## Acids, Bases and Buffers

1(a). This question is about reactions and uses of the weak acids methanoic acid, HCOOH , and ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$.

The $K$ a values of HCOOH and $\mathrm{CH}_{3} \mathrm{COOH}$ are shown in Table 18.1.

| Weak acid | $\boldsymbol{K}_{\mathrm{a}} / \mathbf{~ m o l ~ d m}$ |
| :---: | :---: |
| $\mathbf{- 3}$ |  |
| HCOOH | $1.82 \times 10^{-4}$ |
| $\mathrm{CH}_{3} \mathrm{COOH}$ | $1.78 \times 10^{-5}$ |

Table 18.1

A student adds methanoic acid to ethanoic acid.
An equilibrium is set up containing two acid-base pairs.
Complete the equilibrium and label the conjugate acid-base pairs as A1, B1 and A2, B2.
$\mathrm{HCOOH}+\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons$ $\qquad$ $+$ $\qquad$
$\qquad$
(b). Use Table 18.1 to answer the following questions.
i. The student measures the pH of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ as 2.72.

Show that the concentration of the $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ is $0.204 \mathrm{~mol} \mathrm{dm}^{-3}$.
ii. The student plans to make a buffer solution of pH 4.00 from a mixture of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})$.

The student mixes $400 \mathrm{~cm}^{3}$ of $0.204 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ with $600 \mathrm{~cm}^{3}$ of $\mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})$.

Calculate the concentration of $\mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq})$ needed to prepare this buffer solution of pH 4.00.
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2. This question is about two different types of acid found in organic compounds, carboxylic acids and sulfonic acids, as shown in Fig. 6.1.

| R-C/ | O |
| :---: | :---: |
| OH | R |
| Carboxylic acid | Sulfonic acid |

Fig. 6.1
Ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, and methanesulfonic acid, $\mathrm{CH}_{3} \mathrm{SO}_{2} \mathrm{OH}$, are both monobasic acids. The $\mathrm{p} K_{\text {a }}$ values are shown in the table.

| Acid |  | $\mathbf{p} K_{\mathrm{a}}$ |
| :---: | :---: | :---: |
| Ethanoic acid | $\mathrm{CH}_{3} \mathrm{COOH}$ | 4.76 |
| Methanesulfonic acid | $\mathrm{CH}_{3} \mathrm{SO}_{2} \mathrm{OH}$ | -1.90 |

A student suggests that $1.0 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{SO}_{2} \mathrm{OH}$ should have a lower pH value than 1.0 mol $\mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}$.

Write an equation, showing conjugate acid-base pairs, for the equilibrium of $\mathrm{CH}_{3} \mathrm{SO}_{2} \mathrm{OH}$ with water and explain, with reasons, whether the student is correct.

Label the conjugate acid-base pairs: A1, B1 and A2, B2.
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$\qquad$

3(a). This question is about weak acids.
The $K_{a}$ values of three weak acids are shown in Table 20.1.

| Weak acid | $\boldsymbol{K}_{\mathrm{a}} / \mathbf{m o l ~ d m}^{\mathbf{- 3}}$ |
| :---: | :---: |
| iodic(V) acid, $\mathrm{HIO}_{3}(\mathrm{aq})$ | $1.78 \times 10^{-1}$ |
| propanoic acid, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})$ | $1.35 \times 10^{-5}$ |
| hydrocyanic acid, $\mathrm{HCN}(\mathrm{aq})$ | $6.17 \times 10^{-10}$ |

## Table 20.1

Calculate the pH of $0.0800 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})$.
Give your answer to 2 decimal places.

$$
\mathrm{pH}=
$$

[2]
(b). A student adds a total of $45.0 \mathrm{~cm}^{3}$ of $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}(\mathrm{aq})$ to $25.0 \mathrm{~cm}^{3}$ of $0.0800 \mathrm{~mol} \mathrm{dm}^{-3}$ $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})$ and monitors the pH throughout.
i. Show by calculation that $20.0 \mathrm{~cm}^{3}$ of $\mathrm{NaOH}(\mathrm{aq})$ is required to reach the end point.
ii. Calculate the pH of the final solution.

