

Buffers Calculations

For all buffer calculations the first step is to write out the K_a expression, exactly as you have always done. Using the ever so popular ethanoic acid:

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

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- ✓ remember what we said in the buffers theory tutorial, you **cannot** write $[H^+]^2$ in buffer calculations as the $[H^+]$ and the $[CH_3COO^-]$ are **not** equal.

Calculations types

There are 2 main categories of buffer calculations:

1. Making a buffer

- i) adding the salt directly
- ii) making the salt by the addition of NaOH

These calculations are very different and it is important to appreciate that adding the salt directly does **not involve a reaction** but making the salt involves a **neutralisation reaction**.

2. Addition of acid or base to a buffer

Whether you add acid or base to the buffer, the calculations are very similar.

Examples

1. Making a buffer solution

i.) adding the salt directly

The main point with this type of question is that there is no reaction as the salt is already formed. All you are really doing is putting numbers into the K_a expression:

A buffer solution was prepared by dissolving 0.0236 moles of the salt CH_3COONa in a 50cm^3 of 0.428mol dm^{-3} solution of CH_3COOH . Calculate the pH of the solution. The K_a value is $1.35 \times 10^{-5}\text{mol dm}^{-3}$.

Step 1: write out the K_a expression: $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Step 2: work out the concentrations of acid $[\text{CH}_3\text{COOH}]$ and salt $[\text{CH}_3\text{COO}^-]$.

$$[\text{CH}_3\text{COO}^-] = 50/1000 \times 0.0236 = \mathbf{0.472 \text{ mol dm}^{-3}}$$

$$[\text{CH}_3\text{COOH}] = \mathbf{0.428 \text{ mol dm}^{-3}}$$
 (given in question)

Step 3: put numbers into K_a

$$\begin{aligned} [\text{H}^+] &= 1.35 \times 10^{-5} \times 0.428/0.472 \\ &= \mathbf{1.22 \times 10^{-5}} \end{aligned}$$

Step 4: calculate the pH

$$\text{pH} = -\log[\text{H}^+] \rightarrow \mathbf{4.91}$$

- ✓ as an alternative, they often ask to calculate the amount in grams of the salt added. So they will give you the pH value. This is just the same steps, except that you calculate the $[\text{A}^-]$ value, then use the volume given \rightarrow moles then use the $M_r \rightarrow$ mass.

ii.) additon of NaOH to make the salt

The difference here from the first example is that a neutralisation reaction occurs i.e. acid + base \rightarrow salt + water.

- ✓ The NaOH will react with the weak acid and neutralise *some* of it to form the salt.
- ✓ The weak acid must be in excess otherwise it becomes a strong base question, as there would be no acid left to form the buffer!

the weak acid must be in excess

Calculate the pH of the buffer solution formed when 10cm^3 of 0.1 mol dm^{-3} NaOH is added to 25cm^3 of $0.410 \text{ mol dm}^{-3}$ ethanoic acid ($K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$).

Step 1: write out the K_a expression: $K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

Step 2: work out the original number of moles acid and base:

$$\text{NaOH} = 10/1000 \times 0.1 = \mathbf{1 \times 10^{-3} \text{ moles}}$$

$$\text{Ethanoic acid} = 25/1000 \times 0.41 = \mathbf{0.01025 \text{ moles}}$$

Remember these are the **original moles**. We need the moles of acid at equilibrium:



| | | | |
|-------------|---------------------|---------------------|--------------------------------------|
| Initial | 0.0125 | 1×10^{-3} | 0 |
| Change | -1×10^{-3} | -1×10^{-3} | $+1 \times 10^{-3}$ |
| Equilibrium | 0.00925 | 0 | 1×10^{-3} |

- ✓ Please note that **you need the moles of salt**. This is really important.
- ✓ I wrote out a table as it is easy to see what is going on. You don't have to do this. All you are doing is subtracting from the acid moles and adding to the salt....every time.

Step 3: put the numbers into the K_a expression:

At this stage you *should* work out the **concentrations** of each species from the moles. However, as the values are affected by the same amount (dividing all by the same volume), you can just put the moles values into the K_a expression.

$$K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3} \quad [\text{H}^+] = ? \quad \text{CH}_3\text{COO}^- = 1 \times 10^{-3} \text{ moles} \quad \text{CH}_3\text{COOH} = 0.00925 \text{ moles}$$

$$[\text{H}^+] = K_a \times \text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$$

$$= 1.74 \times 10^{-5} \times 0.00925 / 1 \times 10^{-3}$$

$$= \mathbf{1.62 \times 10^{-4} \text{ mol dm}^{-3}}$$

Step 4: calculate the pH

$$\text{pH} = -\log_{10}(1.62 \times 10^{-4}) = \mathbf{3.79}$$

2. Adding base to a buffer

This is the second “category” of calculation, and is so similar to the calculation we just did.

