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NZQA

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 (▨). 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.

Achievement TOTAL 10

QUESTION ONE

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

$Ag_2SO_{4(aq)} \rightleftharpoons 2Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

(ii) Write the expression for $K_s(Ag_2SO_4)$.

$K_s = [Ag^+_{(aq)}]^2[SO_4^{2-}{}_{(aq)}]$

(iii) Calculate the solubility of Ag_2SO_4 in water at 25 °C, and give $[Ag^+]$ and $[SO_4^{2-}]$.

$K_s(Ag_2SO_4) = 1.20 \times 10^{-5}$

$K_s = [Ag^+]^2[SO_4^{2-}]$

$K_s = [2S]^2 \times [S]$

$K_s = 4S^3$

$S = \sqrt[3]{K_s \div 4}$

$S = \sqrt[3]{1.2\times10^{-5} \div 4}$

$S = 0.0144\ mol L^{-1}$

$[Ag^+] = 2s^2$

$= (2 \times 0.0144)^2$

$= 4.16 \times 10^{-4}\ mol L^{-1}$ (3sf)

$[SO_4^{2-}] = s$

$= 0.0144\ mol L^{-1}$

$= 0.014\ mol L^{-1}$ (3sf)

(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:

$HNO_3(aq)$, $Na_2SO_4(aq)$, $NH_3(aq)$, $KNO_3(aq)$

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

(i) increase the solubility of Ag_2SO_4 when NH_3 is added to a saturated sdution of Ag_2SO_4, the cations react with the NH_3 to form a complex ion as it is basic. The complex ion formed is $[Ag(NH_3)_2]^+$. This will remove some of the Ag^+ product so the equilibrium system will react by favouring the fowards reaction to replenish it. Therefore more Ag_2SO_4 will dissolve and the solubility will increase.

(ii) decrease 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, $Al_2(SO_4)_3$.

$K_s(Ag_2SO_4) = 1.20 \times 10^{-5}$

$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$

$Q_s = [Ag^+]^2[SO_4^{2-}]$

$= [7.52 \times 10^{-3}]^2 \times [8.76 \times 10^{-3}]$

$= 4.953 \times 10^{-7}$

$[Ag^+] = \frac{0.02}{0.05} \times 0.0188$

$= 7.52 \times 10^{-3}$ molL^{-1}

$[SO_4^{2-}] = \frac{0.03}{0.05} \times 0.0146$

$= 8.76 \times 10^{-3}$ molL^{-1}

$Q_s < K_s$ so no 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.

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

Na^+	>	CH_3COO^-	>	CH_3COOH	=	OH^-	>	H_3O^+

(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.

~~$CH_3COO^- + CH_3COOH \rightarrow 2CH_3COO^-$~~

~~$CH_3COOH + CH_3COONa \rightarrow 2CH_3COO^- + HNa$~~

Adding a small amount of acid will increase the amount of H_3O^+ ions. ~~This will~~

(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.

$K_a(CH_3COOH) = 1.74 \times 10^{-5}$ $pK_a(CH_3COOH) = 4.76$ $M(CH_3COONa) = 82.0$ g mol^{-1}

weak acid

$pH = -\log[H_3O^+]$ ~~$[CH_3COOH]$~~

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

$= 10^{-4.11}$

$= 7.762 \times 10^{-5}$ mol L^{-1}

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

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

$K_a = [H_3O^+]^2 \div [CH_3COOH]$

weak base weak acid

(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 ($pK_a = 7.2$) was added, are shown in the table below.

Solution	Electrical conductivity	Colour with bromothymol blue
A	Poor	Yellow
B	Poor	Blue
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.

$CH_3NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_3^+{}_{(aq)} + OH^-{}_{(aq)}$

CH_3NH_2 is a weak base and only partially dissociates into OH^- and $CH_3NH_3^+$ ions. This means the is a low concentration of charged ions ~~and~~ so it is a poor conductor of electricity. Also, it will turn bromothymol blue, yellow as it is a base with a pH similar to the pKa of the indicator. This means it is solution A.

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3COO^-{}_{(aq)}$.

CH_3COOH is a weak acid and only partially dissociates into H_3O^+ and CH_3COO^- ions. The low concentration of ions means it is a poor conductor. Additionaly, the bromothymol blue will not change colour as it does not reach the pKa of 7.2. This means CH_3COOH is solution B.

$NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

NH_4Cl ~~is a strong~~ fully dissociates in NH_4^+ and Cl^- ions. This means there is a high concentration of ions so it will be a good conductor of electricity. Also it will turn bromothymol blue, yellow so it is solution C.

