3

SAMPLE PAPER

NZQA

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Level 3 Chemistry

3.6: Demonstrate understanding of equilibrium principles in aqueous systems

Credits: Five

Check that you have completed ALL parts of the box at the top of this page.

Check that you have been supplied with the resource sheet for Chemistry 3.6.

You should answer ALL parts of ALL questions in this booklet.

If you need more room for any answer, use the space provided at the back of this booklet.

Check that this booklet has pages 2–11 in the correct order and that none of these pages is blank.

YOU MUST HAND THIS BOOKLET TO YOUR TEACHER AT THE END OF THE ALLOTTED TIME.

EXEMPLAR FOR LOW EXCELLENCE

NOTE: These exemplars do not fully show Grade Score Marking (GSM) because of the small sample of student scripts involved, and the absence of a cut score meeting to determine grade boundaries. GSM can be seen in the level 1 and level 2 exemplars from the 2012 examinations, which will be published on the NZQA website when the assessment schedules are published.

You are advised to spend 60 minutes answering the questions in this booklet.

Assessor's use only

QUESTION ONE

(a) Methanoic acid, HCOOH, is a weak acid. A dilute aqueous solution of this acid has a pH of 2.78.

$$pK_a\ (HCOOH) = 3.74$$

(i) Write an equation for the reaction of methanoic acid with water.

$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$

Correct equation.

(ii) List all the species in the aqueous solution of methanoic acid in order of decreasing concentration.

Correct order.

$[H_2O] > [HCOOH] > [H_3O^+] > [HCOO^-] > [OH^-]$

Give reasons for you answer.

Gives partial explanation, omits to identify CH_3COOH as a weak acid.

Water is in the highest concentration. HCOOH ~~reacts~~ dissociates incompletely - only a little bit reacts ∴ $[HCOOH]$ ~ as beginning. H_3O^+ and $HCOO^-$ are produced in equal amounts in the reaction, however H_2O contains some dissociated H_3O^+ and OH^- ions, hence slightly higher $[H_3O^+]$ and presence of OH^- ions

(iii) Calculate the concentration of the methanoic acid solution with a pH of 2.78.

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

$$= \frac{[H_3O^+]^2}{[HCOOH]}$$

$$[HCOOH] = \frac{[H_3O^+]^2}{K_a}$$

$$= \frac{(10^{-2.78})^2}{10^{-3.74}}$$

$$= 0.0151356$$

$$= 0.015\ mol\ L^{-1}$$

(b) Justify the variation in the properties (pH and conductivity) for the four dilute aqueous solutions described in the table below.

Assessor's use only

	pH	Conductivity
HCl	1.0	high
NH_4Cl	5.1	high
NH_3	11.1	low
NaOH	13.0	high

✱ HCl is a strong acid that dissociates completely, leaving many ions in solution — so it has a low pH and high conductivity.
As NH_4Cl becomes NH_4^+ & Cl^- in solution, & NH_4^+ is a weak acid, the pH is reasonably low, whilst the Cl^- concentration is high : conductivity is high.
NH_3 is a weak base that does not completely dissociate, giving a reasonably high pH. However the solution of NH_3 does not contain many ions in solution due to incomplete dissociation : it has a low conductivity
NaOH is a strong base and dissociates completely, leaving ions in solution to carry charge — giving it a high conductivity and pH.

✱ conductivity is high when there are many ions in solution, as there are many charged particles ions to carry the charge. Partially dissociated acids & base produce few ions.

Identifies number of ions being responsible for conductivity.
Correct identification of ions in solution for HC1, NH_4C1, NH_3, NaOH.
No clear explanation for pH.
Correctly explains conductivity for all species.

E7

QUESTION TWO

Assessor's use only

(a) Iron(II) sulfide, FeS, is dissolved in water to make a saturated solution.

(i) Write the equation for the equilibrium present in a saturated solution of FeS.

$FeS \rightarrow Fe^{2+} + S^{2-}$

Incorrrect arrow.

(ii) Write the expression for K_s(FeS).

$K_s = [Fe^{2+}][S^{2-}]$

Correct K_s expression.

(iii) Calculate the solubility of FeS in a saturated solution, in mol L^{-1}.

