

3. Hydrolysis. Equilibria in multi-proton-donating acids. Buffer solutions.

Hydrolysis

Hydrolysis is a reaction of ion(s) with water. This is a particular case of acid-basic properties of water in action. Only ions that are a product of weak acids or weak bases can be a subject to hydrolysis.

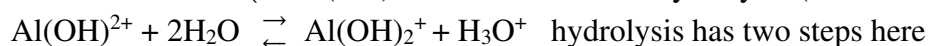
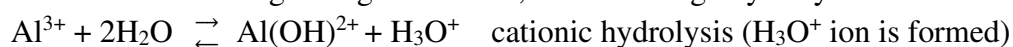
Consider the following salts - what would be the pH of those salts?

a) AlCl_3 $\rightleftharpoons \text{Al}^{3+} + 3\text{Cl}^-$ dissociation produces ions

Which ions are subject to hydrolysis?

Cl^- anion originates from the strong acid HCl , so it is not a subject to hydrolysis. The same applies to all halogen anions: F^- , Br^- , I^- .

Al^{3+} cation is not forming strong base. Thus, it will undergo hydrolysis:



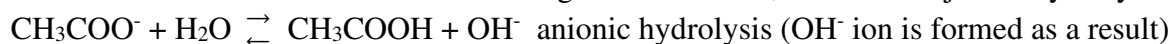
Taking into account the above reactions it can be concluded that pH of AlCl_3 salt is acidic upon dissolving this salt in water. To sum it up: the necessary condition of hydrolysis to take place is dissociation into ions first. Each ion upon the dissociation has to be considered individually. In case of hydrolysis reaction, as long as we want to determine pH of salt in water, we need dissociation chemical equation and corresponding hydrolysis reaction equation.

b) CH_3COONa $\rightleftharpoons \text{CH}_3\text{COO}^- + \text{Na}^+$ dissociation produces ions

Which ions are subject to hydrolysis?

Na^+ ion is known to form strong bases, such as NaOH , so it does not undergo hydrolysis.

CH_3COO^- ion is an acid radical of weak organic acetic acid, so it is a subject to hydrolysis:



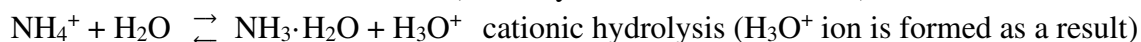
From the above it can be concluded that pH of the CH_3COONa salt is basic.

c) $\text{CH}_3\text{COONH}_4$ $\rightleftharpoons \text{CH}_3\text{COO}^- + \text{NH}_4^+$ dissociation produces ions

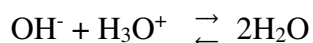
Which ions are subject to hydrolysis?



However, also another ion undergoes hydrolysis - NH_4^+ ion. It is due to the fact that it is a part of weak ammonium base NH_4OH (formally written as a $\text{NH}_3 \cdot \text{H}_2\text{O}$).



From the above it can be concluded that pH of the $\text{CH}_3\text{COONH}_4$ salt is more-less neutral as



d) KCl $\rightleftharpoons \text{K}^+ + \text{Cl}^-$ dissociation produces ions

Both K^+ and Cl^- ions are originating from strong base (KOH) and strong acid (HCl), respectively. Thus, none of those ions is undergo hydrolysis. What would be the resulting pH of this salt's solution in water? pH of KCl water solution is neutral (it does not affect H_3O^+ and OH^- equilibrium).

Buffer systems

Buffer systems are systems made of conjugated pair of acid and base. How such a conjugate pair is formed? One of the components of the buffer system (solution) is usually a weak acid and its salt with a cation of a strong base or a weak base with an anion of a strong acid. For instance: CH_3COOH and CH_3COONa or $\text{NH}_3\cdot\text{H}_2\text{O}$ and NH_4Cl . There also exist buffer systems of salts and acid salts (salts with at least one detachable proton), but we will analyze them in the next chapter on multi-proton-donating (polyprotic) salts equilibria.

Why do we call an acid-base pair for buffer system a conjugated pair? Let's look at the following reactions:

$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$ the protonic form (CH_3COOH) after the reaction with OH^- becomes the basic form (CH_3COO^-).

$\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$ the basic form (CH_3COO^-) after the reaction with H_3O^+ becomes the acidic form (CH_3COOH).

From the above reactions it can be concluded that acid-base pair would cope with the presence of either base or acid.

