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91392



Draw a cross through the box (X) if you have NOT written in this booklet

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Mana Tohu Mātauranga o Aotearoa
New Zealand Qualifications Authority

Level 3 Chemistry 2024

91392 Demonstrate understanding of equilibrium principles in aqueous systems

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 and other reference material are provided in the Resource Booklet L3–CHEMR.

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

Check that this booklet has pages 2–12 in the correct order and that none of these pages is blank.

Do not write in any cross-hatched area (X/X/X). This area will be cut off when the booklet is marked.

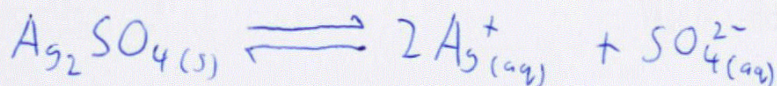
YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Excellence

TOTAL 22

QUESTION ONE

- (a) (i) Write the equation for the equilibrium occurring in a saturated solution of silver sulfate, Ag_2SO_4 .



- (ii) Write the expression for $K_s(\text{Ag}_2\text{SO}_4)$.

$$K_s = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$

- (iii) Calculate the solubility of Ag_2SO_4 in water at 25°C , and give $[\text{Ag}^+]$ and $[\text{SO}_4^{2-}]$.

$$K_s(\text{Ag}_2\text{SO}_4) = 1.20 \times 10^{-5}$$

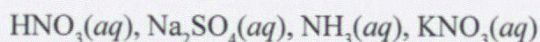
$$K_s = 4s^3 \quad s = \sqrt[3]{\frac{K_s}{4}}$$

$$s = \sqrt[3]{\frac{1.20 \times 10^{-5}}{4}} = 0.0144 \text{ mol L}^{-1}$$

$$[\text{SO}_4^{2-}] = s \quad [\text{SO}_4^{2-}] = 0.0144 \text{ mol L}^{-1}$$

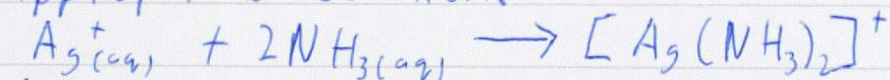
$$[\text{Ag}^+] = 2s \quad [\text{Ag}^+] = 2 \times 0.0144 = 0.0288 \text{ mol L}^{-1}$$

- (b) Below is a list of solutions of the same concentration available for a student to add to a saturated solution of Ag_2SO_4 :



Select and justify, including any relevant equations, an appropriate solution the student could add to:

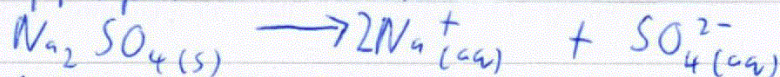
- (i) increase the solubility of Ag_2SO_4 $\text{NH}_3(aq)$ would be an appropriate solution.



Addition of $\text{NH}_{3(aq)}$ would cause the $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion to form which would remove Ag^+ from the solution reducing $[\text{Ag}^+]$. This will cause

the equilibrium from (a)(i) to favour the forward reaction to replace lost Ag^+ thus increasing the solubility of Ag_2SO_4 .

- (ii) decrease the solubility of Ag_2SO_4 $\text{Na}_2\text{SO}_4(\text{aq})$ would be an appropriate solution.



Adding $\text{Na}_2\text{SO}_4(\text{aq})$ would add more SO_4^{2-} thus increasing $[\text{SO}_4^{2-}]$. The equilibrium will respond by favouring the reverse reaction to remove excess SO_4^{2-} thus decreasing the solubility of Ag_2SO_4 .

- (c) Predict, by calculation, whether a precipitate of silver sulfate, Ag_2SO_4 , will form when 20.0 mL of 0.0188 mol L^{-1} silver nitrate, AgNO_3 , is added to 30.0 mL of 0.0146 mol L^{-1} aluminium sulfate, $\text{Al}_2(\text{SO}_4)_3$.

$$K_s(\text{Ag}_2\text{SO}_4) = 1.20 \times 10^{-5}$$

$$[\text{Ag}^+] = 0.0188 \times \frac{20}{50} = 7.52 \times 10^{-3} \text{ mol L}^{-1}$$