$K_s(FeS) = 4.90 \times 10^{-18}$

$s = [FeS] = [Fe] = [S]$

$K_s = s^2$

$s = \sqrt{K_s}$

$= \sqrt{4.90 \times 10^{-18}}$

$= 2.21 \times 10^{-9}$ mol L^{-1}

Correct calculation.

(b) Some sulfides have very low solubility products. When hydrogen sulfide gas is bubbled through solutions of these ions, these ions separate from a mixture of ions.

(i) In a saturated solution of hydrogen sulfide $[H_3O^+]^2[S^{2-}] = 1.10 \times 10^{-23}$

Calculate the sulfide ion concentration when the pH of the solution is 4.20.

$[S^{2-}] = \frac{1.10 \times 10^{-23}}{[H_3O^+]^2}$

$= \frac{1.10 \times 10^{-23}}{(10^{-4.20})^2}$

$= 2.76 \times 10^{-15}$ mol L^{-1}

Correct calculation.

Assessor's use only

(ii) Calculate the solubility of FeS in this solution, in mol L^{-1}.

$[Fe^{2+}] = [FeS]$

$[Fe^{2+}] = \frac{Ks}{[S^{2-}]}$

$= \frac{4.90 \times 10^{-18}}{2.763 \times 10^{-15}}$

$= 1.77339 \times 10^{-3}$

$= 1.77 \times 10^{-3}$ mol L^{-1}

Correct calculation. (Minor error in use of significant figures.)

(c) A solution contains a mixture of the two metal ions Cu^{2+} and Zn^{2+}, both of the same concentration. The solution is saturated with hydrogen sulfide and adding hydrochloric acid lowers the pH of the solution.

$K_s(CuS) = 6.30 \times 10^{-36}$ $K_s(ZnS) = 1.6 \times 10^{-24}$

Account for the fact that at a pH close to 7 all the metal sulfides will precipitate whereas only the most insoluble sulfides precipitate out at a lower pH.

In your answer, you should use equilibrium principles and both Cu^{2+} and Zn^{2+} as examples. **(No calculations are required.)**

$H_2S \rightleftharpoons S^{2-} + 2H_3O^+$

Equilibrium equation.

The lower the pH, the higher the concentration of H_3O^+ ions. The system (H_2S) tries to correct for the increase in H_3O^+ ions by going backwards to produce H_2S. This decreases the S^{2-} ion concentration, and as Ks is dependant of $[S^{2-}]$, when $[S^{2-}]$ is lower, Q is lower, meaning only metal sulfides with a very low Ks will precipitate out at a low pH.

CuS has a lower Ks than ZnS, ∴ requires a smaller $[S^{2-}]$ in order to form a precipitate

Does not compare with pH close to 7.

Correctly explains how pH and therefore [H_3O+] will affect the equilibrium and therefore [S^{2-}].

Relates [S^{2-}] to Q and correctly identifies CuS as more likely to precipiate at low pH.

E7

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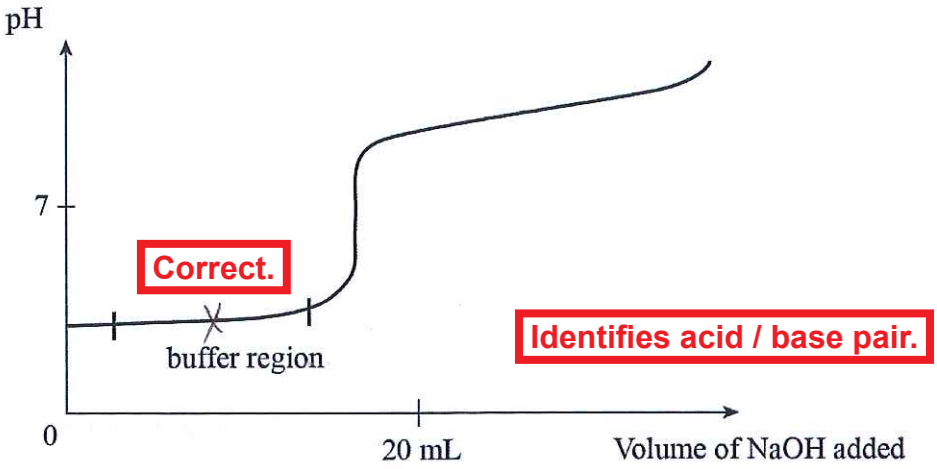
QUESTION THREE

Assessor's use only

20.00 mL of 0.125 mol L^{-1} ethanoic acid is titrated with 0.125 mol L^{-1} sodium hydroxide solution. The equation for this reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

The titration curve for the reaction is given below and the buffer region is marked on the graph.



