

91392



913920


 NEW ZEALAND QUALIFICATIONS AUTHORITY
 MANA TOHU MĀTAURANGA O AOTEAROA

3

SUPERVISOR'S USE ONLY

Level 3 Chemistry, 2014

91392 Demonstrate understanding of equilibrium principles in aqueous systems

 2.00pm Tuesday 11 November 2014
 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.

Merit

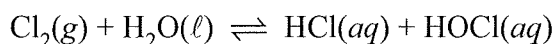
TOTAL

16

ASSESSOR'S USE ONLY

QUESTION ONE

When chlorine gas is added to water, the equation for the reaction is:

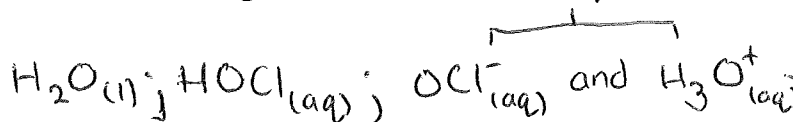


- (a) (i) Write an equation for the reaction of the weak acid, hypochlorous acid, HOCl, with water.



- (ii) List all the species present when HOCl reacts with water, in order of decreasing concentration.

Order of decreasing concentration: least + equal concentration.



Justify your order.

The reaction of hypochlorous acid, HOCl, with water, H₂O, is an equilibrium reaction. HOCl is a weak acid, so ~~it~~ only dissociates partially into H⁺ ions (forming H₃O⁺) and OCl⁻ ions. Hence the majority of the hypochlorous acid does not react. So the concentration of HOCl is greater than those of OCl⁻ and H₃O⁺. The concentrations of OCl⁻ and H₃O⁺ are identical, because according to the equation, for each OCl⁻ ion produced, one H₃O⁺ ion is also produced (1:1). The concentration of H₂O is always the largest in an aqueous system and its concentration is hardly affected by the presence of other species.

- (b) Hypochlorous acid has a pK_a of 7.53. Another weak acid, hydrofluoric acid, HF, has a pK_a of 3.17.

A 0.100 mol L^{-1} solution of each acid was prepared by dissolving it in water.

Compare the pHs of these two solutions.

No calculations are necessary.

A lower pK_a equates to a higher value of K_a , and therefore a greater degree of dissociation. Hence because HF has a lower pK_a than HOCl, it will dissociate more in water, and thus produce more H_3O^+ ions, than HOCl, per volume. A greater concentration of H_3O^+ ions results in a lower pH, according to $\text{pH} = -\log[\text{H}_3\text{O}^+]$, so HF in solution will have a lower pH and be more acidic than HOCl.

- (c) An aqueous solution containing a mixture of HF and sodium fluoride, NaF, can act as a buffer solution.

Calculate the mass of NaF that must be added to 150 mL of $0.0500 \text{ mol L}^{-1}$ HF to give a buffer solution with a pH of 4.02.

Assume there is no change in volume.

$$M(\text{NaF}) = 42.0 \text{ g mol}^{-1} \quad pK_a(\text{HF}) = 3.17$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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

$$= \frac{6.76 \times 10^{-4} \times 0.05 \text{ mol L}^{-1}}{9.55 \times 10^{-5} \text{ mol L}^{-1}}$$

$$= 0.354 \text{ mol L}^{-1} \text{ (3sf)}$$

$$\begin{aligned} n(\text{F}^-) &= c(\text{F}^-) \times V \\ &= 0.354 \text{ mol L}^{-1} \times 0.150 \text{ L} \\ &= 0.0531 \text{ mol (3sf)} \end{aligned}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} \\ &= 10^{-4.02} \end{aligned}$$

