



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 EXCELLENCE**

TOTAL

ASSESSOR'S USE ONLY

19

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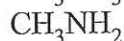
You are advised to spend 60 minutes answering the questions in this booklet.

### 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.



Only 3 equations correct

Order of increasing pH



pH  $\approx$  1

HCl is a strong acid which fully dissociates in water to form  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$ . (equation 1)

Due to its full dissociation its pH is the lowest as  $[\text{H}_3\text{O}^+]$  will be the highest.

(HCl pH  $\approx$  1)

$\text{CH}_3\text{NH}_3\text{Cl}$  also fully dissociates in water to form  $\text{CH}_3\text{NH}_3^+$  and  $\text{Cl}^-$ . (equation 2)

$\text{CH}_3\text{NH}_3^+$  is a weak acid which partially dissociates in (reacts with) water to make the solution slightly

acidic meaning that the pH of  $\text{CH}_3\text{NH}_3\text{Cl}$  solution will have a higher pH than HCl but lower than  $\text{CH}_3\text{NH}_2$ . (pH  $\approx$  5).

$\text{CH}_3\text{NH}_2$  is a weak base that partially dissociates in water. (equation 4)

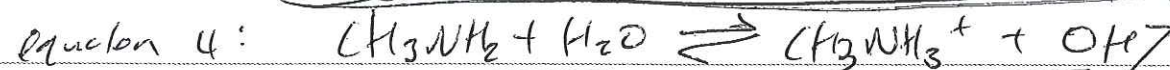
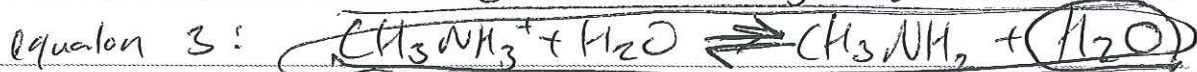
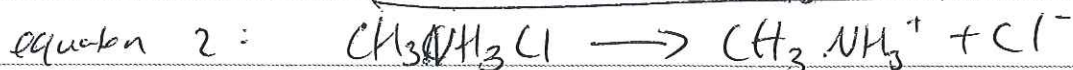
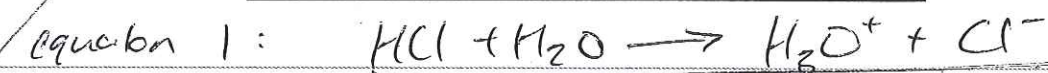
This partial dissociation of  $\text{OH}^-$  means that the pH of  $\text{CH}_3\text{NH}_2$  is greater than 7 and as such it will have the highest pH (due to the lowest conc. of  $\text{H}_3\text{O}^+$  ions). See extra page for equations.

Extra paper if required.

Write the question number(s) if applicable.

ASSESSOR  
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NUMBER

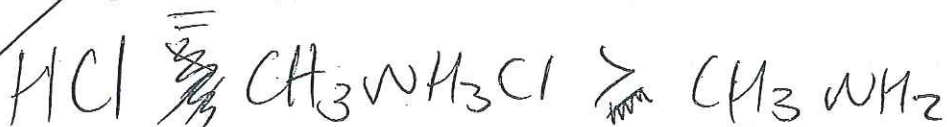
Q1a)



(b) The conductivity of the 1 mol L<sup>-1</sup> solutions formed in (a) can be measured.

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

Order of decreasing conductivity



Compare and contrast the conductivity of each of the 1 mol L<sup>-1</sup> solutions, with reference to species in solution.

Because both HCl and CH<sub>3</sub>NH<sub>3</sub>Cl fully dissociate in water there is a high concentration of ions in the solution and as such these ions can carry a charge which means that HCl and CH<sub>3</sub>NH<sub>3</sub>Cl have high conductivity (conductivity will be equal to each other).

Because CH<sub>3</sub>NH<sub>2</sub> is a weak base it only partially dissociates in water which means that there is very little ions present in the solution which means that CH<sub>3</sub>NH<sub>2</sub> will have the lowest conductivity out of the three solutions.

Fully recognises the role of ions in conductivity and knows that HCl and CH<sub>3</sub>NH<sub>3</sub>Cl will have the same amount of ions

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

(20.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub>Cl and 30.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>2</sub>)

Calculate the pH of the resultant buffer solution.

