18.2.1 Composition of Buffer Solutions
In normal water (non-buffered solution) if you add a small amount of a strong acid or base, it will cause the pH of the water to change significantly. Two drops of 1 mol dm\(^{-3}\) HCl added to water will change the pH from 7 to 4.

**A buffer solution** can be described as a solution, which will resist changes in pH when a small amount of a strong acid or base is added.

**Acidic buffers**
**Composition**
An acidic buffer is composed of a weak acid (HA) and its conjugate base (A\(^-\)) or a weak acid and the salt of the weak acid and a strong base.

**How to make an acidic buffer**
1) Start with a weak acid and strong base of the same concentration (e.g. 0.10 mol dm\(^{-3}\)). Take about 25 cm\(^3\) of a strong base and add an excess moles of a weak acid (50 cm\(^3\)) so that there is a sufficient number of moles of the weak acid to completely neutralize all the moles of strong base.

Excess weak acid is added so that the resulting solution contains the salt (conjugate base), water and excess weak acid.

\[
\text{OH}^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{A}^- (\text{aq}) + \text{H}^+ (\text{aq})
\]

Buffer solution

in the buffer the \([\text{HA}] = [\text{A}^-]\]

OR

2) Add equal concentration and volume (equal moles) of a weak acid (HA) and the salt of the weak acid and a strong base (A\(^-\)).

For example
- 50 cm\(^3\) of 0.10 moldm\(^{-3}\) of the weak acid, CH\(_3\)COOH is reacted with 25 cm\(^3\) of 0.10 moldm\(^{-3}\) and the strong base, NaOH to give a buffer solution containing the weak acid, CH\(_3\)COOH and CH\(_3\)COONa, the salt formed between them.

\[
\text{CH}_3\text{COOH}_{(aq)} + \text{NaOH}_{(s)} \rightarrow \text{CH}_3\text{COONa}_{(aq)} + \text{CH}_3\text{COOH}_{(aq)}
\]

Weak acid 0.0050 mol

strong base 0.0025 mol

Salt of weak acid & strong base 0.0025 mol

OR

Alternatively the salt, sodium ethanoate could be added directly to the ethanoic acid.
In the buffer solution:

\[ n \text{(CH}_3\text{COOH)} = [\text{CH}_3\text{COOH}] \]

\[ [\text{CH}_3\text{COOH}]_{\text{buffer}} = \text{Initial mol 0.0050 weak acid (excess)} - \text{moles NaOH (limiting)} = 0.0050 - 0.0025 = 0.0025 \text{ moldm}^{-3} \]

Since NaOH is limiting 
\[ n \text{(CH}_3\text{COONa)} = [\text{CH}_3\text{COONa}] = 0.0025 \text{ moldm}^{-3} \]
so weak acid \[ [\text{CH}_3\text{COOH}] = \text{salt [ CH}_3\text{COONa] } \]

Reactions in an acidic buffer solution
The weak acid is only partially dissociated, but the salt is fully dissociated into its ions, so the concentration of the ethanoate ions and ethanoic acid is high.

\[
\text{CH}_3\text{COONa(aq)} \rightarrow \text{Na}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

Sodium ethanoate
0.0025 mol

\[
\text{CH}_3\text{COOH(aq)} \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

Weak acid (HA)
Ethanoic acid
0.0025 mol

(\text{NOTE: the exact pH of the buffer depends on the moles of HA and A-})

If a small amount of strong acid is added to the buffer the H\(^+\) ions are removed because they combine with ethanoate ions to form ethanoic acid. Overall the concentration of ions H\(^+\) remains unaltered, because the strong acid H\(^+\) is replaced by the weak acid CH\(_3\)COOH.

\[
\text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \rightarrow \text{CH}_3\text{COOH (aq)}
\]

Ethanoic acid

An alternative explanation is if a small amount of acid is added to the buffer solution the concentration of H\(^+\) ions increases. According to Le Chataliers Principle, the position of equilibrium will shift to the left (reverse direction) to oppose the change and restore equilibrium.

If a small amount of strong base is added the hydroxide ions, OH\(^-\) react with the small amounts of H\(^+\) ions to form water.

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O(l)}
\]

According to Le Chataliers Principle, the position of equilibrium will shift to the right to replacing the lost H\(^+\) ions, causing the pH to remain unchanged.
**Alkali / Basic Buffer**

**Composition**
A basic buffer is composed of a weak base (B) and its conjugate acid (BH⁺) / weak base and the salt of the weak base and a strong acid.

