{1}{r} \right) \quad (32)$$

From $d\pi/dpH = 0$, a third degree equation ($a_0 x'^3 + a_1 x'^2 + a_2 x' + a_3 = 0$) is obtained

$$x'^3 + 3x'^2 + (3-r)x' + 1+r = 0 \quad (33)$$

This is equivalent to consider negligible the ratio K_b/K_a in Eqn. (18). The real positive roots (Nievergelt, 1994), x'_a and x'_c , of the third degree Eqn. (33) allows to calculate the acid minimum, pH'_a , and the central maximum, pH'_c , by taking logarithms in Eqn. (17)

$$pH'_a = pK_a - \log x'_a \quad (34)$$

$$pH'_c = pK_a - \log x'_c \quad (35)$$

By making $x' = z' - a_1/3$, Eqn. (33) is reduced (Uspensky, 1948) to the form $z'^3 + pz' + q = 0$, with $p = a_2 - a_1^2/3 = -r$, $q = 2 a_1^3/27 - a_2 a_1/3 + a_3 = 2r$, and then

$$z'^3 - rz' + 2r = 0 \quad (36)$$

The discriminant, Δ , of Eqn. (35) is given by

$$\Delta = \frac{q^2}{4} + \frac{p^3}{27} = r^2 \left(1 - \frac{r}{27}\right) \quad (37)$$

If $\Delta \leq 0$, then

$$r = \frac{C_A}{K_a} \geq 27 \quad (38)$$

$$pK_a \geq pC_A + 1.4314 \quad (39)$$

Eqn. (33) having two positive roots (three real roots), corresponding to the minimum, a , on the acid side, and the central maximum, c , as we have indicated above. Note that $\log x'$ measures the distance in pH units between the pH at the minimum of the buffer index curve in the acid side, or the pH at the central maximum, and pK_a , respectively, as shown in Table 2, for different values of r . For solving the third degree equation, the following applies ($p = -r$, and $q = 2r$)

$$\rho = \sqrt{\frac{-p^3}{27}} = \frac{r}{3} \sqrt{\frac{r}{3}} \quad (40)$$

Table 2

Location of the central maximum and lateral acid or basic minimum in the buffer index curve for a monoprotic acid

r $= C_A/K_a$	$\log \sqrt{r}$	$\log x'_a = pK_a - pH'_a$	$\log x'_c = pK_a - pH'_c$
10^7	3.5000	3.4997	0
10^5	2.5000	2.4972	0
10^3	1.5000	1.4709	0.0035
10^2	1.0000	0.8915	0.0380
50	0.8495	0.6717	0.0858
27	0.7157	0.3010	0.3010
s $= C_A/K_b$	$\log \sqrt{s}$	$\log y'_b = pH'_b - pK_a$	$\log y'_c = pH'_c - pK_a$

Table 3

Values of r and T'_c as a function of the difference between pK_a and the central maximum pH'_c

$\log x'_c = pK_a - pH'_c$	x'_c	r $= C_A/K_a$	$\log r$	T'_c
0.001	1.0023	3482.37	3.542	0.4991
0.005	1.0116	702.95	2.847	0.4957
0.010	1.0233	355.59	2.551	0.4914
0.015	1.0351	239.86	2.380	0.4871
0.020	1.0471	182.03	2.260	0.4827
$\log y'_c = pH'_c - pK_a$	y'_c	s $= C_A/K_b$	$\log s$	T'_c

$$\theta = \arccos\left(\frac{-q}{2\rho}\right) = \arccos\left(-3\sqrt{\frac{3}{r}}\right) \quad (41)$$

$$z'_j = 2\rho^{1/3} \cos\left(\frac{\theta + 2k\pi}{3}\right) \quad k = 0, 1, 2 \quad (42)$$

and

$$x'_j = z'_j - \frac{a_1}{3} = z'_j - 1 \quad (43)$$

with $j = 1, 2, 3$.

