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91392

913920

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NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

QUALIFY FOR THE FUTURE WORLD
KIA NOHO TAKATŪ KI TŌ ĀMUA AO!

Level 3 Chemistry, 2015

91392 Demonstrate understanding of equilibrium principles in aqueous systems

2.00 p.m. Wednesday 11 November 2015
Credits: Five

Achievement	Achievement with Merit	Achievement with Excellence
Demonstrate understanding of equilibrium principles in aqueous systems.	Demonstrate in-depth understanding of equilibrium principles in aqueous systems.	Demonstrate comprehensive understanding of equilibrium principles in aqueous systems.

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

You should attempt ALL the questions in this booklet.

A periodic table is provided on the Resource Sheet L3–CHEMR.

If you need more room for any answer, use the extra space provided at the back of this booklet and clearly number the question.

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 THE SUPERVISOR AT THE END OF THE EXAMINATION.

Low Achievement

TOTAL 9

ASSESSOR'S USE ONLY

QUESTION ONE

LOW ACHIEVE

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Methylammonium chloride, CH_3NH_3Cl, dissolves in water to form a weakly acidic solution.

$K_a(CH_3NH_3^+) = 2.29 \times 10^{-11}$

(a) (i) Write an equation to show CH_3NH_3Cl dissolving in water.

$CH_3NH_3Cl \rightleftharpoons CH_3NH_2 + Cl^-$ $\cancel{H_3O}$

(ii) Write an equation to show the reaction occurring in an aqueous solution of CH_3NH_3Cl.

$CH_3NH_3Cl + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$

(iii) List all the species present in an aqueous solution of CH_3NH_3Cl, in order of decreasing concentration.

Do not include water.

CH_3NH_3Cl , CH_3NH_2 , H_3O^+

(iv) Calculate the pH of 0.0152 mol L^{-1} CH_3NH_3Cl solution.

$$Ka = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3Cl]}$$

$$Ka = \frac{[H_3O^+]^2}{[CH_3NH_3Cl]} \Rightarrow 2.29 \times 10^{-11} = \frac{[H_3O^+]^2}{[0.0152]}$$

$$[H_3O^+] = \sqrt{(2.29 \times 10^{-11})(0.0152)}$$

$$= 5.8998 \times 10^{-7} \text{ molL}^{-1}$$

~~3.4808 × 10^-13 molL^-1~~

$$-\log(5.8998 \times 10^{-7}) = \boxed{6.23 \text{ pH}}$$

(b) The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same.

ASSESSOR'S USE ONLY

Solution	NaOH	CH_3NH_2	CH_3COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

Compare and contrast the pH and electrical conductivity of these three solutions.

Include appropriate equations in your answer.

pH: $NaOH \rightarrow Na^+ + OH^-$. NaOH has a high pH as it is a strong acid and it fully dissociates to OH^- as Na^+ is a spectator ion. Due to the large concentration of $[OH^-]$ ions, the pH will be larger indicating that it is basic. The OH^- ions contribute to the pH.

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Electrical conductivity:

A3

QUESTION TWO

ASSESSOR'S USE ONLY

Sufficient calcium carbonate, $CaCO_3(s)$, is dissolved in water to make a saturated solution.

(a) (i) Write the equation for the equilibrium occurring in a saturated solution of $CaCO_3$.

$$CaCO_{3(s)} \rightleftharpoons Ca^{+}_{(aq)} + CO_3^{-}{}_{(aq)}$$

(ii) Write the expression for $K_s(CaCO_3)$.

$$Ks = [Ca^+][CO_3^-]$$

(iii) Calculate the solubility product of $CaCO_3$, $K_s(CaCO_3)$.

Ks

The solubility of $CaCO_3$ is 5.74×10^{-5} mol L^{-1}.

~~$Ks = \sqrt[2]{5.74 \times 10^{-5}} = 7.58 \times 10^{-3}$~~

$Ks = s^2$

$= (5.74 \times 10^{-5})^2$

$= 3.29 \times 10^{-9}$ (3sf)

(b) Some marine animals use calcium carbonate to form their shells. Increased acidification of the oceans poses a problem for the survival of these marine animals.

