Homework 5

Exercise 1

- A solution of a weak acid HA with $Ka=10^{-4}$ 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.

$$HA + NaOH \rightarrow Na^{+} + A^{-} + H_2O$$

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)

Here pH= 4.0 → first condition → we can use the Henderson-Hasselback equation for calculating the amount of Ca

$$pH = pKa + \log\frac{Cs}{Ca} \qquad 4 = 4 + \log\frac{0.05}{Ca}$$

→ $Ca_{(t)} = 0.05$ eq when the pH=4.0

At the beginning: $Ca_{(0)} = Ca_{(t)} + OH^{-} = 0.05 + 0.05 = 0.1$ N

Exercise 2

- Calculate the pH of the solution obtained by mixing 75ml of CH_3COOH 0.01 N with 50ml NaOH 0.01 M (Ka= $1.8\cdot10^{-5}$ M at 25°C).

$$CH_3COOH + NaOH \rightarrow Na^+ + CH_3COO^- + H_2O$$

Equivalents of acid: Ca x Va = 0.01 x 0.075 = $7.5\cdot10^{-4}$ eq
Equivalents of base: Cb x Vb = 0.01 x 0.05 = $5.0\cdot10^{-4}$ eq

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

Cs = Eq(base) / V(tot) = $5\cdot10^{-4}$ / (0.075+0.05) = $4\cdot10^{-3}$ N
Ca = [Eq(acid) – Eq(base)] /V(tot) = [(7.5 – 5.0)$\cdot10^{-4}$] / 0.125 = $2\cdot10^{-3}$ N

$$pH = pKa + \log\frac{Cs}{Ca} = 4.74 + \log\frac{4\cdot10^{-3}}{2\cdot10^{-3}} = 4.74 + \log 2 = 4.74 + 0.301 = 5.04$$

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 (Ka=$1.8\cdot10^{-5}$ M at 25°C).

$$CH_3COOH + NaOH \rightarrow Na^+ + CH_3COO^- + H_2O$$

Equivalents of acid: Ca x Va = 0.5 x 0.25 = 0.125 eq
Equivalents of base: Cb x Vb = 0.2 x 0.25 = 0.05 eq

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

Cs = Eq(base) / V(tot) = 0.05 / (0.25+0.25) = 0.1 N
Ca = [Eq(acid) – Eq(base)] /V(tot) = [0.125-0.05] / 0.5 = 0.15 N

$$pH = pKa + \log\frac{Cs}{Ca} = 4.74 + \log\frac{0.1}{0.15} = 4.74 + \log 0.67 = 4.74 - 0.18 = 4.56$$

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 (Ka= $2 \cdot 10^{-4}$M).

$$HCN + KOH \rightarrow K^{+} + CN^{-} + H_2O$$

Equivalents of acid: Ca x Va = 0.2 x 0.5 = 0.1 eq
Equivalents of base: Cb x Vb = 0.2 x 0.5 = 0.1 eq

There is an equivalence of acid and base → in solution there will ONLY be the newly formed salt, which gives a basic hydrolysis → pH > 7.0

$$[OH^{-1}] = \sqrt{Ki \cdot Cs} = \sqrt{\frac{Kw \cdot Cs}{Kb}} = \sqrt{\frac{10^{-14} \cdot 0.1}{2 \cdot 10^{-4}}} = \sqrt{5 \cdot 10^{-11}} = 2.23 \cdot 10^{-6}\,N$$

pOH = -log [OH-] = 5.65 → 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 (Ka= $1.8 \cdot 10^{-5}$ M).

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

$FW_{(CH3COOH)} = 60$ $FW_{(CH3COONa)} = 82$

$Ca = g / (FW \cdot V) = 0.6 / (60 \cdot 1) = 0.01$ N
$Cs = g / (FW \cdot V) = 0.82 / (82 \cdot 1) = 0.01$ N

$$pH = pK + \log \frac{Cs}{Ca} = 4.74 + \log \frac{0.01}{0.01} = 4.74$$

+ H_3O^+

1) $CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$
2) $CH_3COONa \rightarrow Na^+ + CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$

- Therefore: Ca increases and Cs decreases by the same amount of acid added to the solution:

$Eq_{(HCl)} = Ca \cdot Va = 1 \cdot 10^{-3} = 10^{-3}$ eq

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

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

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

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

Exercise 6

- Calculate how many grams of KOH should be added to 400ml of weak acid HA 0.1 M (Ka=$3\cdot10^{-6}$ 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

$$pH = pKa + \log\frac{Cs}{Ca} \qquad [H_3O^{+1}] = Ka\cdot\frac{Ca}{Cs}$$

$$Cb = Cs = Ka\cdot\frac{Ca}{[H_3O^{+1}]} = \frac{3\cdot10^{-6}\cdot0.1}{5.01\cdot10^{-6}} = 0.06\,M$$

g = Cs·FW· V = 0.06·56·0.4 = 1.344g

Exercise 7

- Calculate the pH of a solution made by dissolving 2.8 g of CH_3NH_2 and 5.0 g of CH_3NH_3Br in 500ml of water ($Kb=4.4\cdot10^{-4}$ M).

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

$Cs = g / (FW\cdot V) = 5 / (111.9\cdot0.5) = 0.089$ M
$Cb = g / (FW\cdot V) = 2.8 / (31\cdot0.5) = 0.181$ M

$$pOH = pKb + \log\frac{Cs}{Cb} = 3.36 + \log\frac{0.089}{0.181} = 3.36 - 0.30 = 3.07$$

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 (Ka= $1.8 \cdot 10^{-4}$ M)?

$$HCOOH + KOH \rightleftarrows HCOO^- + K^+ + H_2O$$

Equivalents(acid) = Ca·V = 0.15·0.3 = 0.045 eq
Equivalents(base) = Cb·V = 0.1·0.2 = 0.02 eq

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

Cs = Cb = 0.02 / 0.5 = 0.04 N
Ca = [Eq(a) – Eq(b)] / Vtot = (0.045 – 0.02) / 0.5 = 0.05 N

$$pH = pKa + \log\frac{Cs}{Ca} = 3.74 + \log\frac{0.04}{0.05} = 3.74 - 0.097 = 3.643$$