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

Dilution factor due to <sup>aqueous</sup> solutions being mixed.

$$[\text{CH}_3\text{NH}_3^+] = 1 \times \frac{20}{50} = 0.4 \text{ mol L}^{-1}$$

$$[\text{CH}_3\text{NH}_2] = 1 \times \frac{30}{50} = 0.6 \text{ mol L}^{-1}$$



$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$\therefore pK_a = \text{pH} - \log \frac{[\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}$$

$$\text{so pH} = pK_a + \log \frac{[\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}$$

$$= 10.64 + \log \frac{0.6}{0.4}$$

$$= 10.816$$

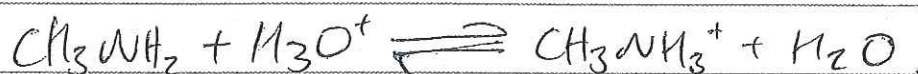
$$= 10.8 \text{ (3sf)}$$

Fully correct and clearly shows working

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

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USE ONLY

When a small amount of acid is added to the buffer solution the conjugate base ( $\text{CH}_3\text{NH}_2$ ) will react with the acid to neutralise it and a change in pH. It does this by reaction with the  $\text{H}_3\text{O}^+$  ions to form  $\text{H}_2\text{O}$  & the acid of the buffer  $\text{CH}_3\text{NH}_3^+$ .



Because the product of the neutralisation is water the  $\Delta$  in pH is negated. However the acid is formed which may slightly increase the pH but it will be a very minimal change in pH.

Recognises that  $\text{CH}_3\text{NH}_2$  reacts with added acid. Gives the correct equation and states that there may be a very small change in the pH.

Although the candidate has not mentioned  $[\text{H}_3\text{O}^+]$ , this was mentioned in part (a). The candidate clearly understands the concept of buffers.

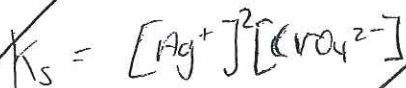
E7

## QUESTION TWO

In an experiment, a saturated solution was made by dissolving  $1.44 \times 10^{-3}$  g of  $\text{Ag}_2\text{CrO}_4$  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.

$$n = \frac{m}{M} = \frac{1.44 \times 10^{-3}}{332} = 4.337 \times 10^{-6} \text{ mol}$$

$$c = \frac{n}{V} = \frac{4.337 \times 10^{-6}}{0.05} = 8.6746 \times 10^{-5} \text{ mol L}^{-1}$$

∴ solubility of  $\text{Ag}_2\text{CrO}_4(s)$  is  $8.67 \times 10^{-5} \text{ mol L}^{-1}$  (3sf)

$$[\text{Ag}^+] = 2 \times 8.674 \times 10^{-5} = 1.73 \times 10^{-4} \text{ mol L}^{-1}$$

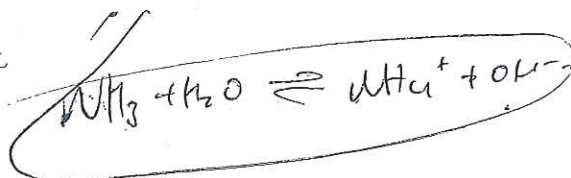
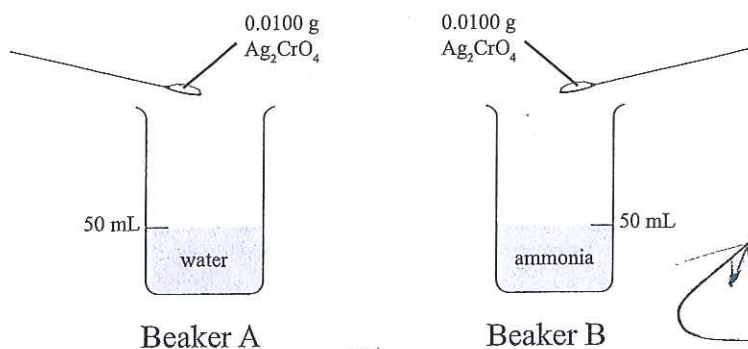
$$[\text{CrO}_4^{2-}] = 8.67 \times 10^{-5} \text{ mol L}^{-1} \quad (3sf)$$

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

$$\begin{aligned} K_s &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ &= (1.73 \times 10^{-4})^2 \times 8.67 \times 10^{-5} \\ &= 2.61 \times 10^{-12} \quad (3sf) \end{aligned}$$

Correct to 3 significant figures

- (c) In another experiment, 0.0100 g of  $\text{Ag}_2\text{CrO}_4$  in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of  $\text{Ag}_2\text{CrO}_4$  was made up to a volume of 50.0 mL with 0.100 mol  $\text{L}^{-1}$  ammonia solution.



