## Acids and bases <br> pH and $K_{\text {w }}$

1. Complete the table below showing some numbers and their common logarithmic values; (1 mark)

| Number (n) | $\boldsymbol{l o g}_{10} \boldsymbol{n}$ |
| :--- | :--- |
| 0.001 | $\ldots \ldots \ldots \ldots$ |
| 0.1 | $\ldots \ldots \ldots .$. |
| $\ldots \ldots \ldots \ldots .$. | 0 |
| $\ldots \ldots$ | 3 |

2. Calculate the pH (to 2 dp ) of each of the solutions below: (3 marks)
(a) $\begin{gathered}{\left[\mathrm{H}^{+}\right]=} \\ 1.00 \times 10^{-10}\end{gathered} \quad \mathrm{pH}=\ldots$
(b) $\begin{aligned} & {\left[\mathrm{H}^{+}\right]=} \\ & 0.200 \times 10^{-2}\end{aligned} \quad \mathrm{pH}=\ldots$
(c) $\begin{gathered}{\left[\mathrm{H}^{+}\right]=} \\ 3.50 \times 10^{-3}\end{gathered} \mathrm{pH}=\ldots \ldots$ $\mathrm{mol} \mathrm{dm}{ }^{-3}$
$\mathrm{mol} \mathrm{dm}^{-3}$
$\mathrm{mol} \mathrm{dm}^{-3}$
3. As water is always slightly ionised, we can write the following equilibrium for water;

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \Delta \mathrm{H}=+ \text { ive }
$$

As only a very small amount of the water is ionised, we define a new equilibrium constant for this equilibrium called the ionic product of water, $\boldsymbol{K}_{\mathbf{w}}$;

$$
K_{\mathrm{w}}=\left[\mathrm{H}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]
$$

Like any other equilibrium constant, the value of $K_{w}$ depends on the temperature of the equilibrium.
(a) Predict what effect increasing the temperature will have on the pH of pure water.
(b) Calculate the pH of pure water (to 2 dp ) at each of the temperatures below;
(i) $10^{\circ} \mathrm{C}, K_{\mathrm{w}}=0.29 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$
(ii) $25^{\circ} \mathrm{C}, K_{w}=1.01 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$
(iii) $40^{\circ} \mathrm{C}, K_{\mathrm{w}}=2.92 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$
(c) Complete the paragraph below;

As the temperature decreases, water becomes (more acidic / less acidic / remains neutral). Explain your answer

## pH and acids

1. Identify the species formed when the following act as acids;
(a) HCl
(b) $\mathrm{NH}_{4}{ }^{+}$
$\qquad$
(c) $\mathrm{HCO}_{3}$ $\qquad$
2. Calculate the pH (to 2 dp ) of the following acids;
(a) $0.25 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCl}$
(b) $0.004 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaHSO}_{4}, K_{\mathrm{a}}$ of $\mathrm{HSO}_{4}^{-}=1.00 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3}$
$\qquad$
$\qquad$
$\qquad$
3. Calculate the concentration of the following acids given their pH .
(a) $\mathrm{HCl}, \mathrm{pH} 0.65$
(b) $\mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{pH} 2.61$ $\qquad$
(c) $\mathrm{CH}_{3} \mathrm{COOH}, \mathrm{pH} 3.40, K_{\mathrm{a}} 1.7 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$

