LECTURE TEXT

Closed-form expressions for monoprotic weak acid aqueous solutions

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Abstract

A general closed-form expression for $[H_3O^+]$ of solutions of a weak acid and a weak acid buffer, as well as their titration with a strong base, has been obtained and mathematically analyzed with the aid of computer algebra systems. This expression is used to evaluate, without the use of numerical approximations, the precision and accuracy of different approximations commonly employed in general chemistry and chemical analysis courses. The closed-form expression for $[H_3O^+]$ of a buffer solution is used to obtain an analytical expression for the pH stability when a strong base is added. Finally, it is shown that the $[H_3O^+]$ expressions for all the systems under study can be obtained from a general closed-form expression in terms of an effective weak acid constant and an effective acid concentration. The formulas found in this work do not display numerical rounding errors and do not require the use of numerical or graphical methods for their evaluation.

Graphical abstract
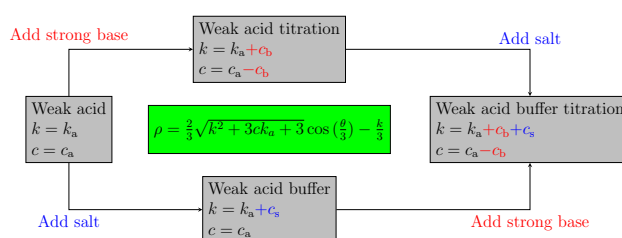
Graphical TOC: A closed-form expression for the weak acid and weak acid buffersolutions and their titrations with a strong base

Keywords Computer algebra systems · Weak acid · Buffer solutions

Introduction

Weak acids are important physical systems of interest in chemistry, biochemistry, chemical engineering, and physiology. A weak acid is a substance that undergone partial protolysis in water to produce undissociated acid molecules, hydronium ions, H_3O^+, and the acid conjugate base. An aqueous weak acid buffer solution is formed by a weak acid and one, or several, of its soluble salts. The equilibrium of a weak acid, or a weak acid buffer, involves four chemical substances and four equations: the dissociation of the acid, the autoionization of water, and the balances of charge and matter. In principle it is possible to obtain the equilibrium concentrations of all the chemical species for the weak acid dissociation or the buffer solution by solving these systems of equations. In practice, these systems of equations involve nonlinear terms making it difficult to obtain exact mathematical expressions for the concentrations. The algebraic manipulation of the systems of equations for the weak acid dissociation or the buffer solution give cubic equations for the concentration of H_3O^+ [1–3]. The equilibrium concentration of H_3O^+ is obtained by finding the roots of these cubic equations. Although there exists a cubic formula that gives the explicit roots of a cubic equation, it is not practical to use because of its complexity [4–6]. The crude use of the cubic formula requires more than 30 arithmetic operations, making its use for hand calculation impractical [6–8]. Macleod and Barling [6, 9, 10] have already reported mathematical

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formulas for the pH of weak acid solutions. Although Macleod's [9] expressions are exact, they show numerical rounding errors, so the Newton–Raphson numerical method is used to calculate the pH. Numerical difficulties with the pH formulas have been observed also in titration models of weak acids [11]. In this work exact simplified formulas for the pH of a weak acid and its buffer are shown and evaluated without numerical rounding errors.

A quadratic equation is obtained for the hydronium ion if the autoionization of water is ignored. Under this approximation, the equilibrium concentration of the H_3O^+ is obtained simply by solving a quadratic equation. The approximation of ignoring water autoionization displays a relative error greater than 10% for weak acids with $K_a < 10^{-6}$, and at low analytical concentrations of the acid or the salt of the acid, $C_{a,s} < 10^{-6}$ M, with $1\,M = 1\,mol\,L^{-1}$. Although the concentrations used in the general chemistry laboratory are generally above 10^{-2} M, there may be situations in chemical analysis where very low concentrations are handled [1, 3, 7, 8].

General purpose computer algebra systems (CAS) allow the algebraic manipulation of equations and inequalities [12]. The use of CAS in mathematical software, with user-friendly graphical interfaces, has extended the use of CAS to all fields of knowledge. Examples of free and non-free CAS are Maple [13], Wolfram Mathematica [14], Maxima [15], and SageMath [16]. Today mathematical software with CAS capability is easily found in research and academic laboratories and classrooms. Complex problems that were considered beyond the scope of the researchers or students can be solved today on the computer by using CAS mathematical software. The mathematical solution of the aqueous dissociation of weak acids or buffer solutions requires functions available in mathematical software. These functions are mainly (i) the simplification and algebraic manipulations of large equations, and inequalities, and (ii) the use of complex analysis, and graphical representation of functions, inequalities, and implicit regions. In this work, Wolfram Mathematica is employed to obtain simplified closed-form expressions for the equilibrium concentrations of the chemical species of four aqueous systems: the weak acid dissociation and its titration by a strong base, the buffer solution and its titration by a strong base [1–3, 17]. The cubic equations for the hydronium ion are analyzed, their roots are obtained by the use of the classical Cardano's method for the associated depressed cubic equations [18, 19]. The direct results of Cardano's method are the cube roots of two complex numbers. The polar representation of these cube roots allows one to obtain only three real roots. These roots are simplified and reduced to closed-form expressions that are simple enough to allow exact pH calculations with only a handheld scientific calculator. The use of Descartes' rule of signs [18–20] allows one to demonstrate that only one root is positive. The pH stability is measured as the change

of the pH as the strong base is added. Finally, a general equation for the concentration of H_3O^+ is presented. This general equation gives the pH for any of the four systems studied in this work in terms of an effective acid constant and an effective acid concentration.