Compare and contrast the solubility of  $\text{Ag}_2\text{CrO}_4$  in beaker A and beaker B.

No calculations are necessary.

in Beaker A the solubility of  $\text{Ag}_2\text{CrO}_4$  will remain the same as it has for previous questions.

Now in Beaker B the solubility of  $\text{Ag}_2\text{CrO}_4$  will increase. This is because in Beaker B the  $\text{Ag}_2\text{CrO}_4$  is added to a solution of ammonia which is a weak base. This means that it also dissociates to form  $\text{OH}^-$  ions and  $\text{NH}_4^+$  ions. Because of the  $\text{OH}^-$  ions, when  $\text{Ag}_2\text{CrO}_4$  is dissolved into the solution the  $\text{Ag}^+$  ions will react with the  $\text{OH}^-$  ions to form  $\text{AgOH}$ .

As such the concentration of  $\text{Ag}^+$  ions will decrease. As  $K_s$  must remain constant, the equilibrium ( $\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$ ) will shift to the right (favoring the forward reaction) and as such more  $\text{Ag}_2\text{CrO}_4$  will dissolve to increase the conc. of  $\text{Ag}^+$  ions.

As such the solubility of  $\text{Ag}_2\text{CrO}_4$  will increase.

Recognises that a great amount dissolves in Beaker B and links this to equilibrium, albeit incorrectly.



## QUESTION THREE

20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide.

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

$$K_a = 10^{-4.76} = 1.7378 \times 10^{-5}$$

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



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Assuming:  $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$   
 $[\text{CH}_3\text{COOH}] \approx 0.0896$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{K_a \times [\text{CH}_3\text{COOH}]} \\ &= \sqrt{1.7378 \times 10^{-5} \times 0.0896} \\ &= 1.2478 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (1.2478 \times 10^{-3}) \\ &= 2.90 \text{ (3sf)} \end{aligned}$$

Correct

- (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.

At the half way to the equivalence point, half of the acid has been neutralised by the addition of sodium hydroxide. (because at equivalence point all acid has been neutralised), so as such half of the ethanoic acid has been converted to ethanoate ion ( $\text{CH}_3\text{COO}^-$ ) which means that  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$

Because  $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$  and  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$  then  $K_a = [\text{H}_3\text{O}^+]$  and so  $\text{p}K_a (-\log K_a)$  will equal  $\text{pH} (-\log [\text{H}_3\text{O}^+])$

Correctly recognises that  $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$  and links this to the equation for  $K_a$

- (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.

As the first 5 ml of NaOH is added to the ethanoic acid, all of it will be neutralised and reacted with the ethanoic acid. However, this neutralisation ~~forms~~ forms  $H_2O$  as a product. This means that the concentration of ethanoic acid has been diluted <sup>so  $[CH_3COOH]$  has decreased</sup>. This neutralisation <sup>reaction</sup> forms  $CH_3COO^-$  as a product and as such the concentration of  $CH_3COO^-$  will increase and as such the conc. of  $CH_3COOH$  will decrease (as  $K_a$  must remain constant).

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

$$c(CH_3COOH) = 0.0896 \times \frac{20}{25} \\ = 0.07168 \text{ mol L}^{-1}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad \text{Assuming } [H_3O^+] = [CH_3COO^-]$$

$$\therefore [H_3O^+] = \sqrt{K_a \times [CH_3COOH]} \\ = \sqrt{1.7378 \times 10^{-5} \times 0.07168} \\ = 1.116 \times 10^{-3} \text{ mol L}^{-1}$$

$$pH = -\log 1.116 \times 10^{-3} \\ = 2.95 \text{ (3sf)}$$

Incorrect

4/3 marks

Recognises the change in concentration of the two species

m6

## Level 3 Chemistry, 2013

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**HIGH EXCELLENCE**

TOTAL

23

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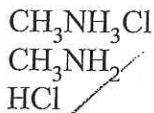
You are advised to spend 60 minutes answering the questions in this booklet.