The central maximum, pH'_c , does not strictly coincides with the pK_a , lying at its left side, $pH'_c \leq pK_a$, because of the self ionization equilibria of water and the magnitude of the difference increases as r decreases, that is to say, as the concentration of the acid decreases, and/or K_a increases (pK_a decreases). Consequently it is untrue (except when $x'_c = 1$) that the buffer capacity is greatest at $T = 0.5$, that is in a solution containing equal formal concentrations of the weak acid and its conjugate base.

Equation (33) on rearrangement leads to

$$r = \frac{(x' + 1)^3}{x' - 1} \quad (44)$$

which allows to calculate the minimum permissible value of r for a given distance ($\log x'_c$) between pK_a and the point of minimum slope of the $d\text{pH}/dT$ curve, where buffer index is at a maximum (Table 3). If an acid of 10^{-2} M concentration is being titrated, its pK_a value must be ≥ 4.847 (4.551) in order to assure a difference

between the central maximum pH'_c and the pK_a less than 0.005 (0.01) as can be deduced from the data in Table 3 ($\text{pK}_a \geq \text{pC}_A + \log r$). The T' values were calculated by applying Eqn. (10) with $\text{OH}^- < \text{H}^+$

$$T = \frac{1}{1+x} - \frac{x}{r} + \frac{y}{s} \approx \frac{1}{1+x} - \frac{x}{r} \quad (45)$$

The maximum or minimum in π are found by substituting in Eqn. (31) for x'_c (maximum) or x'_a (minimum), respectively. When $\text{pH} = \text{pK}_a$, we have $x = 1$, and Eqn. (31) gives

$$|\pi|_{\text{pH}=\text{pK}_a} = \ln 10 C_A \left(\frac{1}{4} + \frac{1}{r} \right) \quad (46)$$

Though the maximum buffer capacity does not strictly coincides with the pH value equals to pK_a , the quotient $\pi(\text{pH} = \text{pH}'_c) / \pi(\text{pH} = \text{pK}_a) \approx 1$ for $r > 27$.

The merging of the minimum with π_{max} as K_a increases above $\text{K}_a = \sqrt{\text{K}_w}(\text{pK}_a < \text{pK}_w/2)$ occurs when $\Delta = 0$, or $r = 27$; Eqn. (33) then gives $x'_1 = x'_2 = 2$, and Eqn. (31) leads to

$$|\pi|_{r=27} = 2 \ln 10 C_A \left(\frac{1}{(1+2)^2} + \frac{1}{27} \right) = \frac{8}{27} \ln 10 C_A \quad (47)$$

Hence, both π_{max} and π_{min} (acid) have increased with decreasing pK_a to this common value. As x approaches 2, the acid minimum a and the central maximum c are displayed towards each other and for $x = 2$ merge into one single maximum. This is well illustrated by the set of curves shown in Fig. 1.

4.4. The alkaline side approximation

For $\text{K}_a < \sqrt{\text{K}_w}(\text{pK}_a > \text{pK}_w/2)$, $\text{H}^+ < \text{OH}^-$, and then, taking into account Eqns. (21) and (23), Eqns. (7) and (16) leads to analogous expressions as Eqns (31) and (32)

$$\pi = \ln 10 C_A y \left(\frac{1}{(1+y)^2} + \frac{1}{s} \right) \quad (48)$$

$$\frac{d\pi}{dpH} = \ln^2 10 C_A y \left(\frac{y-1}{(1+y)^3} - \frac{1}{s} \right) \quad (49)$$

From the condition $d\pi/dpH = 0$ we get

$$y'^3 + 3y'^2 + (3-s)y' + 1 + s = 0 \quad (50)$$

(this is equivalent to consider negligible the ratio K_a/K_b in Eqn. (22)), from which we may calculate the pH corresponding to the central maximum, c, and the minima, b, in the alkaline side, by taking logarithms in Eqn. (21)

$$\text{pH}'_c = \text{pK}_a + \log y'_c \quad (51)$$

$$\text{pH}'_b = \text{pK}_a + \log y'_b \quad (52)$$

The central maximum lies in this situation at the right side of pK_a , $\text{pH}' \geq \text{pK}_a$, because of the self-ionization equilibria of water.

