Historical remarks on the Henderson-Hasselbalch equation: its advantages and limitations and a novel approach for exact pH calculation in buffer region

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Abstract

The theoretical titration curve of a weak acid with a strong base was considered. The limitation of the Henderson-Hasselbalch equation for the calculation of pH in the buffer region was discussed. One novel simple equation for the exact calculation of pH from the beginning of titration up to the equivalence point was derived. By using this equation with one implicit approximation (the dissociation of water), the calculation of pH values after each addition of titrant is possible. A novel equation provides the simple and exact calculation of pH in the range of buffer, and that can be done in a simple and logical way without complex handling of acid-base equilibrium with computer and spreadsheet software. The calculated titration curves for different concentrations of acetic acid and sodium hydroxide were shown.

Keywords: acid-base chemistry; analytical chemistry; Henderson-Hasselbalch equation; titration.

Introduction

These years the Henderson-Hasselbalch equation is celebrating its first century (Henderson 1908, Hasselbalch 1917). The Henderson-Hasselbalch equation is widely used worldwide by chemists for buffer preparation because it is very simple:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \tag{1}$$

where

- $pH = -\log[H_3O^+]$, is the concentration of hydronium ions (it would be more accurate using activity of hydronium ions, $pH = -\log a_{H_3O^+}$)
- $pK_a = -\log K_a$, K_a, is the dissociation constant of weak acid
- $[A^-]$, is the concentration of conjugated base of weak acid
- $[HA]$, is the concentration of weak acid

The biggest advantages of the Henderson-Hasselbalch equation are its simplicity and that the dissociation constant of weak acid, the concentration of weak acid in buffer solution, and the wanted volume of buffer solution known can be easily calculated with the needed mass of the conjugated base of weak acid in the form of salt. During buffer preparation, the required pH value is adjusted by adding a few drops of acid (if the current pH value is above the required pH value) or base (if the current pH value is less than the required pH value) by controlling the pH value with a pH meter. This is one of the limitations of the Henderson-Hasselbalch equation, because it assumes $[HA] = c(HA)$ and $[A^-] = c(A^-)$. As discussed in the succeeding part of this article, this assumption is not true because the true values are

$$[HA] = c(HA) - [H_3O^+] + [OH^-]$$
$$[A^-] = c(A^-) + [H_3O^+] - [OH^-]$$

Furthermore, when the Henderson-Hasselbalch equation is used in acid-base titration, it is unsuitable because, for any used concentration of weak acid and strong base, it gives the same value (full line in Figure 1), and after beginning the titration, and adding the base, according to the Henderson-Hasselbalch equation, pH values are smaller than the starting pH of the weak acid. Decreasing the pH value cannot be reasonably explained by the addition of a strong base because all chemistry handbooks say that after the addition of strong base in a solution of weak acid, the pH value increases (Harvey 2000, Enke 2001, Christian 2004, Kellner et al. 2004, Skoog et al. 2004, Harris 2005). We assume that this unusual and also illogical situation comes from the limitation of the Henderson-Hasselbalch equation. The limitation is that the Henderson-Hasselbalch equation assumes that the sum of concentration of weak acid and the concentration of conjugated base of weak acid are constant during titration. The sum of the concentration of weak acid and concentration of the conjugated base of weak acid would be constant if it does not process the dissociation of acid and if hydrolysis of the conjugated base occurs.

