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- 1 a) $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ [1]
Pair 1: acid – H_2O ; base – OH^- [1]
Pair 2: acid – NH_4^+ ; base – $\text{NH}_3(\text{aq})$ [1]
- b) Sodium chloride is the salt of a strong acid. [1] The chloride ion is a very weak base and does not take protons from water molecules so a solution of sodium chloride is neutral. [1]
Sodium ethanoate is a salt of a weak acid. [1] The ethanoate ion is a strong enough base to take protons from water molecules to produce an alkaline solution with OH^- ions. [1]
- c) The pH of a solution of a weak acid depends on both the concentration of the acid and its degree of ionisation. [1] The acid dissociation constant is an equilibrium constant [1] that applies at all equilibrium mixtures at a given temperature. [1]
- 2 a) $\text{HX}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{X}^-(\text{aq})$ [1]
- b) $K_a = \frac{[\text{H}^+(\text{aq})][\text{X}^-(\text{aq})]}{[\text{HX}(\text{aq})]}$ (1)
- c) i) As the temperature rises the equilibrium shifts in the direction that is endothermic. So the acid ionises more as the temperature rises and this is because the value of K_a increases. [1]
ii) Since the acid ionises more as the temperature rises, the hydrogen ion concentrations rises and the pH decreases. [1]
iii) K_a does not change. K_a is a constant and only varies if the temperature changes. [1]
- 3 a) In water: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$ [1]
 $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$ [1]
- b) i) $[\text{H}^+(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ [1]
Also, in pure water $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$
So: $[\text{OH}^-(\text{aq})] = 1 \times 10^{-7} \text{ mol dm}^{-3}$ [1]
Hence $K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
- ii) The value of K_w becomes more positive as the temperature rises, which means that at a higher temperature the equilibrium shifts to the right, increasing the concentration of hydrogen and hydroxide ions. [1]
This shows that the ionisation of water is endothermic. [1]
- c) i) $[\text{H}^+(\text{aq})] \times 0.30 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
 $[\text{H}^+(\text{aq})] = 3.33 \times 10^{-14} \text{ mol dm}^{-3}$ [1]
 $\text{pH} = 13.48$ [1]
- ii) After dilution $[\text{OH}^-(\text{aq})] = 0.030 \text{ mol dm}^{-3}$ [1]
 $[\text{H}^+(\text{aq})] = 33.33 \times 10^{-14} \text{ mol dm}^{-3}$ [1]
 $\text{pH} = 12.48$ [1]

- ii) Amount of NaOH added to the mixture

$$= \frac{25}{1000} \text{ dm}^3 \times 0.30 \text{ mol dm}^{-3} = 0.0075 \text{ mol [1]}$$

Amount of HCl added to the mixture

$$= \frac{75}{1000} \text{ dm}^3 \times 0.20 \text{ mol dm}^{-3} = 0.0150 \text{ mol [1]}$$

Volume of the solution = 100 cm^3

$$[\text{H}^+(\text{aq})] = 7.5 \times 10^{-2} \text{ mol dm}^{-3} \text{ [1]}$$

$$\text{pH} = 1.12 \text{ [1]}$$

- 4 a) A strong acid ionises completely in aqueous solution. [1]

An example is hydrochloric acid: $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ [1]

A weak acid only ionises to a slight extent in solution. [1]

An example is ethanoic acid: $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$ [1]

- b) i) 2 [1]

- ii) $[\text{OH}^-(\text{aq})] = 0.01 \text{ mol dm}^{-3}$

$$[\text{H}^+(\text{aq})] = \frac{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{0.01 \text{ mol dm}^{-3}} = 1 \times 10^{-12} \text{ mol dm}^{-3} \text{ [1]}$$

$$\text{pH} = 12 \text{ [1]}$$

- c) i) $[\text{H}^+(\text{aq})] = \sqrt{(1.5 \times 10^{-5} \times 0.020)} \text{ mol dm}^{-3}$ [1]

$$\text{pH} = 3.26 \text{ [1]}$$

- ii) Line of sketch graph rises at first from $\text{pH} = 3.3$; partly levels off through buffer region [1]; then rises to give a steeply rising curve when the titre is 25 cm^3 [1]; halfway up the steeply rising portion is above $\text{pH} 7$ [1]; the curve then levels off at about $\text{pH} 12$. [1]

- iii) Thymolphthalein [1]; full colour change must take place within the steeply rising part of the curve. [1]

- 5 a) This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully sustained line of reasoning. Assess the quality of the answer taking into account both the key points made (*up to 4 marks*) and the logic and coherence of the discussion (*up to 2 marks*).