## pH and bases

1. Define;
(a) a Brønsted-Lowry acid
(b) a Brønsted-Lowry base
2. In the following acid-base reactions identify the reactant species (ion or molecule) acting as a Brønsted-Lowry base;
(a) $2 \mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow\left(\mathrm{NH}_{4}{ }^{+}\right)_{2} \mathrm{SO}_{4}{ }^{2-}$
(b) $\mathrm{Ca}(\mathrm{OH})_{2}+\mathrm{H}_{2} \mathrm{CO}_{3} \rightarrow \mathrm{CaCO}_{3}+2 \mathrm{H}_{2} \mathrm{O}$
(c) $\mathrm{Na}_{2} \mathrm{CO}_{3}+2 \mathrm{HCl} \rightarrow 2 \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
3. Calculate the pH (to 2 dp ) of the following basic solutions (take $K_{\mathrm{w}}$ to be $1.00 \times 10^{-14} \mathrm{~mol}^{2}$ $\mathrm{dm}^{-6}$ );
(a) $0.150 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$
(b) $0.261 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{Mg}(\mathrm{OH})_{2}$
4. Calculate the concentration of the following basic solutions (take $K_{w}$ to be $1.00 \times 10^{-}$ ${ }^{14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$ );
(a) $\mathrm{KOH}, \mathrm{pH} 11.00$
$\qquad$
(b) $\mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{pH} 10.45$
5. Ethylamine is a weak base. Draw a curly arrow on the diagram below to show how the ethylamine acts as a base.


## Acid-base tritrations

Some students are carrying out an investigation into the neutralisation reactions between strong acids and bases and weak acids and bases.
They titrate $25 \mathrm{~cm}^{3}$ samples of four different bases against four different acids as shown in the table below.
For each of the titrations 1-4;
(a) Choose the correct titration curve from those shown below,
(b) Name a suitable indicator for the titration,
(c) For titrations 1 and 2, calculate the concentration of the acid.

| Titration | Base | Acid |
| :---: | :---: | :---: |
| $\mathbf{1}$ | $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$ | HCl |
| $\mathbf{2}$ | $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{KOH}$ | HCOOH |
| $\mathbf{3}$ | $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NH}_{3}$ <br> solution | $\mathrm{HNO}_{3}$ |
| $\mathbf{4}$ | $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaHCO}_{3}$ | $\mathrm{CH}_{3} \mathrm{COOH}$ |



Titration number: $\begin{array}{lllll}1 & 2 & 3 & 4\end{array}$
Suitable indicator:
Conc. of acid (if needed): $\qquad$


Titration number: $\begin{array}{lllll}1 & 2 & 3 & 4\end{array}$
Suitable indicator: $\qquad$
Conc. of acid (if needed) $\qquad$


Titration number: $\begin{array}{lllll}1 & 2 & 3 & 4\end{array}$
Suitable indicator: $\qquad$
Conc. of acid (if needed): $\qquad$


Titration number: $\begin{array}{lllll}1 & 2 & 3 & 4\end{array}$
Suitable indicator: $\qquad$
Conc. of acid (if needed): $\qquad$

## Buffer solutions

A buffer solution is a solution that resists a change in pH when a small quantity of acid or base is added.

1. (a) A buffer solution is made by mixing 0.510 mol of methanoic acid with 0.450 mol of sodium methanoate in $500 \mathrm{~cm}^{3}$ of water.
(i) Write an equation to represent the equilibrium established in the buffer solution.
(ii) Calculate the pH of the buffer solution formed. ( $\mathrm{p} K_{\mathrm{a}}$ for methanoic acid $=3.75$ )
(b) Explain how this buffer resists change in pH on;
(i) addition of a small quantity of acid.
(ii) addition of a small quantity of base.
$\qquad$
$\qquad$
2. Mark and Karen are carrying out a science project on the application of buffer solutions in the human body. They have discovered that a buffer of carbonic acid $\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)$ and hydrogen carbonate $\left(\mathrm{HCO}_{3}{ }^{-}\right)$is present in blood plasma to maintain a pH of between 7.35 and 7.45.
(a) They would like to recreate a similar buffer solution in the laboratory. In what proportions should they mix $0.150 \mathrm{~mol} \mathrm{dm}^{-3}$ solutions of carbonic acid and sodium hydrogen carbonate to give a buffer solution with a pH of 7.40 ? $\left(K_{\mathrm{a}}\right.$ for $\mathrm{H}_{2} \mathrm{CO}_{3}$ is $4.5 \times$ $10^{-7} \mathrm{~mol} \mathrm{dm}^{-3}$ ).
(b) Why do you think buffer solutions are needed in the human body?
$\qquad$
$\qquad$
$\qquad$

## More complex buffer calculations

Scientists wish to investigate whether certain bacteria can adapt to live in acidic conditions.

