HL Paper 2

Chloroethene, C₂H₃Cl, is an important organic compound used to manufacture the polymer poly(chloroethene).

d.i.State an equation for the reaction of ethanoic acid with water.	[1]
d.iiCalculate the pH of $0.200~{ m mol}{ m dm}^{-3}$ ethanoic acid $({ m p}K_{ m a}=4.76).$	[3]
e. Determine the pH of a solution formed from adding 50.0 cm^3 of $1.00 \text{ mol } \text{dm}^{-3}$ ethanoic acid, $\text{CH}_3\text{COOH}(\text{aq})$, to 50.0 cm^3 of $0.600 \text{ mol } \text{dm}^{-3}$ sodium hydroxide, NaOH(aq).	[4]
f. (if acid added) ${ m CH_3COO^-} + { m H^+} ightarrow { m CH_3COOH};$	[2]
(if alkali added) $ m CH_3COOH+OH^- ightarrow m CH_3COO^-+H_2O;$	

Explanation marks cannot be awarded without equations.

Markscheme

d.i. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^{-}(aq) + H_3O^{+}(aq);$

OR

 $CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq);$

 $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq);$

Must include \rightleftharpoons .

Ignore state symbols.

d.ii(ii) $K_{\mathrm{a}} = 10^{-4.76}/1.74 imes 10^{-5}/\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log rac{\mathrm{[SALT]}}{\mathrm{[ACID]}};$

$$egin{aligned} 1.74 imes 10^{-5} &= rac{[\mathrm{H}^+]^2}{0.200}/[\mathrm{H}^+] = 0.00187; \ \mathrm{pH} = 2.73; \end{aligned}$$

Award [3] for correct final answer, allow mark for correct conversion of [H⁺] to pH even if [H⁺] incorrect.

e. (initial) $[CH_3COOH]=0.500\ mol\ dm^{-3}$ and) eqm $[CH_3COOH]=0.200\ mol\ dm^{-3};$

(initial) $[CH_3COO^-] = 0.300 \text{ mol } dm^{-3}$ and) eqm $[CH_3COO^-] = 0.300 \text{ mol } dm^{-3}$;

Allow 0.02 moles and 0.03 moles instead of 0.200 and 0.300.

$$[{
m H}^+] = K_{
m a} rac{[{
m CH}_3{
m COOH}]}{[{
m CH}_3{
m COO}^-]} = 1.16 imes 10^{-5}~{
m mol}~{
m dm}^{-3};$$

pH = 4.94;

Award [3 max] for correct final answer if no working shown.

f. [N/A]

Examiners report

d.i. The only issue was that some candidates forgot the reversible arrow in the equation.

d.iiA pleasing number were able to complete the pH calculation successfully.

- e. Only the best candidates scored full marks for the buffer calculation; in some cases an incorrect expression was used, but more often there was no attempt to calculate the equilibrium amounts or concentrations.
- f. There were very few who could write appropriate equations for the buffer action, even though it clearly stated that the answer should include equations many explained buffer action without any equations and scored no marks as a result.

An equilibrium exists between nitrosyl chloride, NOCI, nitrogen oxide, NO, and chlorine, Cl2.

$$2$$
NOCl(g) $\Rightarrow 2$ NO(g) + Cl₂(g)

 20.0 cm^3 of hexane, C_6H_{14} , and 20.0 cm^3 of pentan-1-ol, $C_5H_{11}OH$, were placed separately into two closed containers at 298 K and allowed to reach equilibrium.

Ammonia is a weak base.

(ii)

- a. (i) Deduce the equilibrium constant expression for this reaction.
 - Explain the effect on the position of equilibrium and the value of $K_{\rm c}$ when pressure is decreased and temperature is kept constant.

(iii) 2.00 mol of NOCI was placed in a 1.00 dm^3 container and allowed to reach equilibrium at 298 K. At equilibrium, 0.200 mol of NO was present. Determine the equilibrium concentrations of NOCI and Cl_2 , and hence calculate the value of K_c at this temperature.

- (iv) The value of K_c is 1.60×10^{-5} at 318 K. State and explain whether the forward reaction is exothermic or endothermic.
- b. (i) Compare the two liquids in terms of their boiling points, enthalpies of vaporization and vapour pressures.