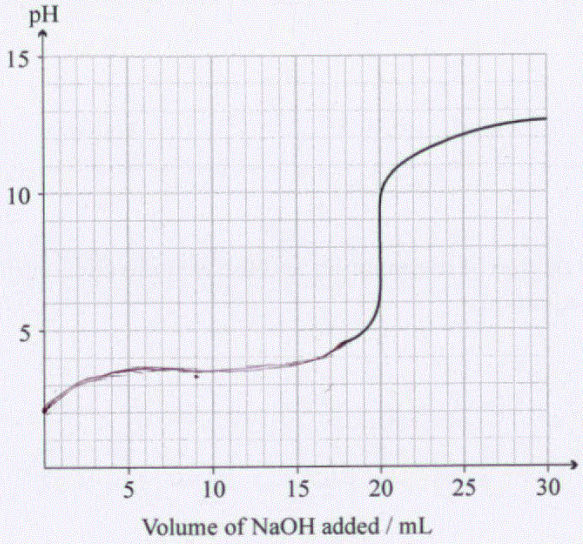
QUESTION THREE

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: weak acid.

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

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



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

$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$

$K_a = \dfrac{[H_3O^+][F^-]}{[HF]}$

$K_a = \dfrac{[H_3O^+]^2}{[HF]}$

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

$= \sqrt{6.76 \times 10^{-4} \times 0.135}$

$= 9.553 \times 10^{-3}$ mol L^{-1}

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

$= -\log [9.553 \times 10^{-3}]$

$= 2.01$

(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.

~~Ka = [NaF]~~

$K_a = \frac{9 \times [H_3O^+]}{1}$

$6.76 \times 10^{-4} = \frac{9 \times [H_3O^+]}{1}$ $\frac{[OH^-]}{}$

$[H_3O^+] = 7.511 \times 10^{-5} mol L^{-1}$

~~pH = -log [H3O+]~~

~~= -log [7.511 x 10^-5]~~

$= 4.$ $\frac{[HA][A^-]}{pK_a < pH}$ A B

$K_W = [H_3O^+][OH^-]$

$1 \times 10^{-14} = [H_3O^+][7.511 \times 10^{-5}]$

$[H_3O^+] = 1.33 \times 10^{-10} mol L^{-1}$

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

$pH = -\log [1.33 \times 10^{-10}]$

$= 9.87$

The pH is greater than the pKa of the buffer so it is more effective against the addition of small amounts of acid.

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

No calculations are necessary.

Between 18mL and 22mL is no longer in the buffer zone this means there is no buffer to act against the change in pH. The equivalence point is met.

Question Three continues on the next page.

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

(ii) In a second titration, 25.0 mL of 0.135 mol L^{-1} ethanoic acid, CH_3COOH, is titrated with the 0.169 mol L^{-1} NaOH solution.

weak acid.

$K_a(CH_3COOH) = 1.74 \times 10^{-5}$ $pK_a(CH_3COOH) = 4.76$

smaller Ka ✓ greater pKa

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

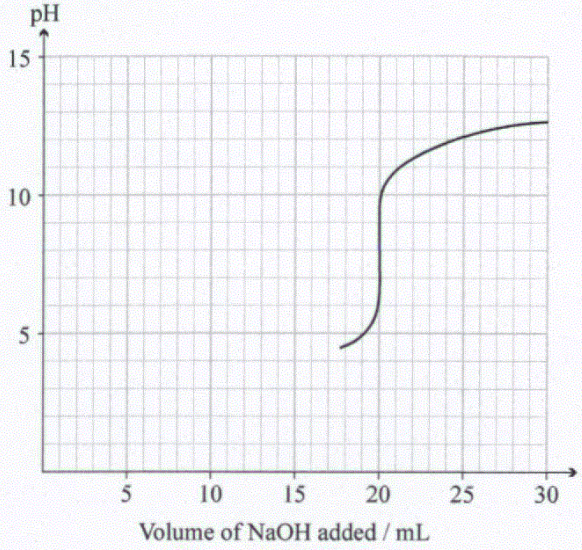
Lower pH **Same pH** **Higher pH**

Explain your choice.

The CH_3COOH is a weak acid that partially dissociates into CH_3COO^- and H_3O^+ ions. However this acid dissociates less than HF so it produces less H_3O^+ ions. This means it is less acidic so it has 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.



Achievement

Subject: Chemistry

Standard: 91392

Total score: 10

Q	Grade score	Marker commentary
One	A4	The candidate was awarded A4 for the following reasons: In part (a), the candidate gave the equilibrium equation and K_s expression, and calculated the solubility. In part (b), the candidate recognised that the addition of ammonia will form a complex ion with Ag^+ ions and therefore decrease $[Ag^+]$. In part (c), the candidate correctly calculated $[Ag^+]$ and compared the ionic product to the solubility product.
Two	N2	The candidate was awarded N2 for the following reasons: In part (a), the candidate listed the correct remaining species present in the solution of sodium ethanoate. In part (b), the candidate explained why a solution of ammonium chloride is a good conductor while solutions of ethanoic acid and methanamine are poor conductors, with reference to the degree of dissociation and concentration of ions.
Three	A4	The candidate was awarded A4 for the following reasons: In part (a), the candidate showed by calculation that the initial pH of the HF solution was 2.02 and accurately sketched the missing portion of the pH curve. In part (b), the candidate recognised that there is no longer an effective buffer present after 18mL. In part (c), the candidate identified that ethanoic acid is weaker than hydrofluoric acid.