The corresponding titration fraction values, T' , when necessary, are now evaluated by applying Eqn (10) with $|\text{OH}^-| > |\text{H}^+|$

$$T \approx \frac{1}{1 + \frac{1}{y}} + \frac{y}{s} \quad (53)$$

When $\text{pH} = \text{pK}_a$, $x = 1$, and then

$$|\pi|_{\text{pH}=\text{pK}_a} = \ln 10 C_A \left(\frac{1}{4} + \frac{1}{s} \right) \quad (54)$$

The required condition for the merging of the maximum with the minimum in the alkaline side is now seen to be

$$s_{\text{lim}} = \frac{C_A}{K_b} = \frac{C_A K_a}{K_w} = 27 \quad (55)$$

As K_a decreases below $\text{K}_a \sqrt{\text{K}_w}(\text{pK}_a > \text{pK}_w/2)$, π_{max} increases and moves to the right occurring at $|\text{H}^+| < \text{K}_a(\text{pH} > \text{pK}_a)$. Thus, the required condition for the appearance of the end point inflection in the titration curve (at 25°C) is

$$\text{pK}_a \leq 12.5686 - \text{pC}_A \quad (56)$$

4.5. Practical applications: the acetic acid and boric acid systems as examples

The possibilities for the analyst to solve various calculating problems have increased drastically with the development of programmable calculators, e.g. it may be possible to handle rigorous formulations (Texas Instruments, 1992) without the tedium of manual solution of higher order equations. Either the five degree Eqns. (18) and

Table 4

pH values corresponding to the minima (pH'_a and pH'_b) and maximum buffer index (pH'_c) calculated by means of the five-degree equations (18) or (22); $C_A = 0.1$ M in all cases

pK_a	pH'_a	pH'_b	pH'_c
3	2.1086	2.9620	8.0022
4	2.5291	3.9965	8.5002
5	3.0088	4.9997	8.9999
6	3.5028	6.0000	9.4997
6.5	3.7515	6.5000	9.7495
7	4.0009	7.0000	9.9991
7.5	4.2505	7.5000	10.2485
8	4.5003	8.0000	10.4972
9	5.0000	9.0003	10.9912
10	5.4998	10.0035	11.4709
11	5.9978	11.0380	11.8915

(22) applied to systems with $C_A = 0.1$ and varying pK_a values ranging from 3 to 11 leads to the maximum and minima pH' values compiled in Table 4.

As a matter of fact, when to approximate, Eqns. (33–35) may be applied to calculate the acid minima and the central maximum in those cases in which $\text{pK}_a < \text{pK}_w/2$. The basic maximum is then calculated from Eqns. (50) and (52). When $\text{pK}_a > \text{pK}_w/2$, the basic minimum and the central maximum are calculated from Eqns. (50–52), whereas the acid minimum is located by applying Eqns. (33) and (34). The same values were obtained by applying either the reduced third degree Eqns. (33) and (50) or the complete five degree Eqns. (18) and (22). Only at extreme dilutions, it

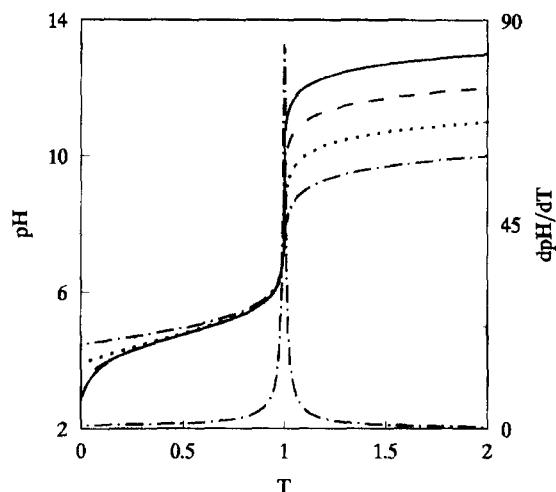


Fig. 4. Titration curves for acetic acid ($\text{pK}_a = 4.75$; $I = 0.1$) for C_A concentrations of 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} M, and derivative curve in the later case.

is necessary to apply the complete equation.