Theory and methods

General equation for the concentration of $[H_3O^+]$

The aqueous dissociation equilibrium of a weak acid HB is given by the chemical equations

$$HB + H_2O \leftrightarrows H_3O^+ + B^-, \tag{1}$$

$$2H_2O \leftrightarrows H_3O^+ + OH^-. \tag{2}$$

These equilibria are altered by the addition of a salt NaB or the addition of a strong base, e.g., NaOH. The salt and the strong base dissociate completely in water to produce the ions Na^+, B^-, and OH^-, through the reactions

$$NaB \xrightarrow{H_2O} Na^+ + B^-, \tag{3}$$

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-. \tag{4}$$

The addition of the salt forms a buffer solution meanwhile the addition of the strong base neutralizes the acidity of the solution. Relevant chemical species are H_3O^+, OH^-, HB, B^-, and Na^+, with molar concentrations $[H_3O^+]$, $[OH^-]$, [HB], $[B^-]$, and $[Na^+]$ respectively [1–3].

A solution of the acid HB, the salt NaB, and the strong base NaOH, with concentrations C_a, C_s, and C_b, respectively, reaches chemical equilibrium. This equilibrium is quantitatively given by five equations [3]. These are the dissociation of the acid K_a, the autoionization of water K_w, the electric neutrality, the matter balance for the acid, and the matter balance for the strong base and salt added:

$$K_a = \frac{[H_3O^+]}{C^\circ} \frac{[B^-]}{C^\circ} \left(\frac{[HB]}{C^\circ}\right)^{-1}, \tag{5}$$

$$K_w = \frac{[H_3O^+]}{C^\circ} \frac{[OH^-]}{C^\circ}, \tag{6}$$

$$[H_3O^+] + [Na^+] = [OH^-] + [B^-], \tag{7}$$

$$C_a + C_s = [HB] + [B^-], \tag{8}$$

$$C_b + C_s = [\text{Na}^+].\tag{9}$$

with $C° = 1\,\text{M}$. Acid constants K_a are dimensionless, with values ranging typically between 10^{-10} and 10^{-1}. It is mathematically convenient to define the variables $x = [\text{H}_3\text{O}^+]/(C°\sqrt{K_w})$, $y = [\text{OH}^-]/(C°\sqrt{K_w})$, $z_0 = [\text{HB}]/(C°\sqrt{K_w})$, $z_1 = [\text{B}^-]/(C°\sqrt{K_w})$, $s = [\text{Na}^+]/(C°\sqrt{K_w})$ and the dimensionless constants $c_a = C_a/\sqrt{K_w}$, $c_b = C_b/\sqrt{K_w}$, $c_s = C_s/\sqrt{K_w}$, $k_a = K_a/\sqrt{K_w}$, and $k_w = 1$. In terms of these dimensionless variables and constants, Eqs. (5)–(9) are replaced by

$$k_a = \frac{xz_1}{z_0},\tag{10}$$

$$x + \bar{c}_b = \frac{1}{x} + z_1,\tag{11}$$

$$\bar{c}_a = z_0 + z_1,\tag{12}$$

with effective base and acid concentrations $\bar{c}_b = c_b + c_s$, and $\bar{c}_a = c_a + c_s$. These effective concentrations are constrained to $\bar{c}_b \geq 0$ and $\bar{c}_a \geq 0$.

The combined use of Eqs. (10) and (12) in Eq. (11) produces after some algebra

$$x^2 + \bar{c}_b x - 1 = \frac{\bar{c}_a k_a x}{x + k_a},\tag{13}$$

which can be conveniently rewritten as

$$(x - \sigma_1)(x - \sigma_2)(x + k_a) = \bar{c}_a k_a x,\tag{14}$$

where $\sigma_{1,2} = \frac{1}{2}\left(-\bar{c}_b \pm \sqrt{\bar{c}_b^2 + 4}\right)$, with $\sigma_1 \geq 1$, $\sigma_2 \leq -1$, $\sigma_1 \sigma_2 = -1$, and $\sigma_1 + \sigma_2 = -\bar{c}_b$.

Expansion of Eq. (13) gives the cubic equation $P = 0$, with

$$P = x^3 + c_2 x^2 + c_1 x + c_0,\tag{15}$$

and coefficients

$$c_3 = 1,\tag{16}$$

$$c_2 = k_a + \bar{c}_b,\tag{17}$$

$$c_1 = -1 + k_a(\bar{c}_b - \bar{c}_a),\tag{18}$$

$$c_0 = -k_a.\tag{19}$$

The 4-tuple of coefficients of P $\text{coef}\,[P] = (c_3, c_2, c_1, c_0)$ gives important information about the roots of the equation $P = 0$. The signs of the $\text{coef}\,[P]$ give the 4-tuple

$$\text{sgn}\,(\text{coef}\,[P]) = \left(\text{sgn}\,c_3,\, \text{sgn}\,c_2,\, \text{sgn}\,c_1,\, \text{sgn}\,c_0\right)$$
$$= (+, +, \pm, -).\tag{20}$$

Regardless of the value of $\text{sgn}\,c_1$, this 4-tuple shows only one change of sign, from positive to negative. Descartes' rule of signs states that the number of positive roots of a polynomial is, at most, equal to the number of sign changes of its ordered list of coefficients [20]. The use of Descartes's rule indicates that $P = 0$ has only one positive root, no matter what system is dealt with—an acid solution, a buffer solution, or the neutralization of any of these solutions.