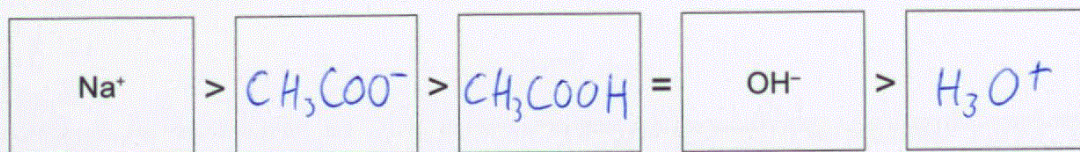
$$[\text{SO}_4^{2-}] = 3 \times 0.0146 \times \frac{30}{50} = 0.02628 \text{ mol L}^{-1}$$

$$Q = (7.52 \times 10^{-3})^2 \times 0.02628 = 1.49 \times 10^{-6}$$

$Q < K_s$ so no Ag_2SO_4 precipitate will form.

QUESTION TWO

- (a) (i) List all the species present in a solution of sodium ethanoate, CH_3COONa , in order of decreasing concentration. Do not include water.



- (ii) Sodium ethanoate can be mixed with ethanoic acid, CH_3COOH , to form a buffer solution.

Explain how this buffer solution would react upon the addition of a small volume of hydrobromic acid, HBr , including a balanced equation(s) to support your answer.

Upon addition of the small volume of HBr it would be neutralised by CH_3COO^-

$$\text{CH}_3\text{COO}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})} \rightarrow \text{CH}_3\text{COOH}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$$

 CH_3COOH is a weak acid so only partly dissociates: $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{CH}_3\text{COO}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$
 Thus increase in $[\text{H}_3\text{O}^+]$ is limited and therefore there is little change in pH.

- (iii) Calculate the mass of sodium ethanoate that must be added to 250 mL of 0.354 mol L^{-1} CH_3COOH to give a buffer solution with a pH of 4.11.

Assume there is no change in volume when the solid is added.

$$K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5} \quad \text{p}K_a(\text{CH}_3\text{COOH}) = 4.76 \quad M(\text{CH}_3\text{COONa}) = 82.0 \text{ g mol}^{-1}$$

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

$$[\text{CH}_3\text{COO}^-] = \frac{1.74 \times 10^{-5} \times 0.354}{10^{-4.11}} = 0.07935 \text{ mol L}^{-1}$$

$$n(\text{CH}_3\text{COO}^-) = 0.07935 \times 0.250 = 0.01984 \text{ mol}$$

$$m(\text{CH}_3\text{COONa}) = 0.01984 \times 82.0 = 1.627 \text{ g}$$

$$m(\text{CH}_3\text{COONa}) = 1.63 \text{ g}$$

- (b) Three colourless 0.110 mol L^{-1} solutions of CH_3NH_2 , CH_3COOH , and NH_4Cl have lost their labels. The solutions are randomly labelled A, B, and C. The electrical conductivity of each solution, and the colour of the solution when the acid-base indicator bromothymol blue ($\text{p}K_a = 7.2$) was added, are shown in the table below.

Solution	Electrical conductivity	Colour with bromothymol blue
CH_3COOH A	Poor	Yellow
CH_3NH_2 B	Poor	Blue
NH_4Cl C	Good	Yellow

Identify the three solutions.

Justify your identification in terms of the degree of dissociation and the relative concentration of ions in each solution, including relevant equations.

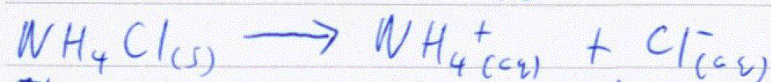
No calculations are necessary.

$A = \text{CH}_3\text{COOH}$ and $C = \text{NH}_4\text{Cl}$. Both CH_3COOH and NH_4^+ are acidic

$$\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$$

$$\text{NH}_4^+_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^+_{(aq)} + \text{NH}_3_{(aq)}$$

so both have $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ thus they will likely show the same result with bromothymol blue indicator (hence both show yellow). NH_4Cl is a salt so dissociates into ions in solution:



Therefore NH_4Cl will have a high ion concentration and thus many free moving charged particles to carry a current and thus be a good conductor.

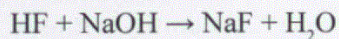
CH_3COOH is a poor conductor as it only partially dissociates so has a low ion concentration and thus few free-moving charged particles to carry a current...