The theory developed above has been applied to the titration of the acetic and boric acids, respectively. The molar fraction of the A^- species and the titration fraction of acid, calculated at each singular pH point (the two minima, a and b, and the maximum c, in the buffer index versus pH curve) are shown in Table 5. Remember that the points a (first), c (middle) and b (end) coincide with the inflection points in the titration $\text{pH} = f(T)$ curve.

Figs. 4 and 5 show a family of titration curves for concentrations ranging from 10^{-1} M to 10^{-4}

Table 5

Location of minima and maximum in the acetic acid ($\text{pK}_a = 4.75$; $I = 0.1$) and boric acid ($\text{pK}_a = 9.1$; $I = 0.1$) systems

C_A	$f_{0,a}$	$f_{0,c}$	$f_{0,b}$	T'_a	T'_c	T'_b	pH'_a	pH'_c	pH'_b
<i>Acetic acid/sodium acetate system</i>									
0.1	0.0135	0.4996	0.9999	0.0005	0.4995	1.0000	2.8869	4.7494	8.8749
0.01	0.0442	0.4964	0.9998	0.0057	0.4946	1.0000	3.4147	4.7437	8.3748
0.001	0.1623	0.4575	0.9992	0.0704	0.4364	1.0000	4.0371	4.6760	7.8743
0.0005	0.2933	0.3704	0.9989	0.2076	0.3099	1.0000	4.3681	4.5196	7.7236
<i>Boric acid/ sodium borate system</i>									
0.1	0.0001	0.5003	0.9886	–	0.5004	0.9996	5.0501	9.1004	11.0400
0.01	0.0003	0.5025	0.9631	–	0.5038	0.9960	5.5502	9.1044	10.5171
0.001	0.0009	0.5283	0.8694	–	0.5424	0.9533	6.0508	9.1492	9.9236
0.0005	0.0013	0.5672	0.7926	–	0.6002	0.8888	6.2016	9.2175	9.6822

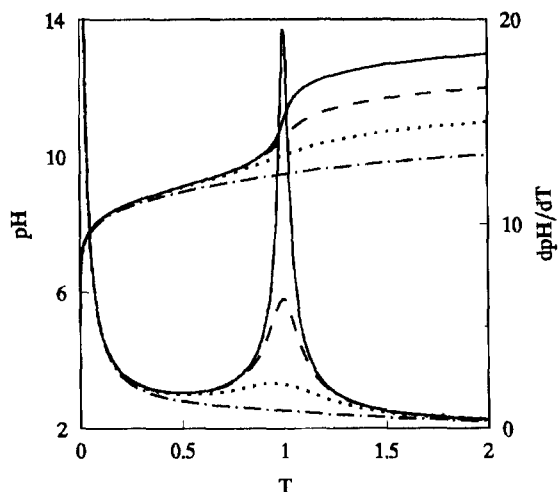


Fig. 5. Titration curves for boric acid ($pK_a = 9.1$; $I = 0.1$) for C_A concentrations of 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} M, and corresponding derivative curves.

M, for acetic ($pK_a = 4.75$, $I = 0.1$) and boric ($pK_a = 9.1$, $I = 0.1$) acids, respectively, obtained by applying Eqn. (10) by means of the reverse approach. The slope (obtained by combining Eqns. (16) and (12)) of the most unfavourable titration curve is also included in Fig. 4, whereas all the corresponding slope titration curves are included in Fig. 5 instead.