**How to make a basic buffer**

1) Start with a weak base and strong acid of the same concentration (e.g. 0.10 moldm⁻³). Take about 25cm³ of a strong acid and add an excess of weak base (about 50 cm³) so that there are sufficient moles of the weak base to neutralize all of the strong acid, leaving excess base in the solution.

\[
\text{OH}^- (aq) + \text{H}^+ (aq) \rightarrow \text{A}^- (aq) + \text{OH}^- (aq)
\]

excess limiting salt excess weak base

buffer solution
in the buffer the \([\text{OH}^-] = [\text{A}^-]\)

OR

2) Add equal concentration and volume (equal moles) of a weak base and the salt of the weak base and a strong acid.

For example

- 0.10 mol of the strong acid HCl and 0.20 mol of the excess of the weak base NH₃ are reacted together to give a buffer solution containing 0.10 mol of the weak base, NH₃ and 0.10 mol of NH₄⁺ ions formed from the salt of ammonia and hydrochloric acid.

\[
\text{NH}_3 (aq) + \text{HCl}(aq) \rightarrow \text{NH}_4\text{Cl}(aq) + \text{NH}_3 (aq)
\]

excess limiting salt excess weak base

0.2 mol 0.1 mol 0.1 mol

buffer

In the buffer solution:

Moles of weak base: \(n (\text{NH}_3) = [\text{NH}_3] = 0.20 - 0.10 = 0.10 \text{ moldm}^{-3}\)

Moles of the salt (conjugate acid): \(n (\text{NH}_4^+) = [\text{NH}_4^+] = 0.10 \text{ moldm}^{-3}\)

so \([\text{NH}_3] = [\text{NH}_4^+]\)
Reactions in the alkali buffer

\[ \text{NH}_4\text{Cl} (aq) \rightarrow \text{NH}_4^+ (aq) + \text{Cl}^- (aq) \]

i. Salt of weak base and strong acid
   \[ \text{NH}_3(aq) + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ (aq) + \text{OH}^- (aq) \]

ii. Weak base
   \[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

(Notice the direction of the arrows)

The weak base is only partially dissociated, but the salt is fully dissociated into its ions, so the concentration of the ammonium ions, \( \text{NH}_4^+ \) and ammonia, \( \text{NH}_3 \) acid is high.

If a small amount of H\(^+\) ions from an acid are added they combine with OH\(^-\) ions to form water, decreasing the concentration of OH\(^-\) ions causing the pH to increase. According to Le Chateliers Principle, the position of equilibrium will shift to the right to replace the OH\(^-\) ions that have been used up causing the pH to remain unchanged.

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]

If a small amount of OH\(^-\) ions from a base are added they will combine with the ammonium ions, \( \text{NH}_4^+ \) removing ammonium ions from the system.

\[ \text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O} \]

In both the acid and alkali buffer the hydrogen ion and hydroxide ion concentration will remain unaltered (constant).

**Important buffer solutions**

Buffer solutions are important living things because if the pH of cellular fluids is not maintained at certain critical levels the plant or animal could die. The internal pH of most cells is close to 7. A slight change in the pH can be extremely harmful to cellular function.

**Blood** is buffered so as to maintain its pH close to 7.4. A change of pH of 0.2 units in either direction is considered life threatening. There are a number of different types of buffers in blood but two of the most important ones are the carbonic acid – hydrogen carbonate ion and hemoglobin buffers.

During aerobic cellular respiration glucose and oxygen combine to form carbon dioxide, water and energy (which is used by the cells reactions).

\[ \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{ATP} \text{ (Energy)} \]

Most of the CO\(_2\) produced diffuses into the red blood cells and combines with water in a catalyzed equilibrium reaction to produce carbonic acid, which dissociates into hydrogen ions and hydrogen carbonate ions. The carbonic acid (weak acid) and hydrogen carbonate ion (salt of the weak acid) form a buffer solution.
The $\text{H}^+$ ions produced (in reaction I) bind to hemoglobin in the blood causing it to release an oxygen molecule (reaction II), which will be used for cellular respiration. Thus, hemoglobin acts as another buffer, removing $\text{H}^+$ ions from the blood, and preventing the pH for changing significantly.

\[
\text{(I)} \quad \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})
\]

\[\text{Weak acid} \quad \text{Carbonic acid} \quad \text{Salt of weak acid} \quad \text{Hydrogen carbonate ion}\]

According to Le Chateliers principle, to counteract the production of extra $\text{H}^+$ ions produced by the carbonate-hydrogen carbonate buffer, the position of equilibrium shifts in the reverse direction (reaction I and II), removing $\text{H}^+$ ions and preventing the pH to change. $\text{CO}_2$ is produced which is removed from the blood via the lungs and released into the air when we exhale.

