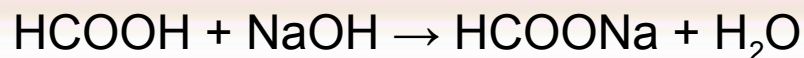


Homework 6

Exercise 1

- ◆ Calculate the pH of a solution prepared by mixing 100 ml of methanoic acid 0.1 M with 25 ml of sodium hydroxyde 0.16 M. (Ka= $1.8 \cdot 10^{-4}$ M at 25°C).



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 → acidic buffer solution (pH < 7.0)
- at equivalence there will only be the salt → basic hydrolysis (pH > 7.0)

$$\text{eq}_{\text{acid}} = C_a \times V_a = 0.1 \times 0.1 = 0.01 = 10 \times 10^{-3}$$

$$\text{eq}_{\text{base}} = C_b \times V_b = 0.16 \times 0.025 = 0.004 = 4 \times 10^{-3}$$

Excess of acid
→ buffer solution!

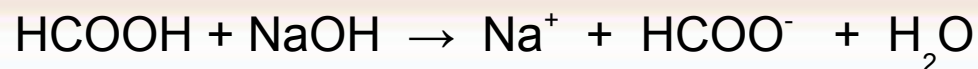
$$\text{eq}_{\text{base}} = \text{eq}_{\text{salt}} = 4 \times 10^{-3}$$

$$\text{eq}_{\text{a-fin}} = \text{eq}_{\text{a}} - \text{eq}_{\text{base}} = (10-4) \times 10^{-3} = 6 \times 10^{-3}$$

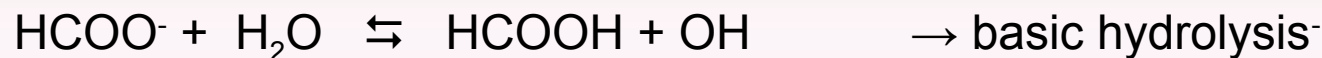
$$\text{pH} = \text{pKa} + \log \frac{C_s}{C_a} = 3.74 + \log \frac{4 \cdot 10^{-3}}{6 \cdot 10^{-3}} = 3.74 - 0.17 = 3.56$$

Exercise 2

- ◆ Calculate the pH of a solution prepared by mixing 100 ml of methanoic acid 0.04 M with 25 ml of sodium hydroxyde 0.16 M. ($K_a = 1.8 \cdot 10^{-4}$ M at 25°C)



$$\left. \begin{array}{l} \text{Equivalents of acid: } C_a \times V_a = 0.04 \times 0.1 = 4 \cdot 10^{-3} \text{ eq} \\ \text{Equivalents of base: } C_b \times V_b = 0.16 \times 0.025 = 4.0 \cdot 10^{-3} \text{ eq} \end{array} \right\} \begin{array}{l} \text{Same quantity} \\ \rightarrow \text{only salt} \end{array}$$



$$[\text{OH}^{-1}] = \sqrt{\frac{K_w}{K_a} \cdot C_s} = \sqrt{\frac{10^{-14} \cdot 4 \cdot 10^{-3}}{1.8 \cdot 10^{-4} \cdot 0.125}} = \sqrt{2.13 \cdot 10^{-12}} = 1.46 \cdot 10^{-6} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 5.83$$

$$\text{pH} = 14 - \text{pOH} = 8.17$$

Exercise 3

- ◆ A solution has been prepared by mixing 450 ml of ammonia 0.1 M with 250 ml of HCl 0.1 M. Which is the pH? ($K_b = 1.8 \cdot 10^{-5}$ M at 25°C)



Equivalents of base: $C_b \times V_b = 0.1 \times 0.45 = 0.045$ eq

Equivalents of acid: $C_a \times V_a = 0.1 \times 0.25 = 0.025$ eq

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

$$C_s = \text{Eq}(\text{acid}) / V(\text{tot}) = 0.025 / 0.7 = 0.0357$$

$$C_b = [\text{Eq}(\text{base}) - \text{Eq}(\text{acid})] / V(\text{tot}) = [0.045 - 0.025] / 0.7 = 0.0286 \text{ N}$$

$$pOH = pK_b + \log \frac{C_s}{C_b} = 4.74 + \log \frac{0.0357}{0.0286} = 4.74 + \log 1.25 = 4.74 + 0.097 = 4.84$$

$$pH = 14 - pOH = 14 - 4.84 = 9.16$$

Exercise 4

- ◆ Calculate the pH of a solution obtained by diluting 1 ml of the commercial solution of ammonia (30%w, $d=0.91\text{ g/ml}$) up to 1 L with pure water. Calculate the pH after having added 1mg of HCl. ($K_b= 1.8 \cdot 10^{-5}\text{ M}$ at 25°C)