Give your answer to $\mathbf{2}$ decimal places.

$$
\mathrm{pH}=
$$

iii. On the axes below, sketch a pH curve for the pH changes during the addition of $45.0 \mathrm{~cm}^{3}$ of $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}(\mathrm{aq})$ to $25.0 \mathrm{~cm}^{3}$ of $0.0800 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})$.

iv. The student considers using the four indicators in Table 20.2 for the titration.

| Indicator | pH range |
| :---: | :---: |
| Cresol red | $0.2-1.8$ |
| Bromophenol blue | $3.0-4.6$ |
| Cresol purple | $7.6-9.2$ |
| Indigo carmine | $11.6-14.0$ |

Table 20.2

Explain which indicator would be most suitable for the titration.
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v. The student repeats the experiment starting with $25.0 \mathrm{~cm}^{3}$ of $0.0800 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HCN}(\mathrm{aq})$ and adding a total of $45.0 \mathrm{~cm}^{3}$ of $0.100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}(\mathrm{aq})$.

Predict one similarity and one difference between the pH curve with $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})$ and the pH curve with $\mathrm{HCN}(\mathrm{aq})$. Use the information in Table 20.1, and your answer to (b)(iii).

Similarity

Difference
$\qquad$
(c). The student calculates the pH of $0.0800 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HIO}_{3}(\mathrm{aq})$. The student assumes that the equilibrium concentration of $\mathrm{HIO}_{3}(\mathrm{aq})$ is the same as the initial concentration of $\mathrm{HIO}_{3}(\mathrm{aq})$.

The student measures the pH , and finds that the measured pH value is different from the calculated pH value.

Explain why the measured pH is different from the calculated pH .
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4. Healthy human blood needs to be maintained at a pH of 7.40 for the body to function normally.
*Carbonic acid, $\mathrm{H}_{2} \mathrm{CO}_{3}$, is a weak acid which, together with hydrogencarbonate ions, $\mathrm{HCO}_{3}{ }^{-}$, acts as a buffer to maintain the pH of blood.

The $\mathrm{p} K_{\mathrm{a}}$ value for the dissociation of carbonic acid is 6.38 .
Explain, in terms of equilibrium, how the carbonic acid-hydrogencarbonate mixture acts as a buffer in the control of blood pH , and calculate the $\left[\mathrm{HCO}_{3}{ }^{-}\right]$: $\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]$ ratio in healthy blood.
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5. A reaction is first order with respect to $\mathrm{H}^{+}$. At a pH of 1 , the initial rate is $2.4 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$. What is the initial rate at a pH of 3 ?
initial rate $=$ $\qquad$ $\mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}[1]$

6(a). Benzoic acid, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$, is added to some foods as a preservative.
A student prepares benzoic acid as outlined below.
The student mixes $4.00 \mathrm{~cm}^{3}$ of phenylmethanol, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{OH}$, (density $=1.04 \mathrm{~g} \mathrm{~cm}^{-3}$ )
Step 1 with sodium carbonate and aqueous potassium manganate(VII), as an oxidising agent. The mixture is heated under reflux.
Step 2 The resulting mixture is cooled and then acidified with concentrated HCI . Impure crystals of benzoic acid appear.
Step 3 The student recrystallises the impure crystals to obtain 1.59 g of pure benzoic acid.

In Step 1, sodium carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3}$, makes the reaction mixture alkaline.
Write an ionic equation to show how carbonate ions form an alkaline solution in water.
(b). In Step 2, explain why the mixture must be acidified so that crystals of benzoic acid appear.
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$\qquad$
(c). Write the overall equation for the preparation of benzoic acid from phenylmethanol.