If the bloods pH gets too low, due to excess hydrogen ions preventing the hemoglobin’s buffering system to work, a condition known as acidosis results. This can be very serious, because many of the chemical reactions that occur in the body, especially those involving proteins, are pH-dependent. Ideally, the pH of the blood should be maintained at 7.4. If the pH drops below 6.8 or rises above 7.8, death may occur. Intravenous injections must also be carefully buffered so as not to change the pH of the blood from its normal value of 7.4.

In the production of beer and wine, the fermentation reaction needs to be carefully buffered so that big changes in pH don’t cause the yeast to die.

Swimming pool water is also buffered to maintain a pH of 7.2 - 7.6. This is because the chance for irritation is greatly reduced when the pH of the pool water is similar to the pH of the skin and eyes. This pH range is also a good range to maximize the sanitizing effect of chlorine and for keeping the water clear from cloudiness.

1.8.2.1 Questions

1. (M07/S) Nitric acid and ammonia may be used to make a buffer solution.
   (i) Describe the behavior of a buffer \[2\]
   (ii) Describe how you would prepare a buffer solution using 0.100 moldm$^{-3}$ solutions of nitric acid and ammonia. \[3\]

2. (M06/S) Describe the composition of a buffer solution. \[1\]

3. (M06/H)
   (i) Identify two substances that can be added to water to form a basic buffer solution. \[1\]
   (ii) Describe what happens when a small amount of acid solution is added to the buffer solution described in (i). Use an equation to support your answer. \[2\]
4. (M05/S) Which substances could be added to a solution of ethanoic acid to prepare an acidic buffer solution.
   I. Hydrochloric acid
   II. Sodium ethanoate
   III. Sodium hydroxide
   A. I and II only
   B. I and III only
   C. II and III only
   D. I, II and III

5. (M04/H)
   A buffer solution can be prepared by adding which of the following to 50cm$^3$ of 0.10 moldm$^{-3}$ solution of CH$_3$COOH.
   I. 50cm$^3$ of 0.10 moldm$^{-3}$ solution of CH$_3$COONa
   II. 25cm$^3$ of 0.10 moldm$^{-3}$ solution of NaOH
   III. 25cm$^3$ of 0.10 moldm$^{-3}$ solution of NaCl
   A. I only
   B. I and II only
   C. II and III only
   D. I, II and III only

6. (N04/H) Which mixture would produce a buffer solution when dissolved in 1.0dm$^3$ of water.
   A. 0.50 mol of CH$_3$COONa and 0.50 mol NaOH
   B. 0.50 mol of CH$_3$COOH and 0.25 mol NaOH
   C. 0.50 mol of CH$_3$COOH and 1.00 mol NaOH
   D. 0.50 mol of CH$_3$COOH and 0.25 mol Ba(OH)$_2$

7. (M03/H) Which is a buffer solution
   I. 0.01 moldm$^{-3}$ solution of HCl and 0.01 moldm$^{-3}$ solution of NaCl
   II. 0.01 moldm$^{-3}$ solution of CH$_3$COOH and 0.01 moldm$^{-3}$ solution of CH$_3$COONa
   A. I only
   B. II only
   C. Both I and II
   D. Neither I nor II

8. (N03/S)
   a) State what is meant by a buffer solution. [2]
   b) State and explain whether each of the following solutions will form a buffer solution.
      (i) A 1.0 dm$^3$ solution containing 0.10 mol NH$_3$ and 0.20 mol HCl [2]
      (ii) A 1.0 dm$^3$ solution containing 0.20 mol NH$_3$ and 0.10 mol HCl [2]
9. M02/H(1) Which one of the following combinations will form a buffer solution?
   I. 20 cm$^3$ 0.10 mol dm$^{-3}$ CH$_3$COOH and 10 cm$^3$ 0.10 mol dm$^{-3}$ CH$_3$COONa
   II. 20 cm$^3$ 0.10 mol dm$^{-3}$ CH$_3$COOH and 10 cm$^3$ 0.10 mol dm$^{-3}$ NaOH
   A. I only
   B. II only
   C. Both I and II
   D. Neither I nor II

10. (N00/H)
    A buffer solution will be formed by combining equal volumes of 0.1 mol dm$^{-3}$ solutions of
    A. Hydrochloric acid and sodium hydroxide
    B. Hydrochloric acid and sodium ethanoate
    C. Ethanoic acid and sodium hydroxide
    D. Ethanoic acid and sodium ethanoate

