

Answers to Practice Questions

1 (a) $\text{pH} = -\lg [\text{H}^+]$

$$[\text{H}^+] = 10^{-3.50} = \underline{\underline{3.16 \times 10^{-4} \text{ mol dm}^{-3}}}$$

(b) $\text{HA}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaA}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$$n_{\text{NaOH}} \text{ reacted} = n_{\text{HA}} \text{ present in apple juice} = \frac{27.50}{1000} \times 0.100 = 2.75 \times 10^{-3} \text{ mol}$$

$$[\text{HA}] \text{ in apple juice} = \frac{2.75 \times 10^{-3}}{25.0} \times 1000 = 0.110 \text{ mol dm}^{-3}$$

Since $[\text{H}^+] \ll [\text{HA}]$, the acid HA in apple juice undergoes only **partial dissociation** and is therefore a **weak acid**.

(c) $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$

$$\begin{aligned} \text{degree of dissociation of HA} &= \frac{n_{\text{HA}} \text{ dissociated in } 1 \text{ dm}^3 \text{ of apple juice}}{\text{initial } n_{\text{HA}} \text{ in } 1 \text{ dm}^3 \text{ of apple juice}} \\ &= \frac{3.16 \times 10^{-4}}{0.110} = \underline{\underline{2.87 \times 10^{-3}}} \end{aligned}$$

$$\begin{aligned} \text{At equilibrium, } [\text{H}_3\text{O}^+] &= [\text{A}^-] = 3.16 \times 10^{-4} \text{ mol dm}^{-3} \\ [\text{HA}] &= 0.110 - 3.16 \times 10^{-4} = 0.1097 \text{ mol dm}^{-3} \end{aligned}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(3.16 \times 10^{-4})^2}{0.1097} = \underline{\underline{9.10 \times 10^{-7} \text{ mol dm}^{-3}}}$$

(d) Since both acids have the same pH (3.50), both acids have the same $[\text{H}^+]$. However, partial dissociation occurs in apple juice, hence the total acid concentration is higher (than hydrochloric acid).

$$[\text{HCl}] = [\text{H}^+] = 3.16 \times 10^{-4} \text{ mol dm}^{-3}$$

From (b): $[\text{HA}] \text{ in apple juice} = 0.110 \text{ mol dm}^{-3}$

In 1 dm^3 , the sample of apple juice will have a greater amount of acid present. Since the volume of H_2 to be produced is proportional to the amount of acid present and a **greater amount of acid** is present in the sample of apple juice, the **apple juice** sample would yield a larger volume of hydrogen gas than the hydrochloric acid sample.

2 (a) (i) $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$

$$\begin{aligned} \text{At equilibrium, } [\text{H}^+] &= [\text{CH}_3\text{COO}^-] \\ [\text{CH}_3\text{COOH}]_{\text{eqm}} &\approx [\text{CH}_3\text{COOH}]_{\text{initial}} = 0.50 \text{ mol dm}^{-3}, \\ &\text{since } \text{CH}_3\text{COOH} \text{ is a weak acid with a small } K_a \end{aligned}$$

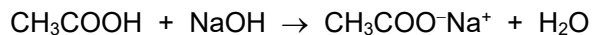
$$\begin{aligned} K_a &= \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]} \\ [\text{H}^+] &= \sqrt{K_a \times [\text{CH}_3\text{COOH}]} = \sqrt{10^{-4.74} \times 0.50} = 3.016 \times 10^{-3} \text{ mol dm}^{-3} \\ \text{pH} &= -\lg(3.016 \times 10^{-3}) = \underline{\underline{2.52}} \end{aligned}$$

(ii) Let volume of CH_3COOH used be $V \text{ dm}^3$.

$$\text{Initial } n_{\text{CH}_3\text{COOH}} = 0.50V \text{ mol}$$

$$\text{Initial } n_{\text{NaOH}} = 0.20V \text{ mol}$$

Upon mixing, the following reaction takes place:



Hence CH_3COOH is in excess.

