## Equilibria

## Question Paper3

| Level | International A Level |
| :--- | :--- |
| Subject | Chemistry |
| Exam Board | CIE |
| Topic | Equilibria |
| Sub-Topic |  |
| Paper Type | Theory |
| Booklet | Question Paper 3 |


| Time Allowed: | 68 minutes |
| :--- | :--- |
| Score: | $/ 56$ |
| Percentage: | $/ 100$ |

Grade Boundaries:

| A* | A | B | C | D | E | U |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $>85 \%$ | $777.5 \%$ | $70 \%$ | $62.5 \%$ | $57.5 \%$ | $45 \%$ | $<45 \%$ |

1 (a) (i) Using the symbol HZ to represent a Brønsted-Lowry acid, write equations which show the following substances acting as Brønsted-Lowry bases.
$\mathrm{NH}_{3}+$
$\rightarrow$
$\mathrm{CH}_{3} \mathrm{OH}+\quad \rightarrow$
(ii) Using the symbol $\mathbf{B}^{-}$to represent a Brønsted-Lowry base, write equations which show the following substances acting as Brønsted-Lowry acids.
$\mathrm{NH}_{3}+$
$\rightarrow$
$\mathrm{CH}_{3} \mathrm{OH}+\quad \rightarrow$
(b) State briefly what is meant by the following terms.
(i) reversible reaction
$\qquad$
(ii) dynamic equilibrium
$\qquad$
$\qquad$
(c) (i) Explain what is meant by a buffer solution.
$\qquad$
$\qquad$
$\qquad$
(ii) Explain how the working of a buffer solution relies on a reversible reaction involving a Brønsted-Lowry acid such as $\mathbf{H Z}$ and a Brønsted-Lowry base such as $\mathbf{Z}$-.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(d) Propanoic acid, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$, is a weak acid with $K_{\mathrm{a}}=1.34 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$.
(i) Calculate the pH of a $0.500 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of propanoic acid.

Buffer solution F was prepared by adding 0.0300 mol of sodium hydroxide to $100 \mathrm{~cm}^{3}$ of a $0.500 \mathrm{~mol} \mathrm{dm}^{-3}$ solution of propanoic acid.
(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.
(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution F.

[propanoic acid] =<br>$\qquad$ $\mathrm{mol} \mathrm{dm}^{-3}$<br>[sodium propanoate] =<br>$\qquad$ $\mathrm{mol} \mathrm{dm}^{-3}$

(iv) Calculate the pH of buffer solution $\mathbf{F}$.

$$
\mathrm{pH}=
$$

$\qquad$
(e) Phenyl propanoate cannot be made directly from propanoic acid and phenol.

Suggest the identities of the intermediate $\mathbf{G}$, the reagent $\mathbf{H}$ and the by-product $\mathbf{J}$ in the following reaction scheme.

$\mathbf{G}$ is $\qquad$
H is $\qquad$
$\mathbf{J}$ is $\qquad$

2 Ethanoic acid can be reacted with alcohols to form esters, an equilibrium mixture being formed.

$$
\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}+\mathrm{ROH} \rightleftharpoons \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{R}+\mathrm{H}_{2} \mathrm{O}
$$

The reaction is usually carried out in the presence of an acid catalyst.
(a) Write an expression for the equilibrium constant, $K_{\mathrm{c}}$, for this reaction, clearly stating the units.
$K_{\mathrm{c}}=$
units
In an experiment to determine $K_{\mathrm{c}}$ a student placed together in a conical flask 0.10 mol of ethanoic acid, 0.10 mol of an alcohol ROH , and 0.005 mol of hydrogen chloride catalyst.
The flask was sealed and kept at $25^{\circ} \mathrm{C}$ for seven days.
After this time, the student titrated all of the contents of the flask with $2.00 \mathrm{moldm}^{-3} \mathrm{NaOH}$ using phenolphthalein indicator.
At the end-point, $22.5 \mathrm{~cm}^{3}$ of NaOH had been used.
(b) (i) Calculate the amount, in moles, of NaOH used in the titration.
(ii) What amount, in moles, of this NaOH reacted with the hydrogen chloride?
(iii) Write a balanced equation for the reaction between ethanoic acid and NaOH .
(iv) Hence calculate the amount, in moles, of NaOH that reacted with the ethanoic acid.
(c) (i) Use your results from (b) to calculate the amount, in moles, of ethanoic acid present at equilibrium. Hence complete the table below.

|  | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ | ROH | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{R}$ | $\mathrm{H}_{2} \mathrm{O}$ |
| :--- | :---: | :---: | :---: | :---: |
| initial <br> amount $/ \mathrm{mol}$ | 0.10 | 0.10 | 0 | 0 |
| equilibrium <br> amount $/ \mathrm{mol}$ |  |  |  |  |

(ii) Use your results to calculate a value for $K_{\mathrm{c}}$ for this reaction.
(d) Esters are hydrolysed by sodium hydroxide. During the titration, sodium hydroxide reacts with ethanoic acid and the hydrogen chloride, but not with the ester.

