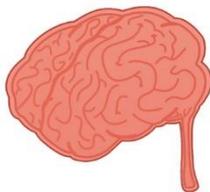**DRAFT ANSWERS – please let us know if you spot any errors**

Level 3 Chemistry

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

You should attempt ALL the questions in this booklet.

A periodic table is provided in the Resource Sheet.

If you need more room for any answer, use the extra space provided at the back of this booklet and clearly number the question.

Check that this booklet has pages 2–8 in the correct order and that none of these pages is blank.

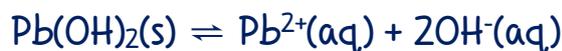YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

TOTAL

QUESTION ONE

(a) Lead hydroxide, $Pb(OH)_2$, is a sparingly soluble, ionic compound.

(i) Write the equation for the dissolving of $Pb(OH)_2$ in water.

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

(ii) Write the expression for the solubility product, K_s, for $Pb(OH)_2$.

$$K_s = [Pb^{2+}(aq)]\,[OH^-(aq)]^2$$

(iii) Calculate the solubility product K_s for $Pb(OH)_2$ given the solubility at 25°C is 3.68×10^{-5} g L^{-1}.
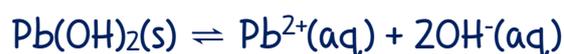
$M(Pb(OH)_2) = 241$ g mol^{-1}

A solubility of 3.68×10^{-5} g L^{-1} so $s = 3.68 \times 10^{-5}/241 = 1.53 \times 10^{-7}$ mol L^{-1}

$K_s = 4s^3 = 4 \times (1.53 \times 10^{-7})^3 = 1.42 \times 10^{-20}$.

(b) The solubility of lead hydroxide, $Pb(OH)_2$, can be altered.

(i) Use equilibrium principles to explain how the solubility of lead hydroxide will change if added to 50 mL of a 1.00 mol L^{-1} lead nitrate solution, $Pb(NO_3)_2(aq)$. *No calculations are necessary.*

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

Lead nitrate solution contains $Pb^{2+}(aq)$ ions, so if lead hydroxide is dissolved in lead nitrate its solubility will be less due to the common ion effect. The lead ion concentration is increased by dissolving the <u>lead</u> hydroxide in <u>lead</u> nitrate solution and the equilibrium responds by favouring the back reaction (to reduce concentration of lead ions) and so less lead hydroxide dissolves.

(ii) A change in pH may lead to the formation of complex ions, such as the plumbate ion, $[Pb(OH)_4]^{2-}$.

Use equilibrium principles to explain what happens to the solubility of lead hydroxide when the pH is greater than 10. *No calculations are necessary.*

$Pb(OH)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2OH^-(aq)$
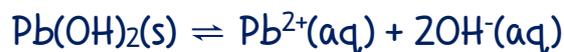
Above pH 10 there is a high concentration of $OH^-(aq)$, enough to form a complex ion with the $Pb^{2+}(aq)$; this effectively reduces the $[Pb^{2+}(aq)]$.

$Pb^{2+}(aq) + 4OH^-(aq) \rightarrow [Pb(OH)_4]^{2-}(aq)$
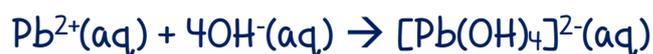
The equilibrium responds by favouring the forward reaction and thus more lead hydroxide dissolves.

(c) Predict whether a precipitate of lead sulfate, $PbSO_4$, will form when the following solutions are mixed:

50.0 mL of 0.00560 mol L^{-1} $Pb(NO_3)_2$ and 70.0 mL 0.00200 mol L^{-1} Na_2SO_4.

$K_s(PbSO_4) = 1.82 \times 10^{-8}$

$IP / Q = [Pb^{2+}(aq)] [SO_4^{2-}(aq)]$

$IP / Q = [50/120 \times 0.00560] [70/120 \times 0.00200]$

$IP / Q = 2.33 \times 10^{-3} \times 1.17 \times 10^{-3} = 2.72 \times 10^{-6}$

Since ionic product > K_s a precipitate will form.

QUESTION TWO

Ethanoic acid, CH_3COOH, is a weak acid. Ka, for ethanoic acid is 1.74×10^{-5}.

(a) What is meant by "ethanoic acid is a weak acid"? Include an equation in your answer.

A weak acid is an acid whose reaction with water is incomplete / only reacts partially with water; it does not totally ionise or dissociate when added to water.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
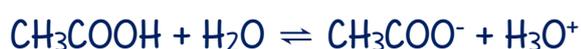
(b) A student titrated 25.0 mL samples of ethanoic acid with 0.200 L^{-1} sodium hydroxide solution added from a burette. The pH was monitored throughout.