Table 6
Locations of the inflection points in weak acid-strong base titrations

K_a	Half point inflection		End-point Inflection	
	Meites and Goldman*	This paper	Meites and Goldman*	This paper
0.1	No inflection	—	—	
0.02	0.065	—	—	
0.01	0.111	—	—	
0.003	0.360	0.3684	—	
0.001	0.463	0.4672	—	
$1 \cdot 10^{-4}$	0.496	0.4970	—	
$1 \cdot 10^{-5}$	0.499	0.4997	—	
$1 \cdot 10^{-7}$	0.5000	0.5000	—	
$1 \cdot 10^{-8}$	—	0.5000	0.9999	
$1 \cdot 10^{-9}$	0.5005	0.5003	0.999	0.9997
$1 \cdot 10^{-10}$	0.506	0.5030	0.990	0.9970
$1 \cdot 10^{-11}$	0.573	0.5328	0.876	0.9641
$5 \cdot 10^{-12}$	No inflection	0.5736	No inflection	0.9183

* Titration of 0.1 F monobasic weak acid with 0.1 F monoacidic strong base

The end inflection point when occurs precedes to the equivalence point, the difference between both points being negligible if the acid is enough strong, but it increases as pK_a and dilution increases, e.g. for boric acid 0.01 M the value of T at the inflection point is 0.996 (-0.4% relative error).

Results obtained by Meites and Goldman (1963) for the titrations of 10^{-1} M of weak acid of various strength, with 10^{-1} M monoacid strong base taking into account dilution effects are shown in Table 6, together with the values obtained using the theory of this paper. As a conclusion, it is clear that the volume change during most titrations is such that the resulting dilution does not change the characteristic aspects of the titration curve.

5. pH values at the points of minima and maximum buffer index

Simple expressions for the pH values at which the buffer index is maximum or minimum may be obtained by making some sort of approximations as shown in the following, thus obtaining well known textbooks expressions. The degree of approximation are also evaluated in each case.

5.1. Acid side minimum

When $\text{pH} < \text{pK}_a$ (but not too low), $x = |\text{H}^+|/K_a \gg 1$, and then, from Eqn.(32) with $d\pi/d\text{pH} = 0$

$$x'_a{}^* = \sqrt{r} = \sqrt{\frac{C_A}{K_a}} \quad (57)$$

By combining Eqns. (17) and (57) we obtain the pH value, pH^* , at the apparent minimum in π , $\pi'_a{}^*$

$$|\text{H}^+|'_a{}^* = x'_a{}^* K_a = \sqrt{C_A K_a} \quad (58)$$

$$\text{pH}'_a{}^* = \frac{1}{2}(\text{p}C_A + \text{p}K_a) \quad (59)$$

The deviation, $\Delta\text{pH}'_a$ from the minimum pH'_a given by Eqn. (34) (third degree approximation) is given by

$$\begin{aligned} \Delta\text{pH}'_a &= \text{pH}'_a{}^* - \text{pH}'_a \\ &= \frac{1}{2}(\text{p}C_A + \text{p}K_a) - (\text{p}K_a - \log x'_a) \\ &= \log x'_a - \frac{1}{2}(\text{p}K_a - \text{p}C_A) = \log x'_a - \log \sqrt{r} \end{aligned} \quad (60)$$

Its follows from the data compiled in the Table 2 that $\text{pH}'_a{}^* < \text{pH}'_a$.

The buffer capacity at the apparent acid minimum, π'_a , takes the value (Eqn. (31) with $x > > 1$)

$$\pi'_a{}^* = \ln 10 C_A x'_a{}^* \left(\frac{1}{x'_a{}^*{}^2} + \frac{1}{r} \right) \quad (61)$$

and taking into account Eqn. (57)

$$\pi'_a{}^* = 2 \ln 10 \frac{C_A}{\sqrt{r}} = 2 \ln 10 \sqrt{C_A K_a} \quad (62)$$

5.2. The alkaline side minimum

If the pH values are not too high but greater than pK_a (basic minimum) $y = K_a/|\text{H}^+| > > 1$, and then $d\pi/d\text{pH} = 0$ requires

$$y'_b{}^* = \sqrt{s} = \sqrt{\frac{C_A K_w}{K_a}} \quad (63)$$

and Eqns. (21) and (63) leads to the apparent basic minimum

$$|\text{H}^+|'_b{}^* = \frac{K_a}{y'_b{}^*} = \sqrt{\frac{C_A}{K_a K_w}} \quad (64)$$

$$\text{pH}'_b{}^* = \frac{1}{2}(\text{p}K_a - \text{p}C_A + \text{p}K_w) \quad (65)$$

