SUPERVISOR'S USE ONLY

3

91392

913920

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

NZQA
Mana Tohu Mātauranga o Aotearoa
New Zealand Qualifications Authority

Level 3 Chemistry 2025

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 the margins (⁄⁄⁄). 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 iron(II) hydroxide, $Fe(OH)_2$.

$$Fe(OH)_2 \rightleftharpoons Fe^{2+} + 2OH^-$$

(ii) Write the expression for $K_s(Fe(OH)_2)$.

$$K_s = [Fe^{2+}][OH^-]^2$$

(iii) Calculate the solubility product, K_s, of $Fe(OH)_2$ in water at 25 °C, given $Fe(OH)_2$ has a solubility of 1.01×10^{-5} mol L^{-1}.

$K_s = [Fe^{2+}][OH^-]^2$

$K_s = 4s^3$

$K_s = 4(1.01 \times 10^{-5})^3$

$K_s = 4.121204 \times 10^{-15}$

$\approx 4.12 \times 10^{-15}$ (3sf)

(iv) Some dilute hydrochloric acid, HCl(*aq*), is added to a saturated solution of $Fe(OH)_2$.

Justify what will happen to the solubility of the $Fe(OH)_2$ in solution.

Include relevant equation(s) in your answer.

No calculations are necessary.

When HCl (aq) is added, the H_3O^+ ions in it's solution will react with the OH^- ions in the $Fe(OH)_2$ solution in a nuetralisation reaction to form water: $H_3O^+ + OH^- \rightleftharpoons 2H_2O$. This will therefore remove OH^- ions from the solution, so the equilibrium will shift to the right to replace these in order to minimise the effect of the change. This will drive the forward reaction, increasing the solubility of $Fe(OH)_2$.

(b) Nickel hydroxide, $Ni(OH)_2$, is another sparingly soluble solid.

(i) A student makes a green precipitate of $Ni(OH)_2$ in a test tube by mixing sodium hydroxide, $NaOH(aq)$, and nickel chloride, $NiCl_2(aq)$. When the student then adds excess sodium cyanide, $NaCN(aq)$, the green precipitate dissolves.

Explain why the green precipitate of $Ni(OH)_2$ dissolves, using equilibrium principles and any relevant equation(s).

$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$

When NaCN (aq) is added, the CN^- ions react with the Ni^{2+} ions in solution to form the complex ion $[Ni(CN)_4]^{2-}$:

~~Ni~~ $Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$

As this complex ion is formed, it removes Ni^{2+} ions from the solution. The equilibrium shifts to the right to replace these, driving the forward reaction and hence causing the $Ni(OH)_2$ precipitate to dissolve.

(ii) Determine whether a precipitate of $Ni(OH)_2$ will form when 55.0 mL of 0.130 mol L^{-1} nickel sulfate, $NiSO_4$, is added to 35.0 mL of potassium hydroxide, KOH, solution of pH 11.7.

$K_s(Ni(OH)_2) = 6 \times 10^{-16}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$IP = [Ni^{2+}][OH^-]^2$

$[Ni^{2+}] = \frac{0.130 \times 55}{90} = 0.07944 \text{ mol} L^{-1}$

$[H_3O^+] = 10^{-11.7} = 1.99526 \times 10^{-12}$

$[OH^-] = \frac{5.01187 \times 10^{-3} \times 35}{90}$

$= 1.94906 \times 10^{-3} \text{ mol} L^{-1}$

$IP = [0.07944][1.94906 \times 10^{-3}]^2$

$= 3.017798... \times 10^{-7}$

$\approx 3.02 \times 10^{-7}$ (3sf)

$IP > K_s$ as $3.02 \times 10^{-7} > 6 \times 10^{-16}$ so a precipitate will form.

QUESTION TWO

Methylammonium chloride, CH_3NH_3Cl, is an acidic salt.

(a) List all the species present in a solution of CH_3NH_3Cl in order of decreasing concentration.

Do not include water.

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

Space for working if required

(b) If CH_3NH_3Cl and methanamine, CH_3NH_2, are mixed in the appropriate quantities, a buffer solution is formed.

$K_a(CH_3NH_3^+) = 2.51 \times 10^{-11}$ $\quad$ $pK_a(CH_3NH_3^+) = 10.6$

(i) When a small volume of dilute sodium hydroxide, NaOH, is added to the buffer, the following reaction occurs:

$$CH_3NH_3^+ + OH^- \rightarrow CH_3NH_2 + H_2O$$

Describe the function of a buffer solution, and explain the significance of this equation in terms of the function of the buffer solution.

Buffer: $CH_3NH_3^+ + H_2O \rightleftharpoons CHNH_2 + H_3O^+$

A buffer is a solution that resists changes in pH when small amounts of acid or base are added. When NaOH is added the $CHNH_3^+$ ions in the buffer solution react with the OH^- ions to neutralise them producing H_2O. As H_2O is neutral and has a pH of 7, it means by doing so it does not alter the pH, and as OH^- is removed to do so, it prevents the pH from increasing due to OH^- ions being added.

