A correction to the Henderson–Hasselbalch equation

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The Henderson–Hasselbalch equation is known to virtually all chemistry students and widely used in practical calculations, since it allows for a direct evaluation of pH of a mixture of a weak acid with its salt, e.g., of a buffer solution. Within a modern general-chemistry course, the Henderson equation:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \qquad (1)$$

is trivially obtained by rearranging terms in the law of mass action for the reversible reaction $HA \rightleftarrows H^+ + A^-$:

$$\frac{[H^+][A^-]}{[HA]} = K_a$$

The Henderson–Hasselbalch equation (2) is the logarithmic form of eq. (1):

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]} \qquad (2)$$

Both both eq. (1) and eq. (2) imply an approximation when *equilibrium* ($[HA]$, $[A^-]$) concentrations of the acid and the salt are replaced by *initial* ones ($[HA]_0$, $[A^-]_0$), which is usually done in practical calculations. In other words,

$$[H^+] \approx K_a \frac{[HA]_0}{[A^-]_0} \qquad (1a)$$

$$pH \approx pK_a + \log_{10} \frac{[A^-]_0}{[HA]_0} \qquad (2a)$$

For a present-days smart undergraduate student accustomed to solve problems in chemical equilibrium, the difference between eqs. (1)–(2) and (1a)–(2a) should not be a secret, although the original authors[1,2] never stressed this point. However, it is not immediately clear how much replacing the equilibrium concentrations by the initial ones would affect the numerical results. Purely numerically, this problem, as well as historical aspects of the Henderson–Hasselbalch equation, were considered in detail previously.[3] Here we propose a different approach. We are going to derive an analytical correction to eqs. (1a)–(2a) to see whether it allows improving the results where eqs. (1a)–(2a) fail.

Analytical solution (neglecting water ionization)

We will first derive an analytical expression for the H^+ concentration, with $[HA]_0$ and $[A^-]_0$ being initial concentration of the acid and its salt, respectively. This derivation given below is quite straightforward and follows, roughly, that in Dickerson, Gray and Haight's *Chemical Principles*.[4] Subsequently, we will make some approximations to obtain formulas similar to (1a) and (2a) with some extra terms. Water ionization will be first neglected.

Let x be the equilibrium proton concentration: $x = [H^+]$. Thus, the equilibrium concentration of the acid will be $[HA] = [HA]_0 - x$ and the equilibrium conjugate base concentration $[A^-] = [A^-]_0 + x$, since the acid dissociation generates equal quantities of H^+ and A^-. From the law of mass action for the acid: $[H^+][A^-]/[HA] = K_a$, the following equation is obtained:[5]

$$\frac{x([A^-]_0 + x)}{[HA]_0 - x} = K_a \qquad (3)$$

A trivial rearrangement of eq. (3) leads to the quadratic equation:

$$x^2 + ([A^-]_0 + K_a)x - K_a[HA]_0 = 0$$

that has the following solution:[1]

$$x = \frac{-([A^-]_0 + K_a) + \sqrt{([A^-]_0 + K_a)^2 + 4K_a[HA]_0}}{2} \qquad (4)$$

A further exact simplification of eq. (3) is not possible and eq. (4) is not directly comparable with Henderson's equation (1a). We will now deal with it in an approximate way.

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[1] The second solution, with a minus at the radical, is discarded because it always results in a negative x.

Approximation to equation (3)

An obvious way of deriving eq. (1a) from eq. (3) is to neglect x *both* in the parentheses in the numerator *and* in the denominator of eq. (3). In this way we obtain $[A^-]_0 x/[HA]_0 = K_a$, the solution of which with respect to x leads directly to the Henderson equation (eq. (1a)).

If we neglect x in the parentheses in the numerator of eq. (3), which is possible when $[A^-]_0 \gg x$, but retain x in the denominator, the following approximation is obtained:

$$\frac{[A^-]_0 x}{[HA]_0 - x} = K_a$$

By solving it with respect to x, we immediately obtain the proton concentration:

$$[H^+] = x = K_a \frac{[HA]_0}{[A^-]_0 + K_a} \qquad (5)$$

We observe that eq. (5) is very similar to eq. (1a) except that the denominator in eq. (5) contains $[A^-]_0 + K_a$ instead of $[A^-]_0$. Thus, the K_a in the denominator is a correction to Henderson's equation eq. (1a). We can cast eq. (5) in a *multiplicative* form:

$$[H^+] \approx K_a \frac{[HA]_0}{[A^-]_0 + K_a} = K_a \frac{[HA]_0}{[A^-]_0} \frac{[A^-]_0}{[A^-]_0 + K_a} = K_a \frac{[HA]_0}{[A^-]_0}\left[\frac{1}{1 + K_a/[A^-]_0}\right] \qquad (6)$$

where the expression in square brackets is a *correction factor* to Henderson's equation. Logarithmising eq. (6), we can write down an equation for pH similar to eq. (2a):

$$pH = -\log_{10}[H^+] \approx pK_a + \log_{10}\frac{[A^-]_0}{[HA]_0} + \log_{10}\left(1 + K_a/[A^-]_0\right) \qquad (7)$$