(continues on back)

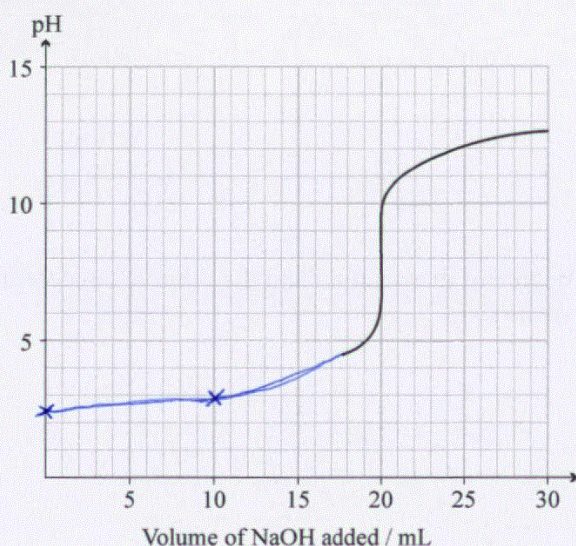
QUESTION THREE

A titration was carried out by adding 0.169 mol L^{-1} sodium hydroxide, NaOH, to 25.0 mL of 0.135 mol L^{-1} hydrofluoric acid, HF.

The equation for the reaction is:



$$K_a(\text{HF}) = 6.76 \times 10^{-4} \quad pK_a(\text{HF}) = 3.17$$



- (a) (i) Show, by calculation, that the initial pH of the HF solution is 2.02.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \quad [\text{H}_3\text{O}^+] = \sqrt{K_a \times [\text{HF}]}$$

$$[\text{H}_3\text{O}^+] = \sqrt{6.76 \times 10^{-4} \times 0.135} = 9.553 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log(9.553 \times 10^{-3}) = 2.0199$$

$$\text{pH} = 2.02$$

- (ii) Sketch the missing portion of the titration curve between 0 and 17.5 mL to complete the curve provided above.

Consider the initial pH after 10.0 mL of NaOH has been added, and the shape of the curve.

If you need to redraw your curve, use the graph on page 9.

- (b) (i) After a certain volume of NaOH has been added, the HF and NaF are present in a 1:9 ratio in the solution.

Calculate the pH of this solution, and evaluate its buffering ability.

$$K_a = [H_3O^+] \times \frac{[NaF]}{[HF]}$$

$$[H_3O^+] = 6.76 \times 10^{-4} \times \frac{1}{9} = 7.511 \times 10^{-5} \text{ mol/L}$$

$$pH = -\log(7.511 \times 10^{-5}) = 4.12$$

pH is within $pK_a \pm 1$ so it is an effective buffer. Due to there being significantly less HF than NaF it will be more effective against the addition of strong acid than the addition of strong base.

- (ii) Justify why the pH increases rapidly between 18.0 mL and 22.0 mL.

No calculations are necessary.

At this point there is very little or no HF left so the solution cannot resist changes in pH due to added strong base. Hence addition of NaOH at this point causes rapid increase in pH. After 22.0 mL the pH is almost completely determined by the NaOH so addition of NaOH after this point ~~only~~ increases it at a slower rate by increasing $[NaOH]$ and thus $[OH^-]$.

Question Three continues
on the next page.

- (c) (i) Calculate the pH at the equivalence point.

$$n(\text{HF}) = 0.025 \times 0.135 = 3.375 \times 10^{-3} \text{ mol}$$

$$V(\text{NaOH}) = \frac{3.375 \times 10^{-3}}{0.169} = 0.01997 \text{ L}$$

$$[\text{HF}] = 0.135 \times \frac{25}{25 + 19.97} = 0.07505 \text{ mol L}^{-1}$$

$$K_b = \frac{[\text{OH}^-][\text{HF}]}{[\text{F}^-]} \quad [\text{OH}^-] = \sqrt{K_b \times [\text{HF}]}$$

$$[\text{OH}^-] = \sqrt{10^{-(14-3.17)} \times 0.07505} = 1.054 \times 10^{-6} \text{ mol L}^{-1}$$

$$\text{pOH} = 5.98$$

$$\text{pH} = 8.02$$

- (ii) In a second titration, 25.0 mL of 0.135 mol L⁻¹ ethanoic acid, CH₃COOH, is titrated with the 0.169 mol L⁻¹ NaOH solution.