(ii) Calculate the mass of CH_3NH_3Cl that should be added to 600 mL of 0.840 mol L^{-1} CH_3NH_2 to produce a solution of pH 12.1.

$M(CH_3NH_3Cl) = 67.5$ g mol^{-1}

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

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

$[H_3O^+] = 10^{-12.1} = 7.9433 \times 10^{-13}$

$$2.51 \times 10^{-11} = \frac{[CH_3NH_2][7.9433 \times 10^{-13}]}{[CH_3NH_3^+]}$$

$[CH_3NH_2] = 0.840$

$$2.51 \times 10^{-11} = \frac{0.840 \times 7.9433 \times 10^{-13}}{[CH_3NH_3^+]}$$

$[CH_3NH_3^+] = 0.02658$ molL^{-1}

$n = c \times v$
$= 0.02658 \times 0.6$
$n = 0.0159\ 5$ mol

$m = n \times M$
$= 0.01595 \times 67.5$
$= 1.0766154$
$m \approx 1.08$ g (3SF)

(iii) Explain why the solution prepared in part (ii) will not function as a buffer.

Outline how the solution could be modified in the laboratory to make it a buffer.

No calculations are necessary.

The buffer solution above has a pH of 12.1. To function as a buffer, the pH must be within ± 1 pH unit of the pKa which is 10.6 so pH range for the buffer is 9.6 – 11.6. Therefore 12.1 is outside this range. To reduce the pH of this solution so it can function as a buffer, it must be made more acidic so the concentration of $CH_3NH_3^+$ should be increased so that pH falls within the buffer range.

(c) The pH of three solutions of equal concentration were ranked in order of increasing pH.

$$HBr \qquad NH_4Cl \qquad CH_3NH_2$$

$$\xrightarrow[\text{increasing pH}]{}$$

Justify the order in terms of the degree of dissociation and the relative concentration of hydronium ions in each solution.

Include relevant equation(s) in your answer.

HBr is a strong acid. It fully dissociates into it's ions: $HBr + H_2O \rightarrow Br^- + H_3O^+$

NH_4Cl is an acidic salt. It fully dissociates into it's ions: $NH_4Cl \rightarrow NH_4^+ + Cl^-$.

NH_4^+ partially dissociates further with H_2O:

NH_4^+ ~~4~~ $+ H_2O \rightleftharpoons NH_3 + H_3O^+$

CH_3NH_2 is a weak base. It partially dissociates into it's ions: $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$.

pH is the measure of $[H_3O^+]$. The greater the $[H_3O^+]$, the lower the pH. As HBr fully dissociates it produces the highest $[H_3O^+]$ so hence has the lowest pH. As NH_4Cl only partially dissociates it produces fewer H_3O^+ ions so it has a higher pH than HBr, however pH is still below 7 as it's acidic. As CH_3NH_2 is basic, it has a pH > 7 as $[H_3O^+] < [OH^-]$ so it hence has the highest pH.

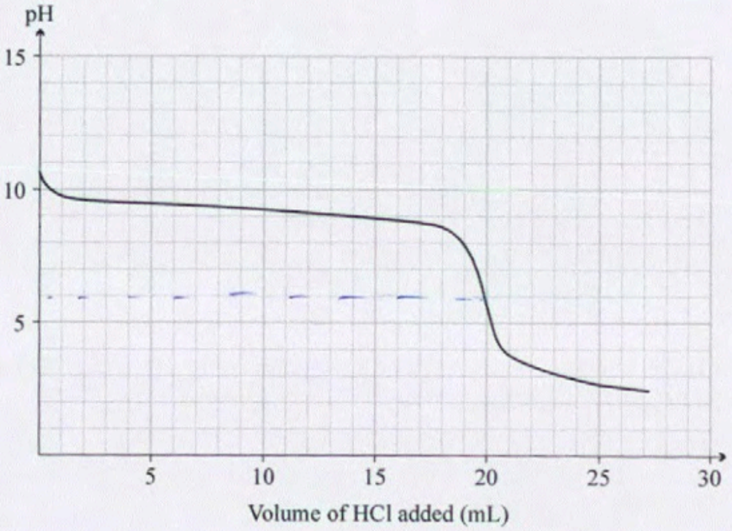
QUESTION THREE

A titration was carried out by adding 0.0174 mol L^{-1} hydrochloric acid, $HCl(aq)$, to 25.0 mL of 0.0139 mol L^{-1} ammonia, $NH_3(aq)$, in a conical flask.