Use [ O ] for the oxidising agent.
$\qquad$
(d). Calculate the percentage yield of benzoic acid.

Give your answer to 3 significant figures.
percentage yield $=$
\% [3]
(e). In Step 3, describe how the student can recrystallise the impure crystals to obtain pure benzoic acid.
$\qquad$
$\qquad$




$\qquad$
$\qquad$
7. This question is about organic reactions.

Compound $\mathbf{A}$ is formed when ethanal is mixed with $\mathrm{OH}^{-}(\mathrm{aq})$ ions, which act as a catalyst.
The balanced equation is shown in reaction 6.1 below.

i. Give the systematic name for compound $\mathbf{A}$.
ii. What type of reaction has taken place?
iii. Reaction 6.1 takes place in two steps. $\mathrm{OH}^{-}$ions act as a catalyst.

In step 1, ethanal reacts with $\mathrm{OH}^{-}$ions to set up an acid-base equilibrium. In step 2, compound $\mathbf{A}$ is formed.
. Complete the equilibrium for step 1 and label the conjugate acid-base pairs as:
A1, B1 and A2, B2.

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$\qquad$
$\qquad$

- Suggest the equation for step 2.
iv. A similar reaction takes place when propanone, $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CO}$, is mixed with $\mathrm{OH}^{-}(\mathrm{aq})$ ions.

Draw the structure of the organic product of this reaction.

8(a). This question is about acids and bases found in the home.
Ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, is the acid present in vinegar.
A student carries out an experiment to determine the $\mathrm{p} K_{a}$ value of $\mathrm{CH}_{3} \mathrm{COOH}$.

- The concentration of $\mathrm{CH}_{3} \mathrm{COOH}$ in the vinegar is $0.870 \mathrm{~mol} \mathrm{dm}^{-3}$.
- $\quad$ The pH of the vinegar is 2.41.
i. Write the expression for the acid dissociation constant, $K$ a, of $\mathrm{CH}_{3} \mathrm{COOH}$.
ii. Calculate the $\mathrm{p} K_{a}$ value of $\mathrm{CH}_{3} \mathrm{COOH}$.

Give your answer to two decimal places.
$\mathrm{p} K_{\mathrm{a}}=$
iii. Determine the percentage dissociation of ethanoic acid in the vinegar.

Give your answer to three significant figures.
percentage dissociation $=$
\% [1]
(b). Many solid drain cleaners are based on sodium hydroxide, NaOH .

- A student dissolves 1.26 g of a drain cleaner in water and makes up the solution to 100.0
$\mathrm{cm}^{3}$.
- The student measures the pH of this solution as 13.48 .

Determine the percentage, by mass, of NaOH in the drain cleaner.
Give your answer to three significant figures.

9(a). This question is about the properties and reactions of ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$. Ethanoic acid is a weak acid with an acid dissociation constant, $K_{\mathrm{a}}$, of $1.75 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$ at 25 ${ }^{\circ} \mathrm{C}$.

A student uses a pH meter to measure the pH of a solution of $\mathrm{CH}_{3} \mathrm{COOH}$ at $25^{\circ} \mathrm{C}$.
The measured pH is 2.440 .
Calculate the concentration of ethanoic acid in the solution.
Give your answer to three significant figures.
concentration $=$ $\qquad$ $\mathrm{mol} \mathrm{dm}^{-3}$ [3]
(b). Ethanoic acid is a weak acid with an acid dissociation constant, $K_{\mathrm{a}}$, of $1.75 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$ at 25 ${ }^{\circ} \mathrm{C}$.

Ethanoic acid is added to another weak acid, fluoroethanoic acid, $\mathrm{FCH}_{2} \mathrm{COOH}\left(K_{\mathrm{a}}=2.19 \times 10^{-3}\right.$ mol dm ${ }^{-3}$ ).
An equilibrium is set up containing two acid-base pairs.
Complete the equilibrium and label the conjugate acid-base pairs as A1, B1 and A2, B2.

