



NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

EXEMPLAR

Level 3 Chemistry, 2013

91392 Demonstrate understanding of equilibrium principles in aqueous systems

2.00 pm Tuesday 19 November 2013
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 space for any answer, use the page(s) provided at the back of this booklet and clearly number the question.

Check that this booklet has pages 2–10 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 MERIT

TOTAL

14

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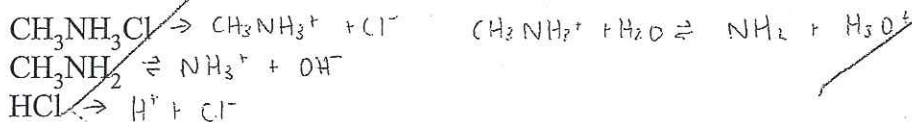
You are advised to spend 60 minutes answering the questions in this booklet.

QUESTION ONE

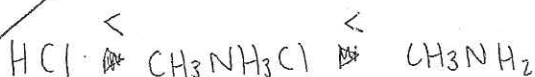
- (a) 1 mol of each of the following substances was placed in separate flasks, and water was added to these flasks to give a total volume of 1 L for each solution.

In the box below, rank these solutions in order of **increasing** pH.

Justify your choice and include equations where appropriate.



Order of increasing pH



HCl will have the lowest pH because it will fully dissociate in water to form H^+ and Cl^- ions and H^+ ions cause acidity.

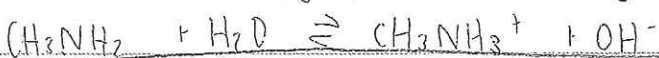
$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ At this level, it is expected that candidates using H_3O^+ , not H^+

$\text{CH}_3\text{NH}_3\text{Cl}$ will first split into its ions and then the NH_3^+ will ^{form an equilibrium} react with water to form H_3O^+ and CH_3NH_2



It is not as strong as HCl because there will always be ~~unreacted~~ CH_3NH_3^+ ions present as it is in equilibrium so a smaller amount of H_3O^+ present, hence higher pH.

CH_3NH_2 forms an equilibrium with water to form OH^- ions which give it the highest pH.



A good answer, spoiled by the use of H^+

(b) The conductivity of the 1 mol L⁻¹ solutions formed in (a) can be measured.

In the box below, rank these solutions in order of **decreasing** conductivity.

Order of decreasing conductivity

~~HCl > CH₃NH₃Cl > CH₃NH₂~~
 HCl > CH₃NH₃Cl > CH₃NH₂

Compare and contrast the conductivity of each of the 1 mol L⁻¹ solutions, with reference to species in solution.

HCl fully dissociates in water so HCl will all split up ^{into H⁺ and Cl⁻} and there will be no HCl left so will be ^{among the best} ~~the best~~ conductor. Conductivity depends on the amount of charged mobile particles (ions) present. HCl will have lots so is ^{among the best} ~~the best~~ conductor. However CH₃NH₃Cl will also fully dissociate into CH₃NH₃⁺ and Cl⁻ making it equally as good of a conductor BUT CH₃NH₃⁺ further reacts with water to form CH₃NH₂ and H₃O⁺. CH₃NH₂ is not charged so there will always be some CH₃NH₂ present meaning the conductivity is not as good as HCl which has all charged particles. CH₃NH₂ forms an equilibrium with water to form CH₃NH₃⁺ and OH⁻ but since it is in equilibrium there will always be some CH₃NH₂ present which is not a charged particle giving it the worst conductivity. CH₃NH₃Cl is a better conductor than CH₃NH₂ because it first splits into ions, then forms an equilibrium so more ions are present (better conductivity)

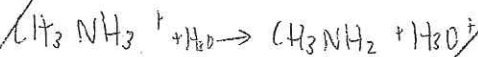
Correctly discusses mobile ions and full dissociation of HCl, and partial dissociation of CH₃NH₂. Fails to recognise that CH₃NH₃Cl has an equivalent concentration of ions to HCl