$$n_{\text{CH}_3\text{COO}^-} \text{ formed} = n_{\text{NaOH}} \text{ reacted} = 0.20V \text{ mol}$$

$$\text{Unreacted } n_{\text{CH}_3\text{COOH}} = 0.50V - 0.20V = 0.30V \text{ mol}$$

$\Rightarrow$ The resultant solution is a buffer.

$$\text{pH of resultant solution} = \text{p}K_a + \lg \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.74 + \lg \left(\frac{0.20V}{0.30V} \right) = \underline{\underline{4.56}}$$

(b) (i) $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$

CH_3COO^- undergoes hydrolysis in water to form OH^- , which causes the solution to be alkaline and pH is above 7. (Note: $[\text{OH}^-] > [\text{H}_3\text{O}^+]$)

$$(ii) K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{10^{-4.74}} = \underline{\underline{5.50 \times 10^{-10} \text{ mol dm}^{-3}}}$$

(iii) $\text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq})$

At equilibrium,

$$[\text{OH}^-] = [\text{CH}_3\text{COOH}]$$

$$[\text{CH}_3\text{COO}^-]_{\text{eqm}} \approx [\text{CH}_3\text{COO}^-]_{\text{initial}} = 0.050 \text{ mol dm}^{-3},$$

since CH_3COO^- is a weak base with a small K_b

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{[\text{OH}^-]^2}{[\text{CH}_3\text{COO}^-]}$$

$$[\text{OH}^-] = \sqrt{K_b \times [\text{CH}_3\text{COO}^-]} = \sqrt{5.50 \times 10^{-10} \times 0.050} = 5.242 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\lg(5.242 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14 - 5.28 = \underline{\underline{8.72}}$$

(c) Let the volume of $\text{CH}_3\text{COO}^-\text{Na}^+(\text{aq})$ needed be $V \text{ dm}^3$.

Amount of $\text{CH}_3\text{COO}^- = V \times 0.10 = 0.10 V \text{ mol}$.

Amount of $\text{CH}_3\text{COOH} = 0.025 \times 0.12 = 0.0030 \text{ mol}$

$$\text{pH of resultant solution} = \text{p}K_a + \lg \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$5.00 = 4.74 + \lg \left(\frac{0.10V}{\frac{0.0030}{V_{\text{total}}}} \right)$$

$$\lg \left(\frac{0.10V}{0.0030} \right) = 0.26$$

$$V = 10^{0.26} \times \frac{0.0030}{0.10} = \underline{\underline{0.0546 \text{ dm}^3}} = \underline{\underline{54.6 \text{ cm}^3}}$$

3 (a) The resultant solution is a buffer.

$$n_{\text{NH}_4^+} \text{ present} = \frac{750}{1000} \times 0.20 = 0.15 \text{ mol}$$

$$n_{\text{NH}_3} \text{ present} = \frac{500}{1000} \times 0.10 = 0.05 \text{ mol}$$

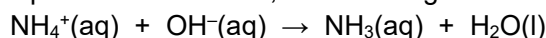
At equilibrium in the resultant solution, $[\text{NH}_4^+]_{\text{eqm}} \approx [\text{NH}_4^+]_{\text{initial}}$ and $[\text{NH}_3]_{\text{eqm}} \approx [\text{NH}_3]_{\text{initial}}$

$$\text{p}K_b = -\lg \left(\frac{K_w}{K_a} \right) = -\lg \left(\frac{1.0 \times 10^{-14}}{6.00 \times 10^{-10}} \right) = 4.778$$

$$\text{pOH of resultant solution} = \text{p}K_b + \lg \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.778 + \lg \left(\frac{0.15}{\frac{0.05}{V_{\text{total}}}} \right) = 4.778 + \lg \frac{0.15}{0.05} = 5.255$$

$$\text{pH} = 14 - 5.255 = 8.745 = \underline{\underline{8.75}}$$

(b) (i) Upon addition of OH^- , the following reaction occurs:



$$n_{\text{NH}_4^+} \text{ present in resultant solution} = 0.15 - 0.002 = 0.148 \text{ mol}$$

$$n_{\text{NH}_3} \text{ present in resultant solution} = 0.05 + 0.002 = 0.052 \text{ mol}$$