The full characterization of the roots of $P = 0$ is given by the discriminant of the polynomial (15), $\Delta[P]$ [18, 19, 21]. The case of $\Delta[P] > 0$ indicates that the three roots of $P = 0$ are all real and different. In the case $\Delta[P] < 0$, one of the roots is real and the other two roots are complex, which are a complex conjugate pair. The case $\Delta[P] = 0$ indicates multiple roots. Although the mathematical expression of $\Delta[P]$ is complicated, the use of the function FullSimplify of Wolfram Mathematica shows that $\Delta[P] > 0$ under the assumptions $\bar{c}_a > 0$, $\bar{c}_b \geq 0$, and $k_a > 0$.

In the supporting information it is shown that ρ_3, the positive root of $P = 0$, is given by

$$\rho = 2\sqrt[3]{\|\zeta\|}\cos(\theta/3) - \frac{k_a + \bar{c}_b}{3},\tag{21}$$

with

$$\sqrt[3]{\|\zeta\|} = \frac{1}{3}\sqrt{(k_a + \bar{c}_b)^2 + 3k_a(\bar{c}_a - \bar{c}_b) + 3},\tag{22}$$

$$\theta = \arctan\left(-\frac{q}{2}, \frac{\Delta[P]}{6\sqrt{3}}\right),\tag{23}$$

$$\Delta[P] = -4p^3 - 27q^2,\tag{24}$$

$$p = -\frac{1}{3}(k_a + \bar{c}_b)^2 - k_a(\bar{c}_a - \bar{c}_b) - 1,\tag{25}$$

$$q = \frac{2}{27}(k_a + \bar{c}_b)^3 + \frac{k_a}{3}(k_a + \bar{c}_b)(\bar{c}_a - \bar{c}_b) + \frac{\bar{c}_b - 2k_a}{3}.\tag{26}$$

The angle θ given in Eq. (23) is restricted to $\theta \in (0, \pi)$. The function $\arctan(x, y)$ used in the definition of θ gives the arc tangent of y/x taking into account which quadrant the point (x, y) is in. This angle θ is related to the trigonometric solution obtained by Nickalls for the roots of the cubic equation [22].

The general Eq. (21) gives the concentration $[\text{H}_3\text{O}^+] = 10^{-7}\rho$, and an approximation to the pH,

$$pH = -\log_{10} a_{H_3O^+}$$

$$\approx -\log_{10} \frac{[H_3O^+]}{C^\circ} \tag{27}$$

$$= 7 - \log_{10} \rho,$$

with $a_{H_3O^+}$ as the activity of the H_3O^+ ion.

Weak acid

The case of a weak acid is described by using $\bar{c}_a = c_a$ and $\bar{c}_b = 0$ in Eq. (21),

$$\rho = \frac{2}{3}\sqrt{k_a^2 + 3c_ak_a + 3} \cos(\theta/3) - \frac{k_a}{3}, \tag{28}$$

with

$$\theta = \arctan\left(-\frac{q}{2}, \frac{\sqrt{\Delta[P]}}{6\sqrt{3}}\right), \tag{29}$$

$\Delta[P] = -4p^3 - 27q^2$, and

$$p = -\frac{k_a^2}{3} - c_ak_a - 1, \tag{30}$$

$$q = \frac{2k_a^3}{27} + \frac{c_ak_a^2}{3} - \frac{2k_a}{3}. \tag{31}$$

The coefficient p is evidently negative, meanwhile q can have positive or negative values. Algebraic manipulation on the inequality $q < 0$ gives $k_a^2 + \frac{9}{2}c_ak_a - 9 < 0$, which can be rearranged to obtain $c_a < \frac{2}{9k_a}(k_a^2 - 9)$. The last inequality implies that negative values of q are obtained with $k_a < 3$, and $c_a < \frac{2}{9k_a}(9 - k_a^2)$. Very weak acids, e.g., HCN ($k_a = 6.2 \times 10^{-3}$) or HOCl ($k_a = 0.4$), would have negative q at micromolar concentrations.

The limit of infinite dilution of θ gives

$$\lim_{c_a \to 0} \theta = \arctan\left(k_a(9 - k_a^2), \sqrt{27}|k_a^2 - 1|\right). \tag{32}$$