Explain why the solubility of $CaCO_3$ is higher in an acidic solution.

Use an equation to support your explanation.

(c) Show, by calculation, that a precipitate of lead(II) hydroxide, $Pb(OH)_2$, will form when 25.0 mL of a sodium hydroxide solution, NaOH, at pH 12.6 is added to 25.0 mL of a 0.00421 mol L^{-1} lead(II) nitrate, $Pb(NO_3)_2$, solution.

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$$K_s(Pb(OH)_2) = 8.00 \times 10^{-17} \text{ at } 25°C$$

$NaOH + Pb(NO_3) \rightarrow Na(NO_3) + Pb(OH)$

conc = shift log (−pH)
= shift log (−12.6)
= 2.51×10^{-13} mol L^{-1} of 25 mL NaOH.

$IP = [Pb^{2+}][OH^-]^2$
$= [0.00421 \times \frac{25}{50}][2.51 \times 10^{-13} \times \frac{25}{50}]$
$= 2.6438 \times 10^{-16}$ ~~mol~~

The ionic product is larger than the Ks value of $Pb(OH)_2$ and therefore a precipitate will form.

n

A3

$HF + H_2O \rightleftharpoons F^- + H_3O^+$

QUESTION THREE

ASSESSOR'S USE ONLY

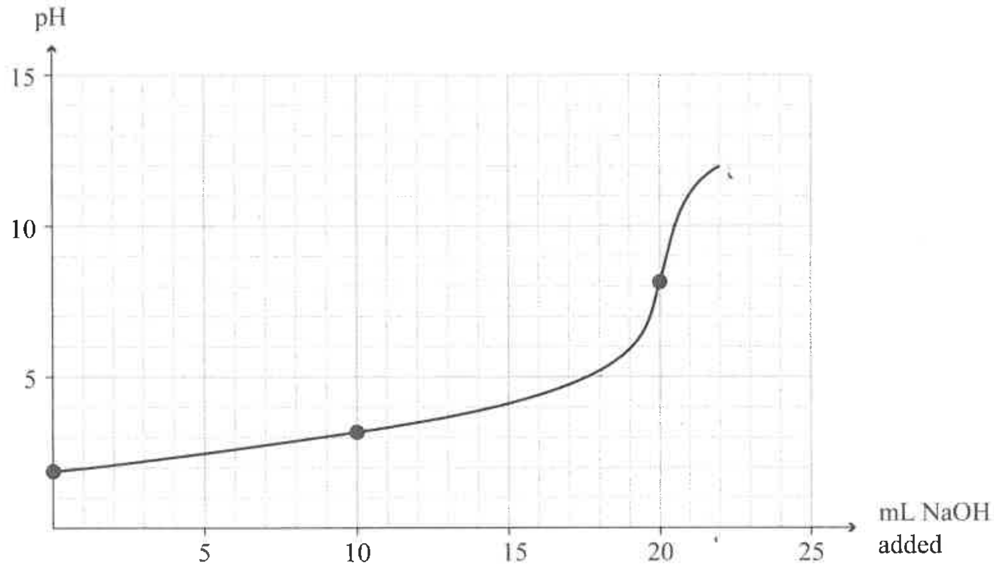
20.0 mL of 0.258 mol L^{-1} hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH, solution.

The equation for the reaction is:

$$HF + NaOH \rightarrow NaF + H_2O$$

$$pK_a(HF) = 3.17$$

The titration curve is given below:



(a) (i) Identify the species in solution at the equivalence point.

Na^+, OH^-, F^-

u

(ii) Explain why the pH at the equivalence point is greater than 7.

Include an equation in your answer.

NaOH is a strong base so has a large concentration of OH^- ions, making the pH higher. The pH is higher than 7 as pH of 7 is considered neutral but NaOH is a strong base and therefore should have a larger pH than 7.

$NaOH \longrightarrow Na^+ + OH^-$ As NaOH is a strong acid it completely dissociates, meaning there is no more NaOH ions present but a large concentration of OH^- and none for Na^+ as Na^+ is a spectator ion.

