## CHEM1612 Worksheet 6: Acids and Bases

## Model 1: Strong and Weak Acids

A strong acid is one that is essentially $100 \%$ dissociated in water: if 0.1 mole of the acid is added to enough water to make a 1.0 L solution, the solution will have $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=0.1 \mathrm{M}$ and will be $\mathrm{pH}=1$.

A weak acid is one that is significantly less than $100 \%$ dissociated in water: if 0.1 mole of the acid is added to enough water to make a 1.0 L solution, the solution will have $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]<0.1 \mathrm{M}$ and will be $\mathrm{pH}>1$.

When an acid HA is placed in water, $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ ions are produced according to the reaction:

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}(\mathrm{aq})
$$

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]\left[\mathrm{A}^{-}(\mathrm{aq})\right]}{[\mathrm{HA}(\mathrm{aq})]}
$$

## Critical thinking questions

1. What are the major species present in a solution of a strong acid like HCl ?
2. What are the major species present in a solution of a weak acid like $\mathrm{CH}_{3} \mathrm{COOH}$ ?
3. Under what pH conditions would $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ be the dominant species in a solution of $\mathrm{CH}_{3} \mathrm{COOH}$ ?
4. Write down the equilibrium expression, $K_{\mathrm{a}}$, for $\mathrm{CH}_{3} \mathrm{COOH}$.
5. What are the major species present in a solution of a weak base like $\mathrm{CH}_{3} \mathrm{NH}_{2}$ ?
6. Under what pH conditions would $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}(\mathrm{aq})$ be the dominant species?
7. The extent of ionization of a drug helps determine how it is distributed in the body because ions are less likely to cross cell membranes than uncharged molecules. Are the two drugs below likely to be absorbed in (i) the acid environment of the stomach or (ii) the basic environment of the intestine?


aspirin

## Model 2: A Solution Containing a Weak Acid

As a strong acid is one that is essentially $100 \%$ dissociated in water: $\mathrm{pH}=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=-\log [\mathrm{HA}]_{\text {initial }}$ As a weak acid is significantly less than $100 \%$ dissociated in water, an equilibrium must be considered:

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}(\mathrm{aq}) \quad K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]\left[\mathrm{A}^{-}(\mathrm{aq})\right]}{[\mathrm{HA}(\mathrm{aq})]}
$$

Calculating the pH requires that the equilibrium value of $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$ be first calculated. To do this, the 'ICE' approach covered in Model 3 of Worksheet 4 can be followed. Consider a 2.00 M solution of $\mathrm{CH}_{3} \mathrm{COOH}$ :

|  | $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ | $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | $\rightleftharpoons$ | $\mathrm{CH}_{3} \mathrm{COO}-(\mathrm{aq})$ | $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| initial | 2.00 | large |  | 0 | 0 |
| change | $-x$ | $-x$ |  | $+x$ | $+x$ |
| equilibrium | $2.00-x$ | large |  | $+x$ | $+x$ |

As hardly any weak acid dissociates, $x$ is very small and so $2.00-x \approx 2.00$. Using this approximation, the equilibrium constant can then be written down as:

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}=\frac{x^{2}}{2.00-x} \approx \frac{x^{2}}{2.00} \quad \text { and so } x=\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=\sqrt{K_{\mathrm{a}} \times 2.00}
$$

After working out $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$, the pH and percentage dissociation of the weak acid can be calculated:

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right] \text { and } \quad \% \text { dissociation }=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]_{\text {initial }}} \times 100 \%
$$

## Critical thinking questions

1. What are the initial and final concentrations of $\mathrm{CH}_{3} \mathrm{COOH}$ in the ICE table above? How are they related when the small $x$ approximation is used?
2. Using your answer to Q1, write down a formula for $x$ for any dilute weak acid for which the small $x$ approximation is valid.
3. Calculate the pH and percentage dissociation of the acetic acid as it is diluted $\left(K_{\mathrm{a}}=10^{-4.76}\right)$.
(a) 2.00 M $\mathrm{pH}=$
(c) $0.500 \mathrm{M} \quad \mathrm{pH}=$

$$
\% \text { dissociation = }
$$

$$
\% \text { dissociation }=
$$

(b) $1.00 \mathrm{M} \quad \mathrm{pH}=$
(d) $0.250 \mathrm{M} \quad \mathrm{pH}=$

$$
\% \text { dissociation }=
$$

$$
\% \text { dissociation }=
$$

4. Complete the graph below showing how the percentage dissociation changes with the initial concentration.

5. Carefully explain in words what happens to the amount of dissociation of a weak acid as it is diluted.
6. What are the major species present in a 1.00 M solution of acetic acid?

## Model 3: Addition of Strong Base to a Solution of a Weak Acid

Model 2 describes the pH and extent of dissociation of a solution of a weak acid. If a strong base, such as NaOH , is added to this solution, it will react with the weak acid.