[4]

(ii) Explain your answer given for part (b)(i).

c.i. Calculate the pH of a $1.50~{ m moldm^{-3}}$ solution of ammonia at 298 K to two decimal places, using Table 15 of the Data Booklet.	[2]
c.ii A buffer solution is made using $25.0~{ m cm}^3$ of $0.500~{ m mol}{ m dm}^{-3}$ hydrochloric acid, HCl (aq), and $20.0~{ m cm}^3$ of $1.50~{ m mol}{ m dm}^{-3}$ ammonia solution,	[2]
$\mathrm{NH}_3(\mathrm{aq}).$	
Describe the meaning of the term buffer solution.	
c.iiiDetermine the pH of the buffer solution at 298 K.	[4]
c.ivA $1.50~{ m mol}{ m dm}^{-3}$ solution of ammonia is added to $25.0~{ m cm}^3$ of a $0.500~{ m mol}{ m dm}^{-3}$ hydrochloric acid solution in a titration experiment.	[1]
Calculate the total volume of the solution at the equivalence point.	
c.v.Calculate the pH of the solution at the equivalence point, using Table 15 of the Data Booklet.	[4]
c.vildentify a suitable indicator for this titration, using Table 16 of the Data Booklet.	[1]

Markscheme

a. (i)
$$(K_{
m c}=)rac{[{
m Cl}_2({
m g})][{
m NO}({
m g})]^2}{[{
m NOCl}({
m g})]^2};$$

Ignore state symbols.

(ii) equilibrium shifts to right as there are more moles (of gas) on product side;

no change to $K_{\rm c}$ as it is a constant at fixed temperature / OWTTE;

(iii)
$$[NOCl(g)] = 1.80 \ (mol \ dm^{-3});$$

$$[\mathrm{Cl}_2(\mathrm{g})] = 0.100 \; (\mathrm{mol} \, \mathrm{dm}^{-3});$$

$$K_{
m c} = \left(rac{0.100 imes (0.200)^2}{\left(1.80
ight)^2}
ight) 1.23 imes 10^{-3} \ ({
m mol} \, {
m dm}^{-3});$$

Award [3] for correct final answer.

- (iv) exothermic as K_c is lower at higher temperature;
- b. (i) hexane has lower boiling point and enthalpy of vaporization than pentan-1-ol / OWTTE;

hexane has higher vapour pressure than pentan-1-ol / OWTTE;

(ii) hexane is non-polar / has only van der Waals'/London/dispersion forces / has weaker intermolecular forces than pentan-1-ol;

pentan-1-ol has hydrogen bonding between molecules;

$$\text{c.i.}\left[\mathrm{OH^{-}}\right] = \sqrt{1.50 \times 1.78 \times 10^{-5}} = 5.17 \times 10^{-3} \; (\mathrm{mol} \, \mathrm{dm^{-3}});$$

$$pH = (14 - pOH = 14 - 2.29 =) 11.71;$$

Award [2] for correct final answer.

Accept correct answer with more than 2 decimal places.

c.ii.solution which resists change in pH / changes pH slightly / OWTTE;

when small amounts of acid or base are added;

$$\begin{split} \mathsf{c.iii}[\mathrm{NH}_3] = \; \left(\frac{(1.50 \times 0.0200) - (0.500 \times 0.0250)}{0.0450} = \right) \; 0.389 \; (\mathrm{mol} \; \mathrm{dm}^{-3}); \\ [\mathrm{NH}_4^+] = \; \left(\frac{(0.500 \times 0.0250)}{0.0450} = \right) \; 0.278 \; (\mathrm{mol} \; \mathrm{dm}^{-3}); \end{split}$$

$$egin{aligned} [\mathrm{OH}^-] &= \left(rac{K_b[\mathrm{NH}_3]}{[\mathrm{NH}_4^+]} =
ight) \; rac{1.78 imes 10^{-5} imes 0.389}{0.278} = 2.49 imes 10^{-5} \; (\mathrm{mol} \, \mathrm{dm}^{-3}); \ \mathrm{pH} &= (14.0 - \mathrm{pOH} = 14.0 - 4.60 =) \; 9.40; \end{aligned}$$

OR

$$egin{aligned} \mathrm{pOH} &= \mathrm{p}K_b + \lograc{[\mathrm{NH}_4^+]}{[\mathrm{NH}_3]} = \mathrm{p}K_b + \lograc{(12.5/1000)}{(17.5/1000)}; \ \mathrm{pOH} &= 4.75 + \log\Bigl(rac{12.5}{17.5}\Bigr) = 4.75 - 0.146 = 4.604; \ \mathrm{pH} &= 14.0 - 4.604 = 9.40; \end{aligned}$$

