

# *Homework 5*

## Exercise 1

- ◆ A solution of a weak acid HA with  $K_a=10^{-4}$  M is titrated with NaOH. After having added 0.05 equivalents of base, the measured pH is 4.0. Calculate the concentration of HA at the beginning.



When a strong base is added to a weak acid:

- at the beginning (before equivalence) there will be a mixture of the acid and its salt  $\rightarrow$  acidic buffer solution ( $\text{pH} < 7.0$ )
- at equivalence there will only be the salt  $\rightarrow$  basic hydrolysis ( $\text{pH} > 7.0$ )

Here  $\text{pH} = 4.0 \rightarrow$  first condition  $\rightarrow$  we can use the Henderson-Hasselback equation for calculating the amount of Ca

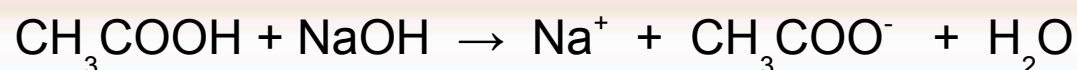
$$\text{pH} = \text{pKa} + \log \frac{C_s}{C_a} \qquad 4 = 4 + \log \frac{0.05}{C_a}$$

$\rightarrow C_{a(t)} = 0.05$  eq when the  $\text{pH} = 4.0$

At the beginning:  $C_{a(0)} = C_{a(t)} + \text{OH}^- = 0.05 + 0.05 = 0.1$  N

## Exercise 2

- ◆ Calculate the pH of the solution obtained by mixing 75ml of CH<sub>3</sub>COOH 0.01 N with 50ml NaOH 0.01 M (K<sub>a</sub>= 1.8·10<sup>-5</sup> M at 25°C).



Equivalents of acid:  $C_a \times V_a = 0.01 \times 0.075 = 7.5 \cdot 10^{-4}$  eq

Equivalents of base:  $C_b \times V_b = 0.01 \times 0.05 = 5.0 \cdot 10^{-4}$  eq

There is an excess of weak acid → in solution there will be the newly formed salt and the remaining acid → BUFFER solution

$$C_s = \text{Eq}(\text{base}) / V(\text{tot}) = 5 \cdot 10^{-4} / (0.075 + 0.05) = 4 \cdot 10^{-3} \text{ N}$$

$$C_a = [\text{Eq}(\text{acid}) - \text{Eq}(\text{base})] / V(\text{tot}) = [(7.5 - 5.0) \cdot 10^{-4}] / 0.125 = 2 \cdot 10^{-3} \text{ N}$$

$$pH = pK_a + \log \frac{C_s}{C_a} = 4.74 + \log \frac{4 \cdot 10^{-3}}{2 \cdot 10^{-3}} = 4.74 + \log 2 = 4.74 + 0.301 = 5.04$$

## Exercise 3

- ◆ 250ml of ethanoic acid 0.5 N are mixed with 250ml of NaOH 0.2 N. Calculate the pH of the final solution ( $K_a=1.8 \cdot 10^{-5}$  M at 25°C).



Equivalents of acid:  $C_a \times V_a = 0.5 \times 0.25 = 0.125$  eq

Equivalents of base:  $C_b \times V_b = 0.2 \times 0.25 = 0.05$  eq

There is an excess of weak acid  $\rightarrow$  in solution there will be the newly formed salt and the remaining acid  $\rightarrow$  BUFFER solution

$$C_s = \text{Eq}(\text{base}) / V(\text{tot}) = 0.05 / (0.25+0.25) = 0.1 \text{ N}$$

$$C_a = [\text{Eq}(\text{acid}) - \text{Eq}(\text{base})] / V(\text{tot}) = [0.125-0.05] / 0.5 = 0.15 \text{ N}$$

$$pH = pK_a + \log \frac{C_s}{C_a} = 4.74 + \log \frac{0.1}{0.15} = 4.74 + \log 0.67 = 4.74 - 0.18 = 4.56$$

## Exercise 4

- ◆ 500 ml of HCN 0.2 N are mixed with 500ml of KOH 0.2 N. Calculate the pH of the final solution ( $K_a = 2 \cdot 10^{-4} M$ ).



Equivalents of acid:  $C_a \times V_a = 0.2 \times 0.5 = 0.1 \text{ eq}$

Equivalents of base:  $C_b \times V_b = 0.2 \times 0.5 = 0.1 \text{ eq}$

There is an equivalence of acid and base  $\rightarrow$  in solution there will ONLY be the newly formed salt, which gives a basic hydrolysis  $\rightarrow \text{pH} > 7.0$

$$[\text{OH}^{-1}] = \sqrt{K_i \cdot C_s} = \sqrt{\frac{K_w \cdot C_s}{K_b}} = \sqrt{\frac{10^{-14} \cdot 0.1}{2 \cdot 10^{-4}}} = \sqrt{5 \cdot 10^{-11}} = 2.23 \cdot 10^{-6} N$$

$$\text{pOH} = -\log [\text{OH}^-] = 5.65 \quad \rightarrow \quad \text{pH} = 14 - 5.65 = 8.35$$

## Exercise 5

- ◆ Calculate the pH of a solution made by dissolving 0.6 g of acetic acid and 0.82 g of sodium acetate in 1L of water. Calculate the pH after having added 1ml of HCl 1M ( $K_a = 1.8 \cdot 10^{-5}$  M).