$K_a = [\ ]$

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(iii) ~~After~~ a certain volume of NaOH solution has been added, the concentration of HF in the solution will be twice that of the F^-.

Calculate the pH of this solution, and evaluate its ability to function as a buffer.

K_a = Shift log (−pK_a)
= Shift log (−3.17) = 6.76×10^{-4} molL^{-1}

$K_a = \frac{[H_3O^+]^2}{[HF]} \Rightarrow 6.76 \times 10^{-4} \times 0.258 \times \frac{20}{42} = [H_3O^+]^2$

$[H_3O^+]^2 = 8.31 \times 10^{-5}$ molL^{-1}
$[H_3O^+] = \sqrt{8.31 \times 10^{-5}} = 9.11 \times 10^{-3}$ molL^{-1}
$-\log(9.11 \times 10^{-3}) = 2.04$ ~~[illegible]~~

A buffer solution resists the change in pH when a small amount of acid or base is added. When a NaOH is added, it works to neutralise the solution.

(iv) Determine by calculation, the pH of the solution after 24.0 mL of 0.258 mol L^{-1} NaOH solution has been added.

Question Three continues on the following page.

$\cancel{CH_3COOH + NaOH \rightarrow Na(H_3COONa' + H_2O)}$

(b) In a second titration, a 0.258 mol L^{-1} ethanoic acid, CH_3COOH, solution was titrated with the NaOH solution.

ASSESSOR'S USE ONLY

Contrast the expected pH at the equivalence point with the HF titration.

$pK_a(CH_3COOH) = 4.76$

No calculations are necessary.

CH_3COOH is a weak acid as it does not fully dissociate. The pKa value is higher indicating that it is a weaker acid in comparison to HF as its pKa is 3.17. At the equivilance point all HF has been converted to F^-.

u

A3

Low Achievement exemplar for 91392 2015			Total score	09
Q	**Grade score**	**Annotation**		
1	A3	This provides evidence for A3 because there are no correct equations in part (a)(i), (ii) & (iii) but in (a) (iv) the calculation is correct. Also in (b) they recognise pH depends on hydroxide ion concentration but only discuss NaOH and do not write any equations. They also do not discuss conductivity.		
2	A3	This provides evidence for A3 because they correctly calculate the solubility product in (a) (iii) and correctly compare an incorrect IP value to Ks in (c). They would have gained an A4 if they had the ion charges correct in (a)(i) & (ii)		
3	A3	This provides evidence for A3 because they correctly identified three ions in (a)(i), described the function of a buffer in (a)(iii) and described ethanoic acid as weaker than hydrofluoric acid in (b)		

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High Achievement

TOTAL 12

ASSESSOR'S USE ONLY

QUESTION ONE HIGH ACHIEVE

ASSESSOR'S USE ONLY

Methylammonium chloride, CH_3NH_3Cl, dissolves in water to form a weakly acidic solution.

$K_a(CH_3NH_3^+) = 2.29 \times 10^{-11}$

(a) (i) Write an equation to show CH_3NH_3Cl dissolving in water.

$CH_3NH_3Cl_{(s)} \longrightarrow CH_3NH_3^+{}_{(aq)} + Cl^-{}_{(aq)}$

(ii) Write an equation to show the reaction occurring in an aqueous solution of CH_3NH_3Cl.

$CH_3NH_3^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons$ $CH_3NH_{3(aq)} + H_3O^+{}_{(aq)}$ ~~$CH_3NH_{2(aq)} + H_3O^+{}_{(aq)}$~~

(iii) List all the species present in an aqueous solution of CH_3NH_3Cl, in order of decreasing concentration.

Do not include water.