$$K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$$

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

Predict how the pH at the equivalence point will compare to the titration with HF by circling one answer below:

Lower pH

Same pH

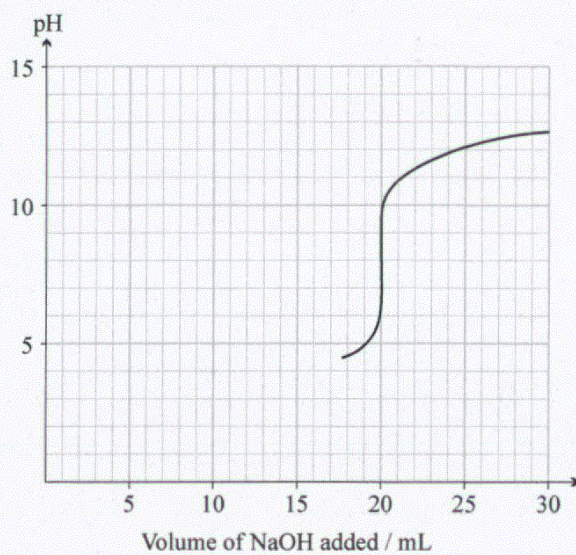
Higher pH

Explain your choice.

CH₃COOH has a ^{lower} ~~higher~~ K_a than HF
so CH₃COO⁻ will have a higher K_b than
F⁻. This means that at the equivalence
point the CH₃COOH will have a
higher [OH⁻] and therefore a
lower [H₃O⁺] and thus have a
higher pH.

SPARE DIAGRAM

If you need to redraw your response to Question Three (a)(ii), use the graph below. Make sure it is clear which answer you want marked.



Extra space if required.

Write the question number(s) if applicable.

QUESTION
NUMBER

Two B = CH_3NH_2 CH_3NH_2 is basic
 (b) $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
 therefore $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ and CH_3NH_2
 will turn bromothymol blue a different
 colour from the acidic solutions (hence blue).
 Like CH_3COOH , CH_3NH_2 is a
 poor electrical conductor as it only
 partly dissociates, meaning it has a
 low ion concentration and therefore
 few charged particles which can
 carry a current.

Excellence

Subject: Chemistry

Standard: 91392

Total score: 22

Q	Grade score	Marker commentary
One	E8	<p>The candidate was awarded E8 for the following reasons:</p> <p>In part (a), the candidate gave the equilibrium equation and K_s expression, and calculated the solubility, including $[\text{Ag}^+]$ and $[\text{SO}_4^{2-}]$.</p> <p>In part (b), the candidate selected and justified the correct solutions to both increase and decrease the solubility of silver sulfate, including the equation to show the formation of the complex ion between silver ions and ammonia.</p> <p>In part (c), the candidate correctly calculated the ionic product and compared it to the solubility product to predict that a precipitate of silver sulfate will not form.</p>
Two	E8	<p>The candidate was awarded E8 for the following reasons:</p> <p>In part (a), the candidate listed the correct remaining species present in the solution of sodium ethanoate, explained how the buffer would react upon addition of HBr, with support from a relevant equation, and calculated the mass of sodium ethanoate required to prepare a buffer.</p> <p>In part (b), the candidate justified the identification of the three solutions in terms of their electrical conductivity and their effect on the colour of bromothymol blue (with reference to the relative $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$).</p>
Three	M6	<p>The candidate was awarded M6 for the following reasons:</p> <p>In part (a), the candidate showed by calculation that the initial pH of the HF solution was 2.02.</p> <p>In part (b), the candidate calculated the pH of the buffer and evaluated its effectiveness. The candidate explained how the solution can no longer resist a change in pH as the NaOH is added between 18 – 22mL since very little HF remains.</p> <p>In part (c), the candidate calculated the pH at the equivalence point. Although the candidate recognised that the conjugate base of CH_3COOH has a higher K_b than the conjugate base of HF, the candidate did not make it clear that it is the conjugate base that is present at the equivalence point and therefore determining the pH. Furthermore, the strength of CH_3COO^- was not linked to its degree of dissociation and therefore the relative $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$.</p>