

The Henderson-Hasselbalch (HH) Equation

(A Year 2 Blog for the week commencing the 5th of April 2020. When a Weak Acid and its Conjugate Base are in a position of dynamic equilibrium, then we can use something called the Henderson-Hasselbalch equation to solve problems about the pH of buffer solutions. However, for this to apply, the reaction must follow certain criteria viz. (i) the ratio of the conjugate base to the weak acid must be between 0.10 and 10, and (ii) both the ratio of the conjugate base and K_a value and the ratio of the acid and the K_a value must exceed 100 (i.e. the acid must be a very **DILUTE WEAK** acid). Please first read last week's Blog on Buffer Solutions.

- If you are going on to study any sort of Medicine at University, then I would advise you to master the Henderson-Hasselbalch (HH) equation; but, before I talk about it let me remind you of two basic log equations.
- Since the multiplication of two numbers can be transformed into the addition of two exponentials then if $A = B \cdot C$ (i.e. B multiplied by C) then, irrespective of the base of the logs taken (i.e. irrespective of whether we use base "10"/base "e"/base "(1.0-10⁻⁷)" i.e. Napier's original construct/etc)

$$\log A = \log B + \log C$$
 and if $A = B \div C$ (i.e. B divided by C) then $\log A = \log B - \log C$.

- We already know that for a **weak acid** that is at dynamic equilibrium (at a given temperature),

$$\text{HA (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{A}^- \text{(aq)} \quad [\text{where } \text{H}^+ \text{(aq)} = \text{H}_3\text{O}^+ \text{(aq)}]$$

there will be an equilibrium constant K_a such that

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

and by rearranging the above equation we get

$$[\text{H}^+ \text{(aq)}] = K_a \times \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]}$$

- Then if we take the logs of both sides of this equation to the base 10 we obtain

$$\log_{10}[\text{H}^+ \text{(aq)}] = \log_{10}[K_a] + \log_{10} \left\{ \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]} \right\}$$

and if we now multiply the whole equation by "-1" we obtain

$$-\log_{10}[\text{H}^+ \text{(aq)}] = -\log_{10}[K_a] + -\log_{10} \left\{ \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]} \right\}$$

which gives $\text{pH} = \text{pK}_a - \log_{10} \left\{ \frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]} \right\}$ **Concentration of the ACID**
Concentration of the SALT

where " $\frac{[\text{HA (aq)}]}{[\text{A}^- \text{(aq)}]}$ " is the concentration of the acid divided by the concentration of its salt

and in log terms we can invert the numerator and the denominator and write the above equation as

$$\text{pH} = \text{pK}_a + \log_{10} \left\{ \frac{[\text{A}^- \text{(aq)}]}{[\text{HA (aq)}]} \right\} \quad \begin{array}{l} \text{Concentration of the SALT} \\ \text{Concentration of the ACID} \end{array}$$

- The latter form (salt ÷ acid) is the most commonly used form of the HH equation i.e. **pH equals pK_a plus the log₁₀ of the ratio of the concentrations of the salt to the acid.**

- Quite often the term “base” or “conjugate base” is used instead of “salt” where the acid is the species that dissociates the proton (e.g. HCO_3^-) and its conjugate base is then the species with the “H” missing (viz. CO_3^{2-}), as in $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$.
- What we are doing is to use the mole reaction ratios of the Salt (or the Conjugate Base) and the Acid (and this will become very clear when we start doing worked examples) – and this should come as no surprise, because the whole point about a reaction (any chemical reaction) is that the amount by which the reactants will react with each other is determined by their stoichiometric reaction ratios (**but the Rate of a Reaction is NOT determined by the stoichiometric ratios of the reaction!**)
- Another thing to notice is that it does not matter which form of the HH equations we use (i.e. **plus** the \log_{10} of the concentrations of Salt \div Acid, or **minus** the \log_{10} of the concentrations of Acid \div Salt) – **the numerical value of the log will still be exactly the same.** (Please use your calculator to find $+\log_{10}$ of “ $4 \div 2$ ” and of $-\log_{10}$ of “ $2 \div 4$ ” and you will get “0.3010” in each case!)
- There is one quite important mathematical fact that arises from the HH equation, therefore let us look at it again (and it does not matter which form of the equation one uses).