The primary textbooks in the field of analytical chemistry contain chapters concerned with acid-base chemistry. In addition, the literature cited includes selected articles (de Levie 1993, 1999, Ault 1999, Barnum 1999, Po and Senozan 2001, Kraft 2003, Pardue et al. 2004) published in the *Journal of Chemical Education*. A new approach in the treatment of experimental data from a potentiometric titration of a single acid or base was discussed recently (Maslarska et al. 2003). Searching the literature, we found no article that solves, in a simple and accurate way, the calculation of pH during the titration of a weak acid with a strong base. In this paper, we give suggestions of a novel equation that can be used for the exact prediction of acid-base titration as a function of the starting concentrations of acid and base and the added volumes of base (dotted lines in Figure 1). All calculations
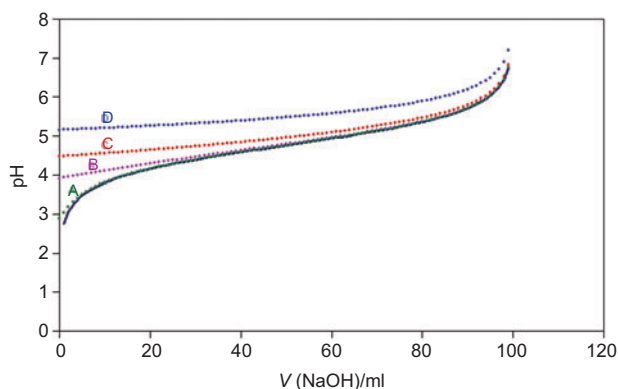
Figure 1   Curve for the titration of acetic acid with sodium hydroxide. Curve A: 0.1 M acid with 0.1 M base. Curve B: 1×10^{-3} M acid with 1×10^{-3} M base. Curve C: 1×10^{-4} M acid with 1×10^{-4} M base. Curve D: 1×10^{-5} M acid with 1×10^{-5} M base. Before equivalence point: full line, Eq. (8); dotted lines, Eq. (11).

in this article were performed using Microsoft® Excel 2002 (10.6871.6870) SP3 (Microsoft Corporation, Redmond, WA, USA). Microsoft® Excel was chosen because of its widespread availability in PCs and its great simplicity, so students can easily do calculations and draw graphic plots of calculated results.

Theoretical part

The first step in each case of acid-base equilibrium is to write the chemical reaction between the analyte and titrant. Then, we use that reaction to calculate the composition of the solution and pH after each addition of titrant. As a simple example, the titration of acetic acid with sodium hydroxide has been examined. The neutralization reaction is
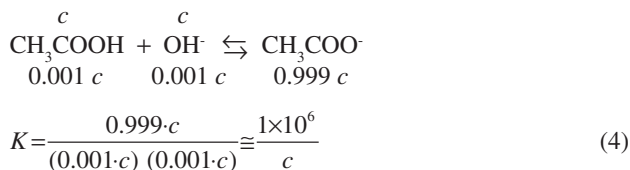
$$CH_3COOH+Na^++OH^-\rightarrow CH_3COO^-+H_2O+Na^+ \qquad (2)$$

The equilibrium constant for this reaction can be expressed and calculated as follows:

$$K=\frac{K_a}{K_w}=\frac{1.75\times10^{-5}}{1\times10^{-14}}=1.75\times10^9\,M^{-1} \qquad (3)$$

where K_a is the dissociation constant of acetic acid (1.75×10^{-5} M) and K_w is the ionization of water (1×10^{-14} M²). The equilibrium constant is so large that we can suppose that the reaction goes to completion after each addition of OH⁻. However, for a required extent of reaction, the appropriate equilibrium constant should be calculated. For an extent of reaction (99.9%) that is very close to completion, we can calculate the equilibrium constant by writing the reaction with the relative concentration before and after neutralization.

$$\begin{array}{cccc} c & & c & \\ CH_3COOH & + & OH^- & \leftrightarrows & CH_3COO^- \\ 0.001\,c & & 0.001\,c & & 0.999\,c \end{array}$$

$$K=\frac{0.999\cdot c}{(0.001\cdot c)\,(0.001\cdot c)}\cong\frac{1\times10^6}{c} \qquad (4)$$

If we substitute K in Eq. (4) with the calculated constant (1.75×10^9 M⁻¹), we obtain for 99.9% extent of reaction, the concentration of reactant should be higher than 5.7×10^{-4} M. As a simple teaching example, our attention is focused on the titration of 100.0 ml of 0.0010 M acetic acid with 0.0010 M sodium hydroxide. The volume of sodium hydroxide needed to reach the equivalence point ($V_{e.p.}$) is also 100.0 ml.