Award [4] for the correct final answer.

$${
m c.iv}\Big({
m V(NH_3)} = rac{25.0 imes 0.500}{1.50} = 8.33~{
m cm}^3\Big)$$

 ${
m V} = {
m V(NH_3)} + {
m V(HCl)} = 8.33 + 25.0 = 33.3~{
m cm}^3/0.0333~{
m dm}^3;$

 $\texttt{c.v.}(NH_4^+ \text{ ions are present at equivalence point } NH_3 + HCl \rightarrow NH_4^+ + Cl^- \text{ at equivalence } n(NH_4^+ \text{ produced}) = n(NH_3 \text{ added}) = n(HCl))$

$$\begin{split} [\mathrm{NH}_4^+] &= \frac{0.500 \times 0.0250}{0.0333} = 0.375 \; (\mathrm{mol} \; \mathrm{dm}^{-3}); \\ (\mathrm{NH}_4^+(\mathrm{aq}) &\rightleftharpoons \mathrm{NH}_3(\mathrm{aq}) + \mathrm{H}^+(\mathrm{aq})/\mathrm{NH}_4^+(\mathrm{aq}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}_3(\mathrm{aq}) + \mathrm{H}_3\mathrm{O}^+(\mathrm{aq}) \\ \mathrm{p}K_{\mathrm{a}}(\mathrm{NH}_4^+) &= 14 - \mathrm{p}K_{\mathrm{b}}(\mathrm{NH}_3) = 14.00 - 4.75 = 9.25) \\ K_{\mathrm{a}} &= \frac{[\mathrm{NH}_3(\mathrm{aq})][\mathrm{H}^+(\mathrm{aq})]}{[\mathrm{NH}_4^+(\mathrm{aq})]} = 5.62 \times 10^{-10}; \\ [\mathrm{H}^+(\mathrm{aq})] &= \sqrt{5.62 \times 10^{-10} \times 0.375} = 1.45 \times 10^{-5} \; (\mathrm{mol} \; \mathrm{dm}^{-3}); \\ \mathrm{pH} &= 4.84; \end{split}$$

Award [4] for the correct final answer.

c.vibromocresol green / methyl red;

ECF for answer in 7(c)(v) if pH given is below 7.

Examiners report

a. The construction and use of equilibrium expressions for K_c showed good understanding. The prediction of the effect of increasing pressure on the position of equilibria by applying Le Chatelier's principle was good, but the fact that K_c remains constant at fixed temperatures was less well known.

pH calculations in c(i), c(ii) and c(v) tended to be very good or completely incorrect.

b. The construction and use of equilibrium expressions for K_c showed good understanding. The prediction of the effect of increasing pressure on the position of equilibria by applying Le Chatelier's principle was good, but the fact that K_c remains constant at fixed temperatures was less well known.

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pH calculations in c(i), c(ii) and c(v) tended to be very good or completely incorrect.

A buffer solution with a pH of 3.87 contains $7.41 \text{ g} \text{ dm}^{-3}$ of propanoic acid, CH_3CH_2COOH , together with an unknown quantity of sodium propanoate, CH_3CH_2COONa .

â	a. Define the term <i>buffer solution</i> .	[2]
k	b. Explain, using appropriate equations, how this solution acts as a buffer solution.	[2]
C	z. Calculate the concentration, in $ m moldm^{-3}$, of sodium propanoate in this buffer solution.	[4]
	The $\mathrm{p}K_\mathrm{a}$ of propanoic acid is 4.87 at 298 K.	

Markscheme

a. a solution that resists changes in pH / changes pH slightly / OWTTE;

when small amounts of an acid/ $\mathrm{H^{+}}$ or a base/alkali/ $\mathrm{OH^{-}}$ are added;

b. addition of acid:

 $CH_3CH_2COO^-(aq) + H^+(aq) \rightarrow CH_3CH_2COOH(aq)$ / propanoate ions combine with H^+ ions to form undissociated propanoic acid; addition of base:

 $CH_{3}CH_{2}COOH(aq) + OH^{-}(aq) \rightarrow CH_{3}CH_{2}COO^{-}(aq) + H_{2}O(l) \text{ / addition of } OH^{-} \text{ removes } H^{+} \text{ and more propanoic acid dissociates/ionizes;}$

Ignore state symbols.