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{FCH}_{2} \mathrm{COOH} \leftrightharpoons
$$

$\qquad$
$+$
(c). The student plans to prepare a buffer solution that has a pH of 4.50. The buffer solution will contain ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, and sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}$.

The student plans to add $9.08 \mathrm{~g} \mathrm{CH}_{3} \mathrm{COONa}$ to $250 \mathrm{~cm}^{3}$ of $0.800 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}$. The student assumes that the volume of the solution does not change.
i. Show by calculation whether, or not, the student's experimental method would produce the required pH .

Show all your working.
ii. When the student prepares the buffer solution, the volume of solution increases slightly.

Suggest whether the pH of the buffer solution would be the same, greater than, or less than your calculated value in (c)(i).

Explain your reasoning.
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$\qquad$

10. This question is about organic molecules that have a strong smell.

Thiols are foul-smelling, organic sulfur compounds with the functional group -SH.
Butane-1-thiol, shown below, contributes to the strong smell of skunks.

i. Thiols are weak acids.

Write the expression for the acid dissociation constant, $K_{\mathrm{a}}$, for butane-1- thiol.
ii. Thiols react with carboxylic acids to form thioesters.

Write an equation for the reaction of butane-1-thiol with ethanoic acid.
Use structures for all organic compounds with the functional groups clearly displayed.
iii. When beer is exposed to light, 3-methylbut-2-ene-1-thiol is formed, which gives an unpleasant smell and flavour to the beer.

Draw the skeletal formula for 3-methylbut-2-ene-1-thiol.
iv. Propane-1,3- dithiol reacts with carbonyl compounds in a condensation reaction to form a cyclic organic sulfur product.

Write an equation for the reaction of propane-1,3-dithiol with propanone.
Use structures for organic compounds.
11. When concentrated sulfuric acid is added to water, dissociation takes place in two stages.

Stage 1: $\quad \mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \mathrm{H}^{+}+\mathrm{HSO}_{4}^{-}$
Stage 2: $\mathrm{HSO}_{4}{ }^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{SO}_{4}{ }^{2-}$
i. $\quad 0.100 \mathrm{~mol} \mathrm{dm}^{-3}$ sulfuric acid has a pH of 0.96 .

Explain this observation. Your answer should include a calculation.
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$\qquad$
$\qquad$

$\qquad$
$\qquad$
ii. A student adds an excess of aqueous sodium carbonate to dilute sulfuric acid.

- Predict what the student would observe.
- Explain what happens to the equilibrium in Stage 2 as the aqueous sodium carbonate is added.

Observation

Explanation
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$\qquad$
$\qquad$
$\qquad$

12(a). This question is about vitamin $\mathrm{C}, \mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6}$.
Vitamin $C$ is a weak monobasic acid with a $K_{a}$ value of $6.76 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.
i. Write the expression for $K_{\mathrm{a}}$ for vitamin C.
ii. Calculate $\mathrm{p} K_{\mathrm{a}}$ for vitamin C , to two decimal places.
iii. A bottle of vitamin C supplements contains tablets, each containing 500 mg of vitamin C .

A student dissolves three vitamin C tablets in water and makes up the solution to a volume of $250.0 \mathrm{~cm}^{3}$.

Calculate the pH of the solution.
Give your answer to two decimal places.
$\mathrm{pH}=$
(b). Low acidity vitamin C tablets are less acidic than tablets containing just vitamin C .

A student dissolves a low acidity vitamin $C$ tablet in water.

- The tablet contains a mixture of 300 mg of vitamin $\mathrm{C}, \mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6}$, and the sodium salt of vitamin $\mathrm{C}, \mathrm{C}_{6} \mathrm{H}_{7} \mathrm{O}_{6} \mathrm{Na}$.
- The pH of the solution is 4.02 .
i. Calculate the ratio $\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{O}_{6}{ }^{-}: \mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6}$ in the solution.