Before any base is added, the solution contains weak acid in water and the pH is determined by the next equilibrium

$$\begin{array}{ccc} CH_3COOH & \rightleftarrows & CH_3COO^- + H^+ \\ c-x & & x \qquad\quad x \end{array} \qquad (5)$$
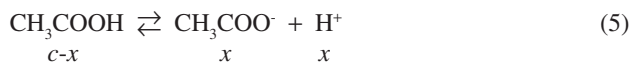
$$\frac{x^2}{0.0010-x}=K_a=1.75\times10^{-5}\,M;\ x=\left[H_3O^+\right]=1.24\times10^{-4}\,M;$$
$$pH=3.91 \qquad (6)$$

This pH concentration of $[H_3O^+]$ from ionization of water can be ignored:

$$\left[H_3O^+\right]_{H_2O}=\left[OH^-\right]_{H_2O}=\frac{1\times10^{-14}}{1.24\times10^{-4}}=8.1\times10^{-11}\,M$$

Calculation of pH in the range of buffer

From the first addition of NaOH, a mixture of CH_3COOH and CH_3COO^- is created by the titration reaction [Eq. (1)]. In different textbooks (Harvey 2000, Christian 2004, Skoog et al. 2004, Harris 2005), the following statement can be found: after various increments of titrant have been added (in quantities up to, but not including, an equivalent amount), the solution consists of a series of buffers. The pH of each buffer can be simply calculated from the analytical concentrations of the conjugate base and the residual concentrations of the weak acid by using the well-known Henderson-Hasselbalch equation as follows:

$$pH=pK_a+\log\frac{[CH_3COO^-]}{[CH_3COOH]} \qquad (7)$$

$$\frac{\left[CH_3COO^-\right]}{\left[CH_3COOH\right]}=\frac{n\left(CH_3COO^-\right)/\left(V_a+V_b\right)}{n\left(CH_3COOH\right)/\left(V_a+V_b\right)}=\frac{n\left(CH_3COO^-\right)}{n\left(CH_3COOH\right)}$$

$$\frac{n\left(CH_3COO^-\right)}{n\left(CH_3COOH\right)}=\frac{V_b\times c_b}{\left(V_{e.p.}-V_b\right)\times c_b}$$

where V_b and c_b are the added volume and concentration of the titrant, strong base. The n denotes the number of moles of acid (CH_3COOH) or conjugate base (CH_3COO^-) in buffer. V_a is the volume of analyte (weak acid) at the beginning of titration, and $V_{e.p.}$ is the volume of titrant at the equivalence point.

Finally, the Henderson-Hasselbalch equation can be written in the following form:

$$pH=pK_a+\log\frac{V_b}{\left(V_{e.p.}-V_b\right)} \qquad (8)$$

From Eq. (8), one can conclude that the calculated pH values before equivalence point do not depend on the concentration of weak acid. Also, when $1/2\ V_{e.p.}$ has been added, pH=pK_a.
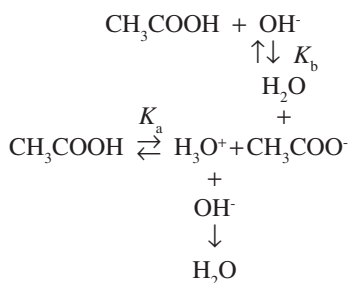
When 1.0 ml of NaOH is added, in our exercise, pH can be calculated by using Eq. (8)

$$pH=4.76+\log\frac{1.0}{100.0\text{-}1.0}=2.76$$

The calculated pH value (2.76) is not logical. After 1 ml of titrant (OH⁻) has been added, [H_3O^+] is increased! We should note that the pH values calculated by using Eq. (8) were less than at the beginning of the titration, up to V=12 ml. At this point, ==it is very important to stress again that there are some significant approximations implicit in the Henderson-Hasselbalch equation. The most significant is the assumption that the concentration of the acid and its conjugate base at equilibrium will remain the same as the total or analytical concentration.== This neglects the dissociation of the acid and the hydrolysis of the base. The dissociation of water itself is also neglected. As shown (Po and Senozan 2001), an exact calculation of [H_3O^+] in a buffer must take into account a set of four independent equations with four unknowns, and [H_3O^+] can be calculated by iterative techniques using spreadsheet software.