Accept reversible arrows.

Award [1 max] if correct equations are given without reference to addition of acid or alkali.

c. $K_{a} = \frac{[H^{+}(aq)][CH_{3}CH_{2}COO^{-}(aq)]}{[CH_{3}CH_{2}COOH(aq)]} / pH = pK_{a} + \log\left(\frac{[base]}{[acid]}\right);$ $K_{a} = 1.3 \times 10^{-5} / 10^{-4.87} \text{ and } [H^{+}] = 1.3 \times 10^{-4} / 10^{-3.87} (mol dm^{-3}) / \log \frac{[CH_{3}CH_{2}COO^{-}]}{[CH_{3}CH_{2}COOH]} = 3.87 - 4.87 = -1;$ $\left([CH_{3}CH_{2}COOH] = \frac{7.41}{74.09} =\right) 0.100 / 1.00 \times 10^{-1} (mol dm^{-3});$ $\left([CH_{3}CH_{2}COONa] =\right) 0.010 / 1.0 \times 10^{-2} (mol dm^{-3});$ Award [4] for correct final answer. $Accept corresponding use of <math>[H_{3}O]^{+}$ for $[H^{+}]$, facid] for $[CH_{3}CH_{2}COOH]$, and [base] or [salt] for $[CH_{3}CH_{2}COO^{-}]$ throughout.

Examiners report

- a. Most candidates were able to give a definition of buffer solutions including the detail that pH does not change significantly when small amounts of acid or alkali are added. The explanation of the action of buffers proved to be more challenging with only the stronger candidates giving a complete response in terms of protonation of the conjugate base and increased dissociation of the acid. The calculation of equilibrium concentrations from pK_a values was better done than in previous sessions, but still proved too difficult for many. The need to change the units of concentration of propanoic acid made this an additional obstacle in this demanding question.
- b. Most candidates were able to give a definition of buffer solutions including the detail that pH does not change significantly when small amounts of acid or alkali are added. The explanation of the action of buffers proved to be more challenging with only the stronger candidates giving a complete response in terms of protonation of the conjugate base and increased dissociation of the acid. The calculation of equilibrium concentrations from pK_a values was better done than in previous sessions, but still proved too difficult for many. The need to change the units of concentration of propanoic acid made this an additional obstacle in this demanding question.
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Buffer solutions are widely used in both chemical and biochemical systems.

b. Determine the pH of a buffer solution, correct to **two** decimal places, showing your working, consisting of 10.0 g of CH₃COOH and 10.0 g of [5] CH₃COONa in 0.250 dm³ of solution. K_a for CH₃COOH = 1.8×10^{-5} at 298 K.

Markscheme

a. (solution containing significant/equal amounts of a) weak acid and its salt / (solution containing) strong base to which excess of weak acid has

been added / OWTTE;

Accept (solution containing) weak acid and conjugate base.

Do not accept descriptions with specific compounds alone (e.g. CH₃COOH and CH₃COONa) unless compounds are stated as <u>weak</u> acid and its salt.

Accept answer such as (solution containing) x mol of <u>weak</u> acid and $\frac{1}{2}x$ mol of strong base.

b. $M_{
m r}(
m CH_3COOH)=60.06$ and $M_{
m r}$ $m CH_3COONa=82.04;$

$$\begin{split} [\mathrm{CH}_3\mathrm{COOH}] &= 6.66 \times 10^{-1}/0.666 \ \mathrm{mol} \ \mathrm{dm}^{-3} \\ [\mathrm{CH}_3\mathrm{COO}^-] &= 4.88 \times 10^{-1}/\ 0.488 \ \mathrm{mol} \ \mathrm{dm}^{-3}; \\ [\mathrm{H}_3\mathrm{O}^+]/[\mathrm{H}^+] &= (1.8 \times 10^{-5} \times 6.66 \times 10^{-1})/4.88 \times 10^{-1} = 2.46 \times 10^{-5}/0.0000246 \ \mathrm{mol} \ \mathrm{dm}^{-3}; \\ \mathrm{pH} &= \left(-\log[\mathrm{H}_3\mathrm{O}^+] = -\log(2.46 \times 10^{-5}) =\right) \ 4.61 \ (\mathrm{2dp}); \\ Award \ \textbf{[5]} \ \textit{for correct final answer of } pH = 4.61 \ \textit{with some working shown.} \\ Award \ \textbf{[2 max]} \ \textit{for } pH = 4.61 \ \textit{without any working at all shown.} \\ \hline \textbf{Two decimal places are required for M5.} \\ \textbf{OR} \end{split}$$