Show your working.

$$
\frac{\left[\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{O}_{6}{ }^{-}\right]}{\left[\mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6}\right]}=\frac{\ldots \ldots \ldots \ldots \ldots \ldots \ldots}{1}
$$

ii. Calculate the mass of $\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{O}_{6} \mathrm{Na}$, in mg, in the low acidity vitamin C tablet.

> mass =
mg [1]
(c). The sodium salt of vitamin $C$ can be made by reacting vitamin $C$ with aqueous sodium hydroxide. An aqueous solution of sodium hydroxide had a pH of 12.72 at 298 K .

Calculate the concentration, in $\mathrm{mol} \mathrm{dm}^{-3}$, of the NaOH solution.
concentration $=$ $\qquad$ $\mathrm{mol} \mathrm{dm}^{-3}$ [2]

13(a). A chemist carries out some experiments using nitrous acid, $\mathrm{HNO}_{2}(\mathrm{aq})$.
$\mathrm{HNO}_{2}$ is a weak acid with a $K_{\mathrm{a}}$ value of $4.69 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$ at the temperature of the chemist's experiments.

Write the expression for $K_{\mathrm{a}}$ for $\mathrm{HNO}_{2}(\mathrm{aq})$.
(b). Calculate the pH of $0.120 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HNO}_{2}(\mathrm{aq})$.

Give your answer to two decimal places.
(c). The chemist prepares $1 \mathrm{dm}^{3}$ of a buffer solution by mixing $200 \mathrm{~cm}^{3}$ of $0.200 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HNO}_{2}$ with $800 \mathrm{~cm}^{3}$ of $0.0625 \mathrm{~mol} \mathrm{dm}^{-3}$ sodium nitrite, $\mathrm{NaNO}_{2}$.
i. Calculate the pH of the buffer solution.

Give your answer to two decimal places.
$\mathrm{pH}=$
ii. Explain how this buffer solution controls pH when:

- a small amount of $\mathrm{HC} /(\mathrm{aq})$ is added
- a small amount of $\mathrm{NaOH}(\mathrm{aq})$ is added.

In your answer, include the equation for the equilibrium in the buffer solution and explain how this equilibrium system controls the pH .
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$\qquad$
(d). The dissociation of water is shown below.
$\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
At $60^{\circ} \mathrm{C}$, the ionic product of water, $K_{\mathrm{w}}$, is $9.311 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$.
At $25^{\circ} \mathrm{C}$, the ionic product of water, $K_{\mathrm{w}}$, is $1.000 \times 10^{-14} \mathrm{~mol}^{2} \mathrm{dm}^{-6}$.
i. Explain whether the dissociation of water is an exothermic or endothermic process.
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$\qquad$
$\qquad$
ii. Predict, using a calculation, whether a pH of 7 at $60^{\circ} \mathrm{C}$ is neutral, acidic or alkaline.
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$\qquad$
iii. $\mathrm{p} K_{\mathrm{w}}, \mathrm{pKa}$ and pH are logarithmic scales.

Calculate $\mathrm{p} K_{\mathrm{w}}$ at $60^{\circ} \mathrm{C}$.
Give your answer to two decimal places.

$$
\mathrm{p} K_{\mathrm{w}}=
$$

iv. $\quad 20.0 \mathrm{~cm}^{3}$ of $0.0270 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$ is diluted with water and the solution made up to 100 $\mathrm{cm}^{3}$ at $60^{\circ} \mathrm{C}$.