~~CH_3NH_3Cl~~, H_3O^+, OH^-

(iv) Calculate the pH of 0.0152 mol L^{-1} CH_3NH_3Cl solution. 3.4808×10^{-13}

~~$K_b = [CH_3NH_3^+][OH^-]$~~

~~$K_a = [CH_3NH_3^+][H_3O^+]$~~

$K_a = \dfrac{[CH_3NH_3^+][H_3O^+]}{[CH_3NH_3Cl]}$

conc. of $CH_3NH_3^+$ and H_3O^+ are fairly similar So use x for both of them

$2.29 \times 10^{-11} = \dfrac{x^2}{0.0152 - x}$

$x^2 = 2.29 \times 10^{-11} \times 0.0152$

conc. of H_3O^+

H_3O^+ in water is negligible

$x = \sqrt{2.29 \times 10^{-11} \times 0.0152}$

$[H_3O^+] = 5.90 \times 10^{-7}$ mol L^{-1}

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

$= -\log(5.90 \times 10^{-7})$

$pH = 6.23$ (3sf)

$\hookrightarrow$ slightly acidic

pH = $-\log H_3O^+$ dissociate $H_3O^+ = 10^{-pH}$ $pK_a = -\log K_a$

(b) The table shows the pH and electrical conductivity of three solutions. The concentrations of the solutions are the same.

Solution	NaOH	CH_3NH_2	CH_3COONa
pH	13.2	11.9	8.98
Electrical conductivity	good	poor	good

Compare and contrast the pH and electrical conductivity of these three solutions.

Include appropriate equations in your answer.

pH. pH is the concentration of $[H_3O^+]$ in solution. The higher the pH, the smaller the $[H_3O^+]$. NaOH is a strong base with a pH of 13.2

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

$[H_3O^+]$ of NaOH $\Rightarrow 10^{-13.2} = 6.31 \times 10^{-14}$ mol L^{-1}

$[H_3O^+]$ of $CH_3NH_2 \Rightarrow 10^{-11.9} = 1.26 \times 10^{-12}$ mol L^{-1}

$[H_3O^+]$ of $CH_3COONa \Rightarrow 10^{-8.98} = 1.04 \times 10^{-9}$ mol L^{-1}

CH_3COONa has the highest $[H_3O^+]$ thus making it a good electrical conductor even though it has the lowest pH. Although NaOH has the lowest $[H_3O^+]$ it fully dissociates thus making it a good electrical conductor

u

Electrical conductivity: NaOH is a good electical conductor (strong electrolyte) as it fully dissociates in water, no reactant is left thus (0.200 mol L^{-1} of ions in solution) the concentration of ions in solution is high. CH_3NH_2 is a poor electrical conductor as it only partially dissociates in water thus there is still some reactant left over, not all of the reactant dissociates thus the concentration of ions is lower than the concentration of ions for NaOH. CH_3COONa is a good electrical conductor as Na^+ (one of products when CH_3COONa is in solution) Na^+ is in group one and all group one compounds are soluble in water. Thus CH_3COONa is a better electrical conductor than CH_3NH_2. ~~NaOH has highest $[H_3O^+]$ thus of~~

u

A4

ASSESSOR'S USE ONLY

ASSESSOR'S USE ONLY

QUESTION TWO

Sufficient calcium carbonate, $CaCO_3(s)$, is dissolved in water to make a saturated solution.

(a) (i) Write the equation for the equilibrium occurring in a saturated solution of $CaCO_3$.

$CaCO_{3(s)} + \cancel{H_2O_{(l)}} \rightleftharpoons \cancel{CaCO_{3(aq)}} + Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

(ii) Write the expression for $K_s(CaCO_3)$.

$\cancel{K_s = [CaCO_{3(aq)}]}$ $K_s = [Ca^{2+}][CO_3^{2-}]$

(iii) Calculate the solubility product of $CaCO_3$, $K_s(CaCO_3)$.

The solubility of $CaCO_3$ is 5.74×10^{-5} mol L^{-1}.

let the solubility of product be s

$[Ca^{2+}] = [CO_3^{2-}]$ ∴ $[Ca^{2+}] = s$

$K_s = s^2$

$K_s = (5.74 \times 10^{-5})^2$

$= 3.29 \times 10^{-9}$

(b) Some marine animals use calcium carbonate to form their shells. Increased acidification of the oceans poses a problem for the survival of these marine animals.

Explain why the solubility of $CaCO_3$ is higher in an acidic solution.

Use an equation to support your explanation.