Figure 1 displays this limit as a function of pK_a for different weak acids. In this limit of infinite dilution, $\lim_{c_a \to 0} \rho = 1$. The left and right extremes of the θ curve shown in Fig. 1 display the infinite dilution of θ for the case of H_3O^+ and H_2O, respectively. Weak acids with higher (lower) dissociation constants are located on the left (right) of the figure. The dashed line is given by acids with $1 \leq k_a \leq 3$. The value $k_a = 1$ gives $\Delta[P] = 0$ and $q < 0$, hence $\theta = 0$ and $\rho = 1$. This case gives one simple root and a double root for $P = 0$. It can be shown that the simple root is $\rho = 1$, and the double root is $\rho = -1$. The particular case of a triple root is impossible since the triple root condition $k_a^2 = -3(1 + c_ak_a)$ cannot be
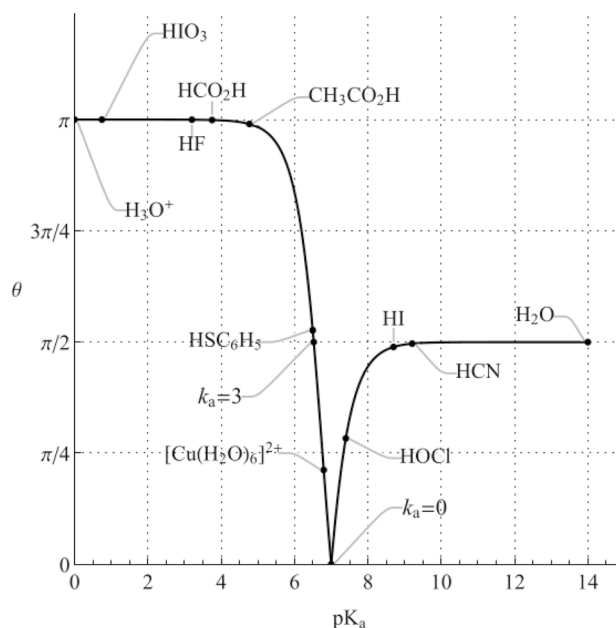

Fig. 1 Angle θ at infinite dilution as a function of the pK_a. The dashed line gives θ for weak acids with $1 \leq k_a \leq 3$. As the concentration of the acid increases, the value of θ tends to $\pi/2$

fulfilled with a real k_a. On the other hand, the value $k_a = 3$ produces $q = 0$ and $\Delta[P] > 0$, hence $\theta = \pi/2$ and $\rho = 1$.

As the concentration c_a is increased, the angle θ tends to $\theta = \pi/2$ for all the acids, regardless of its pK_a. The angle θ displays a maximum as a function of c_a. This maximum is obtained from the condition $\partial\theta/\partial c_a = 0$, which can be shown to give $c_a = 8/k_a$.

The concentration $[H_3O^+]$ is given by $[H_3O^+] = \sqrt{K_w}\rho$, and the pH is

$$pH \approx -\log_{10} \frac{[H_3O^+]}{C^\circ}$$
$$= 7 - \log_{10} \rho, \tag{33}$$

with $C^\circ = 1$ M. The low concentration and weak acid pH limits are given by $\lim_{c_a \to 0} pH = 7$, and $\lim_{k_a \to 0} pH = 7$. Equation (33) is useful to calculate the pH of a weak acid at low concentrations (1–10 μM). We calculate the pH of a diluted ($C_a = 5\,\mu M$) aqueous solution of acetic acid, $K_a = 1.75 \times 10^{-5}$, as an example of the use of these equations. The concentration and dissociation constants are given by $c_a = 5. \times 10^{-6}/10^{-7} = 50$, and $k_a = 1.75 \times 10^{-5}/10^{-7} = 175$. The coefficients p and q are easily calculated by the use of Eq. (30) to obtain $p = -18959.3$ and $q = 907291$. From the values of p and q the discriminant $\Delta[P]$ and θ are given by $\Delta[P] = -4p^3 - 27q^2$ and Eq. (29): $\Delta[P] = 5.03444 \times 10^{12}$, and $\theta = 2.69738$ radians. Finally, Eq. (28) gives $\rho = 40.6076$, for which $pH = 5.3914$. The use of the function NSolve of Wolfram

Mathematica for $P = 0$ gives $\rho = 40.6076$. Although the numerical solution is identical to the analytical solution, the former has a small imaginary part that must be removed to calculate the pH.

Weak acid titration by a strong base

A weak acid titration by a strong base requires one to make $\bar{c}_a = c_a$ and $\bar{c}_b = c_b$ in Eq. (21),

$$\rho = 2\sqrt[3]{\|\zeta\|}\cos\left(\frac{\theta}{3}\right) - \frac{k_a + c_b}{3}, \tag{34}$$

with

$$\sqrt[3]{\|\zeta\|} = \frac{1}{3}\sqrt{\left(k_a + c_b\right)^2 + 3k_a\left(c_a - c_b\right) + 3}, \tag{35}$$

$$\theta = \arctan\left(-\frac{q}{2}, \frac{\sqrt{\Delta[P]}}{6\sqrt{3}}\right), \tag{36}$$

$$\Delta[P] = -4p^3 - 27q^2, \tag{37}$$

$$p = -\frac{1}{3}\left(k_a + c_b\right)^2 - k_a\left(c_a - c_b\right) - 1, \tag{38}$$

$$q = \frac{2}{27}\left(k_a + c_b\right)^3 + \frac{k_a}{3}\left(k_a + c_b\right)\left(c_a - c_b\right) + \frac{c_b - 2k_a}{3}. \tag{39}$$

The contours of $\text{pH} = 7 - \log_{10}\rho$ as a function of $C_a = \sqrt{K_w}c_a$ and $C_b = \sqrt{K_w}c_b$ for acetic acid, $k_a = 180$, are shown in Fig. 2. It is interesting to note that there is a linear relationship between base and acid concentrations at constant pH; in fact, the pH = 7 line has a slope of 1 and passes through the origin $(C_a, C_b) = (0, 0)$. Figure 2 also shows that the C_b-intercept is negative for acidic pH and positive for basic pH. It is also seen in this figure that the slope of the lines $C_b(C_a)$ is less than 1 for acidic pH.

