

91392



NEW ZEALAND QUALIFICATIONS AUTHORITY
 MANA TOHU MĀTAURANGA O AOTEAROA

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SUPERVISOR'S USE ONLY

Level 3 Chemistry, 2014

91392 Demonstrate understanding of equilibrium principles in aqueous systems

2.00 pm 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.

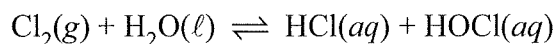
Excellence

TOTAL 22

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QUESTION ONE

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

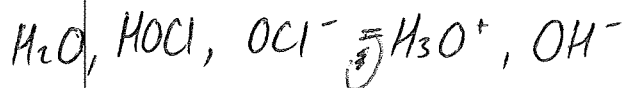


- (a) (i) Write an equation for the reaction of the weak acid, hypochlorous acid, HOCl, with water.



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

Order of decreasing concentration:



Justify your order.

The whole solution is in water so H₂O has the greatest concentration.

Hypochlorous acid is a weak acid so only partially dissociates so there is still a large concentration of HOCl.

OCl⁻ and H₃O⁺ are produced in the same concentrations when HOCl reacts with water.

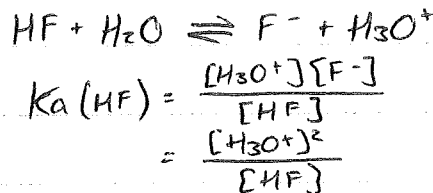
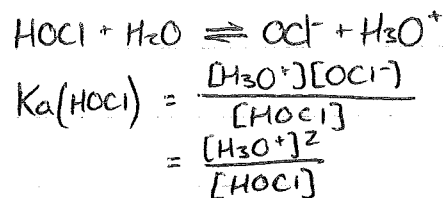
OH⁻ has the smallest concentration because there is more H₃O⁺ produced by the reaction, but OH⁻ is always present.

- (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.



The pK_a values means that HF has the higher K_a value. This means with the same concentrations of each acid, HF has the higher concentration of H_3O^+ ions. This means it has the lower pH.

- (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.

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

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NaF}]}{[\text{HF}]}$$

$$4.02 = 3.17 + \log \frac{[\text{NaF}]}{0.0500}$$

$$\log \frac{[\text{NaF}]}{0.0500} = 0.85$$

$$\frac{[\text{NaF}]}{0.0500} = 7.079\dots$$

$$[\text{NaF}] = 0.3539\dots$$

$$c = \frac{n}{V}$$

$$n = cV = 0.3539\dots \times 0.150 = 0.0530\dots$$

$$n = \frac{m}{M}$$

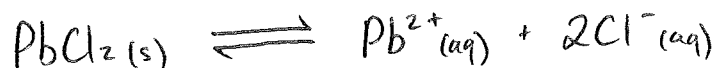
$$m = nM = 0.0530\dots \times 42.0 = 2.230\dots$$

$$\approx 2.23 \text{ g}$$

QUESTION TWO

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 $K_s(\text{PbCl}_2)$.

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

- (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.

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

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

$$= s \times (2s)^2$$

$$= 4s^3$$

$$4s^3 = 1.70 \times 10^{-5}$$

$$s^3 = 4.25 \times 10^{-6}$$

$$s = \sqrt[3]{4.25 \times 10^{-6}}$$

$$= 0.01619\dots$$

$$\approx 0.0162 \text{ mol L}^{-1}$$

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

$$[\text{Cl}^{-}] = 2 \times 0.01619\dots = 0.03239\dots \approx 0.0324 \text{ mol L}^{-1}$$

- (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.