Calculate the pH of the diluted solution of NaOH at $60^{\circ} \mathrm{C}$.
Give your answer to two decimal places.
14. Three redox systems, C, D and $\mathbf{E}$ are shown in Table 6.1.

| $\mathbf{C}$ | $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}+(\mathrm{aq})+\mathrm{e}^{-} \rightleftharpoons \mathrm{Ag}(\mathrm{s})+2 \mathrm{NH}_{3}(\mathrm{aq})$ |
| :--- | :---: |
| $\mathbf{D}$ | $\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{e}^{-} \rightleftharpoons \mathrm{Ag}(\mathrm{s})$ |
| $\mathbf{E}$ | $\mathrm{Ag}(\mathrm{CN})_{2}^{-}(\mathrm{aq})+\mathrm{e}^{-} \rightleftharpoons \mathrm{Ag}(\mathrm{s})+2 \mathrm{CN}^{-}(\mathrm{aq})$ |

Table 6.1
The two cells below were set up in an experiment to compare the standard electrode potentials of redox systems $\mathbf{C}, \mathbf{D}$ and $\mathbf{E}$. The signs on each electrode are shown.


The $\mathrm{CN}^{-}$ion is the conjugate base of a very toxic weak acid.
In aqueous solutions of $\mathrm{CN}^{-}$ions, an acid-base equilibrium is set up.
i. Complete the equation for this equilibrium and label the conjugate acid-base pairs.

ii. Explain, in terms of equilibrium, why acidic conditions should not be used with cells containing $\mathrm{CN}^{-}(\mathrm{aq})$ ions.
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15(a). A student is supplied with $0.500 \mathrm{~mol} \mathrm{dm}^{-3}$ potassium hydroxide, KOH , and $0.480 \mathrm{~mol} \mathrm{dm}^{-3}$ propanoic acid, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$.

The acid dissociation constant, $K_{\mathrm{a}}$, for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ is $1.35 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.
$\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ is a weak Brønsted-Lowry acid.
What is meant by a weak acid and Brønsted-Lowry acid?
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$\qquad$
(b). Calculate the pH of $0.500 \mathrm{~mol} \mathrm{dm}^{-3}$ potassium hydroxide.

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\mathrm{pH}=
$$

(c). The student dilutes $25.0 \mathrm{~cm}^{3} 0.480 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ by adding water until the total volume is $100.0 \mathrm{~cm}^{3}$.
i. Write the expression for $K_{a}$ for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$.
ii. Calculate the pH of the diluted solution.

$$
\mathrm{pH}=
$$

(d). A student prepares a buffer solution containing propanoic acid $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ and propanoate ions,
$\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}$. The concentrations of $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ and $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}$are both $1.00 \mathrm{~mol} \mathrm{dm}^{-3}$.
The following equilibrium is set up.

$$
\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq}) \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq})
$$

The acid dissociation constant, $K_{\mathrm{a}}$, for $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}$ is $1.35 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.
i. Calculate the pH of this buffer solution.

Give your answer to two decimal places.

$$
\mathrm{pH}=
$$

ii. A small amount of aqueous ammonia, $\mathrm{NH}_{3}(\mathrm{aq})$, is added to the buffer solution.

Explain, in terms of equilibrium, how the buffer solution would respond to the added $\mathrm{NH}_{3}(\mathrm{aq})$.
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$\qquad$
iii. The student adds 6.075 g Mg to $1.00 \mathrm{dm}^{3}$ of this buffer solution.

Calculate the pH of the new buffer solution.
Give your answer to two decimal places

16(a). Ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, is a weak Brønsted-Lowry acid.
An acid-base equilibrium is set up when ethanoic acid is added to water.
Write the equation for the equilibrium that would be set up and label the two conjugate acidbase pairs.
$\qquad$ $+$ $\qquad$ $\rightleftharpoons$ $\qquad$ $+$ $\qquad$
(b). An aqueous solution of $\mathrm{CH}_{3} \mathrm{COOH}$ has a pH of 3.060 .