- (c) (i) The following two solutions from part (a) are mixed to form a buffer solution:

20.0 mL of 1 mol L⁻¹ CH₃NH₃Cl and 30.0 mL of 1 mol L⁻¹ CH₃NH₂

Calculate the pH of the resultant buffer solution.

$$pK_a(\text{CH}_3\text{NH}_3^+) = 10.64$$



$$pH = -\log [\text{H}_3\text{O}^+]$$

$$K_a = 2.29 \times 10^{-11}$$

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]} = 2.29 \times 10^{-11}$$

$$= \frac{1 \times \frac{30}{50} [\text{H}_3\text{O}^+]}{1 \times \frac{20}{50}} = 2.29 \times 10^{-11}$$

~~$$pH = -\log 2.29 \times 10^{-11}$$~~

~~$$[\text{H}_3\text{O}^+] = 1.53 \times 10^{-11}$$~~

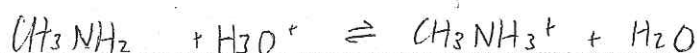
~~$$pH = -\log 1.53 \times 10^{-11}$$~~
~~$$= 10.8$$~~

Correct

(ii) Explain the effect on the solution formed in (i) when a small amount of acid is added.

~~As the pH of the buffer is 10.8, it will work best when small amounts of added acid are added~~

Buffers are able to resist changes in pH so when a small amount of acid is added, the CH_3NH_2 will react to ~~prev~~ use up the added acid



As the pH of the buffer is 10.8, it will be more effective against added base but it will still buffer the effect of added acid

Correct equation that recognises that added acid reacts with CH_3NH_2 . No link to $[\text{H}_3\text{O}^+]$

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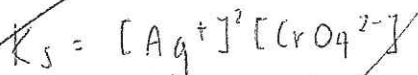
MG

QUESTION TWO

In an experiment, a saturated solution was made by dissolving 1.44×10^{-3} g of Ag_2CrO_4 in water, and making it up to a volume of 50.0 mL.

$$M(\text{Ag}_2\text{CrO}_4) = 332 \text{ g mol}^{-1}$$

- (a) Write the K_s expression for $\text{Ag}_2\text{CrO}_4(s) \rightarrow 2\text{Ag}^+ + \text{CrO}_4^{2-}$



Correct

- (b) (i) Calculate the solubility of $\text{Ag}_2\text{CrO}_4(s)$, and hence give the $[\text{Ag}^+]$ and $[\text{CrO}_4^{2-}]$ in the solution.

$$\begin{aligned} \text{let } [\text{Ag}^+] [\text{CrO}_4^{2-}] &= s & c &= \frac{n}{V} \\ [2s]^2 &= [s] & &= 4.34 \times 10^{-6} \div 0.05 \\ n &= cV & &= 8.67 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} n &= \frac{m}{M} & [\text{Ag}_2\text{CrO}_4] &= 8.67 \times 10^{-5} \text{ mol L}^{-1} \\ &= \frac{1.44 \times 10^{-3}}{332} & [\text{Ag}^+] &= 2.89 \times 10^{-5} \\ & & [\text{Ag}^+] &= 5.78 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

$$n(\text{Ag}_2\text{CrO}_4) = 4.34 \times 10^{-6} \quad [\text{CrO}_4^{2-}] = 2.89 \times 10^{-5} \text{ mol L}^{-1}$$