11. M03/S(1)
    State a suitable mixture that can act as a buffer solution. [2]

12. (M01/H)
    30 cm$^3$ of 0.100 mol dm$^{-3}$ CH$_3$COOH is placed in a beaker and mixed with 10 cm$^3$ of 0.100 mol dm$^{-3}$ NaOH. Explain, with the help of an equation, how the solution formed acts as a buffer solution when a small quantity of acid is added to it. [2]

13. N02/H(2)
    Describe what happens when a small amount of acid is added to a buffer solution. [3]

14. M98/H(1)
    A buffer solution that contains ethanoic acid and sodium ethanoate has a pH=4.0. How could the pH of this solution be changed to 5.0?
    A. Dilute 10 cm$^3$ of the solution to 100 cm$^3$
    B. Add more sodium ethanoate
    C. Add more ethanoic acid
    D. Add equal moles of ethanoic acid and sodium ethanoate

15. (M98/H)
    Give the relative amounts of NaOH and CH$_3$COOH needed to form a buffer solution and outline your reasoning. [no calculations necessary]. [2]

16. An acidic buffer can be made from a weak acid and its conjugate base. Ethanoic acid, CH$_3$COOH, is a weak acid and CH$_3$COO$^-$ is its conjugate base.
   a) Compare the carbon – oxygen bond lengths in CH$_3$COOH and CH$_3$COO$^-$ giving your reasoning. [4]
   b) Deduce the shape and bond angle of the C-O-H and C=O bond angle in ethanoic acid and give a reason. [6]
   c) Write the two Lewis electron dot structures for the CH$_3$COO$^-$ ions and state how the bonding in the ion is related to these structures. [2]
   d) Write an equation for the dissociation of ethanoic acid in water. Identify the Bronsted Lowry conjugate acid-base pairs and their relative strengths.
17. For each of the following species give the shape, bond angle and reason for the shape using VSEPR theory. [9]
   a) NH$_4^+$
   b) H$_3$O$^+$
   c) H$_2$O
18.2.1 Composition of Buffer Solutions Answers

1. (M07/S)
   (i) A buffer solution is a solution which will resist changes in pH; (1)
       when a small amount of a strong acid or base is added; (1)
       (do not accept pH does not change)

   (ii) react excess ammonia with nitric acid; (1)
        stated volumes with about 50% more ammonia solution; (1)
        gives a solution containing a weak base and the salt of the weak base
        and strong acid; (1)
        Accept suitable volumes from about 20cm$^3$ to about 500cm$^3$ for 2$^{nd}$ mark.

2. (M06/S)
   Composition of an acidic buffer
   1. weak acid + salt of weak acid and a strong base (one of these) (1)
   2. excess weak acid + strong base (one of these)
      or
   Composition of an alkali buffer
   1. weak base + salt of weak base and strong acid
   2. excess weak base + strong acid (one of these)

3. (M06/H)
   (i) $\text{NH}_3 + \text{NH}_4\text{Cl}$ (weak base + salt of weak base and strong acid); (1)
       (or $\text{HCl} + \text{NH}_3$ strong acid + excess weak base)

   (ii) pH changes very little / most of the acid is neutralized by the base; (1)
        equation; (1)
        \[
        \begin{align*}
        \text{NH}_3(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \\
        \text{Weak base} & \quad \text{acid} & \quad \text{Strong conj acid} & \quad \text{Conj base}
        \end{align*}
        \]
        \[
        
        \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}
        \]
        If a small amount of $\text{H}^+$ from a strong acid is added they combine with $\text{OH}^-$ ions to
        form water, decreasing the concentration of $\text{OH}^-$ ions causing the pH to increase.
        Alternatively, according to Le Chataliers Principle, the position of equilibrium will
        shift to the right to replace the $\text{OH}^-$ ions that have been used up causing the pH to
        remain unchanged.

4. (M02/H) C (1)
5. (M04/H) B (1)
6. (N04/H) B (1)
7. (M03/H) B
8. (N03/S) B
   a) A **buffer solution** is a solution which will resist changes in pH; (1) when a small amount of a strong acid or base is added; (1) (do not accept pH does not change)

   b) (i) not a buffer solution; (1)
       after reaction the mixture contains - 0.10 mol NH₄Cl and 0.10 mol HCl / NH₃ needs to be in excess to make a basic buffer; (1)

       (ii) buffer solution; (1)
       after reaction the mixture contains - 0.10 mol NH₃ and 0.10 mol NH₄Cl; (1)

9. (M02/H) B
10. (N00/H) D equal volume and concentration = same number moles
11. (M03/S) B
    ammonia and ammonium chloride / ethanoic acid and sodium ethanoate ; (1)
    (weak acid + salt of weak acid / weak base + salt of weak base (1 max) blood (1 max)

