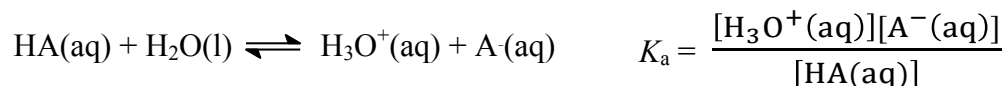


## CHEM1102 Worksheet 9: Weak Acids and Titrations

### Model 1: A Solution Containing a Weak Acid

As a **weak acid** is *significantly* less than 100% dissociated in water, an equilibrium must be considered:



Calculating the pH requires that the equilibrium value of  $[\text{H}_3\text{O}^+(\text{aq})]$  be first calculated. To do this, the 'ICE' approach covered in CHEM1101 can be followed. Consider a 2.0 M solution of  $\text{CH}_3\text{COOH}$ :

	$\text{CH}_3\text{COOH (aq)}$	$\text{H}_2\text{O(l)}$	$\rightleftharpoons$	$\text{CH}_3\text{COO}^-(\text{aq})$	$\text{H}_3\text{O}^+(\text{aq})$
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:

$$K_a = \frac{[\text{CH}_3\text{COO}^-(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00} \quad \text{and so } x = [\text{H}_3\text{O}^+(\text{aq})] = \sqrt{K_a \times 2.00}$$

After working out  $[\text{H}_3\text{O}^+(\text{aq})]$ , the pH and percentage dissociation of the weak acid can be calculated:

$$\text{pH} = -\log[\text{H}_3\text{O}^+(\text{aq})] \quad \text{and} \quad \% \text{ dissociation} = \frac{[\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\%$$

### Critical thinking questions

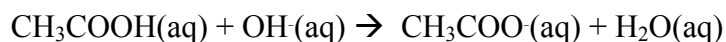
- What are the initial and final concentrations of  $\text{CH}_3\text{COOH}$  in the ICE table above? How are they related when the small  $x$  approximation is used?
- Using your answer to Q1, write down a formula for  $x$  for any dilute weak acid.
- Calculate the pH and percentage dissociation of the acetic acid as it is diluted ( $K_a = 10^{-4.76}$ ).
 

(a) 2.00 M    pH =	(c) 0.500 M    pH =
% dissociation =	% dissociation =
(b) 1.00 M    pH =	(d) 0.250 M    pH =
% dissociation =	% dissociation =

**Model 2: Addition of a Strong Base to a Weak Acid**

In Model 1, you used an “ICE” approach to work out the pH of a solution containing a weak acid. For example, you worked out that a 0.500 M solution of  $\text{CH}_3\text{COOH}(\text{aq})$  has a pH of 2.531.

If a strong base, such as  $\text{NaOH}$ , is added to this solution, it will react with the weak acid.



As long as the amount of  $\text{OH}^-(\text{aq})$  added is *less* than the amount of  $\text{CH}_3\text{COOH}(\text{aq})$  present, the solution will contain both  $\text{CH}_3\text{COO}^-(\text{aq})$  and left over  $\text{CH}_3\text{COOH}(\text{aq})$ . A solution like this containing both a weak acid and its conjugate base is a buffer and its pH is given by the *Henderson-Hasselbalch* equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$$

**Critical thinking questions**

1. If 0.100 mol of  $\text{NaOH}(\text{s})$  is added to a 1.00 L solution of 0.500 M  $\text{CH}_3\text{COOH}$ , it will react to form a solution which is 0.100 M in  $\text{CH}_3\text{COO}^-(\text{aq})$  and 0.400 M  $\text{CH}_3\text{COOH}(\text{aq})$ . What is the pH of this solution? ( $\text{p}K_a(\text{CH}_3\text{COOH}) = 4.76$ ).

2. Complete the table below showing the concentrations of  $\text{CH}_3\text{COOH}(\text{aq})$  and  $\text{CH}_3\text{COO}^-(\text{aq})$  and the pH of the solution as more  $\text{NaOH}(\text{s})$  is added to this solution.

Amount of $\text{NaOH}(\text{s})$ added (mol)	0.000	0.100	0.200	0.300	0.400	0.500
$[\text{CH}_3\text{COOH}(\text{aq})]$ (M)	0.500	0.400				
$[\text{CH}_3\text{COO}^-(\text{aq})]$ (M)	0.000	0.100				
pH	2.531					

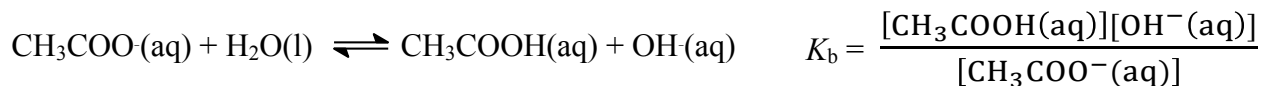
3. To react completely with the original  $\text{CH}_3\text{COOH}$ , 0.500 mol of  $\text{NaOH}$  must be added. What is the pH of the solution when exactly *half* this amount is added?
4. How can you obtain the value for  $\text{p}K_a$  for an acid?

### Model 3: Neutralizing a Weak Acid

Model 2 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 the conjugate base and essentially none of the original acid.

The conjugate base will then set up its own equilibrium:



From the chemical equation:

$$[\text{CH}_3\text{COOH}(\text{aq})]_{\text{equilibrium}} = [\text{OH}^-(\text{aq})]_{\text{equilibrium}}$$

As hardly any base reacts,  $[\text{CH}_3\text{COO}^-(\text{aq})]_{\text{equilibrium}} \approx [\text{CH}_3\text{COO}^-(\text{aq})]_{\text{initial}}$  and so:

$$K_b = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{CH}_3\text{COO}^-(\text{aq})]_{\text{initial}}} \quad \text{and} \quad [\text{OH}^-(\text{aq})] = \sqrt{K_b \times [\text{CH}_3\text{COO}^-(\text{aq})]_{\text{initial}}}$$

After working out  $[\text{OH}^-(\text{aq})]$ , the pOH can be calculated:

$$\text{pOH} = -\log[\text{OH}^-(\text{aq})]$$

Finally, the pH can then be calculated using  $\text{pH} = 14.00 - \text{pOH}$ .

### Critical thinking questions

- To react completely with the original  $\text{CH}_3\text{COOH}$  in Q5, 0.500 mol of NaOH must be added. What will be  $[\text{CH}_3\text{COO}^-(\text{aq})]$  when this occurs?
- Calculate the pH of the solution the reaction produced in Q1.  
(*Hint*: remember that  $\text{p}K_a + \text{p}K_b = 14.00$  or  $K_a \times K_b = 10^{-14.00}$ )
- Correct your entry in the final column of the table in Model 1 if required!
- What is the pH at the equivalence point of the titration of a *strong* acid with a strong base?
- Is the pH at the equivalence point of the titration of a *weak* acid with a strong base less than or higher than 7?

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- Solution A consists of a 0.25 M aqueous solution of hydrazoic acid,  $\text{HN}_3$ , at 25 °C. Calculate the pH of Solution A. The  $\text{p}K_a$  of  $\text{HN}_3$  is 4.63.

**Marks**  
**8**

Answer:

At 25 °C, 1.00 L of Solution B consists of 13.0 g of sodium azide ( $\text{NaN}_3$ ) dissolved in water. Calculate the pH of Solution B.

Answer:

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Answer:

If you wanted to adjust the pH of Solution C to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?