### 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.

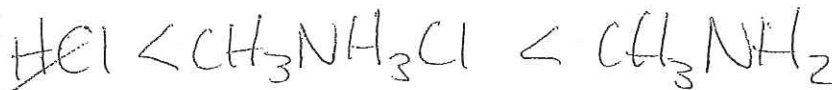
In the box below, rank these solutions in order of **increasing** pH.

Justify your choice and include equations where appropriate.

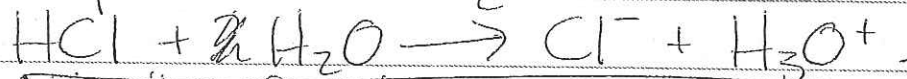


Four equations correct, linked correctly to the degree of dissociation and [H<sub>3</sub>O<sup>+</sup>] [OH<sup>-</sup>]

Order of increasing pH



\* HCl is a strong acid so will completely dissociate in water, donating a proton to H<sub>2</sub>O.

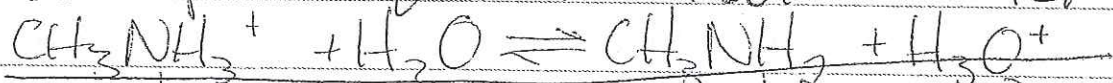


As all of the HCl dissociates to form Cl<sup>-</sup> & H<sub>3</sub>O<sup>+</sup>, the [H<sub>3</sub>O<sup>+</sup>] will be the highest and the pH will be the lowest (pH = -log[H<sub>3</sub>O<sup>+</sup>])

\* CH<sub>3</sub>NH<sub>3</sub>Cl is an ionic solid. In water it will break up completely into it's ions

$$\text{CH}_3\text{NH}_3\text{Cl}_{(s)} \rightarrow \text{CH}_3\text{NH}_3^+_{(aq)} + \text{Cl}^-_{(aq)}$$

CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> is a weak acid so will set up an equilibrium with water



as H<sub>3</sub>O<sup>+</sup> forms (proton donated to H<sub>2</sub>O) the [H<sub>3</sub>O<sup>+</sup>] will be greater than [OH<sup>-</sup>] and pH < 7 however, as it is a weak acid, the pH will be greater than for HCl.

\* CH<sub>3</sub>NH<sub>2</sub> is a weak base that will partially dissociate in water

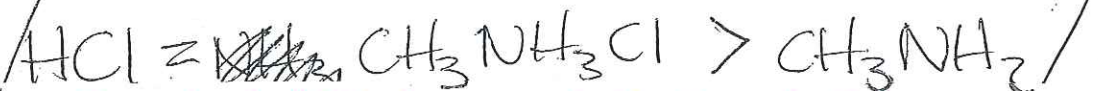
$$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$$

as OH<sup>-</sup> forms [OH<sup>-</sup>] > [H<sub>3</sub>O<sup>+</sup>] and pH > 7

- (b) The conductivity of the 1 mol L<sup>-1</sup> 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 linking ion concentration to conductivity and clearly understands that HCl and CH<sub>3</sub>NH<sub>3</sub>Cl will have equal concentrations of ions

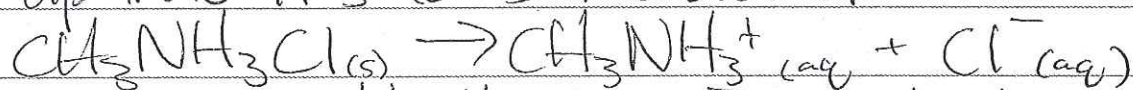
Compare and contrast the conductivity of each of the 1 mol L<sup>-1</sup> solutions, with reference to species in solution.

Conductivity is dependant on the concentration of charged particles (in this case ions) present in solution.