 $M_{
m r}({
m CH_3COOH})=60.06$ and $M_{
m r}~{
m CH_3COONa}=82.04;$

 $\rm [CH_3COOH] = 6.66 \times 10^{-1}/0.666 \ mol \, dm^{-3}$

 $[\mathrm{CH_{3}COO^{-}}] = 4.88 imes 10^{-1} / \ 0.488 \ \mathrm{mol} \ \mathrm{dm^{-3}};$

$$\mathrm{pH} = -\mathrm{log}(1.8 imes10^{-5}) + \mathrm{log}rac{\mathrm{[salt]}}{\mathrm{[acid]}};$$

$$= \left(4.74 + \log rac{0.488}{0.666} = 4.74 - 0.135 =
ight) \; 4.61 \; (
m 2dp);$$

M4 can be scored even if not explicitly stated if M5 is correct based on previous values.

Award [5] for correct final answer of pH = 4.61 with some working shown.

Award [2 max] for pH = 4.61 without any working at all shown.

Two decimal places are required for M5.

Examiners report

- a. This question was based on buffer solutions and was found to be quite challenging for candidates. In part (a), some candidates again failed to read the question, which asked for a description of an acidic buffer solution. Many did not state explicitly that a weak acid is involved (acid alone was not sufficient).
- In part (b), only the best candidates scored all five marks. In addition to conceptual errors, there were also a number of transcription errors (molar mass and arithmetic errors). Candidates also were required to express their answer to two decimal places. A number of candidates used the Henderson-Hasselbalch equation, but often an incorrect equation was given.

Water is an important substance that is abundant on the Earth's surface.

Buffer solutions resist small changes in pH. A phosphate buffer can be made by dissolving NaH_2PO_4 and Na_2HPO_4 in water, in which NaH_2PO_4 produces the acidic ion and Na_2HPO_4 produces the conjugate base ion.

A 0.10 mol dm^{-3} ammonia solution is placed in a flask and titrated with a 0.10 mol dm^{-3} hydrochloric acid solution.

a. (i) State the expression for the ionic product constant of water, $K_{\rm w}$.

- (ii) Explain why even a very acidic aqueous solution still has some OH^- ions present in it.
- (iii) State and explain the effect of increasing temperature on the value of $K_{\rm w}$ given that the ionization of water is an endothermic process.

[7]

[11]

- (iv) State and explain the effect of increasing temperature on the pH of water.
- b. (i) Deduce the acid and conjugate base ions that make up the phosphate buffer and state the ionic equation that represents the phosphate [7] buffer.

(ii) Describe how the phosphate buffer minimizes the effect of the addition of a

strong base, $OH^{-}(aq)$, to the buffer. Illustrate your answer with an ionic equation.

(iii) Describe how the phosphate buffer minimizes the effect of the addition of a

strong acid, $H^+(aq)$, to the buffer. Illustrate your answer with an ionic equation.

- c. (i) Explain why the pH of the ammonia solution is less than 13.
 - (ii) Estimate the pH at the equivalence point for the titration of hydrochloric acid with ammonia and explain your reasoning.
 - (iii) State the equation for the reaction of ammonia with water and write the $K_{\rm b}$ expression for $\rm NH_3(aq)$.
 - (iv) When half the ammonia has been neutralized (the half-equivalence point), the pH of the solution is 9.25. Deduce the relationship between $[NH_3]$ and $[NH_4^+]$ at the

half-equivalence point.

- (v) Determine pK_b and K_b for ammonia based on the pH at the half-equivalence point.
- (vi) Describe the significance of the half-equivalence point in terms of its effectiveness as a buffer.

Markscheme

a. (i) $(K_w) = [H^+][OH^-] / (K_w) = [H_3O^+][OH^-];$

Do not award mark if [] omitted or other brackets are used.

(ii) $[H^+]$ increases, $[OH^-]$ decreases but still some present (K_w constant) / $[OH^-]$ cannot go to zero as equilibrium present / $[OH^-] = \frac{K_w}{[H^+]}$, thus $[OH^-]$ cannot be zero / *OWTTE*;

Accept equilibrium present.