Correct.

Identifies acid / base pair.

Conjugate base not used as identifier.

(a) (i) Explain why the solution in the titration flask can act as a buffer in this marked region. Use an equation in your answer.

As both CH_3COOH & CH_3COO^- ions are present the solution acts as a buffer. However, if all the CH_3COOH reacts in the $NaOH$ it cannot act like a buffer.

when a small amount of CH_3COOH has reacted with the NaOH, CH_3COO^- ions are formed.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The CH_3COOH ions react with strong bases to remove OH^- ions from the solution ($CH_3COOH + A^- \rightleftharpoons CH_3COO^- + HA$)

The CH_3COO^- ions react in strong acids to remove H_3O^+ ions

$$CH_3COO^- + HA \rightleftharpoons CH_3COOH + A^-$$

Because the weak acid (CH_3COOH) and weak base (CH_3COO^-) remove OH^- & H_3O^+ ions from solution the pH does not change dramatically

(ii) Put an **X** on the graph to show at which point the buffering action is the most efficient. Give reasons for your answer.

Because there are equal concentrations of the acid (CH_3COOH) and the base (CH_3COO^-), meaning $pH = pKa$ ($pH = pKa - \log \frac{[acid]}{[base]}$)

Reason for most effective buffer given.

(b) (i) Show that the pH at the equivalence point for this titration is 8.78.

Assessor's use only

$pK_a(CH_3COOH) = 9.24$

Correct calculation of CH_3COO^- concentration.

$n(CH_3COOH) = cV$	$c(CH_3COO^-) = 0.0625\ mol\,L^{-1}$
$= 0.125 \times 0.02$	$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$
$= 2.5 \times 10^{-3}\ mol$	$[H_3O^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$
$n(NaOH) = 2.5 \times 10^{-3}\ mol$	$= \frac{10^{-9.24} \times 0.125}{0.0625}$
$V(NaOH) = \frac{n}{c}$	$= 1.1508798 \times 10^{-9}$
$= \frac{2.5 \times 10^{-3}}{0.125}$	
$= 0.02\ L$	$pH = 8.93897$
$c(CH_3COO^-) = \frac{n}{V}$	$= 8.94$
$= \frac{2.5 \times 10^{-3}}{0.04}$	

(ii) Explain why methyl orange is not a suitable indicator for this titration and why phenolphthalein is a suitable indicator for this titration.

Indicator	pK_a
Methyl orange	3.70
Phenolphthalein	9.30

Methyl orange changes colour when the pH of the solution is much lower ∴ would not give an accurate impression of where the equivalence point is. Phenolphthalein is much closer ∴ would change colour at the right time giving the right pH and calculated volume.

Gives vague reason for use of phenolphthalein.
No use of given pK_a values.

(iii) Phenolphthalein is an acid-base indicator. It is a weak acid and its formula can be represented as HIn. Phenolphthalein is colourless in acidic solutions and purple in basic solutions.

Assessor's use only

$$pK_a\ (HIn) = 9.60$$

Discuss the effect of adding ethanoic acid and sodium hydroxide in turn to a solution containing phenolphthalein. In your answer, you should refer to:

- equilibrium principles
- the species responsible for the colours seen
- the pH range within which this indicator is effective.

Equilibrium equation for indicator given.

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$HIn + H_2O \rightleftharpoons In^- + H_3O^+$

As CH_3COOH produces H_3O^+ ions, therefore causing the HIn equilibrium reaction to go backwards to produce HIn, a colourless solution.

$NaOH \rightarrow Na^+ + OH^-$

As NaOH ~~dissociates~~ produces ~~H^+~~ and OH^- ions, the HIn reaction goes forwards to remove them, producing In^-, which is ~~blue~~ purple in solution. This means it is only effective in high pHs, from 8 - 10

Explains effect of adding CH_3COOH and NaOH on equilibrium and relates to colour of HIn and In^-.

One Excellence answer.