- \* HCl completely dissociates in water  

$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$
 forming ions (H<sub>3</sub>O<sup>+</sup> & Cl<sup>-</sup>), as a result the [ions] is high and conductivity is high

- \* CH<sub>3</sub>NH<sub>3</sub>Cl also completely breaks up into it's ions in water

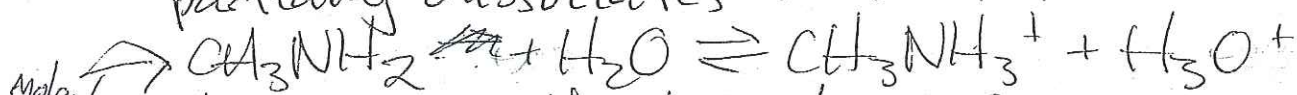


as a result the [ions] is high,

~~approximately the same as HCl, though some CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> does form two ions~~

and the same as for HCl. As a result CH<sub>3</sub>NH<sub>3</sub>Cl has conductivity equally as high, as for HCl.

- \* CH<sub>3</sub>NH<sub>2</sub> is a weak base which only partially dissociates in water



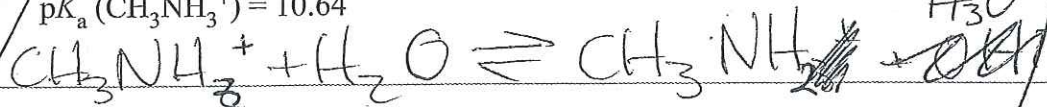
this means that only a few ions form, resulting in a low [ions] and a relatively low conductivity.

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

20.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>Cl and 30.0 mL of 1 mol L<sup>-1</sup> CH<sub>3</sub>NH<sub>2</sub>

Calculate the pH of the resultant buffer solution.

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



$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$\frac{K_a[\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]} = [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = \frac{10^{-10.64} \times 1 \times \left(\frac{20}{50}\right)}{1 \times \left(\frac{30}{50}\right)}$$

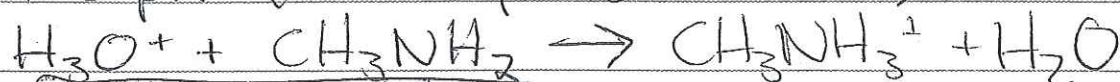
$$= 1.527 \times 10^{-11} \text{ mol L}^{-1}$$

$$\text{pH} = 10.8$$

Fully correct and clearly shows working

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

When a small amount of acid is added to the buffer solution, the solution will resist changes in the pH (resist pH decrease)



as this equation demonstrates, the  $\text{CH}_3\text{NH}_2$  will react with the added  $\text{H}_3\text{O}^+$  to form  $\text{CH}_3\text{NH}_3^+$  and  $\text{H}_2\text{O}$ . This prevents the  $[\text{H}_3\text{O}^+]$  in the solution from changing significantly. However the ratio of  $\text{CH}_3\text{NH}_2$  to  $\text{CH}_3\text{NH}_3^+$  would change slightly. This may cause the  $[\text{H}_3\text{O}^+]$  to be marginally higher

$\left( \frac{K_a [\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]} = [\text{H}_3\text{O}^+] \right)$  resulting in a slightly lower (very slight) pH.

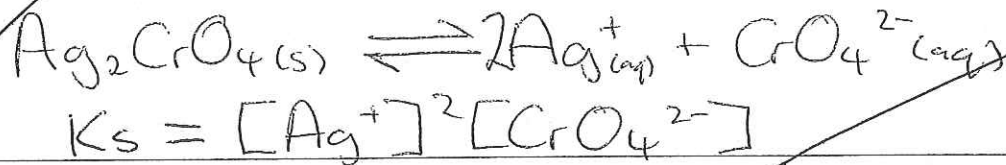
Recognises that  $\text{CH}_3\text{NH}_2$  reacts with added acid. Gives the correct equation and states that there may be a very small change in the pH.

## QUESTION TWO

In an experiment, a saturated solution was made by dissolving  $1.44 \times 10^{-3}$  g of  $\text{Ag}_2\text{CrO}_4$  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  $\text{Ag}_2\text{CrO}_4(s)$ .



- (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.