Correct solubility of Ag_2CrO_4 calculated

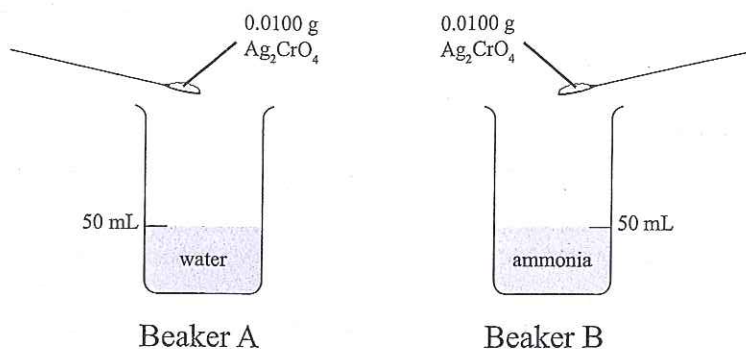
- (ii) Determine the $K_s(\text{Ag}_2\text{CrO}_4)$.

$$K_s = 4s^3$$

$$K_s = 4(5.78 \times 10^{-5})^2 (2.89 \times 10^{-5}) = 9.67 \times 10^{-14}$$

Incorrect solubility for individual ions but has recognised the 2 : 1 ratio

- (c) In another experiment, 0.0100 g of Ag_2CrO_4 in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of Ag_2CrO_4 was made up to a volume of 50.0 mL with 0.100 mol L^{-1} ammonia solution.



Compare and contrast the solubility of Ag_2CrO_4 in beaker A and beaker B.

No calculations are necessary.

In water, Ag_2CrO_4 will split up into its ions Ag^+ and CrO_4^{2-} so will be quite ~~very~~ soluble.

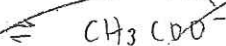
When in ammonia, Ag_2CrO_4 will split up into its ions Ag^+ and CrO_4^{2-} too. However, Ag^+ and NH_3 for react to form a ~~complex ion~~ ~~complex~~ $[\text{Ag}(\text{NH}_3)_2]^+$ ion. By ammonia using up Ag^+ ions, the forward reaction $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$ will be favoured in order to replace lost Ag^+ ions, thus increasing its solubility in ammonia.

Correct equation and tenuously links this to the formation of a complex ion, but clearly discusses the equilibrium

QUESTION THREE

20.0 mL of $0.0896 \text{ mol L}^{-1}$ ethanoic acid is titrated with 0.100 mol L^{-1} sodium hydroxide.

$$pK_a(\text{CH}_3\text{COOH}) = 4.76$$



- (a) Calculate the pH of the ethanoic acid before any NaOH is added.

$$K_{\text{ant}} \quad \text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 10^{-4.76} = 1.74 \times 10^{-5}$$

$$= \frac{[\text{H}_3\text{O}^+]^2}{0.0896} = 1.74 \times 10^{-5}$$

$$\Rightarrow 5.6 \times 10^{-6} \quad [\text{H}_3\text{O}^+] = 1.25 \times 10^{-3}$$

Correct

$$\text{pH} = -\log 1.25 \times 10^{-3}$$

$$= 2.9$$

- (b) Halfway to the equivalence point of the titration, the $\text{pH} = \text{p}K_a$ of the ethanoic acid.

Discuss the reason for this.

This is because the amount of conjugate acid and base are equal. So, the amount of CH_3COO^- is equal to the amount of CH_3COOH present.

Recognises that $[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$

- (c) (i) Discuss the change in the concentration of species in solution, as the first 5.00 mL of NaOH is added to the 20.0 mL of ethanoic acid.

Your answer should include chemical equations.

No calculations are required.

- (ii) Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.

$$K_b = \frac{K_w}{K_a} \quad \text{pH} = -\log [\text{H}_3\text{O}^+] \quad [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

$$[\text{H}_3\text{O}^+] = 1.25 \times 10^{-3} = \frac{K_w}{[\text{OH}^-]} = \frac{1. \times 10^{-14}}{[\text{OH}^-]}$$

$$[\text{OH}^-] = 8.00 \times 10^{-12}$$

$$K_b = \frac{1. \times 10^{-14}}{1.74 \times 10^{-5}} = 5.75 \times 10^{-10}$$

Incorrect

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HIGH MERIT

TOTAL

18

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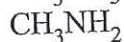
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QUESTION ONE