In solution there are a weak acid and its salt → acidic buffer

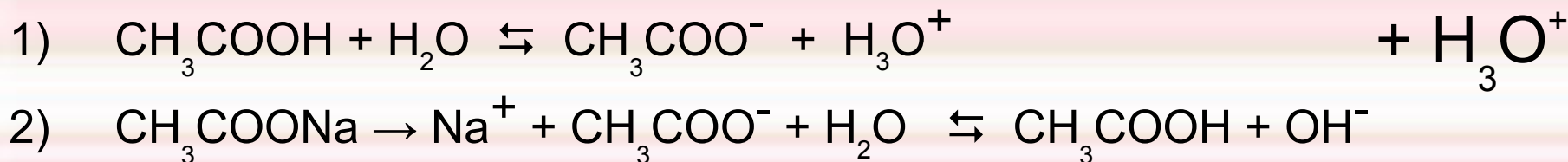
$$FW_{(CH_3COOH)} = 60$$

$$FW_{(CH_3COONa)} = 82$$

$$C_a = g / (FW \cdot V) = 0.6 / (60 \cdot 1) = 0.01 \text{ N}$$

$$C_s = g / (FW \cdot V) = 0.82 / (82 \cdot 1) = 0.01 \text{ N}$$

$$pH = pK + \log \frac{C_s}{C_a} = 4.74 + \log \frac{0.01}{0.01} = 4.74$$



- ◆ Therefore:  $C_a$  increases and  $C_s$  decreases by the same amount of acid added to the solution:

$$Eq_{(HCl)} = C_a \cdot V_a = 1 \cdot 10^{-3} = 10^{-3} \text{ eq}$$

We can approximate the volume to remain constant since we are adding 1ml of acid into 1L of solution

$$C_a = [Eq1 + Eq_{(HCl)}] / V = (0.01 + 0.001) / 1 = 0.011 \text{ N}$$

$$C_s = [Eq2 - Eq_{(HCl)}] / V = (0.01 - 0.001) / 1 = 0.009 \text{ N}$$

$$pH = pKa + \log \frac{C_s}{C_a} = 4.74 + \log \frac{0.009}{0.011} = 4.74 - 0.087 = 4.653$$

## Exercise 6

- ◆ Calculate how many grams of KOH should be added to 400ml of weak acid HA 0.1 M ( $K_a=3 \cdot 10^{-6}$  M) to obtain a solution at pH=5.3.

The exercise is asking to prepare an acidic buffer solution, therefore we can express the Henderson-Hasselback formula without log

$$pH = pK_a + \log \frac{C_s}{C_a} \qquad [H_3O^{+1}] = K_a \cdot \frac{C_a}{C_s}$$

$$C_b = C_s = K_a \cdot \frac{C_a}{[H_3O^{+1}]} = \frac{3 \cdot 10^{-6} \cdot 0.1}{5.01 \cdot 10^{-6}} = 0.06 M$$

$$g = C_s \cdot FW \cdot V = 0.06 \cdot 56 \cdot 0.4 = 1.344g$$



## Exercise 7

- ◆ Calculate the pH of a solution made by dissolving 2.8 g of  $\text{CH}_3\text{NH}_2$  and 5.0 g of  $\text{CH}_3\text{NH}_3\text{Br}$  in 500ml of water ( $K_b=4.4 \cdot 10^{-4}$  M).

Methyl-amine is a weak base, here it is in solution with its salt: basic buffer solution

$$C_s = g / (\text{FW} \cdot V) = 5 / (111.9 \cdot 0.5) = 0.089 \text{ M}$$

$$C_b = g / (\text{FW} \cdot V) = 2.8 / (31 \cdot 0.5) = 0.181 \text{ M}$$

$$pOH = pK_b + \log \frac{C_s}{C_b} = 3.36 + \log \frac{0.089}{0.181} = 3.36 - 0.30 = 3.07$$

$$pH = 14 - pOH = 14 - 3.07 = 11$$

## Exercise 8

- ◆ Which is the pH of a solution obtained after mixing 200 ml of KOH 0.1M with 300ml of formic acid 0.15 M ( $K_a = 1.8 \cdot 10^{-4}$  M)?



$$\text{Equivalents}(\text{acid}) = C_a \cdot V = 0.15 \cdot 0.3 = 0.045 \text{ eq}$$

$$\text{Equivalents}(\text{base}) = C_b \cdot V = 0.1 \cdot 0.2 = 0.02 \text{ eq}$$

There is an excess of weak acid  $\rightarrow$  in solution there will be the newly formed salt and the remaining acid  $\rightarrow$  BUFFER solution

$$C_s = C_b = 0.02 / 0.5 = 0.04 \text{ N}$$

$$C_a = [\text{Eq}(\text{a}) - \text{Eq}(\text{b})] / V_{\text{tot}} = (0.045 - 0.02) / 0.5 = 0.05 \text{ N}$$

$$\text{pH} = \text{p}K_a + \log \frac{C_s}{C_a} = 3.74 + \log \frac{0.04}{0.05} = 3.74 - 0.097 = 3.643$$