~~1.44 g = 1.44 x 10<sup>-3</sup> g~~  
 ~~$n(\text{Ag}_2\text{CrO}_4) = \frac{1.44 \times 10^{-3}}{332}$~~   
 ~~$n(\text{Ag}_2\text{CrO}_4) = \frac{1.44 \times 10^{-3}}{332}$~~   
 ~~$= 4.337 \times 10^{-6} \text{ mol}$~~   
 ~~$[\text{Ag}^+] = 2 \times \frac{4.337 \times 10^{-6}}{0.0500}$~~   
 ~~$= 1.7349 \times 10^{-4} \text{ mol L}^{-1} \Rightarrow 1.73 \times 10^{-4}$~~   
 ~~$[\text{CrO}_4^{2-}] =$~~   
 (see back)

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

$$K_s = (8.67 \times 10^{-5})(1.73 \times 10^{-4})^2$$

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

Correct to 3 significant figures



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

QUESTION  
NUMBER

Two  
(b) i  $n(\text{Ag}_2\text{CrO}_4) = \frac{1.44 \times 10^{-3}}{332}$   
 $= 4.337 \times 10^{-6} \text{ mol}$

$$[\text{Ag}^+] = \frac{2 \times 4.337 \times 10^{-6}}{0.0500}$$

$$= 1.73 \times 10^{-4} \text{ mol L}^{-1}$$

$$[\text{CrO}_4^{2-}] = \frac{4.337 \times 10^{-6}}{0.0500}$$

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

The solubility of  $\text{Ag}_2\text{CrO}_4$  is  
 $8.67 \times 10^{-5}$   $\left( \frac{n(\text{Ag}_2\text{CrO}_4)}{\text{volume}} \right)$

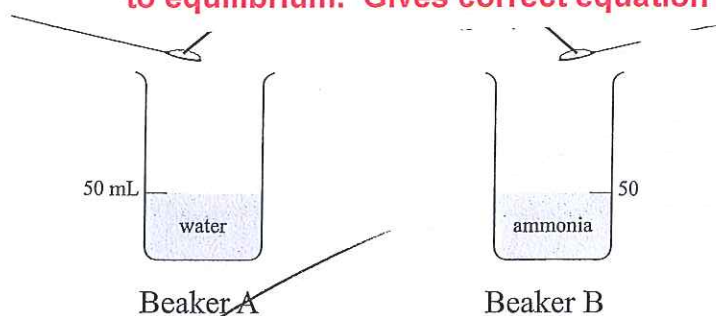
$$[\text{Ag}^+] = 2 \times s$$

$$[\text{CrO}_4^{2-}] = s$$

- (c) In another experiment, 0.0100 g of  $\text{Ag}_2\text{CrO}_4$  in beaker A was made up to a volume of 50.0 mL with water. In beaker B, 0.0100 g of  $\text{Ag}_2\text{CrO}_4$  was made up to a volume of 50.0 mL with 0.100 mol  $\text{L}^{-1}$  ammonia solution.

ASSESSOR'S  
USE ONLY

**Recognises that a great amount dissolves in Beaker B and links this to equilibrium. Gives correct equation for complex ion formation**



Compare and contrast the solubility of  $\text{Ag}_2\text{CrO}_4$  in beaker A and beaker B.

No calculations are necessary.

\* In beaker A, the solubility of  $\text{Ag}_2\text{CrO}_4$  will be normal (~~1.73 x 10<sup>-4</sup> mol L<sup>-1</sup>~~) ( $1.73 \times 10^{-4} \text{ mol L}^{-1}$ )



\* However in beaker B, the solubility of  $\text{Ag}_2\text{CrO}_4$  will be significantly greater. In beaker B, the  $\text{Ag}^+$  that is in solution will form the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$  due to the presence of excess  $\text{NH}_3$ :



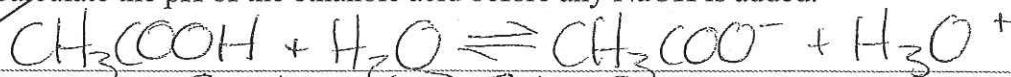
This will decrease the  $[\text{Ag}^+]$ . As a result the solubility equilibrium (1) will favour the forward reaction to increase the  $[\text{Ag}^+]$  in the solution. Obviously this results in more  $\text{Ag}_2\text{CrO}_4$  dissolving and solubility increasing. Hence the solubility of  $\text{Ag}_2\text{CrO}_4$  is significantly greater in Beaker B ~~than in~~ <sup>with</sup> excess  $-0.100 \text{ mol L}^{-1} - \text{NH}_3$  than in beaker A (with water).

## QUESTION THREE

20.0 mL of 0.0896 mol L<sup>-1</sup> ethanoic acid is titrated with 0.100 mol L<sup>-1</sup> sodium hydroxide.