The deviation from the minimum pH'_b given by Eqn. (52), $\Delta\text{pH}'_b$ is equal to

$$\begin{aligned} \Delta\text{pH}'_b &= \text{pH}'_b{}^* - \text{pH}'_b \\ &= \frac{1}{2}(\text{p}K_a - \text{p}C_A + \text{p}K_w) - (\log y'_b + \text{p}K_a) \\ &= \frac{1}{2}(\text{p}K_w - (\text{p}C_A + \text{p}K_a)) - \log y'_b \\ &= \log \sqrt{s} - \log y'_b \end{aligned} \quad (66)$$

The data compiled in Table 2 indicates that $\text{pH}'_b{}^* > \text{pH}'_b$.

The buffer capacity at the apparent basic minimum takes the value (Eqn. (48) with $y > > 1$)

$$\pi'_b{}^* = \ln 10 C_A y'_b{}^* \left(\frac{1}{y'_b{}^*{}^2} + \frac{1}{s} \right) \quad (67)$$

and taking into account Eqn. (63)

$$\pi'_b{}^* = 2 \ln 10 \frac{C_A}{\sqrt{s}} = 2 \ln 10 \sqrt{\frac{C_A K_w}{K_a}} \quad (68)$$

5.3. The central maximum

In the middle range of the pH scale, the pH region where the buffer capacity of water is insignificant, we may neglect both $|\text{H}^+|$ and $|\text{OH}^-|$ in Eqn. (16), and $d\pi/d\text{pH} = 0$ requires

$$x'_c{}^* = y'_c{}^* = 1 \quad (69)$$

and then, from Eqn. (17)

$$|\text{H}^+|'_c{}^* = K_a \quad (70)$$

$$\text{pH}'_c{}^* = \text{p}K_a \quad (71)$$

and taking into account Eqn. (35) the deviation from the minimum pH'_c is given by

$$\begin{aligned} \Delta\text{pH}'_c &= \text{pH}'_c{}^* - \text{pH}'_c = \text{p}K_a - (\text{p}K_a - \log x'_c) \\ &= \log x'_c \end{aligned} \quad (72)$$

being $\Delta\text{pH}'_c < 0.02$ if $r > 185$.

The buffer action, π_{HA} , is shown by means of a well-shaped curve with a maximum $\text{pH}'_c{}^*$ at $\text{p}K_a$ given by the well-known expression

$$\pi_{HA} = \ln 10 \frac{C_A x'_c{}^*}{(1 + x'_c{}^*)^2} = \frac{\ln 10}{4} C_A \quad (73)$$

Table 7

Differences between the inflection points and the equivalence, half equivalence and $\text{pH}_{T=0}$ points, respectively, in the titration curve

C_A	f_0 at $T = 0$	f_0 at $T = 0.5$	f_0 at $T = 1.0$	$\text{pH}'_a - \text{pH}_0$	$\text{pH}'_c - \text{pH}_{0.5}$	$\text{pH}'_b - \text{pH}_{1.0}$
<i>Acetic acid</i>						
0.1	0.0132	0.5002	0.9999	0.0090	-0.0009	-0.0001
0.01	0.0413	0.5018	0.9998	0.0305	-0.0094	-0.0005
0.001	0.1248	0.5166	0.9993	0.1332	-0.1029	-0.0044
0.0005	0.1716	0.5313	0.9990	0.3017	-0.2850	-0.0083
<i>Boric acid</i>						
0.1	-	0.4999	0.9888	-	0.0002	-0.0076
0.01	0.0003	0.4987	0.9651	-	0.0022	-0.0252
0.001	0.0009	0.4880	0.8939	0.0005	0.0284	-0.1020
0.0005	0.0012	0.4770	0.8534	0.0008	0.0776	-0.1829

The graph tends asymptotically to zero at high and low pH values (trivial solutions $f_0 = 0$ and $f_1 = 0$). The function π_{HA} , the contribution of the π curve characteristic of the weak acid itself has no minima to cause acid or basic end point inflection in the $\text{pH} = f(T)$ titration curve.