Buffer solution

The case of a buffer solution requires one to consider $\bar{c}_a = c_a + c_s$ and $\bar{c}_b = c_b + c_s$ in Eq. (21),

$$\rho = 2\sqrt[3]{\|\zeta\|}\cos\left(\frac{\theta}{3}\right) - \frac{k_a + c_b + c_s}{3}, \tag{40}$$

with

$$\sqrt[3]{\|\zeta\|} = \frac{1}{3}\sqrt{\left(k_a + c_b + c_s\right)^2 + 3k_a\left(c_a - c_b\right) + 3}, \tag{41}$$
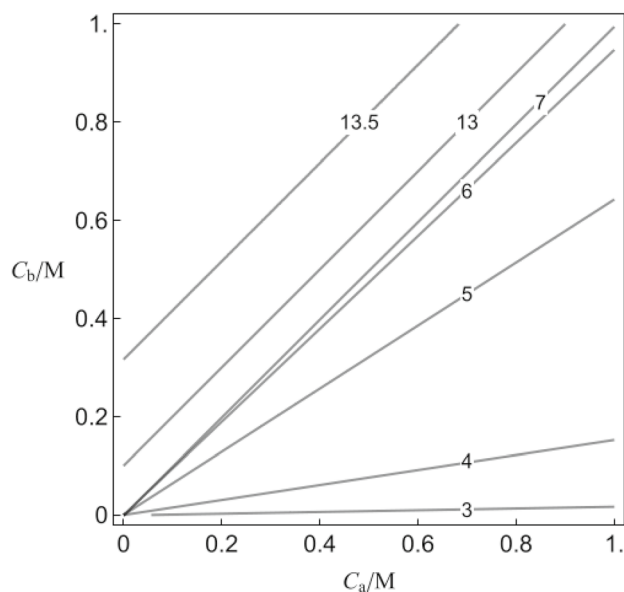

Fig. 2 Lines of constant pH on the C_a–C_b plane for acetic acid and a strong base, at concentrations C_a and C_b, respectively

$$\theta = \arctan\left(-\frac{q}{2}, \frac{\Delta[P]}{6\sqrt{3}}\right), \tag{42}$$

$$\Delta[P] = -4p^3 - 27q^2, \tag{43}$$

$$p = -\frac{1}{3}\left(k_a + c_b + c_s\right)^2 - k_a\left(c_a - c_b\right) - 1, \tag{44}$$

$$q = \frac{2}{27}\left(k_a + c_b + c_s\right)^3 + \frac{k_a}{3}\left(k_a + c_b + c_s\right)\left(c_a - c_b\right) + \frac{c_b + c_s - 2k_a}{3}. \tag{45}$$

By applying the logarithm of the acid dissociation constant K_a, Eq. (5), we obtain, after some algebraic manipulation, the Henderson–Hasselbalch (HH) equation [23–25]

$$\text{pH} = \text{p}K_a + \log_{10}\frac{[\text{B}^-]}{[\text{HB}]}. \tag{46}$$

The right-hand side of this equation is a function of pH and therefore the HH equation is not practical for direct calculation of the pH. It is common to use the approximations $[\text{B}^-] \approx C_s$ and $[\text{HB}] \approx C_a$ to obtain

$$\text{pH}^{(1)} \approx \text{p}K_a + \log_{10}\frac{C_s}{C_a}. \tag{47}$$

Figure 3 shows the absolute error of the pH, for chlorous acid, calculated by the HH equation with respect to the pH calculated using the exact formula, Eq. (40) with $c_b = 0$,
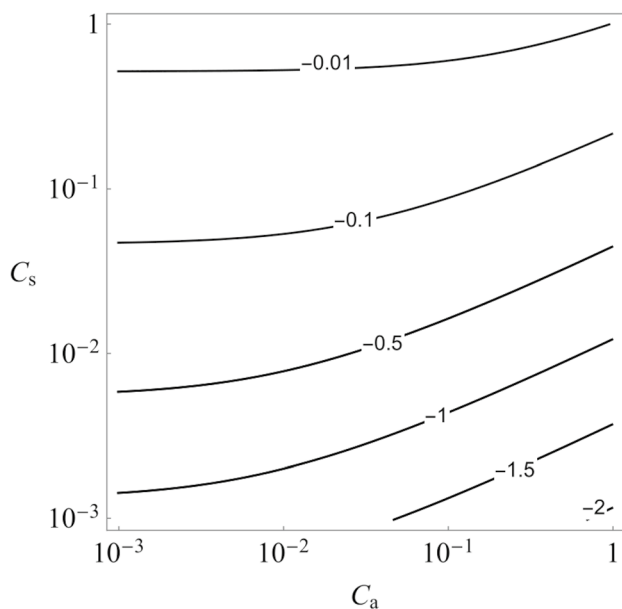
Fig. 3 Absolute error $E^{(pH)}$, in the pH calculated by the Herderson-Hasselbalch equation for a buffer solution of chlorous acid, $K_a = 1.2 \times 10^{-2}$, as a function of the molar concentrations of the acid C_a and the salt C_s

$$E^{(pH)} = pH^{(1)} - \left(7 - \log_{10}\rho\right), \tag{48}$$

with ρ given by Eq. (40). Figure 3 shows that small errors, $E^{(pH)} < 0.1$, are obtained for buffer solutions with high concentration of the salt, $C_s > 0.1\,M$, meanwhile large errors, $E^{(pH)} > 0.5$ are obtained for buffer solutions with $C_s < 0.01\,M$.