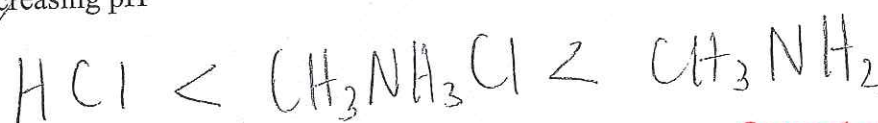
- (a) 1 mol of each of the following substances was placed in separate flasks, and water was added to these flasks to give a total volume of 1 L for each solution.

In the box below, rank these solutions in order of **increasing** pH.

Justify your choice and include equations where appropriate.



Order of increasing pH

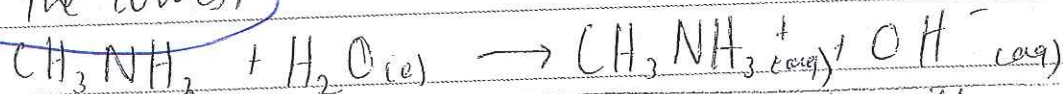


Correct order

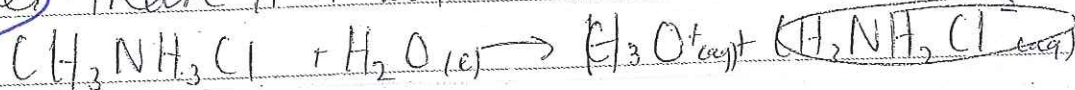
HCl is a strong acid so it fully dissociates into its ions giving it the ^{lowest} highest pH. The pH is based on the number of ions in solution.



CH_3NH_2 is a ~~weak~~ weak base and so it will only partially dissociate into its ions but because it is basic it pH will be the lowest.



$\text{CH}_3\text{NH}_3\text{Cl}$ is a weak acid and so it will only partially dissociate into its ions but because it is a weak acid its pH will be higher than HCl but lower than CH_3NH_2 .



Two correct equations, however, candidate has confused both the acidic and basic end of the pH scale

(b) The conductivity of the 1 mol L⁻¹ solutions formed in (a) can be measured.

In the box below, rank these solutions in order of **decreasing** conductivity.

Order of decreasing conductivity

**Correct
order**



Compare and contrast the conductivity of each of the 1 mol L⁻¹ solutions, with reference to species in solution.

The conductivity of a solution is based on the number of ions in solution.

HCl is a strong acid which fully dissociates into its ions therefore making it a good conductor. H₃O⁺ and Cl⁻ ions in solution.

Both CH₃NH₃Cl and CH₃NH₂ are weak solutions (weak acid/weak base) and therefore will have low conductivity because they only partially dissociate and therefore there are only few ions in solution making them bad conductors.

**Recognises that HCl fully dissociates and CH₃NH₂ only partially dissociates.
Links to concentration of ions determining conductivity**

- (c) (i) The following two solutions from part (a) are mixed to form a buffer solution:
 20.0 mL of 1 mol L⁻¹ CH₃NH₃Cl and 30.0 mL of 1 mol L⁻¹ CH₃NH₂

Calculate the pH of the resultant buffer solution.

$$pK_a(\text{CH}_3\text{NH}_3^+) = 10.64$$

$$C = \frac{1 \times 0.02}{(0.02 + 0.03)} = 0.04 \text{ mol L}^{-1} \text{ for } \text{CH}_3\text{NH}_3\text{Cl}$$

$$C = \frac{1 \times 0.03}{0.05} = 0.06 \text{ mol L}^{-1} \text{ for } \text{CH}_3\text{NH}_2$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3\text{Cl}]}$$

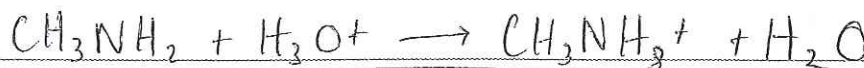
$$\text{pH} = 10.64 + \log \frac{0.06}{0.04}$$

$$\text{pH} = 10.8$$

Correct

(ii) Explain the effect on the solution formed in (i) when a small amount of acid is added.