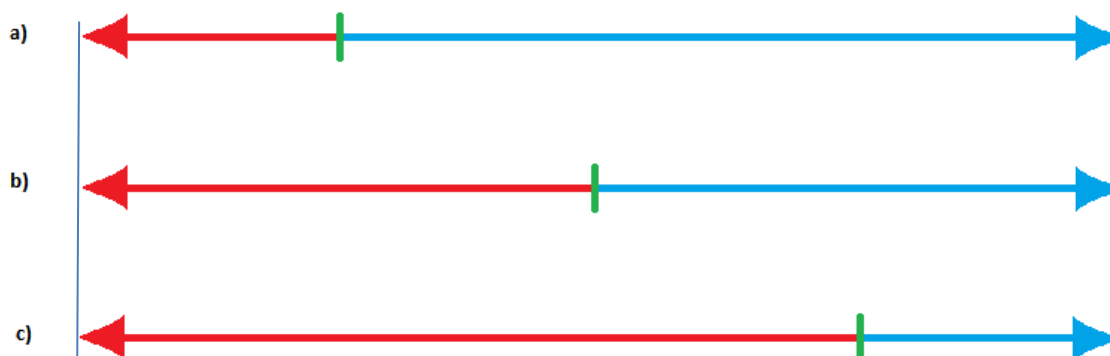
Upon the addition of acid to buffer solution the buffer solution will preserve its pH value close to the initial one up to the point at which most of its basic form will be removed due to the reaction with acid. In case of base addition the buffer solution will keep its initial pH value until most of its acidic form will be removed.

*Attention! Pure acetic acid is dissociating into ions, thus in the pure acetic acid solution there will be also some CH_3COO^- content, but **pure acetic acid is not a buffer solution**, as the acetate anions concentration will be very small in comparison with the acidic form concentration.*

Thus, concentration of both forms should be comparable (of the same order of magnitude) for the buffer to work – ideally, concentrations of both should be the same.

What is a buffer capacity? It is a measure of how much acid or base should be added to the buffer solution in order to change its pH by 1.

Let us consider the following cases of three different buffer solutions:

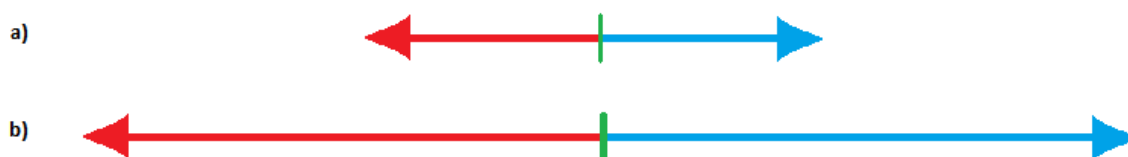


Red arrow represents the amount of acid required in each case to change pH of the given buffer by 1 pH unit (so one order of magnitude of H^+ concentration). Blue arrow represents the required base amount required to change pH of the given buffer by 1 pH unit. In case b) the amount of both acid and base are identical. So what can we say about buffer capacity of the

individual buffer solutions? Which one has the highest buffer capacity? In case a) buffer solution is very resistant toward base addition, but the addition of relatively small amount of the acid will unbalance the buffer solution from the equilibrium and will change its pH by a unit. The buffer capacity by definition is calculated against any of the reagent that can unbalance buffer solution pH („how much it is required to add acid or base to the system”) – so whichever reagent amount is smaller to do so. Thus, in case a) the buffer capacity is determined by the required addition of acid, not the base. It is a result of the fact that buffer solution a) is significantly less resistant to acid influence. Similarly, in case c) buffer solution is more resistant to acid than base. Thus, buffer capacity in case c) is determined by its resistance to base addition. Buffer capacity is determined by its resistance to the reagent to which it is less resistant. It is according to the rule due to which „*We are just as strong as the weakest of us*”.

In comparison to buffer solution a) the red arrow in case b) is much longer (more added acid). The same with blue arrow (base amount) when cases b) and c) are considered. Blue arrow in case c) is shorter than in case b). Thus, buffer solution b) from the above examples has the highest buffer capacity, because in order to unbalance it from the equilibrium and change pH of the system by a unit requires the most acid or base addition (and the same amount).

Are there any other factors influencing buffer capacity? Apparently, yes. **Let us consider the following examples:**



Cases a) and b) are two buffer solutions at their maximum buffer capacity, employing the same acid-base conjugated pair. The only difference between them is its concentration. Buffer solution b) has been diluted fewfold to obtain buffer solution a). As it is visible in the figure above, buffer solution b) has a higher buffer capacity than the diluted buffer a). Thus, the amount of the conjugated acid-base pair affects the buffer capacity. The more buffer solution is diluted, the lower its buffer capacity. For instance, if equal amounts of 1M CH₃COOH and 1M CH₃COONa are mixed, such buffer solution will have a higher buffer capacity than the buffer solution resulting from mixing together equal amounts of 0.1M CH₃COOH and 0.1M CH₃COONa.

It is possible to define buffer solutions equilibria by means of the constants K_a and K_b .

Example I. CH₃COOH and CH₃COO⁻ (from the salt)

In such a system the following equilibria will be formed:

$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$ this reaction is known from the previous descriptions, thus K_a :

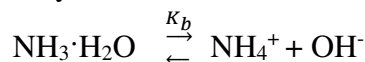
$$K_a = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

K_a constant is called in this case a weak acid dissociation constant, it can be also noted as $K_{\text{CH}_3\text{COOH}}$. If the constant notation includes a specific form, it means that this form in the reaction is on the left side and reacts with water.

