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91392

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NEW ZEALAND QUALIFICATIONS AUTHORITY
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# 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.**

Achievement

TOTAL 12

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## QUESTION ONE

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

$$Cl_2(g) + H_2O(\ell) \rightleftharpoons HCl(aq) + HOCl(aq)$$

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

$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^- + H_3O^+(aq)$

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

Order of decreasing concentration:

$[H_2O] > [OCl^-] = [H_3O^+] > [HOCl]$

Justify your order.

Water will be the greatest concentration as it is present from both reactions, and will not all be used up by either reaction. $OCl^-$ and $H_3O^+$ will be equal in concentration due to each HOCl molecule producing one of each ion. HOCl itself will be lowest in concentration as it is constantly reacting with the abundance of $H_2O$ to be ~~removed~~ hydrolysed ~~and~~

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(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.*

lower pKa corresponds to higher Ka value and higher Ka value indicates a stronger acid. Therefore pH of Hydrofluoric Acid would be lower than that of Hypochlorous acid, indicating Hydrofluoric acid is the stronger of the two.

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(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 mol $L^{-1}$ HF to give a buffer solution with a pH of 4.02.

Assume there is no change in volume.

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

$Ka(HF) = 10^{-pKa} = 10^{-3.17} = 6.76 \times 10^{-4}$.

$Kb = \frac{Kw}{Ka} = \frac{1.00 \times 10^{-14}}{6.76 \times 10^{-4}} = 1.48 \times 10^{-11}$.

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## 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 $PbCl_2$.

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(aq)$

(ii) Write the expression for $K_s(PbCl_2)$.

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

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

$K_s(PbCl_2) = 1.70 \times 10^{-5}$ at 25°C

$K_s = [s][s]^2$

$= 4s^3$

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

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

$s = 0.0162$ mol $L^{-1}$

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

$[Cl^-] = 0.0324$ mol $L^{-1}$

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

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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.

$K_s(PbCl_2) = 1.70 \times 10^{-5}$ $M(Pb(NO_3)_2) = 331$ g $mol^{-1}$

$2Cl^-_{(aq)} + Pb^{2+}_{(aq)} \longrightarrow PbCl_{2(aq)}$ ~~+ ...~~ (aq)

$n = \frac{m}{M}$ $n = \frac{2}{331}$ $n = 6.04 \times 10^{-3}$

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$C = \frac{n}{V}$ $C = \frac{6.04 \times 10^{-3}}{0.5}$ $C = 0.01208$ mol$L^{-1}$ Assume $[Pb^{2+}] = [Pb(NO_3)_2]$

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

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 pH is less than 4, the solution is strongly acidic. This means there will be an abundance of $H_3O^+$ ions. When pH is greater than 10, the solution is strongly basic with an abundance of $OH^-$ ions. Zn(OH) has the ability to attach to an extra $OH^-$ ion to form the zincate ion $[Zn(OH)_4]^{2-}$. This increases the amount of substance that will dissolve.

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## QUESTION THREE

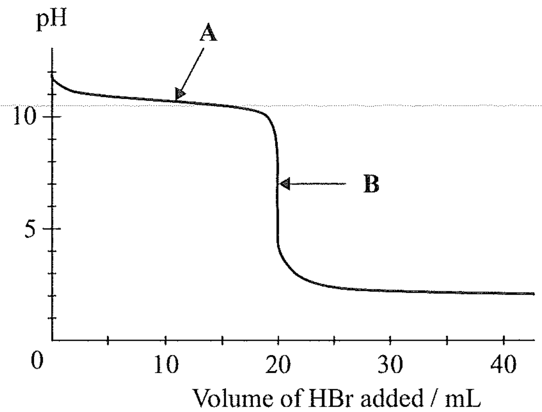
A titration was carried out by adding hydrobromic acid, HBr, to 20.0 mL of aqueous methylamine, $CH_3NH_2$, solution.

The equation for the reaction is:

$$CH_3NH_2 + HBr \rightarrow CH_3NH_3^+ + Br^-$$

$$K_a(CH_3NH_3^+) = 2.29 \times 10^{-11}$$

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.

Because this is a buffer, where addition of either hydronium ions or hydroxide ions will have very little measurable effect on the pH of the solution.

~~$CH_3NH_3^+$ + ... → ...~~

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

$Br^- + H_3O^+ \rightarrow H_2O + HBr$.

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

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

$C = \frac{n}{V}$ ~~$[H_3O^+] = 10^{-pH} = 1.00 \times 10^{-11}$~~ $pOH = 14 - 11.8 = 2.2$.

$[OH^-] = 10^{-2.2} = 6.31 \times 10^{-3}$ mol$L^{-1}$

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

$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$ $K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{2.29 \times 10^{-11}}$

$= 4.37 \times 10^{-4}$

Assume $[CH_3NH_3^+] = [OH^-]$

$[CH_3NH_2] = \frac{(6.31 \times 10^{-3})^2}{4.37 \times 10^{-4}} = 0.0912$ mol$L^{-1}$ (3sf).

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(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.

$CH_3NH_2$. HBr. $CH_3NH_3^+$. $Br^-$.

(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.

A Initially, the ~~species present were~~ only species present was methylamine, $CH_3NH_2$. Concentration was 0.0912 mol$L^{-1}$. We can assume that the initial volume of methylamine was 20mL. Initially, the solution had very poor electrical conductivity due to the lack of ions present in solution.

Point B is the equivalence point. Where all the base

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

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has been reacted with HBr acid. At this point there is 40mL of solution, and electrical conductivity is much better due to the movement of ions in the solution. There are four species present at this point. There ~~[illegible]~~ is also a chemical equilibrium reached. All the acid has been reacted, yet all four species are still present due to the products reacting with the water in solution. Equivalence point is at pH=7 which means the solution is neutral and there will be equal $[H_3O^+]$ and $[OH^-]$ ions.

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Q1. This question is limited to A4 because in part (a) (ii) the candidate does not recognise the presence of hydroxide ions in the solution both in the list of species and the justification. In part (b), if they had added the link to hydrogen ion concentration they would have got Merit. In part (c), they have done one step, calculating $K_a$, but not finished the question.

Q2. This question is limited to A4 because in part (a) (i), they do not use the correct equilibrium arrow. In part (b), they have done one step calculating the moles of lead nitrate but not finished the question. In part (c), they have related high hydroxide concentration to the formation of the complex ion but have not gone on to explain the effect on solubility using equilibrium principles.

Q3. This question is limited to A4 because in part (a), they recognise the buffering properties but write an incorrect equation. In part (c), the species present are not correct, but they do link conductivity to the presence of ions.