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{OH}(\mathrm{aq}) \rightarrow \mathrm{A}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{aq})
$$

$$
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{aq})\right]\left[\mathrm{A}^{-}(\mathrm{aq})\right]}{[\mathrm{HA}(\mathrm{aq})]}
$$

As long as the amount of $\mathrm{OH}^{-}(\mathrm{aq})$ added is less than the amount of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ present, the solution will contain both $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ and left over $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$. A solution like this containing both a weak acid and its conjugate base will have a pH given by the Henderson-Hasselbalch equation:

$$
\mathrm{pH}=\mathrm{p} K_{\mathrm{a}}+\log \frac{[\mathrm{base}]}{[\text { acid }]}=\mathrm{p} K_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{-}(\mathrm{aq})\right]}{[\mathrm{HA}(\mathrm{aq})]}
$$

## Critical thinking questions

1. If 0.100 mol of $\mathrm{NaOH}(\mathrm{s})$ is added to a 1.00 L solution of $0.500 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}$, it will react to form a solution which is $0.100 \mathrm{M}^{2} \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ and $0.400 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$. What is the pH of this solution? $\left(\mathrm{p} K_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76\right)$.
2. Complete the table below showing the concentrations of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ and the pH of the solution as more $\mathrm{NaOH}(\mathrm{s})$ is added to this solution. (Hint: see Model 2 for the first column)

| Amount of $\mathrm{NaOH}(\mathrm{s})$ added (mol) | 0.000 | 0.100 | 0.200 | 0.300 | 0.400 | 0.500 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right](\mathrm{M})$ | 0.500 | 0.400 |  |  |  |  |
| $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right](\mathrm{M})$ | 0.000 | 0.100 |  |  |  |  |
| pH |  |  |  |  |  |  |

3. To react completely with the original $\mathrm{CH}_{3} \mathrm{COOH}, 0.500 \mathrm{~mol}$ of NaOH must be added. What is the pH of the solution when exactly half this amount is added?
4. Using the data from Q 2, complete the graph below showing how the percentage of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ changes with pH . This is called a speciation plot.


## Model 4: Neutralizing a Weak Acid

Model 3 describes the pH changes as a strong base is added to a solution containing a weak acid. The strong base reacts with the weak acid leading to a solution containing the conjugate base of the weak acid and any left over acid. The equivalence point occurs when enough base has been added so that there is no acid left. At this point, the solution contains only the conjugate base.
The pH of the solution of the conjugate base of a weak acid can be calculated by considering the equilibrium it is involved in. The calculation is very similar to that in Model 2.

$$
\mathrm{A}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{HA}(\mathrm{aq})+\mathrm{OH}(\mathrm{aq}) \quad K_{\mathrm{b}}=\frac{[\mathrm{HA}(\mathrm{aq})]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]}{\left[\mathrm{A}^{-}(\mathrm{aq})\right]}
$$

From the chemical equation, at equilibrium:

$$
[\mathrm{HA}(\mathrm{aq})]=[\mathrm{OH}-(\mathrm{aq})] \text { and }[\mathrm{A}(\mathrm{aq})]=[\mathrm{A}(\mathrm{aq})]_{\text {initial }}-[\mathrm{HA}(\mathrm{aq})]
$$

As hardly any base reacts, $[\mathrm{A}(\mathrm{aq})]_{\text {initial }}-[\mathrm{HA}(\mathrm{aq})] \approx[\mathrm{A}(\mathrm{aq})]_{\text {initial }}$ and so:

$$
K_{\mathrm{b}}=\frac{\left[\mathrm{OH}^{-}(\mathrm{aq})\right]^{2}}{\left[\mathrm{~A}^{-}(\mathrm{aq})\right]_{\text {initial }}} \quad \text { and } \quad\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\sqrt{K_{\mathrm{b}} \times\left[\mathrm{A}^{-}(\mathrm{aq})\right]_{\text {initial }}}
$$

After working out $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$, the pOH can be calculated using $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}(\mathrm{aq})\right]$. Finally, the pH can then be calculated using $\mathrm{pH}=14.00-\mathrm{pOH}$.

## Critical thinking questions

1. To react completely with the original $\mathrm{CH}_{3} \mathrm{COOH}$ in $\mathrm{Q} 5,0.500 \mathrm{~mol}$ of NaOH must be added. What will be $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})\right]$ when this occurs?
2. Calculate the pH of the solution in Q1. Correct your entry in the final column of the table in Model 3 if required! (Hint: remember that $\mathrm{p} K_{\mathrm{a}}+\mathrm{p} K_{\mathrm{b}}=14.00$ or $K_{\mathrm{a}} \times K_{\mathrm{b}}=10^{-14.00}$ )