This solution contains both hydrogen ions and hydroxide ions.
i. How can an aqueous solution of an acid contain hydroxide ions?
$\qquad$
$\qquad$
ii. Calculate the concentration of hydroxide ions in this solution of ethanoic acid.
concentration of hydroxide ions =
$\qquad$ $\mathrm{mol} \mathrm{dm}^{-3}$ [2]
(c). A student adds an excess of aqueous ethanoic acid to solid calcium carbonate. The resulting solution is able to act as a buffer solution.
i. Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.
$\qquad$
ii. Explain why this buffer solution has formed.
$\qquad$
$\qquad$
iii. Explain how this buffer solution controls pH when either an acid or an alkali is added.

In your answer you should explain how the equilibrium system allows the buffer solution to control the pH .
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$\qquad$
(d). A biochemist plans to make up a buffer solution with a pH of 5.000.

The biochemist adds solid sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}$, to $400 \mathrm{~cm}^{3}$ of $0.200 \mathrm{~mol} \mathrm{dm}^{-3}$ ethanoic acid.
$K_{a}$ for ethanoic acid $=1.75 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$
Calculate the mass of sodium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

Assume that the volume of the solution remains constant at $400 \mathrm{~cm}^{3}$ on dissolving the sodium ethanoate.

17(a). This question is about different weak acids.
A student carries out a titration to determine the concentration of a solution of ethanoic acid.
The method is outlined below.

- A $25.0 \mathrm{~cm}^{3}$ sample of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ is pipetted into a conical flask.
- The $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ is titrated by adding $0.125 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$ from a burette.
- The pH of the solution is measured continuously, with stirring, as the $\mathrm{NaOH}(\mathrm{aq})$ is added.

The pH titration curve is shown below.

i. How could the student measure the pH continuously as the $\mathrm{NaOH}(\mathrm{aq})$ is added?
ii. Determine the unknown concentration, in $\mathrm{mol} \mathrm{dm}^{-3}$, of the $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$. Show your working.
concentration of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})=$ $\qquad$ mol dm ${ }^{-3}$ [2]
(b). The table shows the pH ranges of four indicators.

| Indicator | congo red | methyl red | brilliant yellow | alizarin yellow R |
| :---: | :---: | :---: | :---: | :---: |
| pH range | $3.0-5.0$ | $4.4-6.2$ | $6.6-7.8$ | $10.1-12.0$ |

i. Choose, with a reason, the indicator from the table that is most suitable for the student's titration in (a).
$\qquad$
ii. An indicator is a weak acid, HA, which has a different colour from its conjugate base, $\mathrm{A}^{-}$.

For methyl red, the HA form is red and the $\mathrm{A}^{-}$form is yellow.
The structure of methyl red is shown below.


Draw the structure of the conjugate base of methyl red and explain, in terms of equilibrium, the colours of methyl red at low pH , at high pH , and at the end point of a titration. You can use HA and $\mathrm{A}^{-}$in your explanation.
explanation: $\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(c). Aspirin is a weak acid with a $p K_{a}$ value of 3.40 and a solubility in water of $1.00 \times 10^{-2} \mathrm{~g} \mathrm{~cm}^{-3}$ at body temperature $\left(37^{\circ} \mathrm{C}\right)$.

The equation for the dissociation of aspirin in aqueous solution is shown below.

i. Calculate the pH of a saturated solution of aspirin in water at body temperature.
$\mathrm{pH}=$ [4]
ii. 'Soluble aspirin' is usually sold as the sodium or calcium salt of aspirin.

Suggest why salts of aspirin are more soluble than aspirin in water.
$\qquad$
$\qquad$
$\qquad$
iii. The stomach contains hydrochloric acid at a pH of about 1-3.

Explain why swallowing soluble aspirin may lead to irritation of the stomach lining.
$\qquad$
$\qquad$
$\qquad$
$\qquad$

18(a). A student investigates the reactions of two weak monobasic acids: 2-hydroxypropanoic acid, $\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}$, and butanoic acid, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOH}$.

The student wants to prepare a standard solution of 2-hydroxypropanoic acid that has a pH of 2.19 .

Plan how the student could prepare $250 \mathrm{~cm}^{3}$ of this standard solution from solid 2hydroxypropanoic acid.