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

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



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \quad \leftarrow \begin{array}{l} \text{assume } [\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] \\ \& [\text{solution}] = [\text{CH}_3\text{COOH}] \end{array}$$

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{10^{-4.76} \times 0.0896}$$

$$= 1.248 \times 10^{-3} \text{ mol L}^{-1}$$

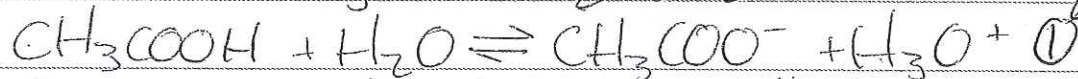
$$\text{pH} = 2.90$$

Correct

- (b) Halfway to the equivalence point of the titration, the pH = pK<sub>a</sub> of the ethanoic acid.

Discuss the reason for this.

halfway to the equivalence point, exactly half of the CH<sub>3</sub>COOH has reacted to form CH<sub>3</sub>COO<sup>-</sup>. As a result



As a result, the concentration of CH<sub>3</sub>COO<sup>-</sup> equals the concentration of CH<sub>3</sub>COOH.

NaOH reacts with the H<sub>3</sub>O<sup>+</sup> that forms when CH<sub>3</sub>COOH donates a proton to H<sub>2</sub>O

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

if [CH<sub>3</sub>COO<sup>-</sup>] = [CH<sub>3</sub>COOH] then

$$K_a = [\text{H}_3\text{O}^+]$$

Correctly recognises that [CH<sub>3</sub>COOH] = [CH<sub>3</sub>COO<sup>-</sup>] and links this to the equation for K<sub>a</sub>

therefore pK<sub>a</sub> = pH

Hence at the half equivalence point pK<sub>a</sub> = pH due to [CH<sub>3</sub>COO<sup>-</sup>] = [CH<sub>3</sub>COOH]

Volume changes so hard to tell

- (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.

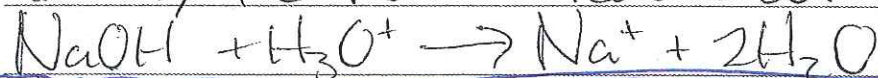
Your answer should include chemical equations:

No calculations are required.

Correct equation  
Recognises the change  
in concentration of the  
two species

when 5 mL of NaOH has been added, the titration curve has still not reach the half equivalence point. Therefore the  $[CH_3COOH] > [CH_3COO^-]$ .

From the start point to 5.0 mL added, the NaOH reacts with  $H_3O^+$

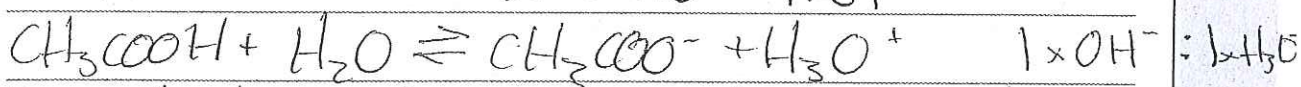


this causes more  $CH_3COOH$  to dissociate ( $[H_3O^+] \downarrow$  so  $\equiv$  'm' will  $\uparrow [CH_3O^-]$

by favouring forward reaction). As a result the ~~amount of  $CH_3COOH$  decreases~~ amount of  $CH_3COOH$  decreases and the amount of  $CH_3COO^-$  increases

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

$$n(\text{NaOH added}) = 0.005 \times 0.100 \\ = 5.00 \times 10^{-4} \text{ mol}$$



$$\Rightarrow n(CH_3COO^-) = 5.00 \times 10^{-4} \text{ mol}$$

$$[CH_3COO^-] = \frac{5.00 \times 10^{-4}}{0.025}$$

$$= 0.0200 \text{ mol L}^{-1}$$

$$\Rightarrow n(CH_3COOH) = 0.0896 \times 0.0200 - 5.00 \times 10^{-4}$$

$$= 1.292 \times 10^{-3} \text{ mol}$$

$$[CH_3COOH] = \frac{1.292 \times 10^{-3}}{0.025}$$

$$= 0.0517 \text{ mol L}^{-1}$$

$$[H_3O^+] = \frac{K_a [CH_3COOH]}{[CH_3COO^-]}$$

$$= 4.490 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = 4.35$$

Correct

E7