The resultant solution is still a buffer.

$$\text{pOH of resultant solution} = \text{p}K_b + \lg \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 4.778 + \lg \left(\frac{0.148}{\frac{0.052}{V_{\text{total}}}} \right) = 4.778 + \lg \frac{0.148}{0.052} = 5.232$$

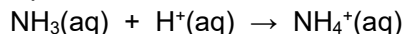
$$\text{pH} = 14 - 5.232 = 8.768$$

$$\text{Change in pH} = 8.768 - 8.745 = \underline{\underline{+0.023}}$$

⇒ There is an **increase in pH of 0.023 units**.

$$(ii) \ n_{H^+} \text{ added} = \frac{1.0}{1000} \times 2.00 = 0.002 \text{ mol}$$

Upon addition of H^+ , the following reaction occurs:



$$n_{NH_4^+} \text{ present in resultant solution} = 0.15 + 0.002 = 0.152 \text{ mol}$$

$$n_{NH_3} \text{ present in resultant solution} = 0.05 - 0.002 = 0.048 \text{ mol}$$

The resultant solution is still a buffer.

$$pOH \text{ of resultant solution} = pK_b + \lg \frac{[NH_4^+]}{[NH_3]} = 4.778 + \lg \left(\frac{0.152}{0.048} \right) = 4.778 + \lg \frac{0.152}{0.048} = 5.279$$

$$pH = 14 - 5.279 = 8.721$$

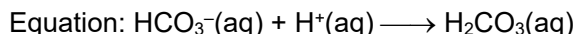
$$\text{Change in pH} = 8.721 - 8.745 = \underline{-0.024}$$

⇒ There is a **decrease in pH of 0.024 units**.

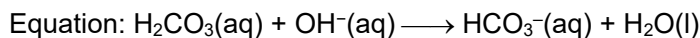
- 4 (a) A buffer solution is a solution which is able to **resist changes in pH** when a **small amount** of an acid or a base is added.

The buffer in blood plasma consists of a mixture of $H_2CO_3(aq)$ and $HCO_3^-(aq)$.

When $[H^+]$ increases, by Le Chatelier's Principle, the equilibrium position of $H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ shift to the left to partially offset the increase in $[H^+]$ by favouring the backward reaction of the equilibrium, resulting in a small decrease in pH.



When $[OH^-]$ increases, by Le Chatelier's Principle, the equilibrium position of $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$ shift to the left to partially offset the increase in $[OH^-]$ by favouring the backward reaction of the equilibrium, resulting in a small increase in pH.



(b) Method 1:

$$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$$7.90 \times 10^{-7} = \frac{[HCO_3^-][10^{-7.40}]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{7.90 \times 10^{-7}}{10^{-7.40}} = \underline{19.8}$$

Method 2:

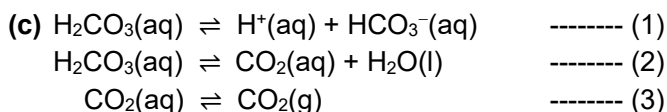
$$pH = pK_a + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$7.40 = -\lg(7.90 \times 10^{-7}) + \lg \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{(7.40 + \lg(7.90 \times 10^{-7}))} = \underline{19.8}$$

Since $[HCO_3^-]$ is higher than $[H_2CO_3]$, the buffer solution is **more effective in resisting pH changes when there is a small increase in the amount of acid (H^+)** than when there is a small increase in the amount of base (OH^-).

[Note: This is probably due to the fact that many reactions in the body produce H^+ and hence the buffer in the blood is required to be more able to resist increase in the amount of H^+ rather than OH^- .]