$CaCO_{3(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

$CO_3^{2-}{}_{(aq)} + H_3O^+ \longrightarrow HCO_3^-{}_{(aq)} + OH^-{}_{(aq)}$

When $CaCO_3$ goes into solution it forms Ca^{2+} and CO_3^{2-} ions. CO_3^{2-} ions can react with acidic (hydronium) ions to produce HCO_3^- ions. Thus if pH of water decreases and becomes more acidic, more $CaCO_3$ can dissolve* ~~[illegible]~~ thus some marine animals will not be able to use $CaCO_3$ to form shells

* increasing amount of ions in solution

pH = pKa + log $\frac{Base}{Acid}$

(c) Show, by calculation, that a precipitate of lead(II) hydroxide, $Pb(OH)_2$, will form when 25.0 mL of a sodium hydroxide solution, NaOH, at pH 12.6 is added to 25.0 mL of a 0.00421 mol L^{-1} lead(II) nitrate, $Pb(NO_3)_2$, solution.

$K_s(Pb(OH)_2) = 8.00 \times 10^{-17}$ at 25°C

ASSESSOR'S USE ONLY

$NaOH_{(aq)} + Pb(NO_3)_{2(aq)} \longrightarrow Pb(OH)_{2(aq)}$ $(+ Na(NO_3)_{2(aq)})$

~~c(NaOH) = $\frac{25}{50}$~~ $c(Pb(NO_3)_2) = \frac{25}{50} \times 0.00421$

at equilibrium $= 0.002105 \text{ mol} L^{-1}$

$n(Pb(NO_3)_2) = c \times V = 0.002105 \times 0.025$
$= 5.26 \times 10^{-5}$ mol

IP must be larger than Ks to form a precipitate

$IP = 0.002105 \times 5.26 \times 10^{-5}$
$= 11.1 \times 10^{-7}$

Ks is larger than IP thus will not form the precipitate $Pb(NO_3)_2$

4

A4

ASSESSOR'S USE ONLY

QUESTION THREE

20.0 mL of 0.258 mol L^{-1} hydrofluoric acid, HF, solution is titrated with a sodium hydroxide, NaOH, solution.

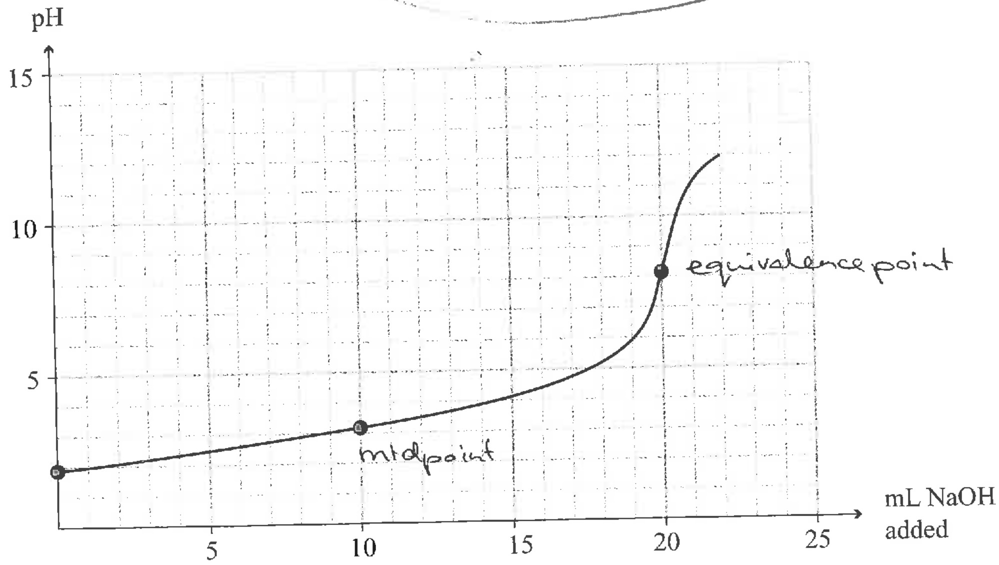
The equation for the reaction is:

$$HF + NaOH \rightarrow NaF + H_2O$$

$$pK_a(HF) = 3.17$$

The titration curve is given below:

~~$HF + H_2O \rightleftharpoons F^- + H_2O$~~



(a) (i) Identify the species in solution at the equivalence point.