The first two terms in eq. (7) correspond to the Henderson–Hasselbalch equation (2a), while the last term is an *additive* correction:

$$\Delta pH = \log_{10}\left(1 + K_a/[A^-]_0\right)$$

Alternatively, eq. (5) can be deduced in a very different manner. Consider the case that the concentrations of both the acid and the salt are much greater than the dissociation constant of the acid: $[A^-]_0 \gg K_a$, $[HA]_0 \gg K_a$, while $[A^-]_0$ and $[HA]_0$ are of comparable order of magnitude. Under these conditions, under the radical in eq. (4), $([A^-]_0 + K_a)^2 \gg 4K_a[HA]_0$, and the following approximation can be applied:[2]

$$\sqrt{X^2 + Y} \approx X + \frac{Y}{2X} \qquad (8)$$

which is valid when $X^2 \gg Y$. Then, using $X = [A^-]_0 + K_a$; $Y = 4K_a[HA]_0$, the expression under the radical in eq. (3) is reduced to $([A^-]_0 + K_a) + 4K_a[HA]_0/2([A^-]_0 + K_a)$. The equation obtained in this way is identical to eq. (5).

$$[H^+] = x \approx \frac{-([A^-]_0 + K_a) + ([A^-]_0 + K_a) + \dfrac{4K_a[HA]_0}{2([A^-]_0 + K_a)}}{2} = K_a \frac{[HA]_0}{[A^-]_0 + K_a}$$

In making such an approximation, *large* terms $([A^-]_0 + K_a)$ cancel, while the remaining term is usually *small*. This is because the denominator is dominated by $[A^-]_0$ (since $[A^-]_0 \gg K_a$), and the entire right-hand side is of order of magnitude of K_a. The advantage of the above derivation of eq. (5) is that it shows a relationship to the exact solution (4).

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[2] A standard way of deriving this approximation is to use the first-order term of the Taylor expansion: $\sqrt{1 + x} \approx 1 + x/2$:

$$\sqrt{X^2 + Y} = X\sqrt{1 + \frac{Y}{X^2}} \approx X(1 + \frac{Y}{2X^2}) = X + \frac{Y}{2X}$$

$$\text{Therefore, } -X + \sqrt{X^2 + Y} \approx \frac{Y}{2X}$$

However, students little familiarity with calculus may want to derive this approximation by means of the elementary mathematics only, by neglecting the $(Y/2X)^2$ term in the left-hand side of the following identity:

$$\sqrt{X^2 + 2X\left(\frac{Y}{2X}\right) + \left(\frac{Y}{2X}\right)^2} = \sqrt{\left(X + \frac{Y}{2X}\right)^2} = X + \frac{Y}{2X}$$

Very obviously, eq. (1a) is not valid when $[A^-]_0$ vanishes, since $[H^+] = \infty$ in this case. However, eq. (5) yields $[H^+] = [HA]_0$ for $[A^-]_0 = 0$. This result is far from reality for a weak acid at a large concentration, but it is still better than infinity!

Water ionization

When $[HA]_0$ is low, water ionization becomes a major source of protons, and two equilibria have to be considered simultaneously

$$HA \rightleftarrows H^+ + A^-$$
$$H_2O \rightleftarrows H^+ + OH^-$$
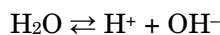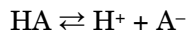
If x is the proton concentration produced from the acid and y is the one generated by the water ionization, then $[H^+] = x + y$ and the equations of equilibrium adopt the following form:

$$\begin{cases} \dfrac{(x + y)([A^-]_0 + x)}{[HA]_0 - x} = K_a \qquad (9) \\ (x + y)y = K_w \end{cases}$$

Substituting $x = K_w / y - y$ from the second equation into the first equation, we obtain:

$$\frac{K_w([A^-]_0 + K_w / y - y)}{y^2 + [HA]_0 y - K_w} = K_a$$

which eventually leads to the cubic equation

$$K_a y^3 + (K_a[HA]_0 + K_w)y^2 - K_w([A^-]_0 + K_a)y - K_w^2 = 0 \qquad (10)$$

Although a cubic equation such as eq. (10) is, in general, hard to solve analytically, a simple and reliable numerical solution is possible (see below). After y is calculated, the proton concentration can be found as $[H^+] = x + y = K_w / y$.