(iii) (changing T disturbs equilibrium) forward reaction favoured / equilibrium shifts to the right;

to use up (some of the) heat supplied;

 $K_{
m w}$ increases (as both $[{
m H}^+]$ and $[{
m OH}^-]$ increase);

(iv) (as $[\mathrm{H^+}]$ increases) pH decreases / $\mathrm{pH} < 7;$

No mark for more acidic.

inverse relationship between pH and $\left[H^{+}\right]/\,pH=-\log\left[H^{+}\right]/\,pH=\log_{10}\frac{1}{\left[H^{+}\right]};$

Accept $[H_3O^+]$ in place of $[H^+]$.

b. (i) Acid:
$$H_2PO_4^-$$
;

(Conjugate) base: HPO_4^{2-} ;

No mark for NaH_2PO_4 or Na_2HPO_4 .

$$\mathrm{H_2PO}_4^-(\mathrm{aq}) \rightleftharpoons \mathrm{H^+}(\mathrm{aq}) + \mathrm{HPO}_4^{2-}(\mathrm{aq});$$

Accept reverse equation or reaction with water.

Ignore state symbols, but equilibrium sign is required.

Accept OH^- (ions) react with H^+ (ions) to form H_2O .

(ii) strong base/ OH^- replaced by weak base (HPO_4^{2-} , and effect minimized) / strong base reacts with acid of buffer / equilibrium in (i) shifts in forward direction;

Accept OH^- added reacts with H^+ to form H_2O .

$$\mathrm{OH^-}(\mathrm{aq}) + \mathrm{H_2PO_4^-}(\mathrm{aq})
ightarrow \mathrm{H_2O}(\mathrm{l}) + \mathrm{HPO_4^{2-}}(\mathrm{aq});$$

Ignore state symbols, accept equilibrium sign.

(iii) strong acid/ H^+ replaced by weak acid ($H_2PO_4^-$, and effect minimized) / strong acid reacts with base of buffer / equilibrium in (i) shifts in reverse direction;

$$\mathrm{H^+(aq)} + \mathrm{HPO}_4^{2-}(\mathrm{aq})
ightarrow \mathrm{H_2PO}_4^{-}(\mathrm{aq});$$

Accept reaction with H_3O^+ .

Ignore state symbols.

c. (i) NH_3 weak(er) base/partial dissociation;

 $[{
m OH}^-] < 0.1(0)/{
m pOH} > 1 \ ({
m thus} \ {
m pH} < 13/{
m pH} + {
m pOH} = 14);$

(ii) around pH = 5;

Accept a value between 4 and 6.

strong acid–weak base titration, (thus acidic) / at equivalence point, NH_4^+ present is acidic / $NH_4^+ \rightleftharpoons NH_3 + H^+;$

(iii)
$$\mathrm{NH}_3(\mathrm{aq}) + \mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}_4^+(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq});$$

Ignore state symbols, but equilibrium sign required.

$$\begin{split} K_{\rm b} &= \frac{[{\rm NH}_4^+][{\rm OH}^-]}{[{\rm NH}_3]}; \\ (\text{iv}) & [{\rm NH}_3] = [{\rm NH}_4^+]; \\ (\text{v}) & {\rm pOH} = 14.00 - 9.25 = 4.75; \\ {\rm p}K_{\rm b} \; (={\rm pOH}) = 4.75; \end{split}$$

$$K_{
m b} = 1.78 imes 10^{-5}$$
;

Ignore units.

Award [3] for correct final answer.

(vi) optimum/most effective/highest buffer capacity/50%-50% buffer/equally effective as an acidic buffer and a basic buffer / OWTTE;

Examiners report

a. This was the second least commonly answered question. With the exception of the part on buffer chemistry where very few appreciated what was

happening, the question was reasonably well done.

While many candidates gave the correct K_w expression, it was not uncommon to either find the value of the constant or $K_w = K_a \times K_b$ given as the answers. A few included $[H_2O]$ in the expression. Candidates recognised that increasing the temperature shifts the equilibrium to the right, but most did not explain why, namely to use up some of the heat supplied.

Candidates generally concluded that formation of more H^+ and OH^- ions gives a higher value of K_w . A significant number of candidates were able to state the effect of increasing temperature on the pH of water (it decreases) but failed to explain why. Some simply incorrectly stated that the pH would not change.