Points to make in the answer:

- a buffer solution evens out the large swings in pH on adding small amounts of acid or alkali which can happen without a buffer
- a typical buffer mixture consists of a solution of a weak acid and one of its salts, for example a mixture of ethanoic acid and sodium ethanoate
- there must be plenty of both the acid and its salt in the buffer mixture
- adding a small amount of strong acid temporarily increases the concentration of $\text{H}^+(\text{aq})$ so the equilibrium shifts to the left to counteract the change

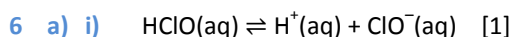
- adding a small amount of strong alkali temporarily decreases the concentration of $\text{H}^+(\text{aq})$ so the equilibrium shifts to the right to counteract the change
- the pH of blood, for example, is closely controlled by buffers within the narrow range 7.35 to 7.45; or chemists use buffers when they want to investigate chemical reactions at a fixed pH.

$$\begin{aligned} \text{b) i) } [\text{H}^+(\text{aq})] &= 1.7 \times 10^{-5} \text{ mol dm}^{-3} \times \frac{0.080 \text{ mol dm}^{-3}}{0.040 \text{ mol dm}^{-3}} [1] \\ &= 3.40 \times 10^{-5} \text{ mol dm}^{-3} \\ \text{pH} &= 4.47 [1] \end{aligned}$$

$$\begin{aligned} \text{ii) } [\text{H}^+(\text{aq})] &= 1.7 \times 10^{-5} \text{ mol dm}^{-3} \times \frac{0.06 \text{ mol dm}^{-3}}{0.06 \text{ mol dm}^{-3}} [1] \\ &= 1.7 \times 10^{-5} \text{ mol dm}^{-3} \\ \text{pH} &= 4.77 [1] \end{aligned}$$

$$\begin{aligned} \text{iii) } [\text{H}^+(\text{aq})] &= \frac{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{0.02 \text{ mol dm}^{-3}} \\ &= 5.0 \times 10^{-12} \text{ mol dm}^{-3} [1] \\ \text{pH} &= 11.30 [1] \end{aligned}$$

- iv) The change of pH is very much less when adding the alkali to a buffer solution than when adding it to water. [1]



$$\text{ii) } K_a = \frac{[\text{H}^+(\text{aq})][\text{ClO}^-(\text{aq})]}{[\text{HClO}(\text{aq})]} [1]$$

$$\begin{aligned} \text{b) } [\text{H}^+(\text{aq})] &= 10^{-7.43} [1] = 3.7 \times 10^{-8} \text{ mol dm}^{-3} [1] \\ K_a &= \frac{(3.7 \times 10^{-8} \text{ mol dm}^{-3})(0.050 \text{ mol dm}^{-3})}{0.050 \text{ mol dm}^{-3}} [1] \\ &= 3.7 \times 10^{-8} \text{ mol dm}^{-3} [1] \end{aligned}$$

- 7 a) i) 10 cm³ of the acid reacts with 10 cm³ of 0.01 mol dm⁻³ solution of sodium hydroxide. [1]
The acid is monobasic. So the acid concentration is 0.01 mol dm⁻³. [1]

ii) At the start pH = 3.5 [1]

- iii) Acid is weak. For a 0.01 mol dm⁻³ monobasic strong acid, pH = 2 [1]

$$\begin{aligned} \text{b) } \text{p}K_a &= 2\text{pH} + \log c_A = (7 - 2) = 5 [1] \\ K_a &= 1 \times 10^{-5} \text{ mol dm}^{-3} [1] \end{aligned}$$

- c) i) The pH did not rise fast between titres of 2.5 cm⁻³ and 7.5 cm⁻³. [1] In this region the flask contains the partly neutralised weak acid and the salt formed by neutralising the acid. [1] This series of mixtures of the acid and its conjugate base are buffer solutions. [1]

ii) Halfway to the end-point, [acid] = [salt] and pH = pK_a. [1]