Buffer capacity

The pH stability of an acid buffer solution is measured by adding a volume V_b of a strong base solution with concentration c_b^0 [3]. The addition of this volume changes the concentrations c_a, c_s, and c_b,

$$c_a = \frac{c_a^0 V_a^0}{V_{ab}^0 + V_b}, \tag{49}$$

$$c_s = \frac{c_s^0 V_s^0}{V_{ab}^0 + V_b}, \tag{50}$$

$$c_b = \frac{c_b^0 V_b}{V_{ab}^0 + V_b}, \tag{51}$$

with c_a^0, c_s^0, and c_b^0, as the concentrations of the acid, salt of acid, and base independent solutions, respectively. The

volumes V_a^0, V_s^0, and $V_{ab}^0 = V_a^0 + V_s^0$ are the initial volumes of the acid, salt, and acid buffer solutions, respectively.

The pH stability, S_{pH}, of a buffer solution is given by

$$\begin{aligned} S_{pH} &= \frac{d(pH)}{dV_b} \\ &= \nabla_c(pH) \cdot \frac{dc}{dV_b}, \end{aligned} \tag{52}$$

with $c = (c_a, c_s, c_b)$ as 3-vector of concentrations, and the gradient of ρ, $\nabla_c \rho$, given by

$$\nabla_c \rho = \left(\frac{\partial \rho}{\partial c_a}, \frac{\partial \rho}{\partial c_s}, \frac{\partial \rho}{\partial c_b}\right). \tag{53}$$

The use in Eq. (52) of the pH definition, $pH = 7 - \log_{10}\rho$, and the concentrations of Eqs. (49)–(51), gives after some algebra

$$S_{pH} = \frac{1}{\ln 10} \frac{1}{\left(V_{ab}^0 + V_b\right)^2} \frac{1}{\rho} \nabla_c \rho \cdot n^0, \tag{54}$$

with

$$n^0 = \left(c_a^0 V_a^0, \ c_s^0 V_s^0, \ -c_b^0 V_{ab}^0\right). \tag{55}$$

The gradient $\nabla_c \rho$ is calculated with respect to the components of c but it must be expressed in terms of the volume of base V_b.

Figure 4 displays the pH stability, S_{pH}, as a function of the pH of the buffer solution. Since the addition of a strong base increases monotonically the pH of the solution, the curves of Fig. 4 contain the same information as the titration curves. To simplify the analysis all the concentrations used to prepare or titrate the buffers, c_a^0, c_s^0 and c_b^0, have the same value c^0. Panel (a) of Fig. 4 displays $S_{pH}/100$ for buffer solutions with concentrations $C^0 = 10^{-7} \times c^0$ ranging from 10^{-2} to 10^{-1} M (from blue to red). Panel (b) of Fig. 4 displays S_{pH} for buffer solutions with concentrations $C^0 = 10^{-7} \times c^0$ ranging from 10^{-7} to 10^{-5} M (from purple to red). In both panels of Fig. 4, curves with lower (higher) values of S_{pH} are for buffer solutions prepared and titrated with solutions of lower (higher) concentrations. The maximum of the curves S_{pH} is higher, and located at higher pH, for buffer solutions at higher concentrations C^0. The highest concentration buffer of Fig. 4a (in red) displays numerical instability for basic pH.