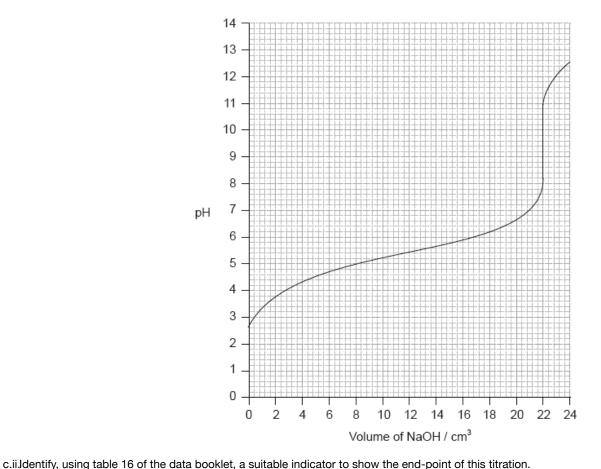
- b. Many candidates gave the wrong formulas for the acid and the conjugate base **ions** of the buffer or offered NaH_2PO_4 and Na_2HPO_4 as the answers. Some candidates gave good answers about the effect of adding a small amount of a strong acid or a strong base, but they could not write correct equations to show these two effects.
- c. Nearly all candidates correctly said that the ammonia solution is a weak base because of partial dissociation and $[OH^-]$ would be less than 0.1 to give a pH less than 13. The majority of candidates correctly identified the pH around 4 6 because it is a titration between a strong acid and a weak base. When writing the equation for the reaction of ammonia and water some candidates did not write the equilibrium sign. The K_b expression was correct in most cases. However, many did not recognise that at the half-equivalence point both the base and the conjugate acid concentrations are equal. The pK_b and K_b were correctly calculated from the pH of the solution by many candidates. However, most failed to realize that at the half-equivalence point the capacity of the buffer is optimum.

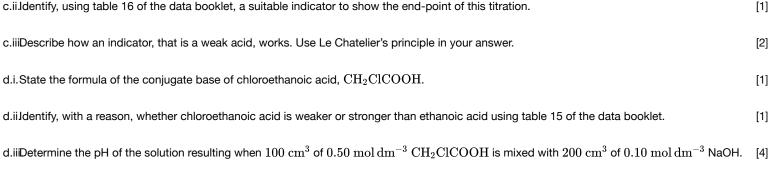
Acids can be described as strong or weak.

a. (i) Outline the difference in dissociation between strong and weak acids of the same concentration.

[4]

- (ii) Describe **three** tests that can be carried out in the laboratory, and the expected results, to distinguish between $0.10 \text{ mol dm}^{-3} \text{ HCl}(aq)$ and $0.10 \text{ mol dm}^{-3} \text{ CH}_3 \text{COOH}(aq)$.
- b. Calculate the pH, using table 15 of the data booklet, of a solution of ethanoic acid made by dissolving 1.40 g of the acid in distilled water to [4] make a 500 cm³ solution.
- c.i. Determine the pH at the equivalence point of the titration and the pK_a of an unknown acid using the acid-base titration curve below. [3]





- e. Describe how chlorine's position in the periodic table is related to its electron arrangement.
- f. SCl₂ and SClF₅ are two sulfur chloride type compounds with sulfur having different oxidation states. Predict the name of the shape, the bond [[N/A angle and polarity of these molecules.

[2]

Markscheme

a. (i) weak acids dissociate only partially and strong acids (are assumed to) dissociate fully;

(ii) measuring electrical conductivity and strong acids have greater electrical conductivity/weak acids have lower electrical conductivity;

Do not accept conductivity for electrical conductivity.

Accept explanation in terms of lightbulb in circuit.

measure pH/use universal indicator and pH higher for weak acid/pH lower for strong acid;

conduct titration with a strong base and equivalence point higher for weak acid / buffer region for weak acid;

adding a reactive metal/carbonate/hydrogen carbonate and stronger effervescence/faster reaction with strong acids;

Accept converse argument.

Accept correct example.

adding a strong base and strong acid would increase more in temperature/weak acids increase less in temperature;

Accept correct example.