Equal ~~conc~~ moles of acid and base
HF and NaOH

(ii) Explain why the pH at the equivalence point is greater than 7.

Include an equation in your answer.

$F^-(aq) + H_2O(l) \rightleftharpoons HF^*(aq) + OH^-(aq)$

A strong base (NaOH) is reacting with a weak acid (HF)'. ~~HF is doesn't fully dissociate and will react with water to form (F⁻) a buffer solution more~~ The F⁻ ions in solution will react with water and produce OH⁻ (aq) ions in the solution, thus decreasing the [H₃O⁺] in solution, making the pH greater than 7.

(iii) After a certain volume of NaOH solution has been added, the concentration of HF in the solution will be twice that of the F^-.

Calculate the pH of this solution, and evaluate its ability to function as a buffer.

$HF_{(aq)} + OH^-_{(aq)} \longrightarrow F^-_{(aq)} + H_2O_{(l)}$

$K_b = \sqrt{\frac{K_a \times K_w}{C_{weak\ base}}}$

$K_s = \frac{x^2}{0.258 - x}$

$n(HF) \Rightarrow CV = 0.258 \times 0.02 = 5.16 \times 10^{-3}$ mol

N

(iv) Determine by calculation, the pH of the solution after 24.0 mL of 0.258 mol L^{-1} NaOH solution has been added.

$n(NaOH) = cV = 0.258 \times 0.024 = 6.19 \times 10^{-3}$ mol

$c(NaOH) = \frac{24}{44} \times 0.258 = 1.41 \times 10^{-1}$ molL

$n(HF) = \frac{20}{44} \times 0.258 = 1.17 \times 10^{-1}$ molL^{-1}

$pH = pKa + \log\left(\frac{[Base]}{[Acid]}\right)$

$= 3.17 + \log\left(\frac{1.41 \times 10^{-1}}{1.17 \times 10^{-1}}\right)$

$= 3.16$

N

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Question Three continues on the following page.

(b) In a second titration, a 0.258 mol L^{-1} ethanoic acid, CH_3COOH, solution was titrated with the NaOH solution.

Contrast the expected pH at the equivalence point with the HF titration.

$pK_a(CH_3COOH) = 4.76$

No calculations are necessary.

The pH of the solution will be higher when ethanoic acid is titrated with NaOH solution than ~~[illegible]~~ the pH at equivalence point was for HF titration. At the midpoint (half of ~~products~~ reactants have been titrated) pKa = pH thus pKa for ethanoic titration is 4.76 which is higher than pH (pKa) at midpoint for HF titration 3.17. Ethanoic acid is a very weak acid and thus at equivalence

ASSESSOR'S USE ONLY

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A4

Extra paper if required.
Write the question number(s) if applicable.

QUESTION NUMBER

ASSESSOR'S USE ONLY

3b point the solution will be alkaline. More NaOH will be needed for all of the ethanoic acid to dissociate (shifting equilibrium in the forward direction).

High Achievement exemplar for 91392 2015		Total score	12
Q	**Grade score**	**Annotation**	
1	A4	This provides evidence for A4 because there is one correct equation in part (a)(i), (ii) & (iii) and in (a) (iv) the calculation is correct. Also in (b) they recognise pH depends on hydronium ion concentration but only discuss NaOH dissociation and do not write any equations. For conductivity they relate conductivity to ion concentration for NaOH but the explanation is unclear for CH_3NH_2 and CH3COONa.	
2	A4	This provides evidence for A4 because they correctly calculate the solubility product in (a) (iii), in (b) they recognise H_3O^+ will remove CO_3^{2-} but provide insufficient explanation. In (c) they correctly compare an incorrect IP value to Ks in (c).	
3	A4	This provides evidence for A4 because they correctly explain why pH is greater than 7 with an equation in (a)(ii), in (a)(iv) they perform one calculation correctly (moles of NaOH) and in (b) recognise the pH will be higher because ethanoic acid has a higher pKa.	