$$\text{pH} = \text{pK}_a + \log_{10} \left\{ \frac{[\text{A}^- (\text{aq})]}{[\text{HA} (\text{aq})]} \right\} \quad \frac{\text{Concentration of the SALT}}{\text{Concentration of the ACID}}$$

- At the half-equivalence point $[\text{A}^- (\text{aq})] = [\text{HA} (\text{aq})]$ therefore $\frac{[\text{A}^- (\text{aq})]}{[\text{HA} (\text{aq})]} = 1$

but, the $\log_{10}(1) = 0$, therefore the HH equation becomes

$$\text{pH} = \text{pK}_a + 0$$

therefore **pH = pK_a**, and this is an important equivalence.

At the half-equivalence point, the pH of a weak acid = its pK_a.

- There is one other thing that will help you in the ‘A’ Level exams. The examiners try to test your knowledge of a range of subjects in the exam, therefore they cannot spend a lot of time on any one topic. It is most unlikely that in any question that involves Equilibria they will ask you to do a complicated calculation. **In most instances therefore, they will set a question that assumes that the initial concentration of the weak acid and its concentration at equilibrium are roughly the same i.e. $[\text{HA}]_{\text{equilibrium}} = [\text{HA}]_{\text{initial}}$** (because the position of dynamic equilibrium lies so far to the left) and that $[\text{H}^+] = [\text{A}^-]$, and then the equation in the ICE table becomes one involving “ x^2 ” instead of one involving a quadratic equation.
- In essence, that is all that there is to HH equations, so let us now do some examples of manipulating HH equations – and if you go on and do a degree involving Medicine, then even if the situation becomes more complex (*as it will do for proteins*), then please remember the basics of the HH equation and you will be able to cope with whatever is thrown at you.

NB Please do understand these calculations and try not to kill any of your patients by accident. The person you kill will almost certainly be loved by somebody and will be devastated by the loss.

- I am going to assume that you have read my Blog on Buffer Solutions (week commencing the 29th of March 2020) and that you know that a Buffer solution consists of either
 - a **WEAK Acid plus a fully dissociated (Strong) salt of that Weak Acid**, or
 - a **WEAK Base plus a fully dissociated (Strong) salt of that Weak Base**
 where the metal cations (M⁺) in the salts of the Acids are usually either Sodium or Potassium and the anions in the salts of the Bases are often Chlorides.

- An example of an **acidic buffer solution** would be

both $\text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$
 and $\text{CH}_3\text{COO}^- \text{Na}^+ \text{(aq)} \longrightarrow \text{Na}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$

 and an example of an alkaline buffer solution would be

$$\text{NH}_3 \text{(aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{NH}_4\text{OH (aq)} \rightleftharpoons \text{NH}_4^+ \text{(aq)} + \text{OH}^- \text{(aq)}^1$$

$$\text{NH}_4\text{Cl (aq)} \longrightarrow \text{NH}_4^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$$

- In an acidic buffer

$$K_a = \frac{[\text{H}^+] \cdot [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$
 therefore
$$[\text{H}^+] = K_a \cdot \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

and in an **alkaline buffer**

$$K_a = \frac{[\text{NH}_4^+] \cdot [\text{OH}^-]}{[\text{NH}_4\text{Cl}]}$$
 therefore
$$[\text{OH}^-] = K_b \cdot \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4^+]}$$

and then you would calculate the pOH, and then use $pH = 14.0 - pOH$ to calculate the pH.

