3

91392

913920

SUPERVISOR'S USE ONLY

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.

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Low Merit

TOTAL 15

ASSESSOR'S USE ONLY

QUESTION ONE

LOW MERIT

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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.

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

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

$CH_3NH_3^+ + H_2O \rightleftharpoons CH_3NH_2 + H_3O^+$

u

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

Do not include water.

$Cl^- > CH_3NH_3^+ > CH_3NH_2 = H_3O^+ > OH^- > CH_3NH_3Cl$

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

$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]}$

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

assuming $[H_3O^+] = [CH_3NH_4]$

$3.48 \times 10^{-13} = [H_3O^+]^2$

$[H_3O^+] = 5.89983... \times 10^{-7}$

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

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

$= 6.229160465$

$= 6.23$ (3 s.f.)

i

ASSESSOR'S USE ONLY

(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: NaOH is a strong base, meaning Na^+ and OH^- ions pretty much completely dissociate, meaning ~~many charged particles are available to carry electrical~~ the concentration of OH^- is high, and pH is high. CH_3NH_2 is a weaker base, and does not dissociate as well as NaOH, so $[OH^-]$ is smaller, and pH ~~slightly~~ lower. CH_3COONa dissociates ~~[illegible]~~ well, but the CH_3COO^- reacts with H_2O to form $CH_3COOH + OH^-$ more sparingly. This means $[OH^-]$ is not as high, ~~[illegible]~~ ~~[illegible]~~ and pH is comparatively lower than the other two.

Electrical conductivity: NaOH almost completely dissociates, so the concentration of ions is high. Many charged particles are therefore available to carry electrical current. Becaus CH_3NH_2 does not dissociate as well, fewer ions are available to carry charge, and conductivity is poor. Although CH_3COONa had a low $[OH^-]$, it has other ions (Na^+, CH_3COO^-) which can carry electrical current, so electrical conductivity is good.

i

i

M5

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 $CaCO_3$.

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

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

$$//K_s = [Ca^{2+}][CO_3{}^{2-}]//$$

u

(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}.

$//K_s = [Ca^{2+}][CO_3{}^{2-}]$ assuming $[Ca^{2+}] = [CO_3{}^{2-}]$

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

$= 3.29476 \times 10^{-9}$

$K_s(CaCO_3) = 3.29 \times 10^{-9}$ (3 s.f.)//

i

(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.

// The Ca^{2+} ion reacts in water forming $Ca(OH)_2 + H_3O^+$, meaning the product side is more acidic. When more H_3O^+ is added, the equilibrium will shift in an effort to minimize the effects of the changes (Le Chatalier's principle), and shift to reactant side, decreasing solubility of $CaCO_3$.

$CO_3{}^{2-} + H_2O \rightleftharpoons H_3O^+ + C$

$Ca^{2+} + 5H_2O \rightleftharpoons 2Ca(OH)_2 + 2H_3O^+$ //

(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. 25.0 mL NaOH

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

// pH = 12.6 ∴ $[H_3O^+] = 10^{-12.6}$

$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-12.6}} = 0.0398107 1706$ [illegible] = [illegible] $[Na^+]$

~~$K_s(Pb(OH)_2) = [Pb^{2+}][OH^-]^2$~~

~~$8.00 \times 10^{-17} = [Pb^{2+}][0.0398]^2$~~

~~Ionic Product = $[Pb^{2+}][OH^-]^2$~~

~~$= [0.00421][0.0398]^2$~~

~~$= 6.67 \times 10^{-6}$ (3 s.f.)~~

~~yes I.P. > K_s ∴ precipitate forms~~

~~$NaOH \rightleftharpoons Na^+ + OH^-$ $[OH^-] = 0.0398107 1706$ mol L^{-1}~~

~~$Pb(NO_3)_2 \rightleftharpoons Pb^{2+} + 2(NO_3^-)$~~

(I.P. = Ionic product)

pH = 12.6 ∴ $[H_3O^+] = 10^{-12.6}$

$[OH^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-12.6}} \times \frac{1}{2} = 0.0199$ (3 s.f.) ($\frac{1}{2}$ as volume doubled)

I.P. $= [Pb^{2+}][OH^-]^2 = \frac{0.0421}{2} \times (0.0199)^2$

$= 8.34 \times 10^{-6}$ (3 s.f.)