When lactic acid is released into blood, $[H^+]$ in blood increases. In accordance to Le Chatelier's principle, the equilibrium position of reaction (1) shifts to the left to decrease $[H^+]$. This leads to an increase in the $[H_2CO_3]$.

This increase in the $[H_2CO_3]$ causes the equilibrium position of reaction (2) to shift to the right, resulting in an increase in $[CO_2(aq)]$.

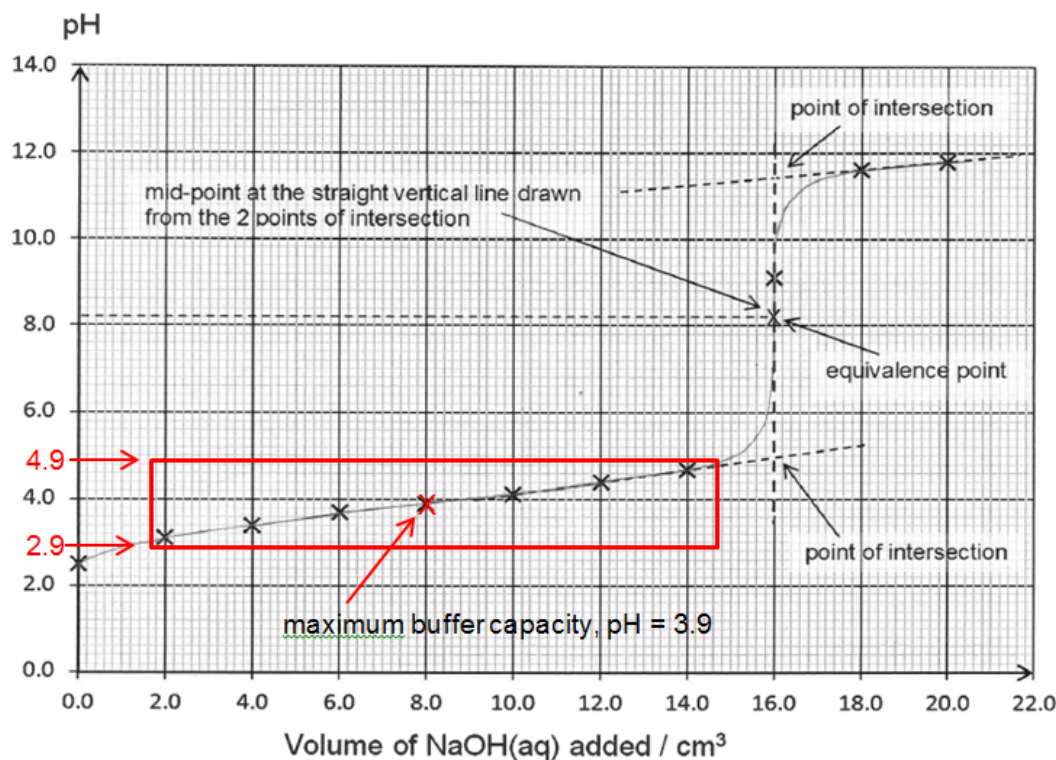
This in turn causes the equilibrium position of reaction (3) to shift right, causing an increase in $[CO_2(g)]$.

When $[CO_2(g)]$ increases, this causes the rate of exhaling $CO_2(g)$ to increase. Thus, the rate of breathing increases as well.

5 (Ans: D)