- Those of you who have grasped what is going on, will want to ask

“Will not the addition and dissociation of the Strong Salt (which is the Conjugate Base of the Weak Acid) in the acid buffer cause the reversible reaction of the Weak Acid to move to the left?” – and if that question did occur to you, then **well done!**”

You are absolutely correct. The position of dynamic equilibrium of the reversible reaction of the Weak Acid will of course move to left when the Strong Salt is added (because the Salt will react with the H⁺ ions and form the Acid and thus move the reaction leftwards) – but, since this is a reversible reaction, the Weak Acid will then spew out more protons which will react with the Strong Salt, and the reaction will keep moving back and forth until a new position of dynamic equilibrium is reached which will be a tiny bit to the left of its original position.

A similar reaction will also happen in the alkaline buffer, but both of these minor movements can be ignored at ‘A’ Level.”

- Let us now do some worked examples of HH equations for a buffer solution.

¹ The release of the hydroxide ions makes the solution basic.

Example 1 (Source : London Metropolitan University)

Can you see that this is a buffer solution?

- Calculate the pH of a **buffer solution** that has 1.35×10^{-3} mol of undissociated formic acid (IUPAC name Methanoic) acid ($K_a = 1.70 \times 10^{-4}$) and 8.75×10^{-4} mol of free formate in 100 cm^3 of water. What would be the effect on the pH of
 - i) diluting the solution to 1 dm^3 ?
 - ii) adding 0.0012 g of NaOH?
 - iii) adding 0.0100 cm^3 10 mol dm^{-3} HCl?

The wording is ambiguous, therefore assume that **EVERYTHING** is in 100 cm^3 of Water.

- “Formic Acid” is today called Methanoic Acid, HCOOH, and since it is a Carboxylic Acid, then it is almost certain to be a **weak acid** where the equilibrium dissociation constant K_a at a given temperature will remain constant – but since we are actually given K_a , then we can be *certain* that the concept of K_a is applicable in this situation.
- The formic acid is undissociated initially therefore the pH of the buffer solution will simply be that of the water of the solution (= 7 at 298K), **and clearly this is not what is being asked**. What the question seeks to find out is the pH of the buffer solution **at equilibrium** at the given temperature.
- If we know what the concentration of the Hydrogen ions are, then we can calculate the pH of the buffer solution.



and at equilibrium $K_a = \frac{[\text{H}^+]_{\text{Eq}} [\text{HCOO}^-]_{\text{Eq}}}{[\text{HCOOH}]_{\text{Eq}}}$ where “Eq” stands for at equilibrium

therefore $[\text{H}^+]_{\text{Eq}} = \frac{K_a \times [\text{HCOOH}]_{\text{Eq}}}{[\text{HCOO}^-]_{\text{Eq}}} = K_a \cdot \frac{\text{Concentration of the acid at equilibrium}}{\text{Concentration of the salt at equilibrium}}$

and we now need to know what the concentrations of the acid and the formate are **at equilibrium**.

- This Buffer Solution consists of a Weak Acid and a Fully Dissociable Strong Salt of the Acid, and
 - 1 **Weak acids hardly dissociate at all**, therefore at equilibrium the concentration of the acid can be taken to be the same as the initial concentration of the acid (= 1.35×10^{-3} moles in 100 cm^3 of solution = and since “Conc. = $N \div \text{Vol.}$ ” we get **$1.35 \times 10^{-2} \text{ mol dm}^{-3}$**), and
 - 2 **A Strong Salt will dissociate to completion** (or almost to completion) therefore at equilibrium the concentration of the Salt is the same as the Initial concentration of the Salt = (8.75×10^{-4} moles in 100 cm^3 of solution) = (**$8.75 \times 10^{-3} \text{ mol dm}^{-3}$**)
- There are two ways of calculating the answer to this question
 - A) use the formula for K_a (and this is the method that I prefer), or
 - B) use the Henderson-Hasselbalch equation.

Answer

(In an exam, you do **not** need to give a long-winded answer like the ones below, and instead you can leave out all the detailed explanations that I am just about to give you.)