1. The scientists make up a buffer solution, by mixing $15.0 \mathrm{~cm}^{3}$ of a
$0.100 \mathrm{~mol} \mathrm{dm}^{-3}$ aqueous solution of NaOH with $35.0 \mathrm{~cm}^{3}$ of a
$0.150 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of propanoic acid. Calculate the pH of the buffer solution formed.
( $K_{\mathrm{a}}$ for propanoic acid has the value $1.35 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$ )
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(4 marks)
2. The scientists wish to test if the solution formed is indeed a buffer solution and will resist change in pH on the addition of small quantities of acid or base possibly formed by the bacteria. They take two separate $10 \mathrm{~cm}^{3}$ aliquots of the buffer solution formed in question 1 and add;
(a) $0.5 \mathrm{~cm}^{3}$ of a $0.05 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of hydrochloric acid to one of the aliquots, and
(b) $0.5 \mathrm{~cm}^{3}$ of a $0.05 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of calcium hydroxide to the other aliquot.

Calculate the pH of each of the new solutions formed.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

## Acids and bases - Answers

1. 

| Number $(\boldsymbol{n})$ | $\log _{10} \boldsymbol{n}$ |
| :--- | :--- |
| 0.001 | $\underline{-3}$ |
| 0.1 | $\underline{-1}$ |
| $\underline{1}$ | 0 |
| $\underline{1,000}$ | 3 |

2. (a) $\mathrm{pH}=10.00$
(b) $\mathrm{pH}=2.70$
(c) $\mathrm{pH}=2.46$
(3 marks, 1 mark for each correct answer given to 2 dp )
3. (a) lonisation of water is endothermic ( $\Delta \mathrm{H}+\mathrm{ive}$ ) so increasing the temperature will favour the forward reaction and hence the $[\mathrm{H}+(\mathrm{aq})]$ will increase. As a result the pH of the water will decrease as the temperature is increased.
(b)
(i) $10^{\circ} \mathrm{C}, K_{\mathrm{w}}=0.29 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6} ;\left[\mathrm{H}^{+}(\mathrm{aq})\right]=5.39 \times 10^{-8} \mathrm{~mol} \mathrm{dm}^{-3} \therefore \mathrm{pH}=7.27$
(ii) $25^{\circ} \mathrm{C}, K_{\mathrm{w}}=1.01 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6} ;\left[\mathrm{H}^{+}(\mathrm{aq})\right]=1.00 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3} \therefore \mathrm{pH}=7.00$
(iii) $40^{\circ} \mathrm{C}, K_{\mathrm{w}}=2.92 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6} ;\left[\mathrm{H}^{+}(\mathrm{aq})\right]=1.71 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3} \therefore \mathrm{pH}=6.77$
(3 marks)
(c) As the temperature decreases, water remains neutral

Water is always neutral as $\left[\mathrm{H}^{+}(\mathrm{aq})\right]=\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ and so there is always an equal number of $\mathrm{H}^{+}$ions and $\mathrm{OH}^{-}$ions.

