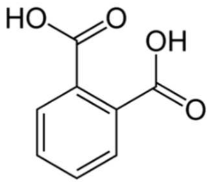
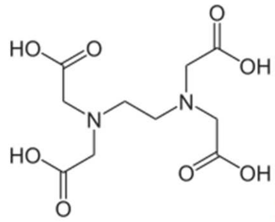
**4. Equilibria in multi-proton-donating acid systems**

The most common multi-proton-donating acids are:
$H_3PO_4$, $H_2CO_3$, $H_2C_2O_4$, phthalic acid, EDTA.


phthalic acid


EDTA

Let us consider equilibria that occur in $H_3PO_4$ acid solutions and its salts:

$H_3PO_4 + H_2O \overset{K_{a1}}{\rightleftarrows} H_2PO_4^- + H_3O^+$  $pK_{a1} = 2.15$

$H_2PO_4^- + H_2O \overset{K_{a2}}{\rightleftarrows} HPO_4^{2-} + H_3O^+$  $pK_{a2} = 7.21$

$HPO_4^{2-} + H_2O \overset{K_{a3}}{\rightleftarrows} PO_4^{3-} + H_3O^+$  $pK_{a3} = 12.34$

Constants can be written in form of, respectively:

$$K_{a1} = \frac{[H_2PO_4^-]\,[H_3O^+]}{[H_3PO_4]} \qquad K_{a2} = \frac{[HPO_4^{2-}]\,[H_3O^+]}{[H_2PO_4^-]} \qquad K_{a1} = \frac{[HPO_4^{2-}]\,[H_3O^+]}{[PO_4^{3-}]}$$

It is possible to write these equilibria in the reverse order of reaction:

$PO_4^{3-} + H_2O \overset{K_{b1}}{\rightleftarrows} HPO_4^{2-} + OH^-$  $pK_{b1} = 14 - pK_{a3} = 14 – 12.34 = 1.66$

$HPO_4^{2-} + H_2O \overset{K_{b2}}{\rightleftarrows} H_2PO_4^- + OH^-$  $pK_{b2} = 7.21 - pK_{a2} = 14 – 7.21 = 6.79$

$H_2PO_4^- + H_2O \overset{K_{b3}}{\rightleftarrows} H_3PO_4 + OH^-$  $pK_{b3} = 12.34 - pK_{a1} = 14 – 2.15 = 11.85$

These equilibria can be written as:

$$K_{b1} = \frac{[HPO_4^{2-}]\,[OH^-]}{[PO_4^{3-}]} \qquad K_{b2} = \frac{[H_2PO_4^-]\,[OH^-]}{[HPO_4^{2-}]} \qquad K_{b3} = \frac{[H_3PO_4]\,[OH^-]}{[H_2PO_4^-]}$$

Let us consider different cases. What would be the pH of the following systems?:

**a) $H_3PO_4$** is an acid, so it will undergo the reaction described by the equilibrium $K_{a1}$.

$H_3PO_4 + H_2O \overset{K_{a1}}{\rightleftarrows} H_2PO_4^- + H_3O^+$  $pK_{a1} = 2.15$

**b) $NaH_2PO_4$** is a salt, which should be considered after its dissociation to the ions: $Na^+$ and $H_2PO_4^-$.
From the hydrolysis reaction equations we can conclude that $H_2PO_4^-$ ion can undergo two types of the reaction:

$H_2PO_4^- + H_2O \overset{K_{a2}}{\rightleftarrows} HPO_4^{2-} + H_3O^+$  $pK_{a2} = 7.21$  or

$H_2PO_4^- + H_2O \overset{K_{b3}}{\rightleftarrows} H_3PO_4 + OH^-$  $pK_{b3} = 12.34 - pK_{a1} = 14 – 2.15 = 11.85$

In order to know which of those two reactions is the dominating one, it is necessary to take into account values of the both reaction equilibrium constants: $pK_{a2} = 7.21$ and $pK_{b3} = 11.85$.
It is hard to conclude at the first glance, so let us look closer at the values of these constants:
$K_{a2} = 10^{-7.21}$ vs. $K_{b3} = 10^{-11.85}$ The question is, which one of those two values is larger?
Now we can easily point out that larger one is $K_{a2}$. Thus, the reaction that will be statistically dominating one is a reaction:

$H_2PO_4^- + H_2O \underset{}{\overset{K_{a2}}{\rightleftarrows}} HPO_4^{2-} + H_3O^+$

As a result of this reaction, the systems (solutions) with this salt will be acidic.

**c) $Na_2HPO_4$** is also a salt, so we can perform simiar consideration as with the previous case. Let us consider ionic dissociation of this salt: $Na_2HPO_4 \rightleftarrows 2Na^+ + HPO_4^{2-}$ Subsequently, we can consider hydrolysis reaction of the $HPO_4^{2-}$ ion.

$HPO_4^{2-} + H_2O \overset{K_{a3}}{\rightleftarrows} PO_4^{3-} + H_3O^+ \quad pK_{a3} = 12.34$

$HPO_4^{2-} + H_2O \overset{K_{b2}}{\rightleftarrows} H_2PO_4^- + OH^- \quad pK_{b2} = 6.79$

Now we compare above equilibrium constants and $K_{a3} = 10^{-12.34}$ is smaller than $K_{b2} = 10^{-6.79}$. Thus, the dominating reaction will be the following reaction:

$HPO_4^{2-} + H_2O \overset{K_{b2}}{\rightleftarrows} H_2PO_4^- + OH^-$

As a result, system with this salt will be basic.

**d) $Na_3PO_4$** is a salt, in which after the dissociation only the $PO_4^{3-}$ ion can undergo hydrolysis reaction. Thus, pH of solutions with this salt will be basic, as the only possible hydrolysis reaction to occur is the one producing $OH^-$ ions.

**Zadanie 4.1**

What will be the pH of the solution resulting from mixing 200 ml of 0.1M phthalic acid (water solution) and 100 ml of 0.2M NaOH? $pK_{a1} = 2.94$; $pK_{a2} = 5.43$

**Answer: pH = 3.3**

**Zadanie 4.2**

What volume of 0.1M KOH is required to fully neutralize 0.5 $dm^3$ of 0.05M carbonic acid? What will be the pH of the resulting solution? $pK_{a1} = 6.35$; $pK_{a2} = 10.33$

*Hint:* Neutralization occurs when $n_{H3O+} = n_{OH-}$

**Answer: 0.5$dm^3$ ; pH = 11.34**

**Zadanie 4.3**

To the 250 $cm^3$ of 0.1M $H_3PO_4$ has been added 150 $cm^3$ of 0.1M NaOH. Calculate what would be the pH of the resulting solution. $pK_{a1}=2.15$

**Answer: pH = 2.32**

**Zadanie 4.4**

Calculate what would be the pH of $NaHCO_3$ salt solution at 0.1M concentration. $pK_{a1} = 6.35$; $pK_{a2} = 10.33$

**Asnwer: pH = 9.67**

**Zadanie 4.5**

Equal volumes of 0.1M $H_3PO_4$ and 0.1M $Na_2HPO_4$ solutions have been mixed together. Calculate the pH of the resulting solution. Write down the reaction equations. $pK_{a1} = 2.15$; $pK_{a2} = 7.21$; $pK_{a3} = 12.34$

*Hint: Take into the account the resulting solution volume.*

**Answer: $H_3PO_4 + Na_2HPO_4 \rightarrow 2NaH_2PO_4$ ; pH = 4.11**