A) Using the formula for K_a



$$\text{therefore} \quad K_a = \frac{[\text{H}^+].[\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$\text{therefore} \quad [\text{H}^+] = K_a \cdot \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

- $[\text{CH}_3\text{COOH}]$ is given in the question as 1.35×10^{-3} mol in 100 cm^3 of Water, therefore
 $[\text{CH}_3\text{COOH}] = 10 \times 1.35 \times 10^{-3}$ mol in $1,000 \text{ cm}^3$ of Water = $1.35 \times 10^{-2} \text{ mol dm}^{-3}$.
- To calculate $[\text{HCOO}^-]_{\text{eq}}$ one can ignore the amount of the Conjugate Base/the Salt that has been contributed by the Weak Acid because it is going to be trivial compared to the amount of Salt that has been contributed by the complete dissolution of the Strong Salt of the Weak Acid. The latter will be massively more important than the former.

$$[\text{CH}_3\text{COO}^-] \text{ is given in the question as } 8.75 \times 10^{-4} \text{ mol in } 100 \text{ cm}^3 \text{ of water, therefore}$$
$$[\text{CH}_3\text{COO}^-] = 10 \times 8.75 \times 10^{-4} \text{ mol in } 1000 \text{ cm}^3 \text{ of water} = 8.75 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{therefore} \quad [\text{H}^+] = (1.70 \times 10^{-4}) \times \frac{1.35 \times 10^{-2} \text{ mol dm}^{-3}}{8.75 \times 10^{-3} \text{ mol dm}^{-3}} = 2.629 \times 10^{-4}$$

$$\text{therefore} \quad \text{pH} = -\log_{10}([\text{H}^+]) = 3.58$$

This is MUCH MUCH EASIER than using the Henderson-Hasselbalch equation – but let us now use the HH equation to find the answer.

B) Using the HH equation



$$\text{therefore} \quad K_a = \frac{[\text{H}^+].[\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$\text{therefore} \quad [\text{H}^+] = K_a \cdot \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

- By taking logs of the above equation we get

$$\log_{10}([\text{H}^+]_{\text{Eq}}) = \log_{10}(K_a) + \log_{10} \left\{ \frac{([\text{HCOOH}]_{\text{Eq}})}{([\text{HCOO}^-]_{\text{Eq}})} \right\}$$

and multiplying across by “-1” we get

$$-\log_{10}([\text{H}^+]_{\text{Eq}}) = -\log_{10}(K_a) - \log_{10} \left\{ \frac{([\text{HCOOH}]_{\text{Eq}})}{[\text{HCOO}^-]_{\text{Eq}}} \right\}$$

and since “pH” of something is “-log₁₀(of that thing)”, then we get

$$\text{pH} = \text{p}K_a - \log_{10} \left\{ \frac{[\text{HA}(\text{aq})]}{[\text{A}^-(\text{aq})]} \right\} \quad \begin{array}{l} \text{Concentration of the ACID} \\ \text{Concentration of the SALT} \end{array}$$

or this can be expressed as the inverse of the Acid to Salt ratio by changing the sign of the log

$$\text{or} \quad \text{pH} = \text{p}K_a + \log_{10} \left\{ \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \right\} \quad \begin{array}{l} \text{Concentration of the SALT} \\ \text{Concentration of the ACID} \end{array}$$

$$\text{therefore} \quad \text{pH} = -\log_{10}(1.70 \times 10^{-4}) + \log_{10} \left\{ \frac{8.75 \times 10^{-3} \text{ mol dm}^{-3}}{1.35 \times 10^{-2} \text{ mol dm}^{-3}} \right\}$$

$$= 3.76956 - 0.188 = \mathbf{3.58} \text{ (and this is the pH of the buffer at equilibrium)}$$

- **The pH of the buffer solution at equilibrium before anything was added is therefore 3.58 – and it did not matter which methodology was used, the answer is still 3.58.**

