Action of a Buffer Solution

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What is a Buffer Solution

Buffer Solution – A solution which resists a change in pH when a small amount of acid or base is added.

Buffer solutions contain large amounts of both a weak acid and its conjugate base or a weak base and its conjugate acid.

The concentrations of both conjugate species in the buffer should be similar (difference should not be more than a factor of 10) – this allows buffer action to occur when either an acid or base is added.

Buffer solutions can be made either by mixing individual solutions of the conjugate acid and base or by reacting the weak acid with a base or the weak base with an acid to produce the required conjugate pair.

Explanation of Buffer Action

The equation for the dissociation of a weak acid (HA) can be given as:

$HA\ (aq) + H_2O\ (l) \rightleftharpoons A^-\ (aq) + H_3O^+\ (aq)$

Hence giving a K_a expression of:

$$K_a = \frac{[H_3O^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}}$$

By rearranging to make $[H_3O^+]_{eqm}$ the subject and taking $-\log_{10}$ of both sides gives:

$$pH = -\log_{10}\left(K_a \frac{[HA]_{eqm}}{[A^-]_{eqm}}\right)$$

Explanation of Buffer Action

If a small amount of acid is added to the buffer solution of HA and A^- then it will react with the A^- to produce HA:

$A^- (aq) + H^+ (aq) \rightarrow HA (aq)$

Since the concentrations of A^- and HA are very large compared to that of H^+ the resultant change in concentration is very small, hence the pH change is also very small.

If a small amount of alkali is added the reverse occurs: HA reacts with the OH^- ions to produce A^-.

This can also be explained in terms of the reaction quotient, Q (however the explanation above appears to be preferred in some past mark schemes – do your own research on this!):

If a small amount of acid is added the concentration of H_3O^+ will increase thus increasing the value of Q.

To reduce the value of Q back to K_a, A^- will react with some H_3O^+ present until $Q = K_a$. This will thus result in a reduction in the concentration of A^- and a corresponding increase in the concentration of HA, however since the amount of acid added is very small in comparison to the amounts of A^- and AH the change in the concentrations of A^- and HA will be very small.

This will hence only lead to a small change in the pH of the solution.

The reverse will occur if a small amount of OH^- is added.

Calculation

HA is a weak acid with a dissociation constant $K_a = 5.62 \times 10^{-5}$ mol dm^{-3}.

A buffer solution contains HA(aq) at a concentration of 0.300 mol dm^{-3}, and its sodium salt, NaA, at a concentration of 0.600 mol dm^{-3}.

Calculate the pH of this buffer solution. (3)

$$K_a = \frac{[H_3O^+]_{eqm}[A^-]_{eqm}}{[HA]_{eqm}} \qquad pH = -\log_{10}\left(K_a \frac{[HA]_{eqm}}{[A^-]_{eqm}}\right)$$

Hence pH = 4.55 (3 s.f.)

Core Practical 9: Determine the K_a of a Weak Acid

Describe an experiment to determine the K_a value of ethanoic acid. (4)

Pipette 25 cm^3 of 0.1 mol dm^{-3} ethanoic acid into a conical flask and add 2-3 drops of phenolphthalein indicator. Titrate the ethanoic acid with 0.1 mol dm^{-3} sodium hydroxide until the equivalence point is reached, then add a further 25 cm^3 of 0.1 mol dm^{-3} ethanoic acid. Measure the pH of the resulting solution with a pH probe. The pH recorded is the pK_a value of the acid. Evaluate 10^{-pKa} to obtain the K_a value.

