Deep Dive: Examples #1, 2, and 3

1. Henderson-Hasselbalch

The Henderson-Hasselbalch (HH) equation itself is fine. After all, the HH equation is just an algebraic rearrangement of the *Law of Mass Action*

$$K_{a} = \frac{\left[H^{+}\right] \cdot [\text{Base}]}{[\text{Acid}]} = \frac{10^{-pH} \cdot [\text{Base}]}{[\text{Acid}]} \qquad \Longleftrightarrow \qquad pH = pK_{a} + \log_{10}\left\{\frac{[\text{Base}]}{[\text{Acid}]}\right\}$$

Caution: In practice approximations to HH are then made. The purpose of this document is (i) to explain these assumptions and (ii) to provide a way to check them.

2. Acetic Acid and Sodium Acetate Solutions

Examples #1, 2, and 3 involve combining acetic acid CH_3COOH and sodium acetate CH_3COONa

> **Example #1:** A buffer is prepared containing 1.00 M acetic acid and 1.00 M sodium acetate. What is its pH?
> **Example #2:** A buffer is prepared containing 0.800 M acetic acid and 1.00 M sodium acetate. What is its pH?
> **Example #3:** A buffer is prepared containing 1.00 M acetic acid and 0.800 M sodium acetate. What is its pH?

The sodium acetate NaAc is assumed to dissociate completely (a very reasonable assumption). The sodium ion Na^+ becomes a spectator ion.

$$NaAc_{(aq)} \longrightarrow Na^{+}{}_{(aq)} + Ac^{-}{}_{(aq)} \qquad K_{sp} \longrightarrow \infty$$

Of course, the acetic acid HAc is a weak acid and experiences this equilibrium reaction

$$HAc_{(aq)} \rightleftharpoons H^{+}{}_{(aq)} + Ac^{-}{}_{(aq)} \qquad K_{a} = 1.77 \times 10^{-5} \tag{2.1}$$
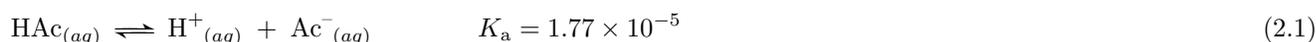
We use the HH equation to solve these three examples. The "Acid" is the acetic acid HAc and the "Base" is its conjugate base the acetate ion Ac^{-}

$$pH = pK_{a} + \log_{10}\left\{\frac{[Ac^{-}]}{[HAc]}\right\} \qquad \text{where} \qquad \begin{array}{rcl} [HAc] &=& \textit{equilibrium concentration of HAc} \\ [Ac^{-}] &=& \textit{equilibrium concentration of } Ac^{-} \end{array}$$

Stoichiometry from eq. (2.1) means we can write

$$pH = pK_{a} + \log_{10}\left\{\frac{[Ac^{-}]_{\circ} + x}{[HAc]_{\circ} - x}\right\} \qquad \text{where} \qquad \begin{array}{rcl} [HAc]_{\circ} &=& \textit{initial concentration of HAc} \\ [Ac^{-}]_{\circ} &=& \textit{initial concentration of } A^{-} \\ x &=& \textit{change in concentration from HAc to } Ac^{-} \end{array} \tag{2.2}$$

Since x is unknown eq. (2.2) is not a quick way to get the pH.

3. Assumptions

So far eq. (2.2) is exact. It follows the same methods used with the *Law of Mass Action* previously. To make eq. (2.2) practical we assume x is very small compared to <u>both</u> of the initial concentrations

$$\textbf{Routine HH Assumption:} \qquad x \ll [HAc]_{\circ} \qquad \text{and} \qquad x \ll [Ac^{-}]_{\circ}$$

The above is routinely assumed **but rarely mentioned**. In other words, the most commonly USED form of the HH equation is

$$pH \approx pK_{a} + \log_{10}\left\{\frac{[\text{Base}]_{\circ}}{[\text{Acid}]_{\circ}}\right\} \tag{3.1}$$

Notice the approximation sign? Again, whether or not mentioned, eq. (3.1) is the most commonly USED form for HH. Indeed, eq. (3.1) is what most people mean by "using the HH equation."

Bottom Line:

Exact: $\quad pH = pK_{a} + \log_{10}\left\{\dfrac{[\text{Base}]}{[\text{Acid}]}\right\}$ **Appoximate:** $\quad pH \approx pK_{a} + \log_{10}\left\{\dfrac{[\text{Base}]_{\circ}}{[\text{Acid}]_{\circ}}\right\}$

4. Approximate Results

For these first three examples, this form of HH is what is used to get the numerical answers

$$\text{pH} \approx \text{p}K_a + \log_{10}\left\{\frac{[\text{Ac}^-]_\circ}{[\text{HAc}]_\circ}\right\} \tag{4.1}$$

Specifically, with $\text{p}K_a = -\log_{10}\left(1.77 \times 10^{-5}\right) = 4.752$ we get

Example #1: $\quad \text{pH} \approx 4.752 + \log_{10}\left\{\dfrac{1.00}{1.00}\right\} \quad \longrightarrow \quad \boxed{\text{pH} = 4.752}$

Example #2: $\quad \text{pH} \approx 4.752 + \log_{10}\left\{\dfrac{1.00}{0.800}\right\} \quad \longrightarrow \quad \boxed{\text{pH} = 4.849}$

Example #3: $\quad \text{pH} \approx 4.752 + \log_{10}\left\{\dfrac{0.800}{1.00}\right\} \quad \longrightarrow \quad \boxed{\text{pH} = 4.655}$

Getting these answers for the pH was very fast.