Analogously to eq. (3), one could attempt to derive an approximation by neglecting x in the denominator in eq. (9). This reduces the problem to a quadratic equation, but, unfortunately, application of the approximation (8) to the solution of this quadratic equation yields again eq. (5), which, obviously does not take into account the water ionization.

Numerical solution of a cubic equation
Let us rewrite eq. (10) in a more general form:

$$f(y) = Ay^3 + By^2 + Cy + D = 0$$

Any iterative solution requires an initial approximation y_0 and a formula for a successive approximation $y_{n+1} = F(y_n)$. An initial approximation can be produced by neglecting either D or A in the above equation, in which case the equation is reduced to a quadratic one ($Ay^2 + By + C = 0$ or $By^2 + Cy + D = 0$, respectively). Subsequently, y_0 is found as a positive root of any of these quadratic equations:

$$y_0 = \frac{-B + \sqrt{B^2 - 4AC}}{2A}$$

$$y_0 = \frac{-C + \sqrt{C^2 - 4BD}}{2B}$$

Successive iterations can be performed by a variety of methods. We favor the conventional Newton–Raphson method, in which case

$$y_{n+1} = y_n - \Delta y$$

where

$$\Delta y = \frac{f(y_n)}{f'(y_n)} = \frac{Ay_n^3 + By_n^2 + Cy_n + D}{3Ay_n^2 + 2By_n + C}$$

The iterative process should be stopped when Δy is small enough with respect to y_n. For instance, the convergence criterion can be formulated as follows:

$$|\Delta y| < \varepsilon \cdot y_n$$

where ε is a small number (10^{-10}, for instance). Such a Newton–Raphson procedure converges very quickly. While it is possible to find a solution by a pocket calculator, it is more instructive for a student to write her or his own code. Any major programming language, e.g., Python, C, Fortran, or Basic would be perfectly suitable for this.

Numerical tests

We performed calculation of the pH of acetate buffer solution in a wide range of concentrations of both the acetic acid and the acetate ion. The results obtained using the Henderson equation (eq. (1a)), the corrected Henderson (eq. (5)), as well the accurate values produced by a numerical solution of the equation system (9) are given in Table 1.

Table 1. pH of the acetate buffer solution at various initial concentrations (mol/L) of acetate $[A^-]_0$ and acetic acid $[HA]_0$ [a]

$[HA]_0 \downarrow$	$[A^-]_0 \rightarrow$	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
1	Henderson (eq. (1a))	4.754	3.754	2.754	1.754	0.754	−0.246	−1.246
	Corrected Henderson (eq. (5))	4.754	3.755	2.755	1.762	0.825	0.195	0.024
	Exact pH (eq. (9))	**4.755**	**3.755**	**2.817**	**2.430**	**2.383**	**2.379**	**2.378**
10^{-1}	Henderson (eq. (1a))	5.754	4.754	3.754	2.754	1.754	0.754	−0.246
	Corrected Henderson (eq. (5))	5.754	4.755	3.755	2.762	1.825	1.195	1.024
	Exact pH (eq. (9))	**5.754**	**4.755**	**3.763**	**3.040**	**2.896**	**2.882**	**2.880**
10^{-2}	Henderson (eq. (1a))	6.754	5.754	4.754	3.754	2.754	1.754	0.754
	Corrected Henderson (eq. (5))	6.754	5.755	4.755	3.762	2.825	2.195	2.024
	Exact pH (eq. (9))	**6.754**	**5.755**	**4.756**	**3.822**	**3.438**	**3.392**	**3.387**
10^{-3}	Henderson (eq. (1a))	7.754	6.754	5.754	4.754	3.754	2.754	1.754
	Corrected Henderson (eq. (5))	7.754	6.755	5.755	4.762	3.825	3.195	3.024
	Exact pH (eq. (9))	**7.754**	**6.755**	**5.755**	**4.769**	**4.064**	**3.922**	**3.908**
10^{-4}	Henderson (eq. (1a))	8.754	7.754	6.754	5.754	4.754	3.754	2.754
	Corrected Henderson (eq. (5))	8.754	7.755	6.755	5.762	4.825	4.195	4.024
	Exact pH (eq. (9))	**8.732**	**7.752**	**6.755**	**5.763**	**4.872**	**4.518**	**4.473**
10^{-5}	Henderson (eq. (1a))	9.754	8.754	7.754	6.754	5.754	4.754	3.754
	Corrected Henderson (eq. (5))	9.754	8.755	7.755	6.762	5.825	5.195	5.024
	Exact pH (eq. (9))	**9.287**	**8.607**	**7.732**	**6.760**	**5.830**	**5.272**	**5.161**
10^{-6}	Henderson (eq. (1a))	10.754	9.754	8.754	7.754	6.754	5.754	4.754
	Corrected Henderson (eq. (5))	10.754	9.755	8.755	7.762	6.825	6.195	6.024
	Exact pH (eq. (9))	**9.368**	**8.848**	**8.287**	**7.613**	**6.799**	**6.198**	**6.040**
10^{-7}	Henderson (eq. (1a))	11.754	10.754	9.754	8.754	7.754	6.754	5.754
	Corrected Henderson (eq. (5))	11.754	10.755	9.755	8.762	7.825	7.195	7.024
	Exact pH (eq. (9))	**9.376**	**8.874**	**8.368**	**7.852**	**7.329**	**6.929**	**6.810**