The titration pH curve is shown below.

volume NaOH(aq) added / mL
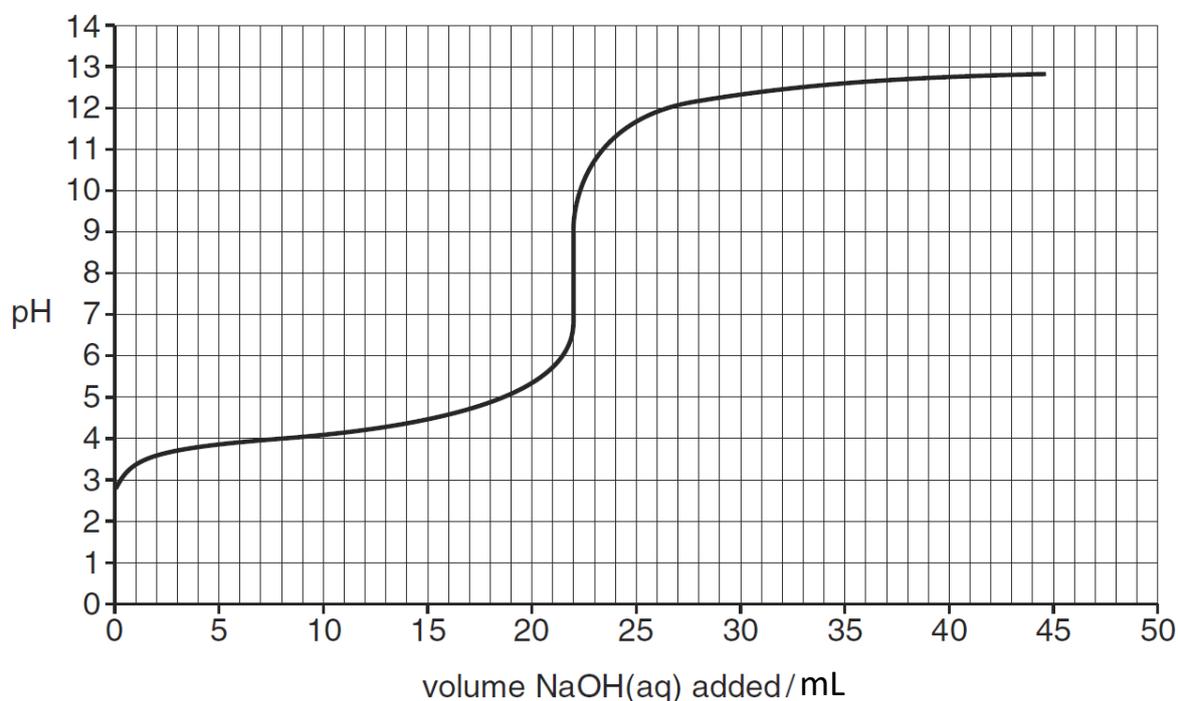
(i) Show that the concentration of the ethanoic acid is 0.176 mol L^{-1}.

Equivalence point is at 22.0 mL of NaOH(aq)

$n(NaOH) = CV = 0.200 \times 0.0220 = 4.40 \times 10^{-3}$ mol. Since 1 mol NaOH reacts with 1 mol CH_3COOH, then $n(CH_3COOH) = 4.40 \times 10^{-3}$ mol

$c(CH_3COOH) = n/V = 4.40 \times 10^{-3} / 0.0250 = 0.176$ mol L^{-1}

(ii) Calculate the pH of the ethanoic acid before any sodium hydroxide is added.

$K_a = [H_3O^+]^2/[HA]$ $1.74 \times 10^{-5} = [H_3O^+]^2/[0.176]$ pH = 2.76

(iii) List all the species present in at equivalence point, in order of decreasing concentration. Do not include water. Justify the order you have given. Include equations, where necessary.

$CH_3COOH + NaOH \rightarrow CH_3COO^- Na^+ + H_2O$

Na^+ does not react any further with water, while CH_3COO^- reacts, as a weak base, with water, reacting only partially.

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

For every mole that reacts, 1 mole CH_3COOH and 1 mole of OH^- is formed. H_3O^+ is present in the lowest concentration as this comes from the dissociation of water only.

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

(c) The pK_a values of three indicators are shown below.
- Cresol purple pKa 8.3
- Bromocresol green pKa 4.7
- Alizarin Yellow pKa 11.0

Discuss your choice of indicator in terms of the composition and function of indicators in acid-base titrations.