Award **[1 max]** for three suitable tests without correct results. Accept specific examples with given strong acid and weak acid. Accept "addition of $AgNO_3(aq)$ **and** white precipitate with HCl (aq)". Do not accept "smell".

b. $\frac{1.40}{60.06}=0.0233~(mol)$ and $\frac{0.0233}{0.500}=0.0466~(mol\,dm^{-3});$

 $({
m p}K_{
m a}=4.76)K_{
m a}=1.7 imes10^{-5};$ $[{
m H}^+]=\sqrt{K_{
m a}}[{
m HA}]=8.9 imes10^{-4};$ Accept $9.0 imes10^{-4}.$

$$pH = 3.05;$$

Award [4] for correct final answer.

Accept alternative methods.

c.i. Equivalence point: pH of 9.5;

Accept values between 9 and 10.

 $\mathrm{p}K_\mathrm{a} = \mathrm{pH}$ at half equivalence point;

$$pK_{a} = 5.4;$$

Accept any value between 5.2 and 5.6.

Award [2] for M2 and M3 if correct pK_a given without explanation.

c.ii.phenolphthalein;

c.iii $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$ and HIn and In^- have different colours;

Ignore state symbols.

equilibrium shifts depending on addition of ${
m H^+}$ and ${
m OH^-}$ / more HIn in acid/low pH / more ${
m In^-}$ in alkali/high pH;

d.i.
$$CH_2ClCOO^-$$
;

d.ii.stronger because $\mathrm{p}K_\mathrm{a}$ of chloroethanoic acid is $<\mathrm{p}K_\mathrm{a}$ of ethanoic acid;

d.iiiConcentration of acid: $\frac{0.030}{0.300} = 0.10 \;(\mathrm{mol}\,\mathrm{dm}^{-3});$

Concentration of base/salt: $\frac{0.020}{0.300} = 0.067 \; (mol \, dm^{-3});$

$$[\mathrm{H^+}] = rac{K_{\mathrm{a}} imes [\mathrm{HA}]}{[\mathrm{A^-}]} / rac{1.3 imes 10^{-3} imes 0.10}{0.067} / 1.9 imes 10^{-3} \ (\mathrm{mol} \ \mathrm{dm}^{-3});$$

$$pH = 2.72;$$

Award [4] for correct final answer.

Accept 2.69, 2.70 or 2.7.

Alternative for M3 and M4 if Henderson-Hasselbalch equation used:

M3:
$$pH=pK_a+lograc{[base]}{[acid]}/$$
 $2.87+log\left(rac{0.067}{0.10}
ight)$

M4: pH = 2.70.

Award [1 max] for $n_{acid}(=100 \times 0.50 \div 1000) = 0.050 mol$ and $n_{base}(=200 \times 0.10 \div 1000) = 0.020 mol.$

e. CI has 7 valence electrons and is in group 7;

Accept "group 17" as suggested by IUPAC.

Cl has 3 occupied (electron) shells/energy levels and so is in period 3;

Molecule	Shape	Bond angle	Polarity
SCI2	bent/angular/ v-shaped	< 109.5° Accept 100° – 108°. Literature value is 103°.	polar
SCIF ₅	Octahedral Accept square bipyramidal.	90° (180°)	polar

Do not accept ECF for bond angles and polarities from incorrect shapes.

Award [3] for all six correct.

f.

Award [2] for four or five correct.

Award [1] for two or three correct.

Examiners report

- a. There is a difference, which candidates should note, between "not fully dissociated" and "partially dissociated" when describing a weak acid. The latter is correct; the former is not accepted as it could mean anything between 1% and 99%. In (ii), many did not state the difference in behaviour of the two acids. Many gained the first mark in (b) for finding the concentration of ethanoic acid. Thereafter either full marks was obtained or there was total confusion. The equivalence point in (c) was better known than the pK_a where an explanation was expected. The best candidates annotated the graph. Almost all candidates identified phenolphthalein in (ii) correctly but in (iii) any answer that did not begin with an equation was likely to score zero. In questions such as (d) (i), candidates should avoid writing a balanced equation (and there were many) unless the actual answer is clearly indicated. Many were able to identify the stronger acid with the correct reason but in (iii) there were few successful conclusions, many not having recognized that a buffer solution was formed. In (e), most were able to explain why chlorine is in group 7, but the explanation for the period, when it was given, often omitted the idea of *occupied* shells. In (f), it was disappointing to note that many thought SCl₂ to be linear and SClF₅ trigonal bipyramidal or square pyramidal. Two respondents commented that the column headed "polarity" was confusing; although we could have expressed this more clearly, the candidates did not seem to have a difficulty with this.
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