[a] Black color: results close to the exact; red color: results substantially deviation from the exact; blue color: results improved with respect to the Henderson equation.

The results show that for the acid concentration $[HA]_0$ from 1 M down to 10^{-4} M and for the salt concentration from 1 M down to 10^{-2} M, the Henderson equation (eq. (1a)) yield quite accurate pH values. The correction (eq. (5)) have virtually no effect on the result in this concentration range. This is because when $[A^-]_0 \gg K_a$, eq. (5) is nearly identical to eq. (1a).

For a large acid concentration combined with a very low salt concentration (10^{-3} M − 10^{-6} M), the Henderson equation fails, strongly underestimating pH. The corrected equation shifts the results in the right direction, but not strongly enough, such that the corrected equation essentially fails, too.

For very low acid concentrations and high salt concentration both equations overestimate pH. However, when the $[HA]_0$ is low but the $[A^-]_0$ is even lower, the corrected equation provides a good approximation to the exact value, while the original Henderson equation still fails. For instance, for $[HA]_0 = 10^{-5}$ M and $[A^-]_0 = 10^{-6}$ M, the exact pH is about 5.16; the corrected Henderson equation yields 5.02, while the original Henderson equation gives a much lower pH value of 3.75. This is easy to understand, since this situation corresponds to a very diluted acid with almost no salt. The acid can be considered as strong under such conditions and we can anticipate that $[H^+] \approx [HA]_0$ and thus pH $\approx -\log_{10} [HA]_0$.

Finally, let us consider a special case when $[HA]_0$ and $[A^-]_0$ are similar and both close to K_a of the acid. In Table 1 this corresponds to the entry $[HA]_0 = [A^-]_0 = 10^{-5}$ M. In this case, the corrected pH value (5.19) is quite close to the exact one (5.27), while the conventional Henderson equation substantially underestimates pH (4.75). Note that eq. (1a) predicts $[H^+] = K_a$ for $[HA]_0 = [A^-]_0$, while eq. (5) gives $[H^+] = K_a/2$ for $[HA]_0 = [A^-]_0 = K_a$.

Conclusions

We presented a simple correction to the Henderson equation and considered the validity of the original Henderson equation and of the corrected one at various concentrations of both the acid and the salt. For the practically important range of concentrations, typical of real buffer solutions, even the original Henderson equation yields an accurate pH value, and the correction does not alter it any significantly. However, for very low salt concentrations, the original Henderson equation fails, while the corrected equation improves the results only partly. Finally, when both acid and salt concentrations are low, the corrected equation provides a significant improvement of the original one, with the calculated pH being quite close to the exact one. The corrected equation is most useful when the acid and the salt concentrations are similar to each other and close to K_a of the acid.

The didactical value of the correction proposed is as follows. A student can learn how to introduce approximations, simply neglecting certain terms in the exact equation, or expanding the solution into a Taylor series. Optionally, the students with even a modest knowledge of computer programming are welcome to implement the exact solution in any suitable programming language. Thus, it the work including the equation derivation, programming, and practical calculations will exploit synergism from subjects such as general chemistry, basic calculus and, if desired, also from computer programming.

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