## pH and acids

1. (a) $\mathrm{HCl} \rightarrow \mathrm{H}^{+}+\underline{\mathrm{Cl}^{-}}$
(b) $\mathrm{NH}_{4}^{+} \rightleftharpoons \mathrm{H}^{+}+\mathrm{NH}_{3}$
(c) $\quad \mathrm{HCO}_{3}^{-} \rightleftharpoons \mathrm{H}^{+}+{\underline{\mathrm{CO}_{3}}}^{2-}$
(3 marks)
2. (a) $\mathrm{pH}=-\log [0.25]=0.60$
(1 mark)
(b) $\quad K_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{SO}_{4}{ }^{2}\right]=\left[\mathrm{H}^{+}\right]^{2} \quad \therefore\left[\mathrm{H}^{+}\right]^{2}=\left(1.0 \times 10^{-2}\right) \times 0.004=4 \times 10^{-5}$ $\left[\mathrm{HSO}_{4}{ }^{-}\right] \quad\left[\overline{\mathrm{HSO}_{4}}\right] \quad\left[\mathrm{H}^{+}\right]=6.32 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=-\log \left[6.32 \times 10^{-3}\right]$
$\therefore \mathrm{pH}=2.20$
(1 mark for $K_{a}$ expression, 1 mark for pH )
3. (a) $\left[\mathrm{H}^{+}\right]=10^{-0.65} \therefore\left[\mathrm{H}^{+}\right]=0.22 \mathrm{~mol} \mathrm{dm}^{-3} \therefore[\mathrm{HCl}]=0.22 \mathrm{~mol} \mathrm{dm}^{-3} \quad$ (1 mark)
(b) $\quad\left[\mathrm{H}^{+}\right]=10^{-2.61} \quad \therefore\left[\mathrm{H}^{+}\right]=2.45 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
$\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow 2 \mathrm{H}^{+}+\mathrm{SO}_{4}{ }^{2-}$ and $\therefore\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]=\left[\mathrm{H}^{+}\right] / 2=\underline{1.23 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}}$
(1 mark)
(c) $\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-} \therefore \mathrm{K}_{\mathrm{a}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]=\left[\mathrm{H}^{+}\right]^{2}$
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right] \quad\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right], \therefore\left[\mathrm{H}^{+}\right]=10^{-3.40}, \therefore\left[\mathrm{H}^{+}\right]=3.98 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$
(1 mark)
$\therefore 1.7 \times 10^{-5}=\left[3.98 \times 10^{-4}\right]^{2} /\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$
$\therefore\left[\mathrm{CH}_{3} \mathrm{COOH}\right]=9.32 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$

## pH and bases

1. (a) A Brønsted-Lowry acid is a proton donor
(b) A Brønsted-Lowry base is a proton acceptor
2. (a) $2 \underline{N H}_{3}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow\left(\mathrm{NH}_{4}{ }^{+}\right)_{2} \mathrm{SO}_{4}{ }^{2-} \quad$ Basic species $=\underline{N H}_{3}$
(b) $\mathrm{Ca}(\underline{\mathrm{OH}})_{2}+\mathrm{H}_{2} \mathrm{CO}_{3} \rightarrow \mathrm{CaCO}_{3}+2 \mathrm{H}_{2} \mathrm{O} \quad$ Basic species $=\underline{\mathrm{OH}^{-}}$
(c) $\mathrm{Na}_{2}{\underline{\mathrm{CO}_{3}}}^{2}+2 \mathrm{HCl} \rightarrow 2 \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$ Basic species $={\underline{\mathrm{CO}_{3}}}^{2-}$
3. (a) $[\mathrm{NaOH}]=0.150 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\therefore\left[\mathrm{OH}^{-}\right]=0.150 \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore 1 \times 10^{-14}=\left[\mathrm{H}^{+}\right][0.150]$ and so, $\left[\mathrm{H}^{+}\right]=6.67 \times 10^{-14} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=-\log \left[6.67 \times 10^{-14}\right]=\underline{13.18}$
(b) $\left[\mathrm{Mg}(\mathrm{OH})_{2}\right]=0.261 \mathrm{~mol} \mathrm{dm}^{-3}$ and $\therefore\left[\mathrm{OH}^{-}\right]=0.261 \times 2=0.522 \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore 1 \times 10^{-14}=\left[\mathrm{H}^{+}\right][0.522]$ and so, $\left[\mathrm{H}^{+}\right]=1.92 \times 10^{-14} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=-\log \left[1.92 \times 10^{-14}\right]=\underline{13.72}$
4. (a) $11.00=-\log \left[\mathrm{H}^{+}\right]$and $\therefore\left[\mathrm{H}^{+}\right]=1.00 \times 10^{-11} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore 1.00 \times 10^{-14}=\left[1.00 \times 10^{-11}\right]\left[\mathrm{OH}^{-}\right]$and so, $\left[\mathrm{OH}^{-}\right]=1.00 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore[\mathrm{KOH}]=1.00 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$
(b) $10.45=-\log \left[\mathrm{H}^{+}\right]$and $\therefore\left[\mathrm{H}^{+}\right]=3.55 \times 10^{-11} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore 1.00 \times 10^{-14}=\left[3.55 \times 10^{-11}\right]\left[\mathrm{OH}^{-}\right]$and so, $\left[\mathrm{OH}^{-}\right]=2.82 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$
Since 1 mol of $\mathrm{Ca}(\mathrm{OH})_{2}$ contains $2 \mathrm{~mol} \mathrm{OH}^{-},\left[\mathrm{Ca}(\mathrm{OH})_{2}\right]=1.41 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$
(1 mark)
5. 