E7

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3.6: Demonstrate understanding of equilibrium principles in aqueous systems

Credits: Five

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EXEMPLAR FOR HIGH EXCELLENCE

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QUESTION ONE

(a) Methanoic acid, HCOOH, is a weak acid. A dilute aqueous solution of this acid has a pH of 2.78.

$$pK_a\,(HCOOH) = 3.74$$

(i) Write an equation for the reaction of methanoic acid with water.

$HCOOH_{(aq)} + H_2O \rightleftharpoons HCOO^-_{(aq)} + H_3O^+_{(aq)}$

(ii) List all the species in the aqueous solution of methanoic acid in order of decreasing concentration.

$H_2O > HCOOH > H_3O^+ \geq HCOO^- > OH^-$

Give reasons for you answer.

H_2O is always in highest concentration in aqueous solutions. Only very little HCOOH dissociates in water (it is a weak acid) so $HCOO^-$ is in second highest concentration. H_3O^+ and $HCOO^-$ dissociated in equal proportion from HCOOH, but there is very slightly more H_3O^+ due to the dissociation of water. There is a very small amount of OH^- from the dissociation of water.

(iii) Calculate the concentration of the methanoic acid solution with a pH of 2.78.

$K_a = \dfrac{[HCOO^-][H_3O^+]}{[HCOOH]}$ $\quad K_a = 10^{-3.74}$

Assume $[HCOO^-] = [H_3O^+]$ and that $[HCOOH]$ in equilibrium equal to initial concentration, as very little dissociates

$[H_3O^+] = 10^{-2.78}$

$K_a \dfrac{[H_3O^+]^2}{[HCOOH]} = 10^{-3.74}$

$\dfrac{(10^{-2.78})^2}{[HCOOH]} = 10^{-3.74}$

$[HCOOH] = 0.0151\ mol\,L^{-1}$

(b) Justify the variation in the properties (pH and conductivity) for the four dilute aqueous solutions described in the table below.

Assessor's use only

	pH	Conductivity
HCl	1.0	high
NH_4Cl	5.1	high
NH_3	11.1	low
NaOH	13.0	high

The pH of a solution depends on the concentration of H_3O^+ ions in solution. HCl is a strong acid, so it fully dissociates in water to form H_3O^+ ions and Cl^-: $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$. Therefore $[H_3O^+] = [HCl]$ so the pH is very low (1.0). Similarly, NaOH is a strong base which fully dissociates in water ($NaOH \xrightarrow{H_2O} Na^+ + OH^-$) so $[OH^-] = [H_3O^+]$ and it has a high pH of 13.0. NH_4Cl firstly separates into NH_4^+ and Cl^- ions when it dissolves, and NH_4^+ is a weak base which partially dissociates in water: $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$. Therefore as the $[H_3O^+]$ is increased the pH is below 7, but only very little NH_4^+ dissociates so the pH is higher than that of HCl. NH_3 is a weak base which also partially dissociates in water: $NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$. So the concentration of OH^- ions in solution is increased so the pH is above 7, but as NH_3 only partially dissociates the pH is lower than that of NaOH.

The conductivity of a solution depends on the concentration of charged particles (ions) in solution which can carry the flow of charge. HCl, NH_4Cl and NaOH all completely separate into cations and anions when they are dissolved in water, so these solutions have a high concentration of ions which carry a current so they all have high conductivity. In a solution of NH_3, however, the only ions present are those formed from the dissociation of the base into OH^- and NH_4^+ ions, and as NH_3 is a weak base only very little dissociates. Therefore the concentration of ions in aqueous NH_3 is low, so it has low conductivity //

States pH depends on [H_3O^+]. Explains each species. States conductivity depends on number of ions and explains for each species.

E8

QUESTION TWO

Assessor's use only

(a) Iron(II) sulfide, FeS, is dissolved in water to make a saturated solution.

(i) Write the equation for the equilibrium present in a saturated solution of FeS.

$FeS_{(s)} \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$

s s

(ii) Write the expression for K_s(FeS).

$K_s = [Fe^{2+}][S^{2-}]$

(iii) Calculate the solubility of FeS in a saturated solution, in mol L^{-1}.

$K_s(FeS) = 4.90 \times 10^{-18}$

$[Fe^{2+}][S^{2-}] = 4.9 \times 10^{-18}$

$(s)\ (s) \quad = 4.9 \times 10^{-18}$

$s^2 \quad = \sqrt{4.9 \times 10^{-18}}$

$s \quad = 2.21 \times 10^{-9}\ mol\ L^{-1}$

(b) Some sulfides have very low solubility products. When hydrogen sulfide gas is bubbled through solutions of these ions, these ions separate from a mixture of ions.