==This article shows that exact calculation of [H_3O^+] in a buffer can be done by using a simple equation derived from the next consideration where only ionization of water is neglected.==

When adding OH⁻, in a form of a strong base as titrant begins, a mixture of CH_3COOH and CH_3COO^- is indeed created not only by the titration reaction [Eq. (2)] but also with the dissociation of acid and hydrolysis of base.

$$CH_3COOH\ +\ OH^-$$
$$\uparrow\downarrow\ K_b$$
$$H_2O$$
$$+$$
$$K_a$$
$$CH_3COOH\ \rightleftarrows\ H_3O^+ + CH_3COO^-$$
$$+$$
$$OH^-$$
$$\downarrow$$
$$H_2O$$

The exact concentration of CH_3COOH and CH_3COO^- can be analyzed and calculated as follows:

$$\frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}=K_a\ \Rightarrow\ [H_3O^+]=K_a\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$[H_3O^+]=K_a\frac{c_a'-[H_3O^+]+[OH^-]}{c_b'+[H_3O^+]-[OH^-]} \tag{9}$$

In the first part of the titration curve, the buffer region, [H^+]>>[OH^-] and [H^+] can be calculated as follows:

$$[H_3O^+]=K_a\frac{c_a'-[H_3O^+]}{c_b'+[H_3O^+]}$$

$$c_a'=\frac{V_a\times c_a\text{-}V_b\times c_b}{V_a+V_b};\quad c_b'=\frac{V_b\times c_b}{V_a+V_b}$$

where c_a denotes the total concentration of weak acid (CH_3COOH) at the beginning of titration, c_a' denotes the concentration of unreacted weak acid (CH_3COOH) after titration began, and c_b' denotes the concentration of conjugated base created by titration (CH_3COO^-).

Solving Eq. (9) gives

$$[H_3O^+]=\frac{-(c_b+K_a)+\sqrt{(c_b+K_a)^2+4\times K_a\times c_a'}}{2} \tag{10}$$

and

$$pH=-\log\left\{\frac{-(c_b+K_a)+\sqrt{(c_b+K_a)^2+4\times K_a\times c_a'}}{2}\right\} \tag{11}$$

When 1.0 ml of titrant is added, we need to calculate the exact concentration of buffer mixture.

$$c_a'=\frac{100.0\times0.0010\text{-}1.0\times0.0010}{100.0+1.0}=9.80\times10^{-4}\ M;$$

$$c_b'=\frac{1.0\times0.0010}{100.0+1.0}=9.90\times10^{-6}\ M$$

Now the "true" [H_3O^+] can be calculated by using Eq. (10)

$$[H_3O^+]=-(9.90\times10^{-6}+1.75\times10^{-5})+$$
$$\frac{\sqrt{(9.90\times10^{-6}+1.75\times10^{-5})^2+4\times1.75\times10^{-5}\times9.80\times10^{-4}}}{2}$$
$$[H_3O^+]=1.18\times10^{-4}\ M$$
$$pH=3.92$$

The calculated value shows an increase of pH from 3.91 to 3.92 after the addition of 1.0 ml of titrant. A summary of the calculations for the titration of 0.0010 M CH_3COOH with 0.0010 M NaOH is shown in Table 1. The values in Table 1 demonstrate that in the part of buffer region, Eq. (11) yields higher pH values than the Henderson-Hasselbalch equation.

For the titration of a weak acid with a strong base, de Levie (de Levie 1997) derived the next approximation for calculation of [H_3O^+] before the equivalence point:

$$[H_3O^+]\approx-c_bV_b-K_a(V_a+V_b)+$$
$$\frac{\sqrt{\{c_bV_b+K_a(V_a+V_b)\}^2+4K_a(V_a+V_b)(c_aV_a-c_bV_b)}}{2(V_a+V_b)}$$

(de Levie equation)

In his last book, de Levie (2008) suggested using a far complex equation (fourth-order polynomial for a monoprotic weak acid) [Eq. (12)], which is hard to solve without using strong mathematical tools, e.g., Wolfram's Mathematica.

Table 1   Changes in pH during the titration of a weak acid with a strong base (100.0 ml of 0.0010 M CH_3COOH with 0.0010 M NaOH).

