

Buffer Solution

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Buffer solutions

A Buffer solution is one where the pH does not change significantly if small amounts of acid or alkali are added to it.

An **acidic** buffer solution is made from a weak acid and a salt of that weak acid (made from reacting the weak acid with a strong base)

Example : ethanoic acid and sodium ethanoate



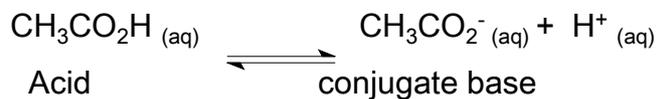
A **basic** buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid)

Example : ammonia and ammonium chloride



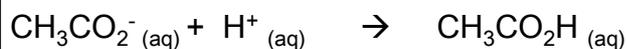
How Buffer solutions work

In an ethanoic acid buffer



In a buffer solution there is a much higher concentration of $\text{CH}_3\text{CO}_2^{-}$ ion than in the pure acid.

If acid is added to the buffer: Then Equilibrium will shift to the left removing nearly all the H^{+} ions added,



As there is a large concentration of the salt ion in the buffer the ratio $[\text{CH}_3\text{CO}_2\text{H}] / [\text{CH}_3\text{CO}_2^{-}]$ stays almost constant, so the pH stays fairly constant.

If alkali is added to the buffer. The OH^{-} ions will react with H^{+} ions to form water. The Equilibrium will then shift to the right to produce more H^{+} ions. Overall the concentration of H^{+} ions and pH remains constant (but some ethanoic acid molecules are changed to ethanoate ions)

Calculating the pH of buffer solutions

The pH can be calculated using the weak acid equation

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

Rearranged to

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

or

$$[H^+_{(aq)}] = K_a \frac{[\text{weak acid}]}{[\text{salt}]}$$

Calculations involving buffers

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

We can use either of the following equations

$$pH = -\log k_a - \log \left(\frac{[\text{acid}]}{[\text{salt}]} \right)$$

Special case: if [acid] is equal to [base] then this equals zero. So $pH = -\log k_a$ or pka

Assumptions to simplify calculation :

1. Initial concentration of the acid has remained constant, because amount that has dissociated or reacted is small
2. The concentration of the base is only due to the salt added in. Ignore any base formed from dissociation of the acid

Calculations with buffers

In order to calculate the pH of a buffer data can be given in several different ways.

1. Given the concentration of the salt and acid in the mixture :- simply put numbers into buffer equation.
2. Given the concentration and volume of the salt and acid before they are mixed: Concentrations will change in the mixture, but if the volume of salt and acid is the same use the original concentrations
3. Given a volume and concentration of acid and a mass of solid salt: The concentration of the acid remains the same, but calculate the concentration of salt from the mass of solid.
4. A buffer solution can be made by adding some sodium hydroxide to a weak acid: the resulting mixture will have unreacted acid and salt formed from the neutralisation

Simple Buffer Calculations

What would be the pH of a buffer made from 45cm³ of 0.1M ethanoic acid and 50cm³ of 0.15 M sodium ethanoate ($K_a = 1.7 \times 10^{-5}$)?

When these two solutions are mixed they will produce a buffer solutions. Their concentrations will change when they are mixed.

- work out number of moles in original weak acid
moles = conc x vol = $0.1 \times 45/1000 = 0.0045\text{mol}$
- work out new concentration weak acid
conc = moles / total new vol = $0.0045 / (95/1000) = 0.047\text{M}$

Do the same for the salt

$$\text{Conc} = \text{old conc} \times \text{old vol} / \text{new vol} = 0.15 \times 50 / 95 = 0.0789$$

Put values of K_a , and concs of acid and salt into equilibrium expression to work out conc of H^+

$$K_a = \frac{[H^+_{(aq)}][CH_3CO_2^-_{(aq)}]}{[CH_3CO_2H_{(aq)}]} \quad [H^+_{(aq)}] = K_a \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \frac{0.047}{0.0789} = 1.01 \times 10^{-5}$$

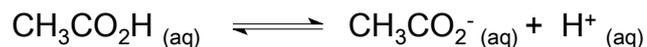
put in pH equation

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log [1.01 \times 10^{-5}] \\ &= 4.99 \end{aligned}$$

Working out pH of a buffer when solid salt is added to weak acid

We start with a weak acid. A known mass of solid salt is added to the acid to make a buffer solution

A buffer solution is made by adding 1.1g of sodium ethanoate into 100 cm³ of 0.4M ethanoic acid. What is its pH? $K_a = 1.7 \times 10^{-5}$



Working out pH of a buffer when solid salt is added to weak acid

First we need to work out how many moles of salt was added.

- work out number of moles in salt added
moles = mass/Mr = 1.1/ 82 = 0.0134mol
- work out concentration of salt formed by dividing the moles of salt by the volume of acid
- Conc $\text{CH}_3\text{COO}^-\text{Na}^+$ = 0.0134/(100/1000) = 0.134M

The concentration of the acid does not change as solid salt is added to it. It remains at 0.4M

Put values of K_a , and concs of acid and salt into equilibrium expression to work out conc of H^+

$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{CH}_3\text{CO}_2^-_{(\text{aq})}]}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]}$$

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

$$[\text{H}^+_{(\text{aq})}] = 1.7 \times 10^{-5} \frac{0.4}{0.134} = 5.07 \times 10^{-5}$$

put in pH equation

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= -\log [5.07 \times 10^{-5}] \\ &= 4.29 \end{aligned}$$

Working out pH of a buffer when some base is added to a **weak acid**

We start with a weak acid. Some of it is neutralised producing a mixture of unreacted acid and salt. i.e. a buffer solution

What is the pH of the buffer solution made when 25cm³ of 0.5M sodium hydroxide is added to 40cm³ of 0.5M ethanoic acid? $K_a = 1.7 \times 10^{-5}$



Working out pH of a buffer when some base is added to a **weak acid**

First we need to work out how many moles of acid is left.

- work out number of moles in original weak acid
moles = conc x vol = $0.5 \times 40/1000 = 0.02\text{mol}$
- work out number of moles in base added
moles = conc x vol = $0.5 \times 25/1000 = 0.0125\text{mol}$
- work out moles of acid left by subtracting base moles from acid moles (will need to convert moles if not 1:1 ratio)
Moles CH_3COOH left = $0.02 - 0.0125 = 0.0075\text{ mol}$

- work out new concentration of remaining acid by dividing the remaining moles by new total volume (vol acid + vol alkali added)

$$\text{Conc CH}_3\text{COOH} = 0.0075 / (65/1000) = 0.115\text{M}$$

- work out moles of salt formed from the balanced equation
1 mole of OH⁻ give 1 mole of salt formed
0.0125 moles OH⁻ gives 0.0125 moles of CH₃COO⁻

- work out concentration of salt formed by dividing the moles of salt by new total volume (vol acid + vol alkali added)

$$\text{Conc CH}_3\text{COO}^- = 0.0125 / (65/1000) = 0.192\text{M}$$

Put values of K_a, and concs of acid and salt into equilibrium expression to work out conc of H⁺

$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{CH}_3\text{CO}_2^-_{(\text{aq})}]}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]}$$

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

$$[\text{H}^+_{(\text{aq})}] = 1.7 \times 10^{-5} \frac{0.115}{0.192} = 1.018 \times 10^{-5}$$

put in pH equation

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ &= -\log [1.018 \times 10^{-5}] \\ &= 4.99 \end{aligned}$$