(i) In a saturated solution of hydrogen sulfide $[H_3O^+]^2[S^{2-}] = 1.10 \times 10^{-23}$

Calculate the sulfide ion concentration when the pH of the solution is 4.20.

$[H_3O^+] = 10^{-4.2}$

$(10^{-4.2})^2 \times [S^{2-}] = 1.1 \times 10^{-23}$

$[S^{2-}] = 2.76 \times 10^{-15}\ mol\ L^{-1}$

(ii) Calculate the solubility of FeS in this solution, in mol L^{-1}. Common ion.

$[Fe^{2+}][S^{2-}] = 4.9 \times 10^{-18}$

$s \times (s + 2.76 \times 10^{-15}) = 4.9 \times 10^{-18}$

$s^2 + 2.76 \times 10^{-15} s = 4.9 \times 10^{-18}$

$s = 2.21 \times 10^{-9}$ mol L^{-1}

Assessor's use only

(c) A solution contains a mixture of the two metal ions Cu^{2+} and Zn^{2+}, both of the same concentration. The solution is saturated with hydrogen sulfide and adding hydrochloric acid lowers the pH of the solution.

$K_s(CuS) = 6.30 \times 10^{-36}$ $K_s(ZnS) = 1.6 \times 10^{-24}$

Account for the fact that at a pH close to 7 all the metal sulfides will precipitate whereas only the most insoluble sulfides precipitate out at a lower pH.

In your answer, you should use equilibrium principles and both Cu^{2+} and Zn^{2+} as examples. **(No calculations are required.)**

$CuS_{(s)} \rightleftharpoons Cu^{2+}_{(aq)} + S^{2-}_{(aq)}$

At a lower pH, $[H_3O^+]$ is increased so hydrogen sulfide is formed. This removes some of the S^{2-} product which causes the equilibrium to favour the forward reaction and the solid CuS moves into solution, so only the most insoluble sulfides in which the IP is still greater than the K_s (because the K_s is very small, ie in CuS). ZnS's higher K_s means that it will not precipitate at.

But at a pH close to 7, hydrogen sulfide is not formed, so the equilibrium strongly favours the base reaction and all metal sulfides precipitate.

Describes effect of increasing [H_3O] on [S^{-2}]. Compares low pH with pH close to 7. Omits equilibrium equation for H_2S.

E7

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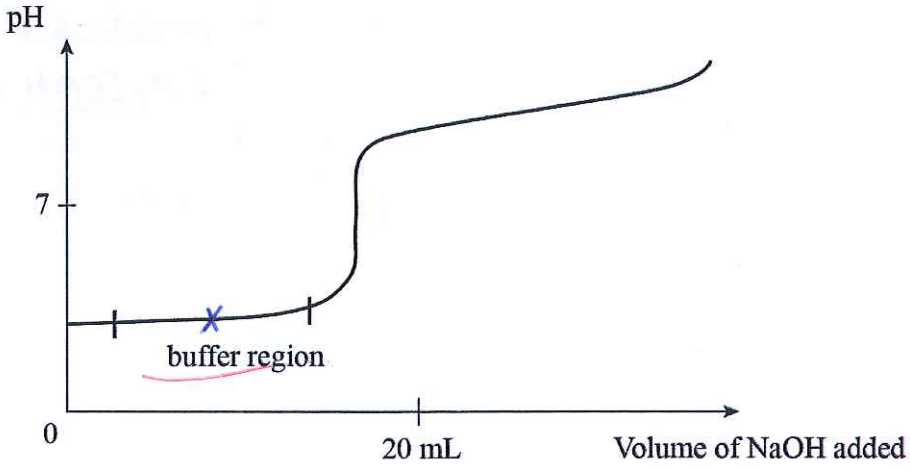
QUESTION THREE

Assessor's use only

20.00 mL of 0.125 mol L^{-1} ethanoic acid is titrated with 0.125 mol L^{-1} sodium hydroxide solution. The equation for this reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O\ (l)$$

The titration curve for the reaction is given below and the buffer region is marked on the graph.



(a) (i) Explain why the solution in the titration flask can act as a buffer in this marked region. Use an equation in your answer.