V (NaOH)/ml	Henderson-Hasselbalch equation, Eq. (8)	pH, Eq. (11)	de Levie equation (de Levie 1997)
1.00	2.76	3.93	3.93
2.00	3.07	3.95	3.95
5.00	3.48	4.00	4.01
10.00	3.80	4.10	4.11
15.00	4.00	4.19	4.21
20.00	4.15	4.29	4.30
25.00	4.28	4.37	4.39
50.00	4.76	4.79	4.80
75.00	5.23	5.25	5.26
99.00	6.75	6.76	6.78

A limited number of points of Figure 1 are shown to save space.

$$\left(V_a+V_b\right)[H_3O^+]^4+\left(K_aV_a+c_bV_b+K_aV_b\right)[H_3O^+]^3$$
$$+\left(K_wV_a-c_aV_aK_a-2K_wV_b+c_bV_bK_a\right)[H_3O^+]^2 \qquad (12)$$
$$+\left(-K_aK_wV_b-c_bV_bK_w\right)[H_3O^+]-V_bK_w^2=0$$

The author did not use Microsoft Excel for solving Eq. (12) in a mathematical way (roots determination) like we suggested for Eq. (11). He calculated V_b using a definite number of pH values ranging from 0 to 14. The proposed way is not intuitive and can be ambigious to students. Despite the stated flaws, we test and discuss that kind of approach in the second part of the paper (Table 2). This approach is suitable for testing any proposed equation.

The pH values calculated by using the Henderson-Hasselbalch equation, derived Eq. (11), and Levie's equation are compared in Table 1.

Curves for the titration of different concentrations of acetic acid with sodium hydroxide are shown in Figures 1 and 2. Figure 1 shows the significant influence of acid concentration on pH values in the buffer region when Eq. (11) instead of the Henderson-Hasselbalch equation was applied. The influence of the concentration of weak acid on the shape of titration curve in the buffer region has been emphasized in some textbooks (Enke 2001, Kellner et al. 2004), but an equation for pH calculation has not been suggested.

Charge balance in buffer solution and checking of Eq. (10)

The state in the solution expressed by Eq. (10) can be analyzed in another complex way without any approximations. Titration of a volume V_a of acetic acid (initial concentration c_a) with a volume V of NaOH of concentration c_b can be considered with a charge balance in the solution as has been shown in the literature (de Levie 1993, 2001, 2008, Harris 1999).

Charge balance: $[H_3O^+]+[Na^+]=[CH_3COO^-]+[OH^-]$ (13)

Concentrations of Na^+ and CH_3COO^- in the buffer solution can be calculated as follows:

$$\left[Na^+\right]=\frac{V_b\times c_b}{V_a+V_b}$$

$$\left[CH_3COO^-\right]=c_{CH_3COOH}\times\alpha_{CH_3COO^-}$$

where α is the fraction of the total (analytical) concentration of acetic acid present in the CH_3COO^- form.

$$c_{CH_3COOH}=\left[CH_3COOH\right]+\left[CH_3COO^-\right]=\frac{V_a\times c_a}{V_a+V_b}$$

Table 2   Comparison between "added" and calculated volume of titrant for acetic acid (0.0010 M) vs. sodium hydroxide (0.0010 M) titration.