$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \xrightleftharpoons{K_b} \text{CH}_3\text{COOH} + \text{OH}^-$ this is a hydrolysis reaction of the acetate ion. It can be noted as follows:

$$K_b = \frac{[\text{CH}_3\text{COOH}] \cdot [\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

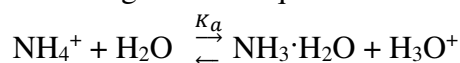
Przykład II. $\text{NH}_3 \cdot \text{H}_2\text{O}$ i NH_4^+ (from the salt)



K_b is a constant describing the above equilibrium. It can be called a weak base dissociation constant. It can be also noted as a $K_{\text{NH}_3\text{aq}}$ or as a $K_{\text{NH}_3 \cdot \text{H}_2\text{O}}$.

$$K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3 \cdot \text{H}_2\text{O}]}$$

It is possible to write down reaction equation and to determine equation for K_a constant which still exist for such system. NH_4^+ ion can undergo a hydrolysis reaction according to the following reaction equation:



Thus, K_a constant is noted as:

$$K_a = \frac{[\text{NH}_3 \cdot \text{H}_2\text{O}] [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

K_a constant in this case can be called NH_4^+ ion hydrolysis constant (K_h), or noted simply as $K_{(\text{NH}_4)^+}$.

Taking the above examples (I and II) into account, consider what would be the pH of a buffer solution that has been prepared from equal amounts of components that together form acid-base conjugated pair. Let us look at the above equation, for instance:

$$K_b = \frac{[\text{NH}_4^+] [\text{OH}^-]}{[\text{NH}_3 \cdot \text{H}_2\text{O}]}$$

What would happen if amounts of NH_4^+ and $\text{NH}_3 \cdot \text{H}_2\text{O}$ in the system would be identical?

Our system could be simplified to the following equation:

$$K_b = [\text{OH}^-] \quad | -\log$$

Thus, if we calculate $\text{pOH} = -\log([\text{OH}^-])$, we can obtain value of $\text{p}K_b$ which is a tabularized constant value for the given base and given temperature (usually 25°C). Thus, it can be stated that diluting buffer solution does not affect pH of the buffer system by much (assuming, for all practical considerations, that buffer components concentrations are significantly higher than 10^{-7} – if not, $[\text{OH}^-]$ resulting from the autodissociation of water starts to have a higher significance).

Task 3.1

Calculate the pH of the buffer solution formed from the equal amounts (volumes) of 0.1M CH₃COOH and 0.2 M CH₃COONa. $pK_a = 4.76$

Answer: pH = 5.06

Task 3.2

What would be the pH of the buffer solution which was made by mixing 0.1M CH₃COOH and 0.2M CH₃COONa solutions in 2:1 volume ratio? $pK_a = 4.76$

Answer: pH = 4.76

Task 3.3

What would be the pH of the buffer solution containing 0.1 mole of NH₄Cl and 0.05 mole of NH₃·H₂O? $pK_b = 4.75$

Answer: pH = 8.95

Task 3.4

Calculate the pH of the buffer solution resulting from mixing 250 ml of 0.1M CH₃COOH with 50 ml of 0.1M NaOH. $pK_a = 4.76$

Hint: CH₃COOH + NaOH → CH₃COONa + H₂O

Answer: pH = 4.16

Task 3.5

The following solutions are given: 0.1M NH₃·H₂O and 0.1M NH₄Cl. Calculate in what volumetric ratio they should be mixed to obtain buffer solution with pH equal to 10.

$pK_b = 4.75$

Answer: Volumetric ratio of NH₃·H₂O to NH₄Cl should be ca. 5:1

Task 3.6

In what volumetric ratio the given solutions should be mixed in order to obtain buffer solution with pH value ca. 4. 0.1M HCOOH and 0.2M HCOONa solutions are given. $pK_a = 3.75$

Hint: First calculate the molar ratio in which those solutions should be mixed.

Answer: Volumetric ratio of HCOOH to HCOONa should be ca. 1:3.5; molar ratio should be ca. 1:7

Task 3.7

What volume of 0.1M NH₄Cl solution should be added to 250 ml of 0.1M NH₃·H₂O solution in order to obtain buffer solution with pH close to 9.5? $pK_b = 4.75$

Answer: ca. 0.14 dm³ of 0.1 M NH₄Cl solution should be added

Task 3.8

Calculate what volume of 0.1M HCl acid solution should be added to 100 ml of 0.1M ammonia solution in order to obtain buffer solution with pH ca. 8.5. $pK_b = 4.75$

Hint: Calculate molar ratio of NH₃·H₂O to NH₄⁺ that is required to obtain the required buffer solution.

Answer: ca. 84.9 ml of 0.1M HCl solution should be added

Task 3.9

Calculate pH of the buffer solution resulting from mixing 100 ml of 0.2M CH₃COOH with 400 ml of 0.08M CH₃COOK.

$pK_a = 4.76$

Answer: pH = 4.96