In the buffer region, both the acid and its conjugate base (CH_3COO^-) are present in solution so when ~~acid~~ base is added, this will react with the CH_3COOH: $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$ and the pH is not changed, and when an acid is added, this will react with the CH_3COO^-: $CH_3COO^- + H_3O^+ \longrightarrow CH_3COOH + H_2O$ and the pH also does not change.

~~Overall equation for buffer solution: $CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$~~

(ii) Put an **X** on the graph to show at which point the buffering action is the most efficient. Give reasons for your answer.

At the centre of the buffer region, the concentrations of acid and conjugate base are equal so the ~~solution~~ highest possible ~~con~~ amounts of acid or base can be added before all of the CH_3COOH or CH_3COO^- is used up and the solution stops buffering.

(b) (i) Show that the pH at the equivalence point for this titration is 8.78.

Assessor's use only

$pK_a(CH_3COOH) = 9.24$

Correct calculation of $[CH_3COO^-]$.

$n(CH_3COOH)$ reacted at equivalence point $= cV = 0.125 \times 20 \times 10^{-3} = 2.5 \times 10^{-3}$ mol

So $V(NaOH)$ added $= \frac{n}{c} = \frac{2.5 \times 10^{-3}}{0.125} = 0.02$ L. Total $V = 0.04$ L

mole ratio = 1:1, ∴ n(NaOH added) = 2.5×10^{-3} mol.

$c(CH_3COO^-)$ at equivalence point $= \frac{n}{V} = \frac{2.5 \times 10^{-3}}{0.04} = 0.0625$ mol L^{-1}

Correct method. Answer incorrect due to incorrect pK_a. $pK_a = 9.24$ should be $pK_a = 4.76$

At equivalence point, salt and water present & following reaction occurs: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$

$[H_3O^+] = \sqrt{\frac{K_a \times K_w}{[base]}}$ $\quad K_a = 10^{-9.24}$

$[H_3O^+] = 9.595 \times 10^{-12}$

$pH = -\log[H_3O^+] = 11.02$ ...

(ii) Explain why methyl orange is not a suitable indicator for this titration and why phenolphthalein is a suitable indicator for this titration.

Indicator	pK_a
Methyl orange	3.70
Phenolphthalein	9.30

The indicator changes colour when pH = pKa.

As the pH at the equivalence point is 8.78, and phenolpht changes colour at a pH of around 9.3 (±1), this indicator will change colour at the equivalence point so the end point is at the equivalence point.

However, methyl orange will change colour at a pH of around 3.7, so in this titration it will change colour before the equivalence point so the end point of the titration will be reache before the equivalence point is, and an incorrect result will be obtained. //

Correct discussion of colour changes for both indicators. Identifies phenolphthalein as most suitable.

(iii) Phenolphthalein is an acid-base indicator. It is a weak acid and its formula can be represented as HIn. Phenolphthalein is colourless in acidic solutions and purple in basic solutions.

Assessor's use only

$$pK_a\ (HIn) = 9.60$$

Discuss the effect of adding ethanoic acid and sodium hydroxide in turn to a solution containing phenolphthalein. In your answer, you should refer to:

- equilibrium principles
- the species responsible for the colours seen
- the pH range within which this indicator is effective.

$HIn + H_2O \rightleftharpoons In^- + H_3O^+$

When ethanoic acid is added, the ethanoic acid dissociates to form H_3O^+ ions, and this increases the concentration of one of the products of the equilibrium reaction (H_3O^+). This drives the equilibrium in the backwards direction ~~which~~ is in order to ~~dec~~ minimise the effects of the change, so the concentration of HIn is increased which is colourless so the solution turns colourless.

When ~~OH^- is adde~~ sodium hydroxide is added, the OH^- ions react with the H_3O^+ ions which are a product to form water, so one of the reaction products is removed. This ~~caus~~ causes the equilibrium to favour the forward reaction so the concentration of In^- increases. In^- is purple, and so the solution turns purple in basic solutions.

The ~~pH~~ indicator changes colour when $[HIn] = [In^-]$, so when $pH = pK_a$. This colour change ~~occurs~~ occurs in a pH of $pK_a \pm 1$, so the indicator is effective in the pH range of about 8·6 – 10·6.

Equilibrium equation for HIn given. Equation used to discuss effect of adding CH_3COOH and NaOH.

E8