I.P. > K_s so precipitate will form //

i

M5

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:

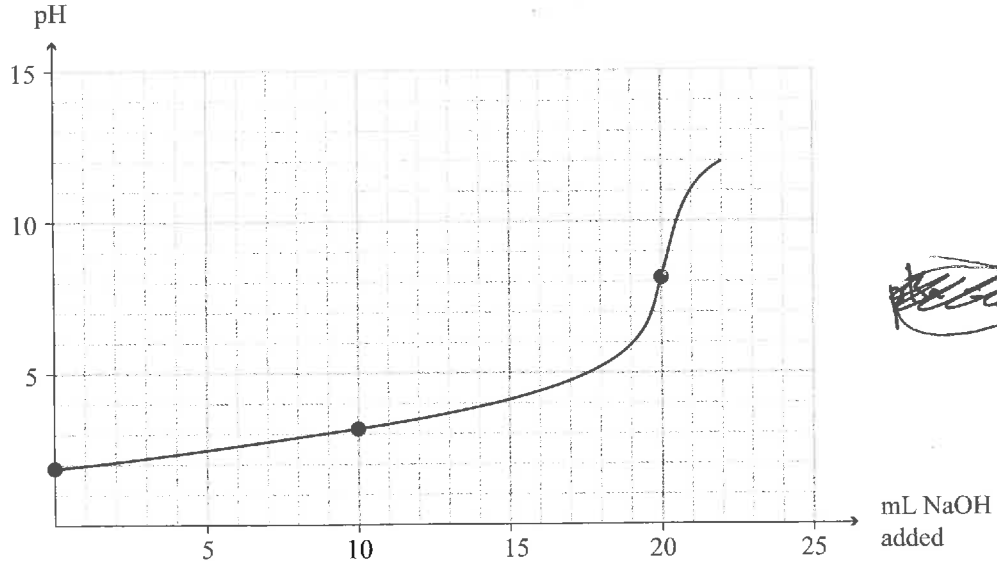
$$HF + NaOH \rightarrow NaF + H_2O$$

$$pK_a(HF) = 3.17$$

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

$NaOH + H_2O \rightleftharpoons Na^+ + OH^-$

The titration curve is given below:



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

$NaF + H_2O$

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

Include an an equation in your answer.

When HF reacts with H_2O to H_3O^+ and F^-, H_2O can react with F^- to form HF and OH^-, forming a slightly basic environment, (the H_3O^+ reacts with OH^- to form $2H_2O$), as H_2O acts as proton donor.

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

Low Merit exemplar for 91392 2015		Total score	15
Q	**Grade score**	**Annotation**	
1	M5	This provides evidence for M5 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 and degree of dissociation for all three substances but do not write any equations. For conductivity they relate conductivity to the presence of ions and dissociation for all three substances but do not write any equations. Had they written correct equations and compared the relative strengths of the weak bases they may have got excellence for both parts.	
2	M5	This provides evidence for M5 because they correctly write the solubility equation and expression in (a)(i) & (ii), calculate the solubility product in (a) (iii), in (c) there is one error in the calculation giving an answer that is a power of ten out. Had they done this correctly they would have gained an excellence and E7 for the question.	
3	M5	This provides evidence for M5 because they correctly explain why pH is greater than 7 with an equation in (a)(ii), in (a) (iii) they correctly calculate the pH of the buffer but do not evaluate its ability. Had they done this they may have gained excellence and E7 for the question. In (a)(iv) they perform one calculation correctly ([H_3O^+] to pH).	

3

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High Merit

TOTAL 18

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QUESTION ONE HIGH MERIT

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.

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

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

$CH_3NH_3^+{}_{(aq)} + H_2O_{(aq)} \rightleftharpoons CH_3NH_2{}_{(aq)} + H_3O^+{}_{(aq)}$

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

Do not include water.