$$= 9.55 \times 10^{-5} \text{ mol L}^{-1} \text{ (3sf)}$$

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

$$= 10^{-3.17}$$

$$= 6.76 \times 10^{-4} \text{ mol L}^{-1} \text{ (3sf)}$$

$$m = nM$$

$$= 0.0531 \text{ mol} \times 42 \text{ g mol}^{-1}$$

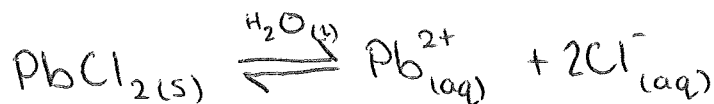
$$= 2.23 \text{ g (3sf)}$$

QUESTION TWO

ASSESSOR'S
USE ONLY

A flask contains a saturated solution of PbCl_2 in the presence of undissolved PbCl_2 .

- (a) (i) Write the equation for the dissolving equilibrium in a saturated solution of PbCl_2 .



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

$$K_s(\text{PbCl}_2) = [\text{Pb}^{2+}] \times [\text{Cl}^{-}]^2$$

- (iii) Calculate the solubility (in mol L^{-1}) of lead(II) chloride in water at 25°C , and give the $[\text{Pb}^{2+}]$ and $[\text{Cl}^{-}]$ in the solution.

$$K_s(\text{PbCl}_2) = 1.70 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

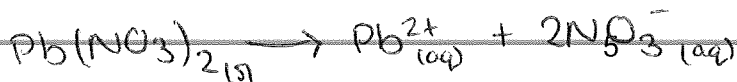
$$K_s = 4s^3$$

$$\therefore s = \sqrt[3]{\frac{1.70 \times 10^{-5}}{4}}$$

$$= 0.0162 \text{ mol L}^{-1} \text{ (3sf)}$$

$$[\text{Pb}^{2+}] = 0.0162 \text{ mol L}^{-1} \text{ (3sf)}$$

$$[\text{Cl}^{-}] = 0.0324 \text{ mol L}^{-1} \text{ (3sf)} \quad (2\text{Cl}^{-} = \text{twice as many particles in solution})$$



$$n = cV$$

- (b) A sample of seawater has a chloride ion concentration of 0.440 mol L^{-1} .

Determine whether a precipitate of lead(II) chloride will form when a 2.00 g sample of lead(II) nitrate is added to 500 mL of the seawater.

$$K_s(\text{PbCl}_2) = 1.70 \times 10^{-5} \quad M(\text{Pb}(\text{NO}_3)_2) = 331 \text{ g mol}^{-1}$$

$$n(\text{Pb}(\text{NO}_3)_2) = \frac{m(\text{Pb}(\text{NO}_3)_2)}{M(\text{Pb}(\text{NO}_3)_2)}$$

$$= \frac{2.00 \text{ g}}{331 \text{ g mol}^{-1}}$$

$$c = n/V$$

$$= \frac{6.04 \times 10^{-3} \text{ mol}}{0.5 \text{ L}}$$

$$= 0.0121 \text{ mol L}^{-1}$$

$$= 6.04 \times 10^{-3} \text{ mol (3sf)}$$

(= $n(\text{Pb}^{2+})$ as per equation above)

$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$= 0.220 \text{ mol L}^{-1} \times (0.440 \text{ mol L}^{-1} + 0.0121 \text{ mol L}^{-1})^2$$

$$= 0.0450 \text{ (3sf)}$$

$Q > K_s$, so a precipitate will form

- (c) The solubility of zinc hydroxide, $\text{Zn}(\text{OH})_2$, can be altered by changes in pH. Some changes in pH may lead to the formation of complex ions, such as the zincate ion, $[\text{Zn}(\text{OH})_4]^{2-}$.

Use equilibrium principles to explain why the solubility of zinc hydroxide increases when the pH is less than 4 or greater than 10.

No calculations are necessary.



According to the equation above, $\text{Zn}(\text{OH})_2$ dissociates to form Zn^{2+} ions and OH^- ions. In solutions with a pH of less than 4, there are many H_3O^+ ions present, which can react with the OH^- ions formed from $\text{Zn}(\text{OH})_2$. This removal of products shifts the equilibrium position to the right, increasing the concentration of products and decreasing that of $\text{Zn}(\text{OH})_2$, the reactant, hence increasing its solubility.