When adding base to a buffer, a **neutralisation** reaction occurs. The base added will **react with the acid** already present.

A buffer solution contains 0.25 moles of propanoic acid and 0.19 moles of sodium propanoate in a 1000 cm³ solution. 0.015 moles of solid NaOH is then added to the solution. $K_a = 1.35 \times 10^{-5}$. What is the new pH?

Step 1: write out the K_a expression: $K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{COOH}]}$

Step 2: we know the number of moles of acid and base initially but we need to know the equilibrium moles. So, work out the new number of moles of acid and salt:



| | | | |
|-------------|--------------|----------|--------------|
| Initial | 0.25 | 0.015 | 0.19 |
| Change | -0.015 | -0.015 | +0.015 |
| Equilibrium | 0.235 | 0 | 0.205 |

As was said above, the NaOH will react with propanoic acid to form more sodium propanoate.

✓ Note how similar this is to the making a buffer example above. The only difference is the original moles of salt is not zero. You are still **subtracting from the acid moles and adding to the salt**.

Step 3: work out the concentrations using the 1000 cm³ volume or just put in the numbers straight into K_a

$$[\text{H}^+] = K_a \times \frac{\text{CH}_3\text{CH}_2\text{COOH}}{\text{CH}_3\text{CH}_2\text{COO}^-} = 1.35 \times 10^{-5} \times \frac{0.235}{0.205} = \mathbf{1.18 \times 10^{-5} \text{ mol dm}^{-3}}$$

Step 4: calculate the pH:

$$\text{pH} = -\log_{10}(1.18 \times 10^{-5}) = \mathbf{4.92}$$

Adding acid to a buffer

If we add extra acid to a buffer, it will **react with the salt** already present.

A buffer solution contains 2.35×10^{-2} moles of methanoic acid and 1.84×10^{-2} moles of sodium methanoate. 5cm^3 of 0.1 mol dm^{-3} HCl is then added. What is the new pH?

This is very similar to the question above except that we now have to **subtract from the salt** moles and **add to the acid** i.e. the opposite of what we did above.

Step 1: write out K_a etc. as for the previous examples.

Step 2: work out how much HCl is being added:

$$\text{Moles of HCl} = 5/1000 \times 0.1 = 5 \times 10^{-4}$$

Step 3: calculate the equilibrium moles.

✓ the equation is slightly different to that in the previous question as the extra acid added reacts with the salt:

| | | | | | | | |
|-------------|---|----------|---------------------|----------|--|----------|-------------|
| | HCOONa | + | HCl | → | HCOOH | + | NaCl |
| Initial | 2.35×10^{-2} | | 5×10^{-4} | | 0.19 | | |
| Change | -5×10^{-4} | | -5×10^{-4} | | $+5 \times 10^{-4}$ | | |
| Equilibrium | 1.79×10^{-2} | | 0 | | 2.4×10^{-2} | | |

Step 4: put these numbers into the K_a expression using 1.78×10^{-4} as the K_a value:

$$[\text{H}^+] = K_a \times \text{HCOOH}/\text{HCOO}^- = 1.78 \times 10^{-5} \times 2.4 \times 10^{-2} / 1.79 \times 10^{-2} = 2.39 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 5: calculate the pH

$$\text{pH} = -\log_{10}(2.39 \times 10^{-5}) = 4.62$$

3. Salt:acid ratio questions

As was discussed in the previous part of the tutorial, the salt:acid ratio dictates the pH. They sometimes ask for this ratio in calculation questions. Just rearrange the K_a expression:

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

Therefore all we need to do is divide the K_a value by the $[H^+]$.

*A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate ions. The pH of the solution is 4.9 and the $K_a = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$. What is the hydrogen ion concentration in the shampoo and hence the **ratio of methanoate ions to methanoic acid**?*

The $[H^+]$ can be worked out from the pH by using $\text{pH} = -\log_{10}[H^+]$, which is **$1.26 \times 10^{-5} \text{ mol dm}^{-3}$** .

We know the values for K_a and $[H^+]$ so we can put them into the K_a expression to give:

$$\frac{[HCOO^-]}{[HCOOH]} = \frac{1.6 \times 10^{-4}}{1.26 \times 10^{-5}} = 12.7$$

The answer is therefore **12.7:1** or 13:1.

- ✓ students often ask where the '1' comes from. From the calculation we are saying there are 12.7 x more A^- ions than HA, therefore it has to be :1.

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