From the graph pK_a = 5.0 [1]

Hence K_a = 1 × 10⁻⁵ mol dm⁻³

- d) i) The equivalence point is at pH = 8.5, which is halfway up the near vertical part of the curve. [1]
- ii) At the equivalence point the flask contains a solution of the sodium salt of a weak acid. The anion in the salt is the conjugate base of the weak acid. [1] If an acid is weak its conjugate base is relatively strong and so gives an alkaline solution in water. [1]
- 8 a) i) $[H^+(aq)] = \sqrt{1.5 \times 10^{-5} \text{ mol dm}^{-3} \times 0.1 \text{ mol dm}^{-3}} = 1.23 \times 10^{-3} \text{ mol dm}^{-3}$ [1]
pH = 2.91 [1]
- ii) Trichloroethanoic acid: $[H^+(aq)] = \sqrt{2.3 \times 10^{-1} \text{ mol dm}^{-3} \times 0.1 \text{ mol dm}^{-3}} = 0.15 \text{ mol dm}^{-3}$ [1]
pH = 0.82 [1]
- b) i) Fluoroethanoic acid > chloroethanoic acid > iodoethanoic acid > ethanoic acid [1]
- ii) Substituting an electronegative atom [1] on the carbon atom next to the –COOH group makes the acid stronger. [1] The more electronegative the atom, the greater the effect. [1] A possible explanation is that the electronegative atom pulls electrons away from the carboxylic acid group so that it holds onto to its proton less strongly. [1]
- c) i) Trichloroethanoic acid > dichloroethanoic acid > chloroethanoic acid > ethanoic acid [1]
- ii) This is consistent with (b) (ii). Increasing the number of electronegative atoms [1] pulling electrons away from the carboxylic acid group [1] increases the strength of the acid.
- d) i) 2-chlorobutanoic acid > 3-chlorobutanoic acid > 4-chlorobutanoic acid > butanoic acid [1]
- ii) Substituting electronegative chlorine atoms into the hydrocarbon chain increases the acid strength of butanoic acid. [1] However, the effect falls away as the chlorine atom gets further from the carboxylic acid group. [1] The effect is most marked when the chlorine atom is on the carbon atom next to the –COOH group. [1]
- 9 a) Use an insulated container: polystyrene cup or vacuum flask. [1]
- b) This question assesses a student's ability to show a coherent and logically structured answer with linkages and fully sustained line of reasoning. Assess the quality of the answer taking into account both the key points made (*up to 4 marks*) and the logic and coherence of the discussion (*up to 2 marks*).
- Points to make in the answer:
- In the mixtures with 0 cm³ to 67 cm³ NaOH(aq), the acid was in excess.
 - The reaction is exothermic.
 - The more alkali there is in these mixtures, the more the energy is given out and the greater the temperature rise.
 - In the mixtures with 67 cm³ to 100 cm³ NaOH(aq), the alkali was in excess.
 - The more acid there is in these mixtures, the more energy is given out and the greater the temperature rise.
 - So there are two rising lines meeting at the point corresponding to exact neutralisation.

- c) i) 67 cm^3 of 2.0 mol dm^{-3} NaOH(aq) reacts with 33 cm^3 of the 2.0 mol dm^{-3} acid. [1]
ii) 2 mol NaOH reacts with 1 mol of the acid. [1] The acid is dibasic, H_2X . [1]
- d) i) 16 K [1]
ii) Energy given out = $100 \text{ g} \times 16 \text{ K} \times 4.18 \text{ J g}^{-1} \text{ K}^{-1}$ [1]
 $= 6690 \text{ J} = 6.69 \text{ kJ}$ [1]
iii) Amount of acid in the mixture = $0.033 \text{ dm}^3 \times 2 \text{ mol dm}^{-3} = 0.066 \text{ mol}$ [1]
Energy change per mole of the acid (exothermic) = $6.69 \text{ kJ} \div 0.066 \text{ mol} = 102 \text{ kJ mol}^{-1}$ [1]
 $\Delta_r H^\ominus = -102 \text{ kJ mol}^{-1}$
- iv) For the neutralisation of a monobasic acid $\Delta H^\ominus \approx -57.5 \text{ kJ mol}^{-1}$. [1] The value for H_2X is much less than twice this value. This suggests a weak acid. [1]