Further aspects of Equilibria - 2021

1. Nov/2021/Paper_41/No.2

Solution **Y** is hydrochloric acid, $HCl(aq)$. Solution **Z** is aqueous 4-chlorobutanoic acid, $Cl(CH_2)_3CO_2H(aq)$. The pK_a of $Cl(CH_2)_3CO_2H(aq)$ is 4.52. The pH of both solutions is 4.00.

(a) (i) Write an expression for the K_a of $Cl(CH_2)_3CO_2H(aq)$.

K_a =

[1]

(ii) Write a mathematical expression to describe the relationship between K_a and pK_a.

.... [1]

(iii) Calculate [H^+] in solutions **Y** and **Z**.

[H^+] = ... mol dm^{-3} [1]

(iv) Calculate the ratio $\dfrac{[HCl] \text{ dissolved in solution } \mathbf{Y}}{[Cl(CH_2)_3CO_2H] \text{ dissolved in solution } \mathbf{Z}}$.

$\dfrac{[HCl] \text{ dissolved in solution } \mathbf{Y}}{[Cl(CH_2)_3CO_2H] \text{ dissolved in solution } \mathbf{Z}}$ = ... [2]

(b) A buffer solution of pH 5.00 is produced by adding sodium propanoate to 5.00 g of propanoic acid in 100 cm^3 of distilled water.

Calculate the mass of sodium propanoate that must be used to produce this buffer solution. The K_a of propanoic acid is 1.35×10^{-5} mol dm^{-3}.

[M_r: propanoic acid, 74.0; sodium propanoate, 96.0]

mass of sodium propanoate = ... g [3]

(c) Some dilute sulfuric acid is mixed with a small sample of the buffer solution described in **(b)**. The final pH of the mixture is close to 1.

Explain this observation.

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.... [2]

[Total: 10]

2. Nov/2021/Paper_42/No.2

Ethoxyethane, $C_2H_5OC_2H_5$, can dissolve both in water and in octan-1-ol. The expression and numerical value for the partition coefficient of ethoxyethane between water and octan-1-ol are given. Water and octan-1-ol are immiscible.

$$K_{pc} = \frac{\text{concentration of } C_2H_5OC_2H_5 \text{ in octan-1-ol}}{\text{concentration of } C_2H_5OC_2H_5 \text{ in water}} = 6.760 \text{ at } 20\,°C$$

(a) In an experiment, octan-1-ol at 20 °C is added to a solution of ethoxyethane in water at 20 °C. The mixture is analysed immediately and a value of K_{pc} is calculated.

The calculation is performed correctly; the value calculated is 5.625.

Explain why the value calculated is **less** than 6.760.

....

.... [2]

(b) A second experiment is performed and the value of K_{pc} is found to be 6.760. The concentration of ethoxyethane in the octan-1-ol layer is 7.62 g dm^{-3}.

(i) Calculate the concentration, in g dm^{-3}, of ethoxyethane in the aqueous layer.

.... g dm^{-3} [1]

(ii) 100 cm^3 of the octan-1-ol layer is taken and shaken with 100 cm^3 of water.

Calculate the maximum amount, in mol, of ethoxyethane that can be extracted into the water.

.... mol [3]

(c) An aqueous solution of lead(II) nitrate is mixed with an aqueous solution of sodium iodide. A yellow precipitate of lead(II) iodide is formed and is filtered out, leaving solution **X**.

The concentration of Pb^{2+} in solution **X** is 5.68×10^{-3} mol dm^{-3}.

The concentration of I^{-} in solution **X** is 4.20×10^{-4} mol dm^{-3}.

(i) Use these data to calculate a value for the solubility product, K_{sp}, of lead(II) iodide.

State the units of K_{sp}.

K_{sp} = ...

units = ... [2]

(ii) Potassium iodide is very soluble in water.

Describe and explain what is seen if a few drops of saturated potassium iodide solution are added to a portion of solution **X**.

....

....

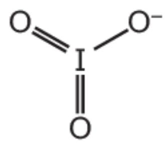
.... [2]

[Total: 10]

3. March/2021/Paper_42/No.3

Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



Explain, with reference to the qualitative model of electron-pair repulsion, why the IO_3^- anion has a pyramidal shape.

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.... [1]

(b) The reaction of iodine and hot aqueous sodium hydroxide is similar to that of chlorine and hot aqueous sodium hydroxide. Sodium iodate, $NaIO_3$, is formed as one of the products.

Suggest an equation for the reaction of iodine and hot aqueous sodium hydroxide.

.... [1]

(c) The decomposition of hydrogen peroxide, H_2O_2, is catalysed by acidified IO_3^-.

H_2O_2 reduces acidified IO_3^- as shown.

$$5H_2O_2 + 2H^+ + 2IO_3^- \rightarrow I_2 + 5O_2 + 6H_2O$$

This reaction is followed by the oxidation of I_2 by H_2O_2.

half-equation	$E^\ominus$/V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+1.19
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68

(i) Use the data to show that the separate reactions of H_2O_2 with IO_3^- and with I_2 are both feasible under standard conditions.