6. pH at the single normalised 0, 0.5 and 1.0 values of the fraction titrated

Equation (10) on rearrangement gives the cubic

$$|H^+|^3 + (TC_A + K_a)|H^+|^2 - (K_a C_A(1 - T) + K_w)|H^+| - K_a \cdot K_w = 0 \quad (74)$$

and taking into account Eqns. (17) and (21) we get, respectively,

$$x^3 + (Tr + 1)x^2 - \left(r(1 - T) + \frac{K_b}{K_a}\right)x - \frac{K_b}{K_a} = 0 \quad (75)$$

$$-y^3 - (s(1 - T) + 1)y^2 + \left(Ts + \frac{K_a}{K_b}\right)y + \frac{K_a}{K_b} = 0 \quad (76)$$

Equations (75) and (76) in combination with Eqn. (17) and (21), respectively, allow the calculation of the pH_0 , $\text{pH}_{0.5}$ and $\text{pH}_{1.0}$ values corresponding to the points at which the fraction titrated T takes the single normalised values 0, 0.5 and 1.0. The

f_{0T} values and the $\text{pH}'_i - \text{pH}_T$ differences ($T = 0, 1, 2$; $i = a, c, b$) obtained for both the acetic acid and the boric acid systems are compiled in Table 7. Some conclusions follow. The initial pH value is always lower than the value of the minimum pH'_a in the acid side. The $\text{pH}_{0.5}$ values lies to the right of the central maximum pH'_c for $\text{p}K_a < \text{p}K_w/2$, and to the left for $\text{p}K_a > \text{p}K_w/2$ values. However, for most analytical purposes (when solutions are not too diluted) the value of $\text{p}K_a$ can be estimated with satisfactory accuracy from the pH value at $T = 0.5$, i.e. when approximately half of the acid has been titrated. The minimum pH'_b in the alkaline side, that is the inflexion end point, always precedes (when occurs) to the equivalence $\text{pH}_{1.0}$ point.

7. Inflexion points in the buffer index versus pH curves.

By differentiating Eqn. (16) with respect to pH

$$\frac{d^2\pi}{dpH^2} = \ln^3 10 \left[\frac{C_A |H^+| \left(1 + \frac{|H^+|^2}{K_a^2} - 4 \frac{|H^+|}{K_a} \right)}{\left(1 + \frac{|H^+|}{K_a} \right)^2} + |H^+| + |OH^-| \right] \quad (77)$$

and taking into account Eqn. (17)

$$\frac{d^2\pi}{dpH^2} = \ln^3 10 \left(\frac{C_A x(1+x^2-4x)}{(1+x)^4} + |H^+| + |OH^-| \right) \quad (78)$$

$d^2\pi/dpH^2 = 0$ leads to a six-degree equation

$$\begin{aligned} x''^6 + 4x''^5 + \left(6+r + \frac{K_b}{K_a}\right)x''^4 \\ + 4\left(1-r + 4\frac{K_b}{K_a}\right)x''^3 + \left(1+r + 6\frac{K_b}{K_a}\right)x''^2 \\ + 2\frac{K_b}{K_a}x'' + \frac{K_b}{K_a} = 0 \end{aligned} \quad (79)$$

Although the inflection points are of doubtful interest themselves, we attempt to calculate them. However, in order to make more tractable the problem, we may neglect $|OH^-|$ with respect to $|H^+|$ when $pK_a < pK_w/2$, and then (K_b/K_a being negligible)

$$x''^4 + 4x''^3 + (r+6)x''^2 + 4(1-r)x'' + 1+r = 0 \quad (80)$$

Exact roots of Eqn (80) may be obtained by the Ferrari's method (Uspensky, 1948) for various values of r as can be seen in Table 8. Two inflection points were obtained, one on the acid side, pH_a'' , and the other in the alkaline direction, pH_b'' . Note that $\log x_a''$ and $\log x_b''$ denotes the distance in pH units between pK_a and the acid, and basic inflection $\pi = f(pH)$ points, respectively. The necessary steps to calculate exact roots of four degree equations by the method of Ferrari are indicated in the following. Let the equation