12. (M01/H)

    \[
    \text{CH}_3\text{COOH}_{(aq)} + \text{NaOH}_{(s)} \rightarrow \text{CH}_3\text{COONa}_{(aq)} + \text{H}_2\text{O}_{(l)}
    \]

    Weak acid 0.003 mol  strong base 0.001 mol  Salt of weak acid & strong base 0.001 mol

The weak acid is only partially dissociated, but the salt is fully dissociated into its ions, so the concentration of the ethanoate ions and ethanoic acid is high.

\[
\text{CH}_3\text{COONa}_{(aq)} \rightarrow \text{Na}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}
\]

Sodium ethanoate 0.001 mol Ethanoate ions 0.001 mol

\[
\text{CH}_3\text{COOH}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}
\]

Weak acid Ethanoic acid 0.002 mol
If a small amount of acid is added to the buffer solution the concentration of $H^+$ ions increases. According to Le Chataliers Principle, the position of equilibrium will shift to the left to oppose the change and restore equilibrium; (1)

**OR**

The added $H^+$ ions are removed because they combine with ethanoate ions to form ethanoic acid; (Overall the concentration of ions $H^+$ remains unaltered, so the pH does not change)

$$\text{CH}_3\text{COO}^- (aq) + H^+ (aq) \rightarrow \text{CH}_3\text{COOH} (aq)$$

Ethanoic acid

(1 mark for equation)

13. (N02/H)

An acidic buffer is composed of a weak acid (HA) and its conjugate base (A⁻) / weak acid and the salt of the weak acid and a strong base; (1)

If a small amount of acid is added to the buffer the $H^+$ ions are removed because they combine with ethanoate ions to form ethanoic acid / position of equilibrium will shift to the left to oppose the change and restore equilibrium; (1)

Overall the concentration of ions $H^+$ remains unaltered, because the strong acid $H^+$ is replaced by the weak acid CH₃COOH; (1)

$$\text{CH}_3\text{COO}^- (aq) + H^+ (aq) \rightarrow \text{CH}_3\text{COOH} (aq)$$

Ethanoic acid

14. (N98/H) B

If you add more salt (conjugate base) the buffer solution becomes more basic & pH will become closer to 14. If you add more acid the buffer solution becomes more acidic, the pH will become closer to 1.

15. (M98/H)

Fewer moles of NaOH than CH₃COOH; (1)

CH₃COOH should be in excess so the final solution contains both CH₃COO⁻ and CH₃COOH; (1)

$$\text{NaOH (aq)} + \text{CH}_3\text{COOH(aq)} \rightarrow \text{CH}_3\text{COONa (aq)} + \text{CH}_3\text{COOH(aq)}$$

limiting excess salt excess weak acid

buffer solution

17. (M00/H)

a) CH₃COOH

one is longer than the other / C=O double bond is shorter than C-O single bond; (1)

extra electron pair makes the C=O bond stronger and therefore shorter; (1)
CH$_3$COO$^-$
C-O bonds of the same length ;
Because of delocalization / resonance ;
(ethanoic acid does not have delocalized electrons whereas its ion does)

b) around C=O trigonal planar ; (1)
120º ; (1)
3 negative charge centers repel each other equally; (1)
around C-O bent; (1)
104º (1)
2 lone pairs & 2 bonding pairs
according to VSEPR theory in order to minimize repulsion Lone pair / lone pair > bonded pair / lone pair > bonded pair / bonded pair repulsion ; (1)

c) Show for ethanoic acid

\[ \text{AND} \]

2 Lewis dot diagrams of the resonance structures ; (2)
(Partial Lewis structures showing bonding pairs as lines is acceptable)
(Lone pairs of electrons on O atoms must be shown, if missing [0])
accept 1 ½ bonds / $\pi$ electrons spread across C-O bonds

17.

a) NH$_4^+$
tetrahedral; (1)
109.5º ; (1)
0 lone pair, 4 bonding pairs of electrons ; (1)
To minimize the repulsion between them, the four bonding pairs repel each other equally bonding pairs repel each other equally to minimize repulsion ; (1)

b) H$_3$O$^+$
trigonal pyramid; (1)
107º ; (1)
1 lone pair, 3 bonding pairs of electrons
To minimize the repulsion bonded pair-lone pair > bonded pair- bonded pair repulsion ; (1)
c) $\text{H}_2\text{O}$
bent; (1)
$104.5^\circ$; (1)
2 lone pair, 2 bonding pairs of electrons
To minimize the repulsion Lone pair-lone pair > bonded pair-lone pair > bonded pair-bonded pair repulsion; (1)