Figure 5 displays the titration curves for the same buffer solutions as in Fig. 4. To simplify the analysis, the concentrations of the solutions to prepare, and titrate, the buffer are the same, $C^0 = 10^{-7}c^0$. All the titration curves of panels (a) and (b) of Fig. 5 intercept at $V_b = 1\,L$ and $pH = 7$. Buffers of higher concentrations, in red, display the largest changes of pH as the solution is titrated with
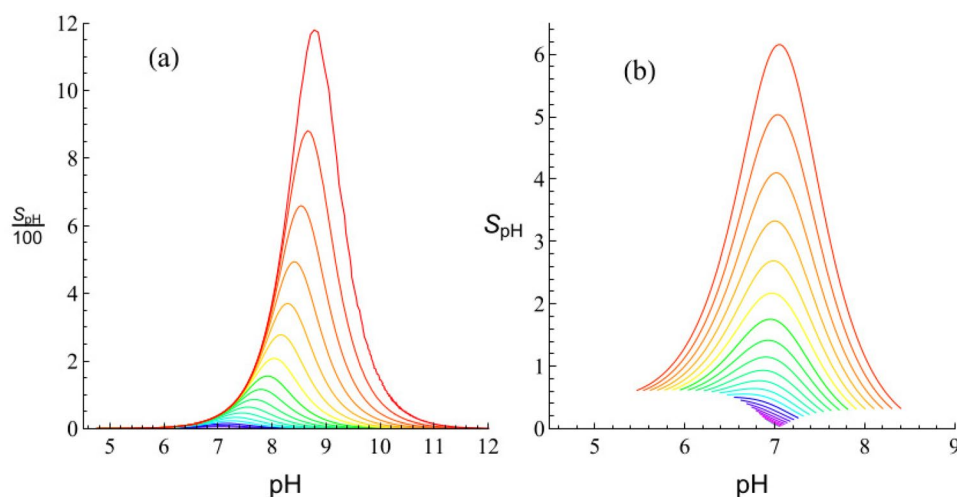
Fig. 4 pH stability S_{pH} as a function of the pH for buffer solutions of acetic acid ($k_a = 175$) and sodium acetate titrated with NaOH. To simplify the analysis, the initial concentrations c_a^0, c_s^0, and c_b^0, are equal to c^0. Panel (**a**) displays $S_{pH}/100$ for solutions with concentrations $C^0 = 10^{-7} \times c^0$ from 10^{-5} to 10^{-1} M. The lowest curves (blue color) are at lower concentrations, the highest curves (red color) are for higher concentrations. Panel (**b**) displays S_{pH} for solutions with concentrations $C^0 = 10^{-7} \times c^0$ from 10^{-7} to 10^{-5} M. The lowest curves (purple color) are for low concentration buffers, the highest curves (red color) for higher concentrations
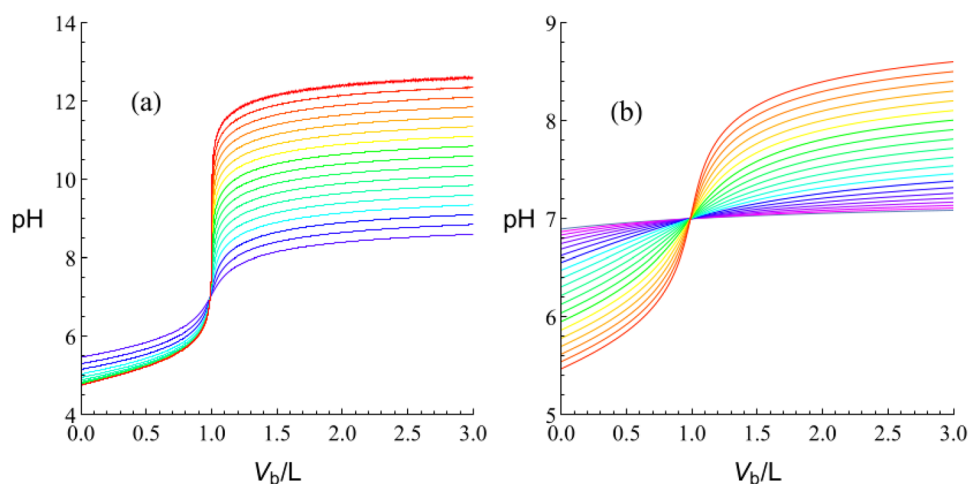
Fig. 5 Buffer titration as a function of the volume of base added, V_b/L. To simplify the analysis, the concentrations of the solutions to prepare, and titrate, the buffer are the same, $C^0 = 10^{-7} \times c^0$. Panel (**a**) displays the pH for solutions with concentrations $C^0 = 10^{-7} \times c^0$ from 10^{-5} to 10^{-1} M. The blue blue curves are at lower concentrations, the red curves are for higher concentrations. Panel (**b**) displays pH for solutions with concentrations $C^0 = 10^{-7} \times c^0$ from 10^{-7} to 10^{-5} M. The purple curves are for low concentration buffers, the red curves for higher concentrations

strong base. It is observed in Fig. 5(a) that the steepest change in the pH is given for pH ≈ 9, as shown in Fig. 4a.

The use of Figs. 4a and 5a indicates that the lower the concentration of the solutions of acid and salt of the acid (blue curves), the lower the change in pH as the base is added.

Systematic analysis relating the pH expressions

The four cubic equations for $x = [H_3O^+]/\sqrt{K_w}$ of the systems under study can be written as

Table 1 Coefficients of the polynomials for the systems studied: weak acid (w.a.), weak acid titration by a strong base (w.a. + s.b.), weak acid buffer (w.a.b.) and titration of a weak acid buffer by a strong base (w.a.b. + s.b.)

System	$c_2 = k$	c_1	c_0	c
w.a.	k_a	$-c_a k_a - 1$	$-k_a$	c_a
w.a. + s.b.	$k_a + c_b$	$-c_a k_a - 1 + c_b k_a$	$-k_a$	$c_a - c_b$
w.a.b.	$k_a + c_s$	$-c_a k_a - 1$	$-k_a$	c_a
w.a.b. + s.b.	$k_a + c_b + c_s$	$-c_a k_a - 1 + c_b k_a$	$-k_a$	$c_a - c_b$

The second and fifth columns give the effective acid constant k and concentration c, respectively

$$x^3 + c_2 x^2 + c_1 x + c_0 = 0. \tag{56}$$

The coefficients of the four systems under study are given by the rows of Table 1.

The concentration x is given by the only positive root of these polynomials,

$$x = \frac{2}{3}\sqrt{k^2 + 3ck_a + 3}\cos(\theta/3) - \frac{k}{3}, \tag{57}$$

with c and k as effective concentrations and acid dissociation constants, given by the fifth and second columns of Table 1, respectively. The angle θ is given by the expression

$$\theta = \arctan\left(-\frac{q}{2}, \frac{\sqrt{\Delta}}{6\sqrt{3}}\right), \tag{58}$$

with discriminant $\Delta = -4p^3 - 27q^2 > 0$, and

$$p = -\frac{1}{3}k^2 - k_a c - 1, \tag{59}$$

$$q = \frac{2}{27}k^3 + \frac{k}{3}\left(1 + k_a c\right) - k_a. \tag{60}$$

The values of k and c from Table 1 show that $k \geq k_a$ and $c \leq c_a$. Equations (57)–(60) with the data of Table 1 give the full description of the pH for the systems studied.