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

$$I.P. = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$= 0.01208... \times 0.440^2$$

$$= 2.339... \times 10^{-3}$$

$$\approx 2.34 \times 10^{-3}$$

$$n(\text{Pb}(\text{NO}_3)_2) = \frac{m}{M} = \frac{2.00}{331}$$

$$= 6.042... \times 10^{-3}$$

$$c(\text{Pb}(\text{NO}_3)_2) = \frac{n}{V} = \frac{6.042... \times 10^{-3}}{0.500}$$

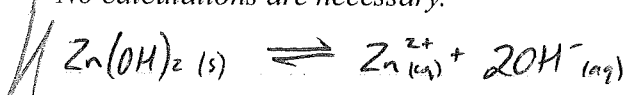
$$= 0.01208...$$

As $I.P. > K_s$, a precipitate of lead chloride 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.



When the pH is greater than 10 the concentration of OH^- ions will increase.

This means the complex ion $[\text{Zn}(\text{OH})_4]^{2-}$ will form, decreasing the concentration of OH^- ions. The equilibrium will respond by moving to the right to replace these 'lost' ions, increasing the solubility.

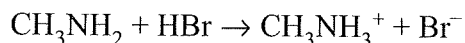
When the pH is less than 4, H_3O^+ ions will be present in the solution.

The concentration of OH^- ions will decrease as they react with the H_3O^+ ions to form water. This means the equilibrium will respond to replace these ions, increasing the solubility. //

QUESTION THREE

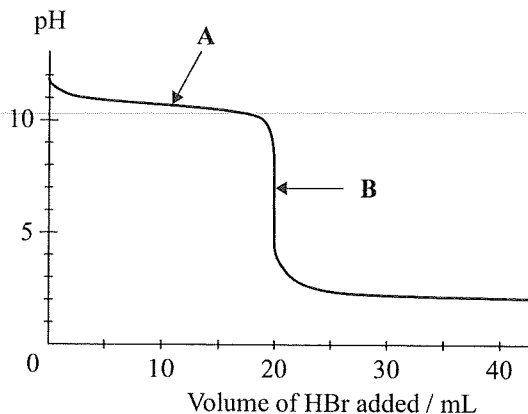
A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, CH_3NH_2 , solution.

The equation for the reaction is:



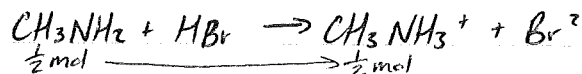
$$K_a(\text{CH}_3\text{NH}_3^+) = 2.29 \times 10^{-11}$$

The curve for this titration is given below:

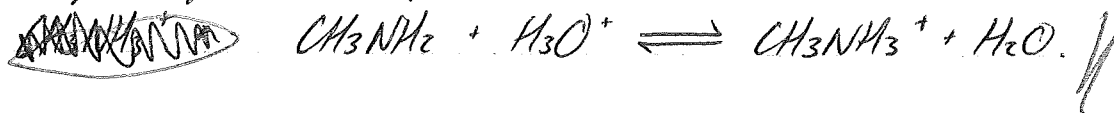


- (a) Explain why the pH does not change significantly between the addition of 5 to 15 mL of HBr (around point A on the curve).

Include any relevant equation(s) in your answer.



When the HBr is added this reacts with the same number of moles of CH_3NH_2 which produces this number of moles of CH_3NH_3^+ which is its conjugate acid. Once 5 to 15 ml of HBr is added, a buffer solution is formed. This is because $[\text{CH}_3\text{NH}_2] \approx [\text{CH}_3\text{NH}_3^+]$ so the equilibrium responds to resist change in pH around point A.



- (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 $0.0912 \text{ mol L}^{-1}$.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-11.8} = 1.584... \times 10^{-12} \text{ mol L}^{-1}$$

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

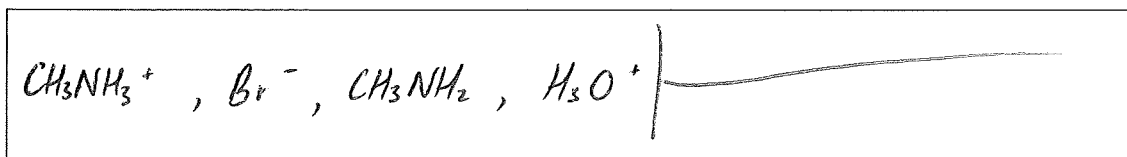
$$\frac{1.584... \times 10^{-12}}{\sqrt{\frac{2.29 \times 10^{-11} \times 1 \times 10^{-14}}{[\text{CH}_3\text{NH}_2]}}} = 2.511... \times 10^{-24}$$

$$[\text{CH}_3\text{NH}_2] = \frac{2.29 \times 10^{-11} \times 1 \times 10^{-14}}{2.511... \times 10^{-24}}$$

$$= 0.09116...$$

$$\approx 0.0912 \text{ mol L}^{-1}$$

- (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.