- i) This next bit of the question that was set was **not** a “trick” question. The question seeks to ascertain whether or not you truly understand what it is that you are doing. The whole point about “K_a” is that for a reversible reaction that is in dynamic equilibrium at a given temperature, **there is a number/a constant that does not change no matter (within certain limits) how much the concentrations of the reactants and the products alter.** You will remember that if the concentration of a reactant in a reaction that is dynamic equilibrium is altered, then the position of equilibrium will change and (provided that the temperature is not altered) it is possible to determine the effect on the other reactants because **K_a is an unvarying constant for a given reaction at a given temperature.**

The answer to this bit of the question therefore is that although the concentrations of the reactants and products has changed, **the K_a has not altered** and (since everything has been diluted by the same amount) the ratio of the concentration of the acid to the concentration of the salt has not changed **therefore the pH of the buffer at equilibrium will still be**

$$\text{pH} = -\log_{10}(1.70 \times 10^{-4}) + \log_{10} \{0.64815\} = \mathbf{3.58}$$

- ii) 1 mol of NaOH has a mass of roughly 40g,² therefore
 X mol 0.0012g
 where X = $\frac{1 \text{ mol} \times 0.0012\text{g}}{40\text{g}} = 3.0 \times 10^{-5} \text{ mol}$

- The concentration of the NaOH in 100cm³ (or 0.1 dm³) of water is given by C = N ÷ V, therefore [NaOH (aq)] = $3.0 \times 10^{-5} \text{ mol} \div 0.1 \text{ dm}^3 = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$.

² At University you would need to use a more precise RMM, but at ‘A’ Level I am not going to bother to do so.



and an addition of a strong alkali, NaOH, will cause a reaction between the OH⁻ in the alkali and the H⁺ in the acid and thus neutralise the alkali. (The negatively charged OH⁻ ion cannot react with the negatively charged HCOO⁻ (aq) ion, and if it were to react with the positively charged M⁺ ion, then since MOH (aq) is fully dissociable, the OH⁻ ion would be spewed straight back out into the buffer solution where it would react with the H⁺ ion.)

- Each ionic unit of NaOH that has been added will dissociate one OH⁻ ion, and each OH⁻ ion will react with one H⁺ ion to form one molecule of water (H₂O); but, as each H⁺ ion is taken out of the buffer solution by an OH⁻ ion, the Formic Acid will dissociate a new H⁺ ion and the position of equilibrium of the reversible reaction will move a tiny amount to the right. It is important to note therefore that for every OH⁻ ion that is put into the buffer solution (and which reacts with an H⁺ ion), the Formic Acid loses one H⁺ ion (i.e. the one that the Acid dissociates to replace the one that has been neutralised by the OH⁻ ion).
- The H⁺ ion and the OH⁻ ion react and form Water, and thus the volume of water increases by a tiny amount – but at ‘A’ Level you can ignore this increase in the dilution.

NB You will not have time to think about all this in the exam therefore please make sure that you understand what is happening.

- However, we do not know what the concentrations of the reactants and the products are at equilibrium, and we will have to work out what these are.
- In the table below, the assumption being made is that the amount and the **initial concentration** of the formate ion (before any dissociation occurs) **is contributed effectively entirely by the fully dissociated salt**, and that none of it is provided by the acid.
- The three substances HCOOH (aq), M⁺HCOO⁻ (aq) and NaOH (aq) are all in exactly the same volume of water therefore the ratios of their concentrations is exactly the same as their mole reaction ratios.
- One mole of NaOH will dissociate one mole of OH⁻ ions, and one mole of OH⁻ ions will react with one mole of H⁺ ions, therefore we can now fill in the middle line of the ICE table because we know that 3.0 x 10⁻⁴ moles of OH⁻ ions will react with 3.0 x 10⁻⁴ moles of H⁺ ions to form 3.0 x 10⁻⁴ moles of Water and the Formic Acid will now have to dissociate 3.0 x 10⁻⁴ moles of H⁺ ions to replace the H⁺ ions that have been used up to form the Water, and in doing so it will increase the number of Formate ions (but the number of H⁺ ions will remain unaltered overall).
- If you put five lines of working into your ICE table for your HH equations, then you will never go wrong.