| V (NaOH)/ml, "added"	[H⁺], calculated, Eq. (10)	$\alpha_{CH_3COO^-}$, calculated, Eq. (14)	Φ, calculated, Eq. (16)	V (NaOH)/ml, calculated, Eq. (17)
1.00	1.26×10^{-4}	0.1285	0.0099	0.99
2.00	1.13×10^{-4}	0.1341	0.0211	2.11
5.00	9.91×10^{-5}	0.1500	0.0509	5.09
10.00	7.95×10^{-5}	0.1803	0.1008	10.08
15.00	6.40×10^{-5}	0.2147	0.1506	15.06
20.00	5.18×10^{-5}	0.2524	0.2005	20.05
25.00	4.23×10^{-5}	0.2927	0.2504	25.04
50.00	1.64×10^{-5}	0.5165	0.5002	50.02
75.00	5.66×10^{-6}	0.7557	0.7501	75.01
99.00	1.74×10^{-7}	0.9902	0.9901	99.01
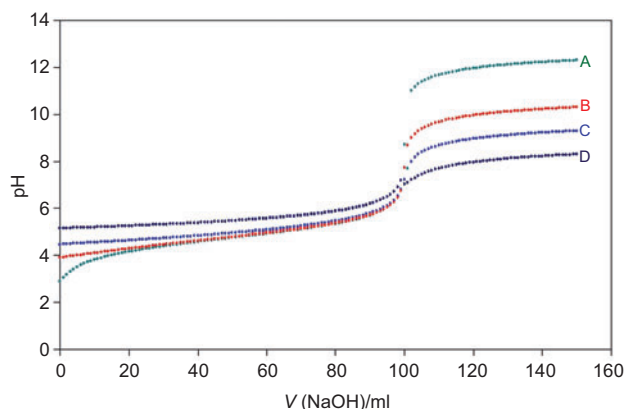
Figure 2 Curve for the titration of acetic acid with sodium hydroxide. Curve A: 0.1 M acid with 0.1 M base. Curve B: 1×10^{-3} M acid with 1×10^{-3} M base. Curve C: 1×10^{-4} M acid with 1×10^{-4} M base. Curve D: 1×10^{-5} M acid with 1×10^{-5} M base.

$$\left[CH_3COO^-\right]=\frac{V_a\times c_a}{V_a+V_b}\times\alpha_{CH_3COO^-}$$

$$\alpha_{CH_3COO^-}=\frac{K_a}{\left[H_3O^+\right]+K_a}\tag{14}$$

Substituting for [Na$^+$] and [CH$_3$COO$^-$] in the charge balance gives

$$\left[H_3O^+\right]+\frac{V_b\times c_b}{V_a+V_b}=\frac{V_a\times c_a}{V_a+V_b}\times\alpha_{CH_3COO^-}+\left[OH^-\right]\tag{15}$$

If the last equation is rewritten in the next form

$$\Phi=\frac{V_b\times c_b}{V_a\times c_a}=\frac{\alpha_{CH_3COO^-}-\dfrac{\left[H_3O^+\right]-\dfrac{K_w}{\left[H_3O^+\right]}}{c_a}}{1+\dfrac{\left[H_3O^+\right]-\dfrac{K_w}{\left[H_3O^+\right]}}{c_b}}\tag{16}$$

where Φ is the fraction of the way to the equivalence point.

$$\Phi=\frac{V_b\times c_b}{V_a\times c_a}\tag{17}$$

Eq. (16) works backward from the usual way of thinking. If we choose pH values during titration, this equation can be used for calculating the volume of titrant added, V. Eq. (16), which is based on a charge balance consideration without any approximations, has been used for examination accuracy of [H$_3$O$^+$] calculated by using Eq. (10) based on one approximation. Ten volumes of titrant were selected, and for each "added" volume, [H$_3$O$^+$] was calculated and tabulated in the second column of Table 2. Then substituting the [H$_3$O$^+$] value from the second column into Eq. (16), the fraction of the way

to the equivalence point Φ was calculated. Finally, the volumes of the titrant needed to reach [H$_3$O$^+$] were calculated and tabulated in the last column of Table 2. Table 2 shows excellent agreement between the "added" volume of the titrant and the volume values calculated by using Eq. (17).

Conclusion

From the beginning of weak acid vs. strong base titration, up to the equivalence point, the derived Eq. (11) provides a calculation of pH values, which generate a smooth titration curve for any concentration of weak acid. Using this equation with one implicit approximation (the dissociation of water) and a simple electronic calculator, we are able to calculate the pH of reaction solution after each addition of titrant. A novel equation derived in this article provides simple and exact calculations of pH in the range of the buffer, and that can be done on a simple and logical way without complex handling of acid-base equilibrium with computer and spreadsheet software. The proposed equation can be used for the titration studied to construct a graph showing how the pH changes as titrant is added. If we include this in teaching programs, students will understand what is happening during the titration, and they will be able to interpret an experimental titration curve.

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