Core Practical 9: Determine the K_a of a Weak Acid

Explain how the method described allows the calculation of the K_a value for ethanoic acid. (2)

At the equivalence point all of the original ethanoic acid ($25\times10^{-3} \times 0.1 = 2.5\times10^{-3}$ moles) has been converted into ethanoate ions (this explains why on the titration curve the pH at this point is greater than 7 since the ethanoate ions are basic while sodium ions are not really acidic at all). Then a further 2.5×10^{-3} moles of ethanoic acid is added, hence $[CH_3COOH] = [CH_3COO^-]$ thus by:

$$pH = -\log_{10}\left(K_a \frac{[CH_3COOH]_{eqm}}{[CH_3COO^-]_{eqm}}\right)$$

$pH = pK_a$

Simple Factual Question

Define the term buffer solution. (2)

A solution which resists a change in pH when small amounts of acid or alkali are added.

Explanation Question

Nitrous acid, HNO_2, is a weak acid with an acid dissociation constant $K_a = 4.70 \times 10^{-4}$ mol dm $^{-3}$ at 4 °C.

$HNO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + NO_2^-\,(aq)$

Suggest why a mixture of nitrous acid and sodium nitrite can act as a buffer solution whereas a solution of sodium nitrite on its own does not.(2)

In a buffer solution there must be a large amount of both an conjugate acid-base pair compared to H_3O^+ and OH^-, however in a mixture of sodium nitrite on its own the concentration of nitrous acid will be very small.

Extended Answer

Equal volumes of 0.500 mol dm^{-3} methanoic acid and 0.250 mol dm^{-3} sodium methanoate solution are mixed to make a buffer solution. Explain, with the aid of equations, how this mixture acts as a buffer solution. (4)

Extended Answer

The methanoic acid is a weak acid and is partially dissociated in solution:

$HCOOH\ (aq) + H_2O\ (l) \rightleftharpoons HCOO^-\ (aq) + H_3O^+\ (aq)$

And the sodium methanoate exists as ions in solution:

$HCOONa\ (aq) \rightarrow HCOO^-\ (aq) + Na^+\ (aq)$

If acid is added:

$HCOO^-\ (aq) + H^+\ (aq) \rightarrow HCOOH\ (aq)$

If alkali is added:

$HCOOH\ (aq) + OH^-\ (aq) \rightarrow HCOO^-\ (aq) + H_2O\ (l)$

The amounts of the acid and salt are large relative to the amount of acid or alkali added, hence their concentrations change very little and the pH of the solution changes very little.

Bonus Question

Suggest why the pH at the equivalence point for a weak acid – strong base titration is greater than pH 7. (2) Note: Self formulated question.

When a weak acid dissociates its conjugate base is generally a slightly strong base, however the conjugate acid of a strong base is very, very weak.

This hence results in a pH of greater than 7 at the equivalence point since the presence of the conjugate base of the weak acid will slightly increase the pH of the solution while the presence of the conjugate acid of the strong base has next to no effect on the pH of the solution. See next slide for another (maybe clearer) explanation.

Bonus Question

Using ethanoic acid as an example:

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$

$$K_a = \frac{[H_3O^+]_{eqm}[CH_3COO^-]_{eqm}}{[CH_3COOH]_{eqm}}$$

Hence for the reverse:

$$K_b = \frac{[CH_3COOH]_{eqm}}{[H_3O^+]_{eqm}[CH_3COO^-]_{eqm}}$$

Thus since $K_w = K_a \times K_b$ or alternatively $pK_w = pK_a + pK_b$, the smaller the value of K_a the larger the value of K_b, hence the conjugate bases of weak acids are quite strong and conversely the conjugate acids of strong bases are very weak. Hence at the equivalence point for a titration between ethanoic acid and sodium hydroxide some of the ethanoate ions will associate to form ethanoic acid hence reducing the pH of the solution since this reaction 'consumes' H_3O^+ ions (see the backwards reaction of the above equation).

A Quick Note on Terminology

Acids may dissociate in solution and the extent of the dissociation dictates if the acid is described as strong or weak.

Organic bases may associate in solution and the extent of this association dictates if the base is strong or weak.

Inorganic bases which are ionic e.g. $Ca(OH)_2$ dissolve in solution (as long as they are fairly soluble in water) to give the metal ion and hydroxide ions (using the earlier example this is a Ca^{2+} ion and two OH^- ions.