CONTINUED ON EXTRA PAGES

Extra paper if required.

Write the question number(s) if applicable.

ASSESSOR'S
USE ONLYQUESTION
NUMBER

2 c) In solutions with a pH of greater than 10, excess OH^- ions in solution react with the Zn^{2+} ions to form $[\text{Zn}(\text{OH})_4]^{2-}$:



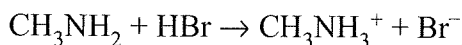
This reduces the Zn^{2+} and OH^- concentrations, driving the $\text{Zn}(\text{OH})_2$ to Zn^{2+} and OH^- equilibrium to shift to the right. This causes it to increase product concentrations (of Zn^{2+} and OH^-), and decrease that of $\text{Zn}(\text{OH})_2$, increasing its solubility. //

QUESTION THREE

~~Strong acid to weak base~~ASSESSOR
USE ONLY

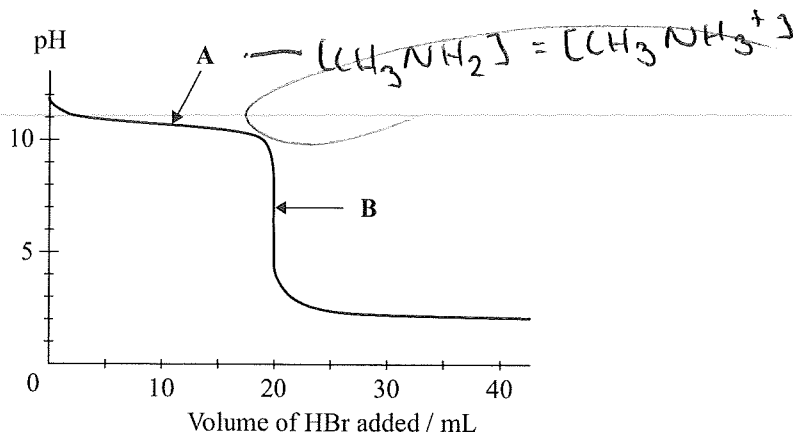
A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH_3NH_2 , solution.

The equation for the reaction is:



$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

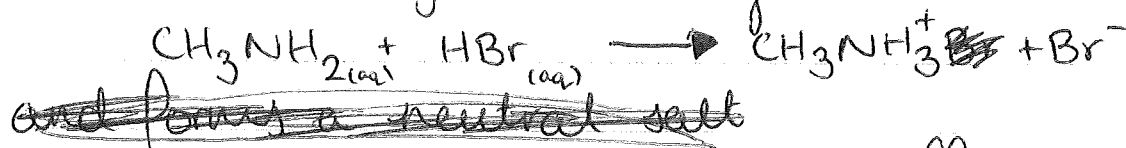
The curve for this titration is given below:



- (a) Explain why the pH does not change significantly between the addition of 5 to 15 mL of HBr (around point A on the curve).

Include any relevant equation(s) in your answer.

This area is the buffer zone, where CH_3NH_2 and its conjugate acid, CH_3NH_3^+ are present in equal concentrations. Hence as acid is added in this area, it is neutralised by the methylamine:



This prevents any significant effect on the solution's pH, as there is no effect on the concentration of H_3O^+ ions (acid does not form H_3O^+ ions, instead forming CH_3NH_3^+ ions).

$$\sqrt{\frac{K_a \times K_w}{[H_3O^+]}}$$

7

- (b) The aqueous methylamine, CH_3NH_2 , solution has a pH of 11.8 before any HBr is added.

Show by calculation that the concentration of this solution is $0.0912 \text{ mol L}^{-1}$.