In your answer, give the equation for the reaction of H_2O_2 with I_2.

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.... [3]

(ii) Write the overall equation for the decomposition of H_2O_2 catalysed by acidified IO_3^-.

.... [1]

(d) A student collects some data for the reaction of H_2O_2 with acidified IO_3^-, as shown in the table.

experiment	$[H_2O_2]$ / mol dm^{-3}	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
1	0.0500	0.0700	0.025	1.47×10^{-5}
2	0.100	0.0700	0.050	2.94×10^{-5}
3	0.100	0.140	0.025	5.88×10^{-5}
4	0.150	0.140	0.025	8.82×10^{-5}

(i) Use the data to determine the order of reaction with respect to $[H_2O_2]$, $[IO_3^-]$ and $[H^+]$.

Show your reasoning.

order with respect to $[H_2O_2]$ = ...

....

....

....

order with respect to $[IO_3^-]$ = ...

....

....

....

order with respect to $[H^+]$ = ...

....

....

....

[3]

(ii) Use your answer to **(d)(i)** to write the rate equation for this reaction.

rate = ... [1]

(iii) Calculate the value of the rate constant, k, using data from experiment 4 and your answer to **(d)(ii)**.

Give the units of k.

k = ...

units = ...
[2]

(e) $Pb(IO_3)_2$ is only sparingly soluble in water at 25 °C.

The solubility product, K_{sp}, of $Pb(IO_3)_2$ is 3.69×10^{-13} $mol^3\,dm^{-9}$ at 25 °C.

(i) Write an expression for the solubility product of $Pb(IO_3)_2$.

K_{sp} =

[1]

(ii) Calculate the solubility, in $mol\,dm^{-3}$, of $Pb(IO_3)_2$ at 25 °C.

solubility = ... $mol\,dm^{-3}$ [2]

(f) NH_4IO_3 is an unstable compound that readily decomposes when warmed. The decomposition reaction is shown.

$$NH_4IO_3(s) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}I_2(g) + 2H_2O(l) \qquad \Delta H = -154.6\,kJ\,mol^{-1}$$

(i) Use the data in the table to calculate the entropy change of reaction, ΔS, of the decomposition of $NH_4IO_3(s)$.

compound	$S / J\,K^{-1}\,mol^{-1}$
$NH_4IO_3(s)$	42
$N_2(g)$	192
$O_2(g)$	205
$I_2(g)$	261
$H_2O(l)$	70

ΔS = ... $J\,K^{-1}\,mol^{-1}$ [2]

(ii) This reaction is feasible at all temperatures.

Explain why, using the data in **(f)** and your answer to **(f)(i)**.

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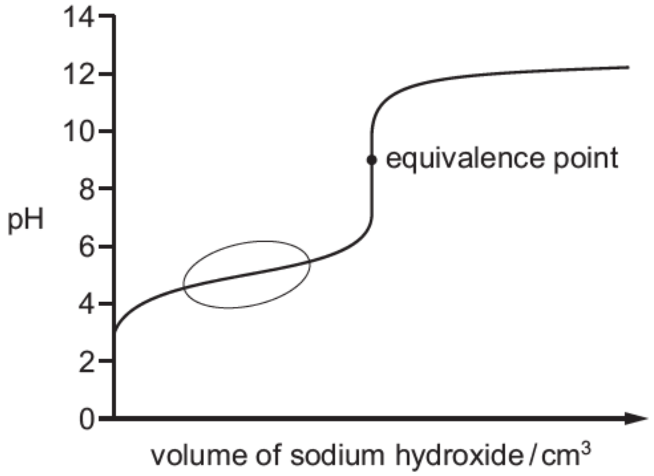
.... [1]

[Total: 18]

4. June/2021/Paper_41/No.8

(a) The sketch graph for the titration of ethanoic acid, CH_3CO_2H, with sodium hydroxide is shown.



(i) In the region circled on the graph, identify the **two** organic species that are present in the solution. Explain why the pH of the mixture only changes slowly and gradually in this region when sodium hydroxide is being added.

two species present ....

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....

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.... [3]

(ii) The equivalence point in this acid-base titration is where the two solutions have been mixed in exactly equal molar proportion.

Suggest why the pH is greater than 7 at the equivalence point in this titration.

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.... [1]

(b) An impure sample of ammonium vanadate(V), NH_4VO_3, with mass 0.150 g, is dissolved in an excess of dilute acid.

In this solution all vanadium is present as VO_2^+ ions. An excess of zinc powder is added to the solution and all the VO_2^+ ions are reduced to V^{2+} ions. The mixture is filtered to remove any remaining zinc powder.

$$VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$$

When the resulting solution is titrated, 20.10 cm^3 of 0.0250 $mol\,dm^{-3}$ acidified MnO_4^- oxidises all V^{2+} ions back to VO_2^+ ions.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Calculate the percentage by mass of NH_4VO_3 in the 0.150 g impure sample of NH_4VO_3.

Give your answer to **three** significant figures.

[M_r: NH_4VO_3, 116.9]

percentage by mass of NH_4VO_3 = ... % [3]

[Total: 7]