5. Exact Results

If we do NOT assume that x is very small compared to the initial concentrations, then we need to use the *Law of Mass Action* without any further approximations

$$K_a = \frac{x \cdot ([\text{Ac}^-]_\circ + x)}{[\text{HAc}]_\circ - x} \tag{5.1}$$

Using the above we would get

Example #1: $\quad 1.77 \times 10^{-5} = \dfrac{x \cdot (1 + x)}{1 - x} \quad \Longrightarrow \quad x \approx 1.770 \times 10^{-5} \quad \Longrightarrow \quad \text{pH} \approx 4.752 \quad \checkmark$

Example #2: $\quad 1.77 \times 10^{-5} = \dfrac{x \cdot (1 + x)}{0.8 - x} \quad \Longrightarrow \quad x \approx 1.416 \times 10^{-5} \quad \Longrightarrow \quad \text{pH} \approx 4.849 \quad \checkmark$

Example #3: $\quad 1.77 \times 10^{-5} = \dfrac{x \cdot (0.8 + x)}{1 - x} \quad \Longrightarrow \quad x \approx 2.212 \times 10^{-5} \quad \Longrightarrow \quad \text{pH} \approx 4.655 \quad \checkmark$

The above took much more time to calculate. For these three examples, we see pH's using the approximate HH equation eq. (4.1) match the exact pH's using eq. (5.1) to at least three sig figs.

6. Five-Percent Rules

But what do we do if we only use the approximate HH equation eq. (4.1)? We still would like to check our answers. We now define a 5% rule. Start with these assumptions

$$\frac{x}{[\text{Acid}]_\circ} < 5\% \qquad \underline{\text{and}} \qquad \frac{x}{[\text{Base}]_\circ} < 5\%$$

Taking the negative logarithm of both sides of the Acid version we get

$$-\log_{10}\left\{\frac{x}{[\text{Acid}]_\circ}\right\} > -\log_{10}(0.050) \qquad \Longrightarrow \qquad \log_{10}[\text{Acid}]_\circ + \text{pH} > 1.3$$

Thus, a 5% rule requires for the initial concentration of both the Acid and Base that

$$\boxed{\log_{10}[\text{Acid}]_\circ + \text{pH} > 1.3 \qquad \underline{\text{and}} \qquad \log_{10}[\text{Base}]_\circ + \text{pH} > 1.3} \tag{6.1}$$

We apply these checks to the examples. The initial concentrations were 1.00 M and 0.800 M so we have

$$\log_{10}(1.00) = 0 \qquad \text{and} \qquad \log_{10}(0.800) = -0.097$$

The approximate pH's were 4.752, 4.655, and 4.849. We can see (without a calculator) that these pH's are large enough that adding either 0 or -0.097 will still be greater than 1.3. This means these approximate pH's from eq. (4.1) are good to within 5%. (Of course, we knew this already because we calculated the exact results.)

7. A Case That Fails

Here is an example where the approximations fail. Consider the case of $[\text{HAc}] = 1.0 \times 10^{-3}$ M and $[\text{NaAc}] = 1.0 \times 10^{-4}$ M. The approximation form of HH gives

$$\text{pH} \approx \text{p}K_\text{a} + \log_{10}\left\{\frac{[\text{Ac}^-]_\text{o}}{[\text{HAc}]_\text{o}}\right\} \approx 3.74$$

Next, we check with $\log_{10}[*]_\text{o} + \text{pH} > 1.3$

$$\log_{10}[\text{Acid}]_\text{o} + \text{pH} = -3 + 3.74 = 0.74$$
$$\log_{10}[\text{Base}]_\text{o} + \text{pH} = -4 + 3.74 = -0.26$$

Since both 0.74 and -0.26 are less than 1.3, the approximate pH is off by more than 5%. So we need to use the *Law of Mass Action*. Doing this we find the exact result is pH ≈ 4.06. So for this example, the HH approximation would have an error of about 8%. There is no way we would have known this unless we check using $\log_{10}[*]_\text{o} + \text{pH} > 1.3$.

8. Summary

The following equation is exact but only useful if we already know the equilibrium concentrations of the acid and base

Exact: $$\text{pH} = \text{p}K_\text{a} + \log_{10}\left\{\frac{[\text{Base}]}{[\text{Acid}]}\right\} \qquad (8.1)$$

The following equation is approximate and useful if we want to estimate the final pH using just the initial concentrations

Approximate: $$\text{pH} \approx \text{p}K_\text{a} + \log_{10}\left\{\frac{[\text{Base}]_\text{o}}{[\text{Acid}]_\text{o}}\right\} \qquad (8.2)$$

Important: People write eq. (8.1) when solving buffer problem but it is really eq. (8.2) that they use.

The pH estimated using eq. (8.2) has an error of less than 5% provided both initial concentrations $[*]_\text{o}$ and estimated pH satisfy

Equation (8.2) Has Less Than 5% Provided That: $$\log_{10}[*]_\text{o} + \text{pH} > 1.3$$

The above check indicates that small initial concentrations $[*]$ and/or small pH's may cause more than 5% error. The error involved using eq. (8.2) instead of eq. (8.1) will increase as

(i) acid strength increases
bigger K_a lead to bigger x so the initial concentrations may be far off from those at equilibrium

(ii) initial concentrations $[*]_\text{o}$ decrease
smaller starting concentrations means that percentage-wise changes are more significant