$Cl^- \approx CH_3NH_3^+ > CH_3NH_2 = H_3O^+ > OH^-$

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

$Ka = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]} = 2.29 \times 10^{-11}$

$[CH_3NH_3Cl] = [CH_3NH_3^+]$ as completely dissociates in water

weak acid = assume $[CH_3NH_2] = [H_3O^+]$

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

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

$= \underline{6.23}$

(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:
$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ Solution completely dissociates
∴ high concentration of OH^- ions in solution as
$Kw = [OH^-][H_3O^+] = 1\times10^{-14}$, low conc. of $[H_3O^+]$ so high pH = 13.2
$CH_3NH_{2(aq)} \rightleftharpoons CH_3NH^+_{3(aq)} + OH^-_{(aq)}$ partial dissociation of
$CH_3NH_{2(aq)}$ so lower conc. of $OH^-_{(aq)}$ in solution ∴ higher
$[H_3O^+]$ than NaOH so slightly lower pH = 11.9
$CH_3COONa_{(aq)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ - full dissociation into ions
$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$ - partial dissociated into OH^- ions
very small concentration $[OH^-]$ is closer to $[H_3O^+]$
than other two solutions ∴ pH lower, closer to 7 (ie neutral)
pH = 8.98. //

/

Electrical conductivity: NaOH is a good conductor as it completely dissociates into ions, which are able to carry a charge ie conduct electricity. $NaOH_{(aq)} \rightarrow Na^+_{(aq)}, OH^-_{(aq)}$
CH_3NH_2 only partially dissociates into ions meaning it is a poor conductor. $CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + OH^-$
CH_3COONa fully dissociates into ions able to carry charge so good conductor =
$CH_3COONa_{(aq)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$ //

4

M5

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 $CaCO_3$.

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

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

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

4

(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}.

$CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ completely dissociate ∴
's' s s Solubility of $CaCO_{3(s)}$ = $Ca^{2+}_{(aq)}$ = $CO_3^{2-}{}_{(aq)}$

so $K_s = [5.74 \times 10^{-5}][5.74 \times 10^{-5}]$

$K_s(CaCO_3) = 3.29 \times 10^{-9}$

(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.

① $CaCO_{3(s)} \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

② $CO_{3(aq)}^{2-} + H_2O_{(l)} \rightleftharpoons HCO_{3(aq)}^{-} + OH^{-}(aq)$

added acid neutralises $OH^-(aq)$ ∴ drives equation 2 equilibrium to the right to minimise change. Therefore decrease of $CO_3^{2-}(aq)$ in equation ~~two~~, and in equation one. ∴ to minimise change equilibrium of equation one shifts to the right to produce more $CO_3^{2-}(aq)$ so increased solubility of $CaCO_{3(s)}$ in acidic solution.

(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

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Equation =

$(Q_s(Pb(OH)_2))$ $Pb(OH)_{2(s)} \rightarrow Pb^{2+}_{(aq)} + 2OH^-_{(aq)}$

$= [Pb^{2+}][OH^-]^2$

$= \left[\frac{0.00421}{2}\right]\left[\frac{3.98 \times 10^{-2}}{2}\right]$

$NaOH_{(aq)} \rightarrow Na^{2+}_{(aq)} + OH^-_{(aq)}$

$[OH^-] = 3.98 \times 10^{-2}$ mol L^{-1}

$Q_s = 4.19 \times 10^{-5}$

$\therefore Q_s > K_s$ (of $(Pb(OH_2))$)

$\therefore$ precipitate forms ($Pb(OH)_2$)

1

M6

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.

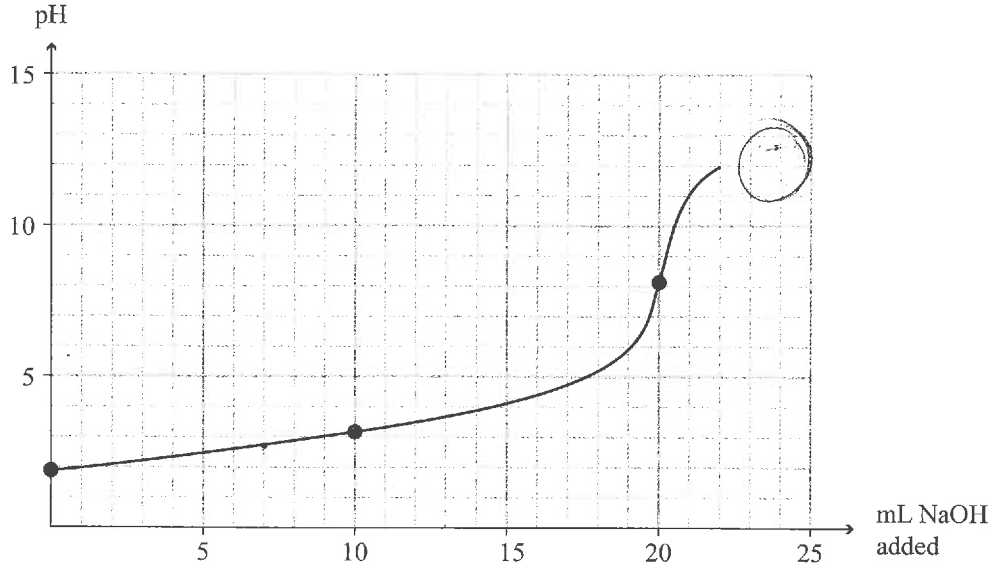
The equation for the reaction is:

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

$$pK_a(HF) = 3.17$$

$HF \rightleftharpoons H^+ + F^-$
$F^- \rightleftharpoons OH^- + HF$
$NaOH \rightarrow Na^+ + OH^-$

The titration curve is given below:



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

F^-, Na^+, OH^-

4

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

Include an equation in your answer.

$HF_{(aq)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$ basic salt formed $NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ fully dissociates so higher concentration $[OH^-]$ present at equivalence point.

(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.

~~When ... of NaOH has been added, the nHF = nF~~

$Ka(HF) = \frac{\boxed{F^-}\boxed{H_3O^+}}{\boxed{HF}}$ so $[F^-] = $'s' $[HF] = 2s$

$\therefore [H_3O^+] = 2 \times Ka$
$= 1.35 \times 10^{-3}$ mol L^{-1}

pH = 2.87

Can function as buffer as relatively noticeable similar ~~volume~~ amount of HF and conjugate base F^- present in solution. ✓

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

~~$nHF = \left(\frac{0.258 \times 0.02}{0.044}\right) = 0.117$ mol~~
~~$nNaOH = (0.258 \times 0.024) = 0.141$ mol~~
~~At 24mL added = 0.044~~

$c\,NaOH = \frac{0.001032}{0.044} = 2.35 \times 10^{-2}$ mol L^{-1}

as $NaOH \rightarrow Na^+ + OH^-$ $[NaOH] = [OH^-]$

$[OH^-] = \frac{Kw}{\boxed{H_3O^+}}$ so $[H_3O^+] = 4.26 \times 10^{-13}$

$c = \frac{n}{V}$

pH = 12.37

	HF	+ NaOH	→ NaF	+ H_2O
n initial =	0.00516	0	0	0
n added =	0	0.006192	0	0
n final =	0	0.001032	→ 0.001032	

C

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.

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.

pKa of CH_3COOH is 4.76, higher than pKa of HF which is = 3.17. ∴ CH_3COOH ~~has~~ ~~is~~ a weaker acid meaning $[H_3O^+]$ is lower meaning pH of acid is higher ∴ at equivalence point, weaker ~~base~~ acid so higher pH than HF titration

u

E7

High Merit exemplar for 91392 2015			Total score	18

Q	Grade score	Annotation
1	M5	This provides evidence for M5 because the equations and species list are correct in part (a)(i), (ii) & (iii) and in (a) (iv) the calculation is correct. Also in (b), although they recognise pH depends on hydronium ion concentration and degree of dissociation for all three substances, the CH_3NH_2 equation is incorrect and they do not compare the relative strengths of the weak bases. For conductivity they relate conductivity the presence of ions and dissociation for all three substances but do not specify amounts or concentrations of ions.
2	M6	This provides evidence for M6 because they correctly write the solubility equation and expression in (a)(i) & (ii) and calculate the solubility product in (a)(iii). In (b) they recognise H_3O^+ will remove CO_3^{2-} and provide insufficient explanation. In (c) they follow correct process but make an error in the calculation giving an incorrect IP which they correctly compare to Ks.
3	E7	This provides evidence for E7 because they correctly calculate the pH of the buffer but do not evaluate its ability and in (a)(iv) they correctly calculate the pH. Had they evaluated the buffer they may have gained excellence and E8 for the question.