The pH at the equivalence point is approximately 8.5 as seen on the titration curve. Indicators change colour over 2 pH units (pKa +/- 1). The bromocresol green changes colour over pH 3.7-5.7 and alizarin yellow over a pH range of 10.0 – 12.0. This means bromocresol green would therefore change colour before the equivalence point and alizarin yellow would change colour after the equivalence point and therefore be unsuitable for this titration. Cresol purple will change colour over a pH range of 7.3 – 9.3 which includes the pH at the equivalence point and so would be a suitable indicator to detect the endpoint.

(d) Ethanoic acid can be used to make buffer solutions.

- Calculate the pH of the buffer solution formed when 16.0 mL of a 0.250 mol L^{-1} solution of sodium hydroxide is added to 24.0 mL of a 0.200 mol L^{-1} solution of ethanoic acid.
- Evaluate the effectiveness of this solution acts as a buffer. Include equations in your answer.

pH = pKa + log [base]/[acid] pk_a = -log K_a = 4.76

n(NaOH) = CV = 0.250 x 0.0160 = 4.00 x 10^{-3} mol

n(CH$_3$COOH) = CV = 0.200 x 0.0240 = 4.80 x 10^{-3} mol

Therefore there would be 4.00 x 10^{-3} mol of CH$_3$COONa formed in a volume of 40 mL. c(CH$_3$COONa) = 4.00 x 10^{-3} / 0.0400 = 0.100 mol L^{-1}.

n(CH$_3$COOH) unreacted = 0.800 x 10^{-3} mol in a volume of 40.0 mL. c(CH$_3$COOH) = n/V = 0.800 x 10^{-3}/0.0400 = 0.0200 mol L^{-1}

pH = pKa + log [base]/[acid] pk_a = -log K_a = 4.76

pH = 4.76 + log [0.100]/[0.0200]   **pH = 5.46**

*could just calculate in mol ratio of CH$_3$COO$^-$ to CH$_3$COOH as both now in same 40 mL volume.

Since the concentrations of base is much greater than that of the acid the buffer be much more effective against added acid than base.

If acid is added: CH$_3$COO$^-$ + H$_3$O$^+$ → CH$_3$COOH + H$_2$O

If base is added: CH$_3$COOH + OH$^-$ → CH$_3$COO$^-$ + H$_2$O

QUESTION THREE

(a) List all the species in each of the following 1.00 mol L^{-1} solutions in order of decreasing concentration. Do not include water.

1.00 mol L^{-1} solutions	Species formed in order of decreasing concentration
NaCl	$Na^+ = Cl^- > H_3O^+ = OH^-$
NH_4Cl	$Cl^- > NH_4^+ > NH_3 = H_3O^+ > OH^-$

(b) Explain why a 1.00 mol L^{-1} solution of ammonium chloride, NH_4Cl, is a strong electrolyte while a 1.00 mol L^{-1} solution of ammonia, NH_3, is a weak electrolyte.

Electrical conductivity relates to the concentration of mobile charged particles present. NH_4Cl completely dissolves in water to produce a high concentration of ions, so its conductivity will be high. Since NH_3 is a weak base, it partially reacts with water to produce only a few ions in the solution, making it a poor electrical conductor.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

(c) (i) Calculate the pH of the 0.850 mol L^{-1} ammonium chloride solution.

pK$_a$ (NH$_4^+$) = 9.25

K$_a$ (NH$_4^+$) = 5.62 x 10^{-10}

NH$_4^+$ + H$_2$O $\rightleftharpoons$ NH$_3$ + H$_3$O$^+$, i.e. salt solution is acidic.

K$_a$ = [H$_3$O$^+$]^2 / [acid]   5.62 x 10^{-10} = [H$_3$O$^+$]^2 / [0.850]   so pH = 4.66

(ii) Calculate **the change in pH** if the ammonium chloride concentration in part (c)(i) is doubled (100% change) and, by considering the pK$_a$ value, explain why the pH change is very small.

5.62 x 10^{-10} = [H$_3$O$^+$]^2 / [1.70]   so pH = 4.51

So the difference is that the solution is only 0.15 pH units more acidic.

This is because the pK$_a$ value was high which means that the NH$_4^+$ ion is a very weak acid indeed and so the equilibrium position lies very much to the left, meaning little breaks down to form H$_3$O$^+$ ions with water even if the ammonium chloride is (100%) more concentrated.

Extra paper if required.

Write the question number(s) if applicable