Suggest a reason for this.
$\qquad$
$\qquad$
(e) What would be the effect, if any, on the amount of ester present if all of the water were removed from the flask and the flask kept for a further week at $25^{\circ} \mathrm{C}$ ?

Explain your answer.
$\qquad$
$\qquad$
$\qquad$

3 (a) State briefly what is meant by the following terms.
(i) reversible reaction
$\qquad$
(ii) dynamic equilibrium
$\qquad$
$\qquad$
(b) Water ionises to a small extent as follows.

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \Delta H=+58 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

(i) Write an expression for $K_{\mathrm{c}}$ for this reaction.
$\qquad$
(ii) Write down the expression for $K_{\mathrm{w}}$, the ionic product of water, and explain how this can be derived from your $K_{\mathrm{c}}$ expression in (i).
$\qquad$
$\qquad$
(iii) State and explain how the value of $K_{w}$ for hot water will differ from its value for cold water.
$\qquad$
$\qquad$
(c) $K_{\mathrm{w}}$ can be used to calculate the pH of solutions of strong and weak bases.
(i) Use the value of $K_{\mathrm{w}}$ in the Data Booklet to calculate the pH of $0.050 \mathrm{moldm}^{-3}$ NaOH .

$$
\mathrm{pH}=
$$

$\qquad$
Ammonia ionises slightly in water as follows.

$$
\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

The following expression applies to this equilibrium.

$$
\left[\mathrm{H}_{2} \mathrm{O}\right] \times K_{\mathrm{c}}=\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right] /\left[\mathrm{NH}_{3}\right]=1.8 \times 10^{-5} \mathrm{moldm}^{-3}
$$

(ii) Calculate $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$ in a $0.050 \mathrm{moldm}^{-3}$ solution of $\mathrm{NH}_{3}$. You may assume that only a small fraction of the $\mathrm{NH}_{3}$ ionises, so that $\left[\mathrm{NH}_{3}\right]$ at equilibrium remains at $0.050 \mathrm{moldm}^{-3}$.
$\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=$
(iii) Use the value of $K_{\mathrm{w}}$ in the Data Booklet, and your answer in (ii), to calculate [ $\left.\mathrm{H}^{+}(\mathrm{aq})\right]$ in $0.050 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NH}_{3}(\mathrm{aq})$.

$$
\left[\mathrm{H}^{+}(\mathrm{aq})\right]=
$$

(iv) Calculate the pH of this solution.

$$
\mathrm{pH}=
$$

4 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.

(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

| experiment <br> number | $\left[\mathrm{CH}_{3} \mathrm{CHO}\right]$ <br> $/ \mathrm{moldm}^{-3}$ | $\left[\mathrm{CH}_{3} \mathrm{OH}\right]$ <br> $/ \mathrm{moldm}^{-3}$ | $\left[\mathrm{H}^{+}\right]$ <br> $/ \mathrm{moldm}^{-3}$ | relative rate |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 0.20 | 0.10 | 0.05 | 1.00 |
| 2 | 0.25 | 0.10 | 0.05 | 1.25 |
| 3 | 0.25 | 0.16 | 0.05 | 2.00 |
| 4 | 0.20 | 0.16 | 0.10 | 3.20 |

(i) Use the data in the table to determine the order with respect to each reactant.
order with respect to $\left[\mathrm{CH}_{3} \mathrm{CHO}\right]$ $\qquad$
order with respect to $\left[\mathrm{CH}_{3} \mathrm{OH}\right]$ $\qquad$
order with respect to $\left[\mathrm{H}^{+}\right]$
(ii) Use your results from part (i) to write the rate equation for the reaction.
$\qquad$
(iii) State the units of the rate constant in the rate equation $\qquad$
(iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are $0.20 \mathrm{moldm}^{-3}$.
$\qquad$
(b) The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

|  | $\left[\mathrm{CH}_{3} \mathrm{CHO}\right]$ <br> $/ \mathrm{moldm}^{-3}$ | $\left[\mathrm{CH}_{3} \mathrm{OH}\right]$ <br> $/ \mathrm{moldm}^{-3}$ | $\left[\mathrm{H}^{+}\right]$ <br> $/ \mathrm{moldm}^{-3}$ | $[$ acetal A] <br> $/ \mathrm{moldm}^{-3}$ | $\left[\mathrm{H}_{2} \mathrm{O}\right]$ <br> $/ \mathrm{moldm}^{-3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| at start | 0.20 | 0.10 | 0.05 | 0.00 | 0.00 |
| at equilibrium | $(0.20-\boldsymbol{x})$ |  |  | $\boldsymbol{x}$ |  |
| at equilibrium |  |  |  | 0.025 |  |

(i) Complete the second row of the table in terms of $\boldsymbol{x}$, the concentration of acetal $\mathbf{A}$ at equilibrium. You may wish to consult the chemical equation opposite.
(ii) Using the [acetal A] as given, $0.025 \mathrm{moldm}^{-3}$, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.
(iii) Write the expression for the equilibrium constant for this reaction, $K_{\mathrm{c}}$, stating its units.
 $\qquad$
(iv) Use your values in the third row of the table to calculate the value of $K_{c}$.

$$
K_{\mathrm{c}}=
$$

$\qquad$
[Total: 15]