## Acid-base titrations



Titration number: $\begin{array}{lllll}1 & 2 & 3 & 4\end{array}$
Suitable indicator: phenolphthalein or methyl orange

Conc. of acid (if needed):

$$
\mathrm{NaOH}+\mathrm{HCl} \rightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}
$$

Moles in $25 \mathrm{~cm}^{3} 0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}=2.5 \times 10^{-3}$
Volume of HCl needed for neutralisation $=14 \mathrm{~cm}^{3}$
Conc. of $\mathrm{HCl}=2.5 \times 10^{-3} / 0.014 \mathrm{dm}^{3}=\underline{0.18 \mathrm{~mol} \mathrm{dm}^{-3}}$


Titration number: $\begin{array}{llll}1 & \underline{2} & 3 & 4\end{array}$
Suitable indicator: phenolphthalein
Conc. of acid (if needed):

$$
\mathrm{KOH}+\mathrm{HCOOH} \rightarrow \mathrm{HCOO}^{-} \mathrm{K}^{+}+\mathrm{H}_{2} \mathrm{O}
$$

Moles in $25 \mathrm{~cm}^{3} 0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{KOH}=2.5 \times 10^{-3}$
Volume of HCOOH needed for neutralisation $=42 \mathrm{~cm}^{3}$
Conc. of $\mathrm{HCOOH}=2.5 \times 10^{-3} / 0.042 \mathrm{dm}^{3}$

$$
=\underline{0.060 \mathrm{~mol} \mathrm{dm}^{-3}}
$$



Titration number: $\begin{array}{lllll}1 & 2 & \underline{3} & 4\end{array}$

Suitable indicator: methyl orange
Conc. of acid (if needed): N/A


Titration number: $\begin{array}{lllll}1 & 2 & 3 & 4\end{array}$
Suitable indicator: none
Conc. of acid (if needed): N/A
(1 mark for correct identification of each titration,
1 mark for each suitable indicator named,
1 mark for each calculation of acid concentration)

## Buffer solutions

1. (a) (i) $\mathrm{HCOOH}(\mathrm{aq}) \rightleftharpoons \mathrm{HCOO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})$
(ii) $\mathrm{p} K_{\mathrm{a}}=-\log K_{\mathrm{a}}, \therefore \underline{K}_{\mathrm{a}}=10^{-3.75}=1.78 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]\left[\mathrm{H}^{+}(\mathrm{aq})\right]}{[\mathrm{HCOOH}(\mathrm{aq})]}
$$