Conclusions

A systematic algebraic analysis has been applied on the ideal aqueous chemical equilibrium of three acid–base systems of academic and practical interest. The weak acid dissociation, the titration of a weak acid solution by a strong base, the acid buffer solution and its titration by a strong base have been algebraically analyzed without approximations. Simple closed-form expressions for the roots of the cubic equations for the $[H_3O^+]$ are obtained. These analytical expressions for $[H_3O^+]$ are simple enough to calculate the pH with a handheld scientific calculator. It has been shown that all the systems under study have one real positive root and two negative roots, no complex roots were obtained. The existence of only one positive root, with physical meaning, was proved in several ways: by analyzing the discriminant of the cubic polynomials, and by using Descates' rule of signs on the polynomial and its derivative. The cubic equations for the systems of interest were solved by the method of the depressed cubic equation of Vieta and Cardano. For all the systems under study, $[H_3O^+]$ is the subtraction of two terms: the first term is the product of a trigonometric function and the square root of a quadratic form of the acid dissociation constant, k_a, and the concentrations, c_a, c_s, and c_b; the second term is simply one-third of the sum of the acid constant and the concentrations. The analytical forms of $[H_3O^+]$ for the four systems analyzed are easily related by simple mathematical substitutions.

In addition to the expression for $[H_3O^+]$, the stability of the pH S_{pH} has been obtained and studied. The expression obtained for the pH stability S_{pH} allows one to quantify precisely the pH stability of a buffer solution when a strong base is added.

The exact pH has been compared against the approximate expression commonly used for calculating the pH. The error of these approximations is analyzed in detail. It has been shown that the Henderson–Hasselbalch (HH) equation exhibits large error for buffer solutions with salt concentrations $C_s < 0.01$ M.

Declarations

References

1. Denbigh KG (1981) The principles of chemical equilibrium: with applications in chemistry and chemical engineering, 4th edn. Cambridge University Press
2. Burgot J-L (2012) Ionic equilibria in analytical chemistry. Springer
3. Skoog DA, West DM, Holler FJ, Crouch SR (2022) Fundamentals of analytical chemistry, 10th edn. Cengage
4. Ladd MFC (1980) Dissociation of a weak acid. J Chem Educ 57:669
5. McNaught IJ, Peckham GD (1986) [A-] in weak acid solution. J Chem Educ 63:597
6. Barling PM (2012) The pH of very dilute solutions of strong acids—a calculation for a medical or biomedical class involving the application of simple numerical skills. IeJSME 6:32–8
7. Bellová R, Melicherčíková D, Tomčík P (2018) Approximate relations in pH calculations for aqueous solutions of extremely weak acids: a topic for problem-based learning. J Chem Educ 95:1548–1553
8. Wildman RJ, Coleman WF (2002) Acid-base equilibria in aqueous solutions. J Chem Educ 79:1486
9. Macleod AJ (1984) The calculation of pH. Int J Math Educ Sci Technol 15:691–696
10. Barling PM (2014) The pH of very dilute solutions of weak acids—a calculation involving the application of numerical skills to the solution of a cubic equation. IeJSME 8:24–29
11. Glaister P (1994) A titration model-an analysis and solution. Int J Math Educ Sci Technol 25:399–406
12. Albrecht R, Buchberger B, Collins G, Loos R (2013) Computer Algebra: symbolic and algebraic computation. Computing Supplementa; Springer Vienna
13. Maplesoft, a division of Waterloo Maple Inc., Maple. https://www.maplesoft.com/. Accessed 6 July 2023
14. Wolfram Research, Inc. (2022) Mathematica, Version 12.1, Champaign, IL. https://www.wolfram.com/mathematica. Accessed 6 July 2023
15. Joyner D (2006) OSCAS: maxima. ACM Commun Comput Algebra 40:108–111
16. Stein W, Joyner D, Kohel D, Cremona J (2020) Eröcal, B. SageMath, version 9.0. http://www.sagemath.org. Accessed 6 July 2023
17. Levie R (2001) The formalism of titration theory. Chem Educ 6:272–276
18. Dickson LE (1914) Elementary theory of equations, 1st edn. Wiley
19. Dickson LE (1922) First course in the theory of equations, 1st edn. Wiley
20. Curtiss DR (1918) Recent extentions of descartes' rule of signs. Ann Math 19:251–278
21. Irving RS (2004) Integers, polynomials, and rings: a course in algebra, 1st ed. Springer, New York
22. Nickalls RWD (1993) A new approach to solving the cubic: Cardan's solution revealed. Math Gaz 77:354–359
23. Henderson LJ (1908) Concerning the relationship between the strength of acids and their capacity to preserve neutrality. Am J Physiol 21:173–179
24. Hasselbalch K (1917) Die Berechnung der Wasserstoffzahl des Blutes aus der freien und gebundenen Kohlensäure desselben, und die Sauerstoffbindung des Blutes als Funktion der Wasserstoffzahl. Biochem Z 78:112–144
25. Po HN, Senozan NM (2001) Henderson-Hasselbalch equation: its history and limitations. J Chem Educ 78:1499–1503