We need to convert from %w into Molar concentration, then we shall proceed to dilute the weak base:

30%w = 30g of ammonia in 100g of solution

100g of solution can be converted into a Volume of solution through the density (g/V)

$$\rightarrow V = g / d = 100 / 0.91 = 109.9 \text{ ml} = 0.1099 \text{ L}$$

$$C_b = g / (\text{FW} \cdot V) = 30 / (17 \cdot 0.1099) = 16.06 \text{ M}$$

When we dilute the number of moles remains constant:

$$n_1 = n_2 \quad \rightarrow \quad C_1 \cdot V_1 = C_2 \cdot V_2 \quad \rightarrow \quad 16.06 \cdot 10^{-3} = C_2 \cdot 1 \quad \rightarrow \quad C_2 = 0.016 \text{ M}$$

$$[\text{OH}^{-1}] = \sqrt{K_b \cdot C_b} = \sqrt{1.8 \cdot 10^{-5} \cdot 0.016} = \sqrt{2.88 \cdot 10^{-7}} = 5.29 \cdot 10^{-4}$$

$$\text{pOH} = -\log [\text{OH}^{-1}] = 3.28$$

$$\text{pH} = 14 - \text{pOH} = 10.72$$

If we add 1 mg of HCl, then the base will react with it to form the salt NH_4Cl

$$Eq_{\text{base}} = C_b \cdot V_b = 0.016 \cdot 1 = 0.016$$

$$Eq_{\text{acid}} = g / \text{FW} = 10^{-3} / 36.5 = 2.7 \cdot 10^{-5}$$

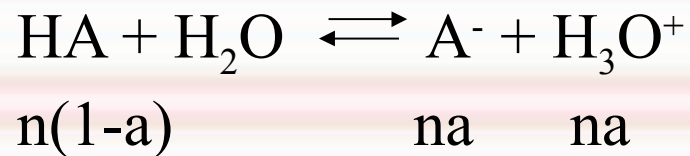
Basic buffer in solution:

$$\text{pOH} = \text{pK}_b + \log (C_s / C_b) = 4.74 + \log (2.7 \cdot 10^{-5} / 0.016) = 4.74 - 2.77 = 1.97$$

$$\text{pH} = 14 - 1.97 = 12.03$$

Exercise 5

- ◆ Calculate the formula weight and the dissociation coefficient of a weak monoprotic acid, whose solution made by dissolving 1g in 1 L of pure water has pH=4.0. (Ka=3·10⁻⁶M)



$$K_a = \frac{[\text{H}_3\text{O}^{+1}]^2}{C_a}$$

$$C_a = \frac{[\text{H}_3\text{O}^{+1}]^2}{K_a} = \frac{(10^{-4})^2}{3} \cdot 10^{-6} = 3.3 \cdot 10^{-3} \text{ M}$$

$$C_a = \frac{g}{FW \cdot V}$$

$$FW = \frac{g}{C_a \cdot V} = \frac{1}{3.3 \cdot 10^{-3} \cdot 1} = 303.03 \text{ Da}$$

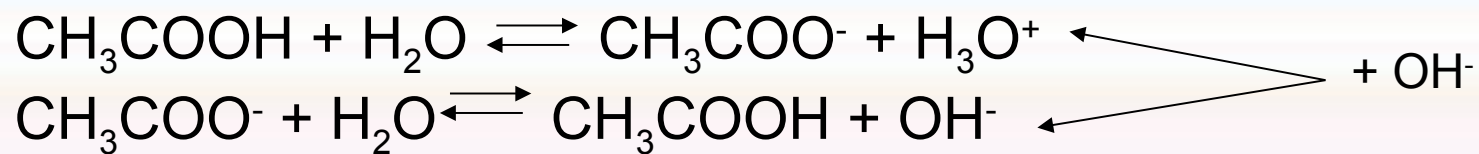
$$[\text{H}_3\text{O}^+] = n \cdot \alpha / V = C_a \cdot \alpha$$

$$\rightarrow \alpha = [\text{H}_3\text{O}^+] / C_a = 10^{-4} / 3.3 \cdot 10^{-3} = 0.03$$