This buffer solution consists of a weak base / weak acid. If a small amount of acid is added the base will neutralise the effect of the acid, as it will form its conjugate acid.



Correct equation that recognises that the acid reacts with the base

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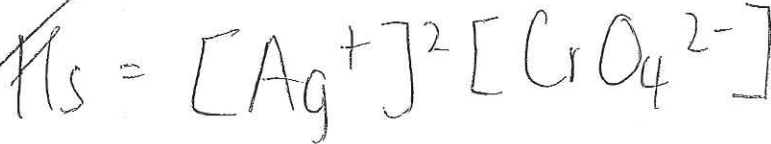
M6

QUESTION TWO

In an experiment, a saturated solution was made by dissolving 1.44×10^{-3} g of Ag_2CrO_4 in water, and making it up to a volume of 50.0 mL.

$$M(\text{Ag}_2\text{CrO}_4) = 332 \text{ g mol}^{-1}$$

- (a) Write the K_s expression for $\text{Ag}_2\text{CrO}_4(s)$.



Correct

- (b) (i) Calculate the solubility of $\text{Ag}_2\text{CrO}_4(s)$, and hence give the $[\text{Ag}^+]$ and $[\text{CrO}_4^{2-}]$ in the solution.

$$n = \frac{m}{M} \quad n = \frac{1.44 \times 10^{-3}}{332}$$

$$n = 4.3373 \times 10^{-6} \text{ mol}$$

$$s = \frac{n}{V} \quad s = \frac{4.3373 \times 10^{-6}}{0.05}$$

$$s = 8.67 \times 10^{-5} \text{ mol L}^{-1}$$

$$K_s = [2s]^2 [s]$$

- (ii) Determine the $K_s(\text{Ag}_2\text{CrO}_4)$.

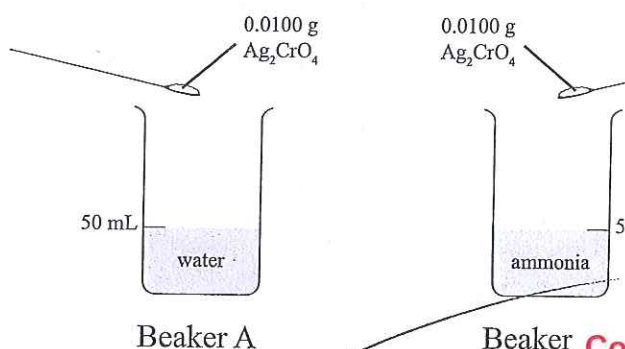
$$K_s = 4s^3$$

$$K_s = 4(8.67 \times 10^{-5})^3$$

$$K_s = 2.61 \times 10^{-12}$$

Correct, however, failed to calculate $[\text{Ag}^+]$ and $[\text{CrO}_4^{2-}]$

- (c) In another experiment, 0.0100 g of Ag_2CrO_4 in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of Ag_2CrO_4 was made up to a volume of 50.0 mL with 0.100 mol L^{-1} ammonia solution.

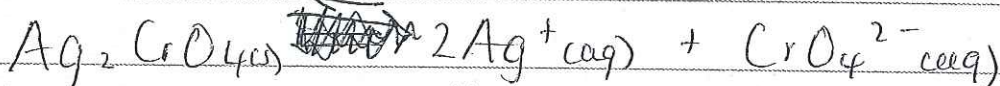


Correct equation for the formation of the complex ion
Correct equilibrium equation linked to the formation of the complex ion

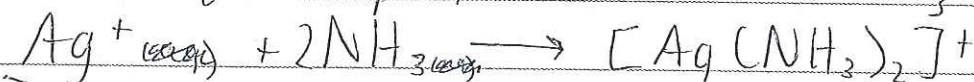
Compare and contrast the solubility of Ag_2CrO_4

No calculations are necessary.