Option A	Incorrect. The correct pH of the buffer solution is: $pH = pK_a + \lg \frac{[\text{lactate}]}{[\text{lactic acid}]} = -\lg(1.4 \times 10^{-4}) + \lg \frac{0.5}{1.5} = 3.38$
Option B	Incorrect. Upon dilution with some water, the pH of the buffer solution should remain the same as the amount of lactic acid and sodium lactate in the buffer solution remains unchanged (although their concentrations decrease). $pH = pK_a + \lg \frac{[\text{lactate}]}{[\text{lactic acid}]} = pK_a + \lg \frac{n(\text{lactate}) / V_{\text{buffer}}}{n(\text{lactic acid}) / V_{\text{buffer}}} = pK_a + \lg \frac{n(\text{lactate})}{n(\text{lactic acid})}$ (If the buffer solution is infinitely diluted with water, the $[H^+]$ in the buffer solution tends towards that of pure water (i.e. $10^{-7} \text{ mol dm}^{-3}$) and pH increases and approaches 7.) Hence, pH of the buffer solution will not decrease upon dilution with water.
Option C	Incorrect. Buffering capacity depends on the amount of lactic acid and sodium lactate in the buffer solution. Since the amount of lactic acid and sodium lactate in the buffer solution remains unchanged upon dilution, the buffering capacity remains the same.
Option D	Correct. Since the buffer solution has a greater amount of lactic acid (weak acid) than the lactate ions (conjugate base), the buffer solution is more effective in buffering the effect of addition of small amounts of base than acid.

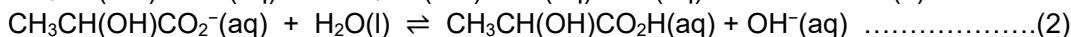
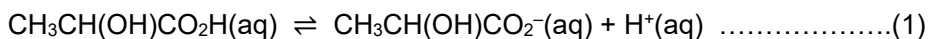
6 (a)



[Note: marking out the equivalence point on the graph is not required]

The two major organic species are $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$ and $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2^-$.

In the solution, the following equilibria exist,

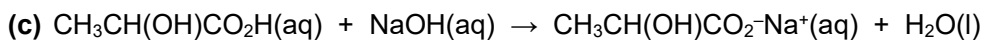


When a small amount of OH^- ions is added to the solution, concentration of OH^- increases. By Le Chatelier's Principle, the position of equilibrium 2 shift to the left to partially offset the increase in concentration of OH^- by favouring the backward reaction of the equilibrium, resulting in a small increase in pH.

(b) (i) **Thymol blue (or thymolphthalein)** may be used for this **weak acid–strong base titration**.

Its **pH range** (around pH 8.0 – 9.6, or 9.4 – 10.6 for thymolphthalein) **coincides** with the region of the **rapid pH change** (about pH 7.5 – 10.5) of the titration. Thus it will **change colour sharply** when near the equivalence point.

(ii) The colour change will be from **yellow to green (or colourless to light blue for thymolphthalein)**.



From the graph, volume of NaOH required to reach equivalence point = **16.00 cm³**

$$n_{\text{lactic acid present}} = n_{\text{NaOH used for neutralisation}} = \frac{16.00}{1000} \times 0.050 = 8.00 \times 10^{-4} \text{ mol}$$

$$[\text{lactic acid}] = \frac{8.00 \times 10^{-4}}{10.0} \times 1000 = \underline{\mathbf{0.0800 \text{ mol dm}^{-3}}}$$

[Note: Accept all sensible answers (e.g. 15.80 cm³) based on the titration curve drawn. Some titration curves will be drawn without a vertical straight line portion.]

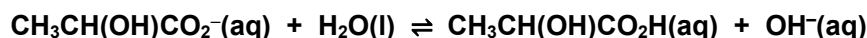
- (d) From (c), volume of NaOH needed to neutralise half of the lactic acid present = (1/2)(16.00) = **8.00 cm³**

When 8.00 cm³ of NaOH is added, the resultant solution is a buffer with maximum buffer capacity, i.e. [CH₃CH(OH)CO₂H] = [CH₃CH(OH)CO₂⁻] and **pH = pK_a = 3.9**.

$$\text{Hence } K_a = 10^{-3.9} = \underline{\mathbf{1.26 \times 10^{-4} \text{ mol dm}^{-3}}}$$

- (e) At the equivalence point of the titration, the resultant solution is **CH₃CH(OH)CO₂⁻Na⁺(aq)**.

Being the conjugate base of a weak acid, CH₃CH(OH)CO₂⁻ **undergoes hydrolysis to produce OH⁻ ions.**



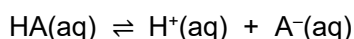
The OH⁻ ions generated by the hydrolysis reaction causes the solution to be basic.