$$Ax^4 + Bx^3 + Cx^2 + Dx + E = 0 \quad (81)$$

Table 8

Distance (in pH units) between pK_a and the acid and basic inflection, respectively, for different r values with $OH^- \ll H^+$

r	$\log x_a''$	$\log x_b''$
10^7	0.5719	-0.5719
10^5	0.5718	-0.5719
10^3	0.5560	-0.5707
10^2	0.4578	-0.5597
50	0.3876	-0.5471
27	0.3010	-0.5249

By dividing through A we get

$$x^4 + ax^3 + bx^2 + cx + d = 0 \quad (82)$$

Let y_0 be a root of the auxiliary cubic equation

$$y^3 + by^2 + (ac - 4d)y - (d(a^2 - 4b) + c^2) = 0 \quad (83)$$

Then the coefficients A, B and C are given by

$$A = \frac{a^2}{4} + b + y_0 \quad (84)$$

$$B = \frac{ay_0}{2} - c \quad (85)$$

$$C = \frac{y_0^2}{4} - d \quad (86)$$

Making

$$\alpha = \sqrt{A} \quad (87)$$

$$\beta = \sqrt{C} \quad (88)$$

we get for the exact roots of the four degree equation the following expressions

$$x_1 = \frac{1}{2} \left(-\left(\frac{a}{2} - \alpha\right) + \sqrt{\left(\frac{a}{2} - \alpha\right)^2 - 4\left(\frac{y_0}{2} - \beta\right)} \right) \quad (89)$$

$$x_2 = \frac{1}{2} \left(-\left(\frac{a}{2} - \alpha\right) - \sqrt{\left(\frac{a}{2} - \alpha\right)^2 - 4\left(\frac{y_0}{2} - \beta\right)} \right) \quad (90)$$

$$x_3 = \frac{1}{2} \left(-\left(\frac{a}{2} + \alpha\right) + \sqrt{\left(\frac{a}{2} + \alpha\right)^2 - 4\left(\frac{y_0}{2} + \beta\right)} \right) \quad (91)$$

$$x_4 = \frac{1}{2} \left(-\left(\frac{a}{2} + \alpha\right) - \sqrt{\left(\frac{a}{2} + \alpha\right)^2 - 4\left(\frac{y_0}{2} + \beta\right)} \right) \quad (92)$$

In those cases in which $|H^+|$ and $|OH^-|$ may be neglected, Eqn (78) reduces to

$$\frac{d^2\pi}{dpH^2} = \ln^3 10 \frac{C_A x(1+x^2-4x)}{(1+x)^4} \quad (93)$$

and $d^2\pi/dpH^2 = 0$ requires

$$x''^2 - 4x'' + 1 = 0 \quad (94)$$

and then

$$x'' = 2 \pm \sqrt{3} \quad (95)$$

$$\log x'' = \pm 0.5719 \quad (96)$$

as shown recently by Asuero, 1992 in this journal.

8. Conclusion

Although the principles of potentiometric titrations are described in some detail in almost every modern textbook of analytical chemistry, some aspects concerning to relevant aspects of the buffer index behaviour have been frequently omitted. However, the buffer index expressions are extremely useful in discussing the general nature of titration curves. At each maximum or minimum in the π versus pH curve corresponds an inflection point in the titration curve which requires $C_A < 27 K_a$ in the acid side, or $C_A K_a > 27 K_w$ in the alkaline one. On the other hand, the maximum buffer capacity does not strictly coincides with the pH value equals to pK_a . Though it is assumed that there is no volume change this is in fact possible in some situation, e.g. the titrant may, for example, be assumed to be generated directly in the titration vessel. In any case, the volume change does not substantially affect the characteristic aspects of the titration curve.

Acknowledgements

Financial support received from DGICYT through Research Line N° PB92-0678 is gratefully acknowledged.

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