The equation for the reaction is:

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

$K_a(NH_4^+) = 5.75 \times 10^{-10}$ $\qquad$ $pK_a(NH_4^+) = 9.24$



(a) Explain, with reference to the titration curve, why methyl red (pK_a 5.1) would be a better indicator to detect the equivalence point than thymol blue (pK_a 1.7).

From the graph, the pH at the equivalance point can be approximated as ~~56~~ 5.8-6. An effective indicator must be a pka within a ± 1 pH range of the pH at the equivalance point, so approximately 5 - 7. This is within the upright portion of the graph. Methyl red has a pka that falls within this range so it would be a better indicator than thymol blue as it's pka is less than this range so will change colours too early.

(b) (i) Calculate the pH at equivalence point.

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$

$5.75 \times 10^{-10} = \frac{[H_3O^+]^2}{[NH_4^+]}$

$[NH_4^+] = \frac{0.0139 \times 25}{45} = 7.7222 \times 10^{-3}$ $molL^{-1}$

$[H_3O^+] = \sqrt{4.4403... \times 10^{-12}}$

$= 2.1072... \times 10^{-6}$

$pH = -\log(2.1072... \times 10^{-6})$

$= 5.67629...$

≈ 5.68 (3sf)

(ii) Compare the electrical conductivity of the solution in the conical flask before HCl is added, and after 20 mL of HCl is added.

Include relevant equation(s) in your answer.

Before any HCl is added, the solution is only NH_3 which is a weak base. It partially dissociates into it's ions: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$. After 20mL of HCl is added, the equivalance point it reached. At the equivalance point, the solution is made up of the products of the titration: $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$. Therefore there is a high concentration of ions at this point.

In order to be a good conductor of electricity a solution must have a high concentration of free moving charged particles. At the beginning, there is a low concentration of ions as NH_3 only partially dissociates whereas after 20mL of HCl is added there is a high concentration of ions so the solution is a better conductor at this point than in the beginning.

(c) (i) Calculate the pH in the conical flask after 25.0 mL of 0.0174 mol L^{-1} HCl has been added.

5 mL of ~~0.0174~~ HCl is unreacted:

$$[H_3O^+] = \frac{5 \times 0.0174}{50}$$

$$= 1.74 \times 10^{-3}$$

$$pH = -\log(1.74 \times 10^{-3})$$

$$= 2.75945...$$

$$\approx 2.76 \text{ (3sf)}$$

(ii) The 0.0174 mol L^{-1} HCl in the burette has a pH of 1.76.

Explain why the pH calculated in part (i) is higher than 1.76.

No calculations are necessary.

~~After 25 mL of HCl is added, this amount is diluted by the 25mL of~~ other

The 5mL of unreacted HCl has been diluted by the other solutions in the titration, meaning it is a weaker acid than the orginal ~~HCl~~, undiluted HCl ~~in~~ in the burette, hence a higher pH.

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

QUESTION NUMBER

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

QUESTION NUMBER

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

QUESTION NUMBER

91392

Merit

Subject: L3 Chemistry

Standard: 91392

Total score: 22

Q	Grade score	Marker commentary
One	E8	The candidate was awarded E8 for the following reasons: In part (a), the candidate used equilibrium principles to justify why adding a strong acid to a saturated solution of iron(II) hydroxide caused its solubility to increase. In part (b), the candidate used equilibrium principles to explain why the formation of a complex ion caused the nickel hydroxide precipitate to dissolve. Furthermore, the candidate correctly calculated the ionic product, and compared it to the solubility product to predict that a precipitate of nickel hydroxide would form.
Two	E7	The candidate was awarded E7 for the following reasons: In part (b), the candidate calculated the correct mass of methylammonium chloride required to prepare a solution of pH 12.1. The candidate subsequently explained why the solution at a pH of 12.1 would not function as a buffer, and outlined how the solution could be modified to function as a buffer by increasing the concentration of $[CH_3NH_3^+]$. In part (c), the candidate justified the order in pH of the three solutions, with reference to the degree of dissociation and $[H_3O^+]$, supported by three relevant equations. To gain E8, the candidate needed to be more specific about how the solution in part (b) could be modified in the laboratory to function as buffer by adding either a strong acid or more solid methylammonium chloride.
Three	E7	The candidate was awarded E7 for the following reasons: In part (b), the candidate correctly calculated the pH at the equivalence point. Furthermore, the candidate compared the electrical conductivity of the initial ammonia solution with the acidic salt solution present at the equivalence point by explaining the degree of dissociation and the [ions] for each solution, supported by relevant equations. In part (c), the candidate correctly calculated the pH after 25.0 mL of HCl had been added. In addition, the candidate explained that dilution caused the difference in pH between the solution in the burette and the solution in the conical flask after 25.0 mL of HCl had been added.

		To gain E8, the candidate needed to further explain that the increase in pH in part (c)(ii) was due to a decrease in $[H_3O^+]$ caused by dilution.