At point B is the equivalence point, this means an equivalent amount of HBr has been added to the amount of CH_3NH_2 which was present initially. This means there is no unreacted CH_3NH_2 or HBr, the only species immediately present are CH_3NH_3^+ and Br^- . However $\text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+$ so there ~~is~~ also CH_3NH_2 and H_3O^+ present.

Originally there was only CH_3NH_2 but $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$.

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

So the only difference is species present is the Br^- ions at point B.
However the concentrations will be different.

(ignoring
water)

Initially: $[\text{CH}_3\text{NH}_2] > [\text{CH}_3\text{NH}_3^+] = [\text{OH}^-] > [\text{H}_3\text{O}^+]$

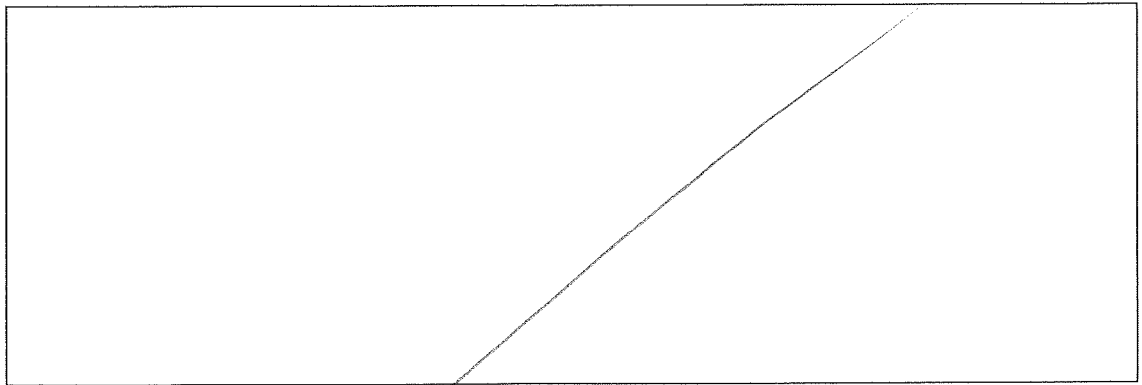
At B: $[\text{Br}^-] > [\text{CH}_3\text{NH}_3^+] > [\text{CH}_3\text{NH}_2] = [\text{H}_3\text{O}^+] > [\text{OH}^-]$

Conductivity of a solution is directly linked to the ^{concentration of} ions present.

Originally there ~~is~~ ^{are} only a small number of ions present because as CH_3NH_2 is a weak base it only partially dissociates so a small concentration of CH_3NH_3^+ and OH^- are produced and an even smaller amount of ~~the~~ H_3O^+ ions.

At point B there is 1 mol of Br^- and slightly less than 1 mol of CH_3NH_3^+ as some partially dissociates to produce H_3O^+ ions and small amounts of OH^- ions are present.

So point B has approximately 2 moles of ions while originally there ~~are~~ ^{is} less than 1 mole of ions. This means ~~there is a~~ B has a greater electrical conductivity. κ



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Q1. This question provides evidence for E7 rather than E8 because in part (a) (ii), the low OH^- is not fully related to either the solution being acidic or the relationship between Hg^{2+} , OH^- and K_w .

Q2. This question provides evidence for E7 rather than E8 because in part (c), the explanation needs to also outline that the formation of the complex ion reduces the Zn^{2+} concentration.

Q3. Both Excellence opportunities fully answered for E8.