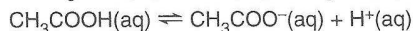
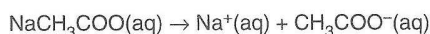


Buffers

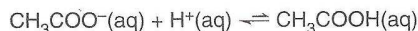
BUFFER SOLUTIONS

A buffer solution resists changes in pH when small amounts of acid or alkali are added to it.

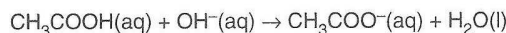
An acidic buffer solution can be made by mixing a weak acid together with the salt of that acid and a strong base. An example is a solution of ethanoic acid and sodium ethanoate. The weak acid is only slightly dissociated in solution, but the salt is fully dissociated into its ions, so the concentration of ethanoate ions is high.



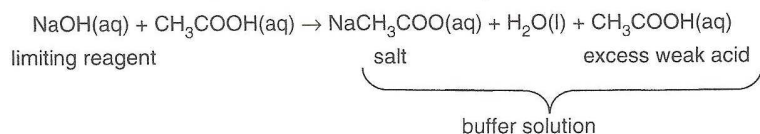
If an acid is added the extra H^+ ions coming from the acid are removed as they combine with ethanoate ions to form undissociated ethanoic acid, so the concentration of H^+ ions remains unaltered.



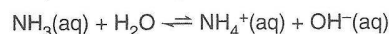
If an alkali is added the hydroxide ions from the alkali are removed by their reaction with the undissociated acid to form water, so again the H^+ ion concentration stays constant.



In practice acidic buffers are often made by taking a solution of a strong base and adding excess weak acid to it, so that the solution contains the salt and the unreacted weak acid.



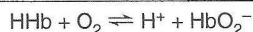
An alkali buffer with a fixed pH greater than 7 can be made from a weak base together with the salt of that base with a strong acid. An example is ammonia with ammonium chloride.



If H^+ ions are added they will combine with OH^- ions to form water and more of the ammonia will dissociate to replace them. If more OH^- ions are added they will combine with ammonium ions to form undissociated ammonia. In both cases the hydroxide ion concentration and the hydrogen ion concentration remain constant.

BLOOD

An important buffer is blood which only functions correctly within a very narrow pH range. Blood is a complex buffering system, which is responsible for carrying oxygen around the body. One of the components of the system is that the oxygen adds on reversibly to the haemoglobin in the blood.



If the pH increases ($[\text{H}^+]$ falls) the equilibrium will move to the right and the oxygen will tend to be bound to the haemoglobin more tightly. If the pH decreases ($[\text{H}^+]$ increases) the oxygen will tend to be displaced from the haemoglobin. Both of these processes are potentially life threatening.

BUFFER CALCULATIONS

The equilibrium expression for weak acids also applies to acidic buffer solutions,

e.g. ethanoic acid/sodium ethanoate solution.

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

The essential difference is that now the concentrations of the two ions from the acid will not be equal.

Since the sodium ethanoate is completely dissociated the concentration of the ethanoate ions in solution will be almost the same as the concentration of the sodium ethanoate, as very little will come from the acid.

If logarithms are taken and the equation is rearranged then:

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Two facts can be deduced from this expression. Firstly the pH of the buffer does not change on dilution, as the concentration of the ethanoate ions and the acid will be affected equally. Secondly the buffer will be most efficient

when $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$. At this point, which equates to the half equivalence point when ethanoic acid is titrated with sodium hydroxide, the pH of the solution will equal the $\text{p}K_a$ value of the acid.

Calculate the pH of a buffer containing 0.200 mol of sodium ethanoate in 500 cm^3 of 0.100 mol dm^{-3} ethanoic acid (given that K_a for ethanoic acid = $1.8 \times 10^{-5} \text{ mol dm}^{-3}$).

$$[\text{CH}_3\text{COO}^-] = 0.400 \text{ mol dm}^{-3}; [\text{CH}_3\text{COOH}] = 0.100 \text{ mol dm}^{-3}$$

$$K_a \approx \frac{[\text{H}^+] \times 0.400}{0.100} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{H}^+] = 4.5 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = 5.35$$

Calculate what mass of sodium propanoate must be dissolved in 1.00 dm^3 of 1.00 mol dm^{-3} propanoic acid ($\text{p}K_a = 4.87$) to give a buffer solution with a pH of 4.5.

$$[\text{C}_2\text{H}_5\text{COO}^-] = \frac{K_a \times [\text{C}_2\text{H}_5\text{COOH}]}{[\text{H}^+]} = \frac{10^{-4.87} \times 1.00}{10^{-4.5}} = 0.427 \text{ mol dm}^{-3}$$

$$\text{Mass of NaC}_2\text{H}_5\text{COO required} = 0.427 \times 96.07 = 41.0 \text{ g}$$