Substances in mol dm ⁻³	[HCOOH (aq)]	[H ⁺ (aq)] from the Acid	[HCOO ⁻ (aq)] Formate ions from M ⁺ HCOO ⁻
Initial Concentrations	1.35 x 10⁻²	c. (1.35 x 10 ⁻²)	8.75 x 10⁻³
The addition of OH ⁻ ions removes H ⁺ ions ∴	-3.0 x 10 ⁻⁴	H ⁺ + OH ⁻ becomes water	+3.0 x 10 ⁻⁴
Equilibrium Concentrations	1.32 x 10⁻²	1.35 x 10 ⁻²	9.05 x 10⁻³

- The H^+ and OH^- react to form water and this will reduce the concentration of all the substances by a small amount, but at 'A' Level this can be ignored.
- Now we can use the HH equation

$$pH = pK_a + \log_{10} \left\{ \frac{[A^-(aq)]}{[HA(aq)]} \right\} \quad \begin{array}{l} \text{Concentration of the SALT} \\ \text{Concentration of the ACID} \end{array}$$

- Therefore $pH = -\log_{10}(1.70 \times 10^{-4}) + \log_{10} \left\{ \frac{[HCOO^-(aq)]}{[HCOOH(aq)]} \right\}$ at equilibrium

$$= -\log_{10}(1.70 \times 10^{-4}) + \log_{10} \left\{ \frac{9.05 \times 10^{-3}}{1.32 \times 10^{-2}} \right\}$$

$$= -\log_{10}(1.70 \times 10^{-4}) + \log_{10} 0.68561$$

$$= 3.76955 - 0.16393$$

$$= 3.60 \text{ (and of course the pH will rise if you add an alkali)}$$

- Let me just summarise what has happened. We have put one of the strongest alkalis in Chemistry (NaOH) into this buffer solution (and we would expect the pH of the resulting mixture to go up dramatically because alkalis have high pH values!) – and the resulting pH has indeed gone up *but only by a very small amount (from 3.58 to 3.60)*. **THAT is what a buffer solution is all about!**
- Mind you, you must appreciate that a buffer solution can cope with only **small amounts** of strong acids or small amounts of strong alkalis. If you stick a large amount of either a strong acid or a strong alkali (i.e. a soluble base that generates OH^- ions) into the buffer solution (in for example your eye), **then nothing on earth is going to prevent the pH of the resulting mixture from going to a level which will shred your eye to pieces! Please always wear your safety goggles when conducting experiments in the lab! You would not like it if you were to go blind!**
- Please could you now do Section (iii) where you add 0.0100 cm^3 10 mol dm^{-3} HCl to the buffer solution (and if you add acid to the buffer solution, then you would expect a tiny fall in the pH).
- OK, I have shown in massive detail the workings of HH equations. Now could you please go and do a large number of examples from any of the textbooks that I have recommended. You might also like to have a look at Chemteam's excellent videos of HH examples on <http://www.chemteam.info/AcidBase/AcidBase-Problems&Video.html>
If you do, then you will see that problems concerning HH equations can be done in half a dozen lines of workings. I took many pages to do the example above because I wanted you to understand exactly what you are doing. I do not want you to kill one of your patients by accident merely because you did not understand
 - how HH equations work, or
 - how to manipulate logs, or
 - how to set things out in an ICE table.
- *Obviously if you spend 48 hours on the trot at a weekend as a junior doctor and you are so tired that by Sunday afternoon you do not know what the hell you are doing, then it is the fault of our stupid system if you accidentally kill one of your patients. Strangely enough, my wife immediately forgave the Junior Doctor who nearly killed her (because she was such a lovely human being), but (even after all these years) the memory of what he did still causes me enormous pain.*