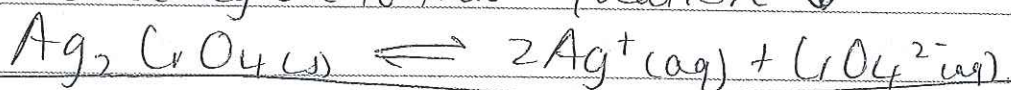
In beaker A where Ag_2CrO_4 is mixed with water it would dissolve the Ag_2CrO_4 into its ions



In beaker B where there is an ammonia solution the silver ions (the Ag^+ (silver ions)) will form a complex ion with the NH_3



In reference again to this equation ↓



due to the formation of the complex ion Ag^+ ions would be removed from the ^{equilibrium} and ~~the~~ to restore this concentration the ^{equilibrium} would shift to the right therefore ^{increasing the solubility} dissolving more of the Ag_2CrO_4 . Therefore in comparison, the Ag_2CrO_4 in beaker B is more soluble than the Ag_2CrO_4 in beaker A

QUESTION THREE

20.0 mL of 0.0896 mol L⁻¹ ethanoic acid is titrated with 0.100 mol L⁻¹ sodium hydroxide.

$$pK_a(\text{CH}_3\text{COOH}) = 4.76$$

- (a) Calculate the pH of the ethanoic acid before any NaOH is added.

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times c(\text{HA})}$$

$$K_a = 10^{-4.76}$$

$$K_a = 1.7378 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = \sqrt{1.7378 \times 0.0896}$$

$$= 1.2478 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pH} = 2.90$$

Correct

- (b) Halfway to the equivalence point of the titration, the pH = pK_a of the ethanoic acid.

Discuss the reason for this.

halfway to the equivalence point half of the ethanoic acid has reacted with the NaOH that has been titrated. This is also when there is an equal equi-molar amount of the weak acid and its conjugate base.

$$\text{re. } [\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$$

Correct

placing this into our formula.

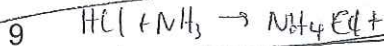
$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

these two are in equal amounts one then

$$\text{pH} = \text{p}K_a + \log [1]$$

$$\text{the } \log [1] = 0$$

$$\therefore \text{pH} = \text{p}K_a \text{ of ethanoic acid.}$$



- (c) (i) Discuss the change in the concentration of species in solution, as the first 5.00 mL of NaOH is added to the 20.0 mL of ethanoic acid.

Your answer should include chemical equations.

No calculations are required.

~~The equation of the titration is~~



The pH of the titration mixture increases as more NaOH is added because it is a strong base. The concentration of ethanoic acid decreases since more NaOH is added (it is diluted with NaOH).

Correctly states that $[\text{CH}_3\text{COOH}]$ decreases

- (ii) Calculate the pH of the titration mixture after 5.00 mL of NaOH has been added.

~~$$\text{pH} = \text{pK}_a + \log \frac{[\text{B}]}{[\text{A}]}$$~~

~~$$c(\text{B}) = \frac{0.1 \times (0.005 - 0)}{(0.005 + 0.02)} = 0.02 \text{ mol l}^{-1}$$~~

~~$$c(\text{A}) = \frac{0.0896 \times (0.02 - 0)}{(0.005 + 0.02)} = 0.07168 \text{ mol l}^{-1}$$~~

~~$$\text{pH} = \text{pK}_a + \log$$~~

~~$$\text{pH} = 4.76 + \log \frac{[0.02]}{[0.07168]}$$~~

~~$$\text{pH} = 4.21$$~~

Correctly calculated 'n' for the wrong base at the start (CH_3COO^- instead of NaOH)

U

M5