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

$$= 10^{-11.8}$$

$$[H_3O^+] = 1.58 \times 10^{-12} \text{ mol L}^{-1} \text{ (3sf)}$$

$$[H_3O^+] = \sqrt{\frac{K_a \times K_w}{[A^-]}}$$

$$\therefore (1.58 \times 10^{-12} \text{ mol L}^{-1})^2 = \frac{K_a \times K_w}{[A^-]}$$

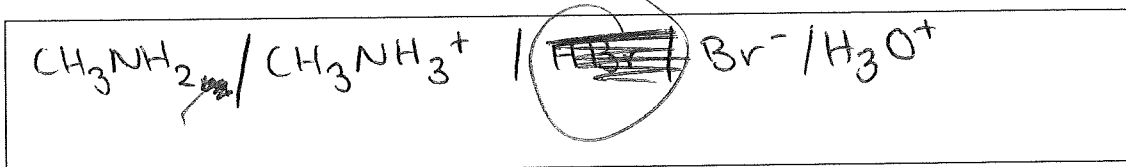
$$[CH_3NH_2] = \sqrt{\frac{2.29 \times 10^{-11} \times 10^{-14}}{1.58 \times 10^{-12} \text{ mol L}^{-1}}}$$

~~Handwritten scribbles~~

$$\therefore [CH_3NH_2] = \frac{2.29 \times 10^{-11} \times 10^{-14}}{1.58 \times 10^{-12} \text{ mol L}^{-1}}$$

$$= 0.0912 \text{ mol L}^{-1} \text{ (3sf)}$$

- (c) (i) Write the formulae of the four chemical species, apart from water and OH^- , that are present at the point marked **B** on the curve.



- (ii) Compare and contrast the solution at point **B** with the initial aqueous methylamine solution.

In your answer you should include:

- a comparison of species present AND their relative concentrations
- a comparison of electrical conductivity linked to the relevant species present in each solution
- equations to support your answer.

The initial solution contained only aqueous CH_3NH_2 . At point B, CH_3NH_2 is still present, but its concentration is ~~25%~~ ^{far reduced} from the original, due to ~~half~~ ^{at least} of it reacting ~~and the volume doubling~~ from the initial solution to that at point B. This new solution also contains

There is more space for your answer to this question on the following page.

~~A low concentration of~~ ^{NO} ~~HBr~~, as ~~most~~ ^{all} of this has also reacted to form Br^- and CH_3NH_3^+ . ~~Here the~~ CH_3NH_2 and ~~Br~~ ~~HBr~~ concentrations are ~~also~~ ^{identical}, as ~~the solution is neutral with a pH of 7~~. CH_3NH_3^+ and Br^- are present in ~~the~~ a much larger concentration, ~~again the~~ ~~same~~ because the two original species have ~~mostly~~ reacted to form them at a ratio of 1:1 according to the equation:

$$\text{CH}_3\text{NH}_2_{(aq)} + \text{HBr}_{(aq)} \rightarrow \text{CH}_3\text{NH}_3^+_{(aq)} + \text{Br}^-_{(aq)}$$

Because the dominant species in solution are both ions, there is a very large concentration of charged particles able to carry a charge, and hence the solution at point B is a good conductor. The

original solution is a poor conductor, due to a very low concentration of ions or other charged particles.

* Some of (a very small amount of) the CH_3NH_3^+ produced reacts with water:



This means there is less CH_3NH_3^+ ions present at point B than Br^- ions, as some of them react, and it means there is a very low concentration of CH_3NH_2 and of H_3O^+ ions.

Merit 16

Q1. This question is limited to M5 because in part (a) (ii), they do not recognise the presence of hydroxide ions in the solution, both in the list of species and the justification.

Q2. This question is limited to M6 because in part (b), although they have used the correct process and made a correct prediction based on their answer, there is a calculation error giving an incorrect value for K_s .

Q3. This question is limited to M5 because in part (a), they do not write the correct equation but rewrite the one at the top of the question. In part (c), the species are not fully compared and not all the relevant equations are written.