Exercise 6

- ◆ Calculate which volume of NaOH 1M needs to be added to a buffer solution containing acetic acid 0.01 M and sodium acetate 0.01 M in order to adjust the pH to 5.0 ($K_a = 1.8 \cdot 10^{-5}$ M at 25°C, approximate the volume to remain constant).

$$\text{pH}_1 = \text{pK}_a + \log (C_s/C_a) = 4.74 + \log (0.01/0.01) = 4.74$$



$$\text{pH}_2 = \text{pK}_a + \log (C_s+x/C_a-x) \rightarrow [H^+] = K_a \frac{(eq_a - x)/V}{(eq_s + x)/V}$$

$$Eq_a = C_a \cdot V_a = 0.01 \cdot 1 = 0.01$$

$$Eq_s = C_s \cdot V_s = 0.01 \cdot 1 = 0.01$$

$$[H^+] = K_a \frac{(eq_a - x)/V}{(eq_s + x)/V} \quad 10^{-5} = 1.8 \cdot 10^{-5} \frac{\frac{0.01 - x}{1}}{\frac{0.01 + x}{1}}$$

$$10^{-5} = 1.8 \cdot 10^{-5} \frac{\frac{0.01 - x}{1}}{\frac{0.01 + x}{1}}$$

$$10^{-5} (0.01 + x) = 1.8 \cdot 10^{-5} (0.01 - x)$$

$$10^{-7} + 10^{-5} x = 1.8 \cdot 10^{-7} - 1.8 \cdot 10^{-5} x$$

$$2.8 \cdot 10^{-5} x = 0.8 \cdot 10^{-7}$$

$$x = 0.8 \cdot 10^{-7} / 2.8 \cdot 10^{-5} = 2.86 \cdot 10^{-3} \text{ eq}$$

$$V = \text{eq} / N = 2.86 \cdot 10^{-3} / 1N = 2.86 \cdot 10^{-3} \text{ L} = 2.86 \text{ ml}$$

Exercise 7

- ◆ A solution of HNO_2 is made by dissolving 3.53 g in 500 ml of pure water at 25°C . Calculate its dissociation coefficient, knowing that this solution has an osmotic pressure of 3.87 atm.



$$\Pi = CRT[1+\alpha(v-1)]$$

$$C = g / \text{PM} \cdot V = 3.53/47 \cdot 0.5 = 0.15\text{M}$$

$$\pi = CRT[1+\alpha(v-1)]$$

$$3.87 = 0.15 \cdot 0.082 \cdot 298[1+\alpha(2-1)]$$

$$3.87 = 3.66[1+\alpha]$$

$$3.87 = 3.66 + 3.66\alpha$$

$$3.66\alpha = 3.87 - 3.66$$

$$\alpha = 0.21/3.66 = 0.057$$

Exercise 8

- ◆ Calculate the osmotic pressure of a solution of potassium acetate at 25°C, knowing that its pH is 9.02. ($K_a = 1.8 \cdot 10^{-5} \text{ M}$)



$$\frac{K_w}{K_a} = K_i = \frac{[\text{HCOOH}][\text{OH}^{-1}]}{[\text{HCOO}^{-1}]} = \frac{[\text{OH}^{-1}]^2}{C_s}$$

$$[\text{OH}^-] = 10^{-(14-\text{pH})} = 10^{-4.98} = 1.047 \cdot 10^{-5}$$

$$C_s = \frac{[\text{OH}^{-1}]^2 K_a}{K_w} = \frac{(1.047 \cdot 10^{-5})^2 \cdot 1.8 \cdot 10^{-5}}{10^{-14}} = \frac{1.096 \cdot 10^{-10} \cdot 1.8}{10^{-9}} = 0.197 \text{ M}$$

$$\pi = CRT[1 + \alpha(v-1)] = 0.197 \cdot 0.082 \cdot 298 \cdot [1 + 1(2-1)] = 9.63 \text{ atm}$$