$\left[\mathrm{HCOO}^{-}(\mathrm{aq})\right]=0.450 \mathrm{~mol} / 0.5 \mathrm{dm}^{3}=0.90 \mathrm{~mol} \mathrm{dm}^{-3}$
$[\mathrm{HCOOH}(\mathrm{aq})]=0.510 \mathrm{~mol} / 0.5 \mathrm{dm}^{3}=1.02 \mathrm{~mol} \mathrm{dm}^{-3}$
Substituting these values in we get, $1.78 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}=0.90 \times\left[\mathrm{H}^{+}(\mathrm{aq})\right] / 1.02$
$\therefore\left[\mathrm{H}^{+}(\mathrm{aq})\right]=2.02 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=3.70$
(b) (i) On the addition of $\mathrm{H}^{+}$ions, according to Le Châtelier's principle, the equilibrium shifts to the left to remove the extra $\mathrm{H}^{+}$ions added and maintain the pH approximately constant.
(ii) On the addition of $\mathrm{OH}^{-}$ions, the $\mathrm{OH}^{-}$ions react with the HCOOH to produce water molecules and more $\mathrm{HCOO}^{-}$;

$$
\mathrm{HCOOH}+\mathrm{OH}^{-} \rightarrow \mathrm{HCOO}^{-}+\mathrm{H}_{2} \mathrm{O}
$$

This removes the $\mathrm{OH}^{-}$and so the pH remains approximately constant.
2. (a) $\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}) \rightleftharpoons \mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})$
pH of desired buffer $=7.40$, $\mathrm{so}\left[\mathrm{H}^{+}(\mathrm{aq})\right]=10^{-7.40}=3.98 \times 10^{-8} \mathrm{~mol} \mathrm{dm}^{-3}$

$$
\begin{aligned}
& K_{\mathrm{a}}=\frac{\left[\mathrm{HCO}_{3}^{-}(\mathrm{aq})\right]\left[\mathrm{H}^{+}(\mathrm{aq})\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})\right]} \\
& \therefore \quad \underset{\left[\mathrm{HCO}_{3}^{-}(\mathrm{aq})\right]}{[\mathrm{H} 2 \mathrm{CO} 3(\mathrm{aq})}=\frac{K}{[\mathrm{H}+(\mathrm{aq})]}=\frac{4.5 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3}}{3.98 \times 10-8 \mathrm{~mol} \mathrm{dm}-3}=\frac{11.3}{1}
\end{aligned}
$$

Since both stock solutions are of an equal concentration they should mix the two in a ratio of 11.3: $1 \mathrm{HCO}_{2}{ }^{-}: \mathrm{H}_{2} \mathrm{CO}_{3}$
(b) Many reactions in the human body rely on enzymes. Enzymes work only under very precise conditions. If the pH moves outside of a narrow range, the enzymes slow or stop working and can be denatured. Hence maintaining a constant pH is essential.

## More complex buffer calculations

1. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{NaOH} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-} \mathrm{Na}^{+}+\mathrm{H}_{2} \mathrm{O}$

Moles of $\mathrm{NaOH}=0.015 \mathrm{dm}^{3} \times 0.100 \mathrm{~mol} \mathrm{dm}^{-3}=1.5 \times 10^{-3} \mathrm{~mol}$
$\therefore$ moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$ will decrease by $1.5 \times 10^{-3} \mathrm{~mol}$ and moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-} \mathrm{Na}^{+}$ will increase by $1.5 \times 10^{-3} \mathrm{~mol}$.

Initial moles
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$

$0.035 \mathrm{dm}^{3} \times 0.150 \mathrm{~mol}$$\rightleftharpoons \quad$| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}$ | $+\mathrm{H}^{+}$ |
| :--- | :--- |
| 0 mol | 0 mol | $d m^{-3}$ $=5.25 \times 10^{-3} \mathrm{~mol}$