- (f) See the graph in (a).

[Note: Effective buffer range is pK_a ± 1 i.e. from pH 2.9 to 4.9.]

- 7 (a) C₆H₅CO₂H(aq) ⇌ C₆H₅CO₂⁻(aq) + H⁺(aq)

- (b) Let HA denote C₆H₅CO₂H.



At equilibrium, [H⁺] = [A⁻]
 [HA]_{eqm} ≈ [HA]_{initial} = 0.010 mol dm⁻³,
 since benzoic acid is a weak acid with a small K_a

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]^2}{[\text{HA}]}$$

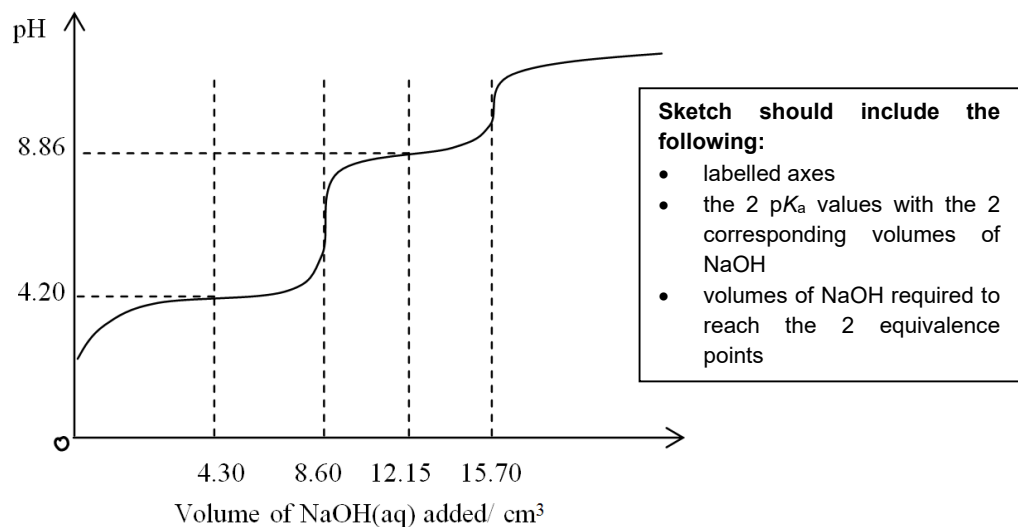
$$[\text{H}^+] = \sqrt{K_a \times [\text{HA}]} = \sqrt{10^{-4.20} \times 0.010} = 7.943 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg(7.943 \times 10^{-4}) = \underline{\mathbf{3.10}}$$

- (c) Benzoic acid is a **stronger acid** than phenylboronic acid.

This is because benzoic acid has a **smaller pK_a** (or a larger K_a) than phenylboronic acid, which indicates that benzoic acid **dissociates to a greater extent** in aqueous solution.

(d) (i) A sketch of the titration curve.



(ii) When the first indicator changes colour, benzoic acid (the stronger acid) is completely neutralised.

$$n_{\text{benzoic acid present}} = n_{\text{NaOH used for neutralisation}} = \frac{8.6}{1000} \times 0.050 = 4.30 \times 10^{-4} \text{ mol}$$

$$[\text{benzoic acid}] \text{ in X} = \frac{4.30 \times 10^{-4}}{10.0} \times 1000 = \underline{\underline{0.0430 \text{ mol dm}^{-3}}}$$

$$n_{\text{phenylboronic acid present}} = n_{\text{NaOH used for neutralisation}} = \frac{7.1}{1000} \times 0.050 = 3.55 \times 10^{-4} \text{ mol}$$

$$[\text{phenylboronic acid}] \text{ in X} = \frac{3.55 \times 10^{-4}}{10.0} \times 1000 = \underline{\underline{0.0355 \text{ mol dm}^{-3}}}$$