In your answer you should provide detail of the practical procedure that would be carried out, including appropriate quantities and necessary calculations.
$K_{a}$ for 2-hydroxypropanoic acid is $1.38 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$ at $25^{\circ} \mathrm{C}$.
$\qquad$
$\qquad$
$\qquad$

$\qquad$
$\qquad$
(b). 2-Hydroxypropanoic acid is a slightly stronger acid than butanoic acid. The two acids are mixed together and an acid-base equilibrium is set up.

Suggest the equilibrium equation and identify the conjugate acid-base pairs.
$\mathrm{CH}_{3} \mathrm{CH}(\mathrm{OH}) \mathrm{COOH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COOH} \rightleftharpoons$ $\qquad$
(c). To prepare a buffer solution, $75.0 \mathrm{~cm}^{3}$ of $0.220 \mathrm{~mol} \mathrm{dm}^{-3}$ butanoic acid is reacted with $50.0 \mathrm{~cm}^{3}$ of $0.185 \mathrm{~mol} \mathrm{dm}^{-3}$ sodium hydroxide.
$K_{a}$ for butanoic acid is $1.5 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$ at $25^{\circ} \mathrm{C}$.
i. Calculate the pH of $0.185 \mathrm{~mol} \mathrm{dm}^{-3}$ sodium hydroxide at $25^{\circ} \mathrm{C}$.

Give your answer to two decimal places.
ii. Calculate the pH of the buffer solution at $25^{\circ} \mathrm{C}$.

Give your answer to two decimal places.
Show all your working.
$\mathrm{pH}=$
19. Methanoic acid is added to water. An acid-base equilibrium is set up containing two acid-base pairs.

Suggest a mechanism for the forward reaction in this equilibrium.

Your mechanism should use displayed formulae and curly arrows, and show all species present at equilibrium.
20. The complex ion, $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$, behaves as a weak Brønsted-Lowry acid in aqueous solution. The equation below represents the dissociation of aqueous $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ ions, together with the $K_{a}$ value.

$$
\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}(\mathrm{aq}) \rightleftharpoons\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{OH}\right]^{2+}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \quad K_{\mathrm{a}}=6.00 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}
$$

i. Write the expression for the acid dissociation constant, $K_{\mathrm{a}}$, for $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$
ii. Calculate the pH of a $0.100 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ to two decimal places.
$\mathrm{pH}=$
21. The dissociation of water is measured by the ionic product of water, $K_{w}$. The value of $K_{w}$ varies with temperature as shown in the graph below.


Calculate the pH of water at body temperature, $37^{\circ} \mathrm{C}$.
$\mathrm{pH}=$ $\qquad$ [3]

22(a). This question is about acids and bases.
Nitric acid, $\mathrm{HNO}_{3}$, and nitrous acid, $\mathrm{HNO}_{2}$, are two Brønsted-Lowry acids containing nitrogen.
A student measures the pH of $0.0450 \mathrm{~mol} \mathrm{dm}^{-3}$ solutions of $\mathrm{HNO}_{3}$ and $\mathrm{HNO}_{2}\left(\mathrm{pK} \mathrm{K}_{\mathrm{a}}=3.35\right)$ and found that the acids had different pH values.
i. Explain why the pH values are different.
$\qquad$
$\qquad$
ii. Calculate the pH value of $0.0450 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HNO}_{3}$ to two decimal places.

Show your working.
$\mathrm{pH}=$
iii. Calculate the pH value of $0.0450 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HNO}_{2}$ to two decimal places.

### 5.1.3 Acids, Bases and Buffers

Show your working.
$\mathrm{pH}=$
[3]
(b). Rubidium hydroxide, RbOH , is a strong alkali. A technician is asked to prepare a $250.0 \mathrm{~cm}^{3}$ solution of RbOH with a pH of 12.500 .

Calculate the mass of RbOH that the technician needs to use.