Change in $\quad-1.5 \times 10^{-3} \mathrm{~mol}$
$+1.5 \times 10^{-3} \quad ?$
moles
Equilibrium
$3.75 \times 10^{-3} \mathrm{~mol}$
mol
$1.5 \times 10^{-3} \mathrm{~mol}$ ? moles
$K_{\mathrm{a}}=\underset{\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}_{3}^{-}\right]\left[\mathrm{CH}^{+} \mathrm{COOH}\right]}{\left[\mathrm{CH}^{2}\right]}=\frac{\left(1.5 \times 10^{-3} \mathrm{~mol} / 0.05 \mathrm{dm}^{3}\right) \times\left[\mathrm{H}^{+}\right]=1.35 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}}{\left(3.75 \times 10^{-3} \mathrm{~mol} / 0.05 \mathrm{dm}^{3}\right)}$
$\therefore\left[\mathrm{H}^{+}\right]=3.38 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=4.47$
2. In a $10 \mathrm{~cm}^{3}$ aliquot ( $=1 / 5 \mathrm{th}$ ) of the buffer solution made above;
moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}=7.5 \times 10^{-4} \mathrm{~mol}$; moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}=3.0 \times 10^{-4} \mathrm{~mol}$
(a) No. of moles of acid added $=0.0005 \mathrm{dm}^{3} \times 0.05 \mathrm{~mol} \mathrm{dm}^{-3}=2.5 \times 10^{-5} \mathrm{~mol}$

$$
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}
$$

$\therefore$ moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$ will increase by $2.5 \times 10^{-5} \mathrm{~mol}$ and moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}$will decrease by $2.5 \times 10^{-5} \mathrm{~mol}$.
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH} \quad \rightleftharpoons \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{H}^{+}$

Initial moles
$7.5 \times 10^{-4} \mathrm{~mol}$
Change in moles $+2.5 \times 10^{-5} \mathrm{~mol}$
Equilibrium $\quad 7.75 \times 10^{-4} \mathrm{~mol}$
moles
$3.0 \times 10^{-4} \mathrm{~mol}$
$-2.5 \times 10^{-5} \mathrm{~mol}$ ?
$2.75 \times 10^{-4} \mathrm{~mol}$ ?
$\therefore 1.35 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}=\frac{\left(2.75 \times 10^{-4} \mathrm{~mol} / 0.0105 \mathrm{dm}^{3}\right) \times\left[\mathrm{H}^{+}\right]}{\left(7.75 \times 10^{-4} \mathrm{~mol} / 0.0105 \mathrm{dm}^{3}\right)}$
$\therefore\left[\mathrm{H}^{+}\right]=3.80 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=4.42$
(b) No. of moles of $\mathrm{Ca}(\mathrm{OH})_{2}$ added $=0.0005 \mathrm{dm}^{3} \times 0.05 \mathrm{~mol} \mathrm{dm}^{-3}=2.5 \times 10^{-5} \mathrm{~mol}$
$\therefore$ no. of moles of $\mathrm{OH}^{-}$added $=2 \times 2.5 \times 10^{-5} \mathrm{~mol}=5.0 \times 10^{-5} \mathrm{~mol}$
(1 mark)

## $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}+\mathrm{OH}^{-} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}$

$\therefore$ moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$ will decrease by $5.0 \times 10^{-5} \mathrm{~mol}$ and moles of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}$will increase by $5.0 \times 10^{-5} \mathrm{~mol}$.
(1 mark)

## $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COOH}$ <br> $\rightleftharpoons \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{COO}^{-}$ <br> $+\mathrm{H}^{+}$

Initial moles
$7.5 \times 10^{-4} \mathrm{~mol}$
$3.0 \times 10^{-4} \mathrm{~mol}$

| Change in moles | $-5.0 \times 10^{-5} \mathrm{~mol}$ |
| :---: | :---: |
|  | $+5.0 \times 10^{-5}$ |$?$

Equilibrium moles $7.0 \times 10^{-4} \mathrm{~mol}$
$3.5 \times 10^{-4} \mathrm{~mol}$
?
$\therefore 1.35 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}=\frac{\left(3.5 \times 10^{-4} \mathrm{~mol} / 0.0105 \mathrm{dm}^{3}\right) \times\left[\mathrm{H}^{+}\right]}{\left(7.0 \times 10^{-4} \mathrm{~mol} / 0.0105 \mathrm{dm}^{3}\right)}$
$\therefore\left[\mathrm{H}^{+}\right]=2.7 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$
$\therefore \mathrm{pH}=4.57$

