UNIVERSITY of LIFE SCIENCES in Lublin

FACULTY OF VETERINARY MEDICINE

Mechanism of Buffer Action

Adding a drop of strong acid to 10 ml of water causes sharp decline in pH of water of a few units. Meanwhile, a living organism constantly produces the substantial amounts of carbonic acid, lactic acid, pyruvic acid, uric acid, etc., and the pH of body fluids is maintained at a constant level.

What is more, a potential change of pH of blood, e.g. in dogs from 7.4 to 7.3 - a difference of only 0.1 pH unit – is a symptom of metabolic disorders called acidosis.

Therefore, the maintenance a constant pH level in the body fluids has a crucial importance for living organism. This is achieved by the existence of systems having buffering properties called buffers.

Question about the mechanism of buffer action occurs very often in the inorganic chemistry test. Here is the pattern of answer to the question aforementioned:

Definition. Buffers are the solutions containing the mixture of a weak acid and the salt of this acid and strong base, or the mixture of a weak base and the salt of this base and strong acid, or the mixture of the two salts of polyprotic acid.

The role of buffer solutions is to prevent rapid changes of pH during dilution, or adding small amounts of acids and bases.

The mechanism of action will be described based on acetate buffer (the mixture of acetic acid and sodium acetate), as an example. Acetic acid is dissolved in water and it dissociates. *Dissociation is the process in which molecules split into ions.* It is well known that acetic acid is a representative of weak acids. The term weak or strong acids is associated with a value of its degree of dissociation. *The degree of dissociation(α) is the ratio of the number of particles split into ions (n) to all the molecules in solution – N).*

$$\alpha = \frac{n}{N}$$

Weak electrolytes dissociate only partially, below 0,05 (5%). Therefore, in acetic acid solution there are 3 components: mainly undissociated acetic acid molecules CH_3COOH, and small amounts ($\leq 5\%$) of acetate ions CH_3COO^- and protons H^+. Adding the salt CH_3COONa to this solution disturbs the existing balance, because the salt dissociates and sodium ions and extra acetate

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ions CH_3COO^- appear. Degree of dissociation depends on the presence of other ions in solution and changes so-called "The Equilibrium Law" (Chatelier's principle) says that if the system is removed from a state of equilibrium, it tends to counteract the change. Thus, if one of the products of dissociation of acetic acid arrives, then the system going to reduce the concentration of reaction products and increase the concentration of the substrate. Ratios of the newly formed state of equilibrium are determined by the dissociation constant. *Dissociation constant($K_{c\ kw}$) is the ratio of the concentration of ions generated during dissociation to the concentration of undissociated molecules.*

$$K_{c\ kw} = \frac{[A^-]\,[H^+]}{[HA]}$$

Dissociation constant, as the name suggests, is a constant value, it does not depend on the presence of other ions in the solution. Therefore, after pouring sodium acetate to the solution, dissociation of acetic acid regresses. Then, in the solution remain mainly the molecules of undissociated acid, acetate and sodium ions and small amount of H^+ ions derived from dissociation of acetic acid. Moreover, sodium acetate hydrolyzes, which means that the acetate ions generated during dissociation process have the ability to bind protons and to produce undissociated molecules of acetic acid. This process in a buffer system is inhibited by an excess acetate ions derived from acetic acid. As we can see, the resulting balance between the amount of the individual components of this system is very unstable – there are several systems constantly ready to bond or donate protons. Therefore, e.g. during adding small amounts of acid to the buffer system there is an action as shown in the following reaction:

CH_3COO^- + H^+ → CH_3COOH
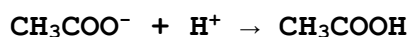
It happens due to the fact, that the dynamic equilibrium of the dissociation of acetic acid was disturbed by addition of H^+ ions, and that the dissociation constant remained constant value, the system aims to reduce the concentration of acetate ions and H^+ ions and to increase the concentration of CH_3COOH molecules. We can see, that adding an acid to the buffer system did not decrease pH, because H^+ ions – responsible for the acidity of the solution – have been bound and acetic acid was formed. Despite the presence of increased amounts of acetic acid in the solution, the pH is not reduced, because the molecules of acid remain undissociated.(*pH is the negative of the logarithm to base 10 of the activity of the hydrogen ion. It follows that, if the*

hydrogen ion concentration changes 10 times, the pH changes by one unit, when it a hundredfold rises or falls, the pH changes by 2 units, etc.). Similarly, the addition of the base containig OH^- ions to the buffer system, also do not change pH value, because these ions will be „neutralized" by the H^+ ions released from undissociated acetic acid:

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$
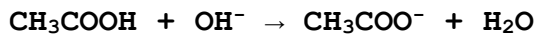
More precisely, hydroxyl ions bind to H^+ ions existing in the buffer system, which interferes with the buffer equilibrium and in place of neutralized H^+ ions, new ions derived from dissociation of acetic acid are released. It remains to clarify only one issue: does the concentration of OH^- ions in the solution affects the pH? Of course yes, it does – as the concept of pH is derived from the concept of the ionic product of water, which implies that, in any aqueous solution the product of the concentrations of H^+ and OH^- is constant, which means that if OH^- ions arrive, thus proportionally the concentration of H^+ ions must decreases, and vice versa. The concept of the ionic product of water is nothing but a simplified formula for the dissociation constant of water:

$$K_{cw} = \frac{[H^+] [OH^-]}{[H_2O]}$$

from which the denominator has been removed, as the concentration of the pure water is constant:

$$K_w = [H^+] [OH^-]$$

There is only the product of the concentrations of H^+ and OH^- ions in the numerator, which is also a constant value. Accurate measurements showed, that the value of the constant K_w is 10^{-14}; $K_w=[H^+][OH^-]=10^{-14}$ (at 25°C). In pure water hydroxide ion concentration is the same as the hydrogen ion concentration, because they're formed in equal amounts during the autoionization reaction.

The concentration of H^+ ions in the neutral solution is 10^{-7} (because $10^{-14} = 10^{-7}$ x 10^{-7}). And finally in our discussion returning to the concept of pH, negative logarithm of 10^{-7} is 7, so pH of the neutral solutions has that value. Increasing the concentration of H^+ ions in the solution 10x (up to the value 10^{-6}) causes the decrease of pH to 6, which means the decrease of one unit. Solutions with a pH less than 7 are acidic, solutions with a pH greater than 7 are basic.

The change in hydrogen ion concentration in the acid solution can be obtained, e.g. by dilution with water. The change of concentration of strong acid solution from 0,01 to 0,001 increases pH value from 2 to 3. Whereas dilluting buffer solution did not change its pH, because pH of the buffer depends on the rating how components of the buffer are mixed. E.g. For buffers built on a weak acid formula for calculating pH is as follows:

$$pH = pK_a + \log \frac{[CA]}{[CS]}$$

where: pK_a is a negative logarithm of the acid dissociation constant, CA – acid concentration, CS – salt concentration.

As we can see, pH of the buffer do not directly depend on the concentration of H^+ ions.

For buffers built on a weak basis formula for calculating pH is as follows:

$$pH = 14 - (pK_b - \log \frac{[CB]}{[CS]})$$

where: pK_b is a negative logarithm of the base dissociation constant, CB – base concentration, CS – salt concentration.

While we're on the topic of buffers based on the bases, we will show additionally the mechanism of action of **ammonium buffer**:
Composition: weak base - NH_4OH, salt - NH_4Cl.
There is a mixture of undissociated NH_4OH molecules and ions: NH_4^+, OH^- and Cl^- in water solution.
When acid is added, H^+ ions are bound by OH^- ions present in the solution, and in place of these ions new one are released, thanks to dissociation of ammonium base, which simply can be presented as follows:
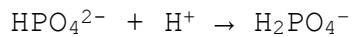
$NH_4OH + H^+ \rightarrow NH_4^+ + H_2O$
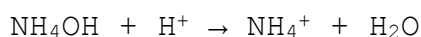
… and when base is added:

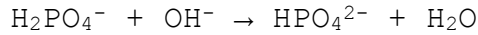$NH_4^+ + OH^- \rightarrow NH_4OH$
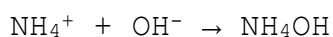
Analogously act buffers built on polyprotic acid salts, e.g. phosphoric acid. This buffer consists of $H_2PO_4^-$ ions – act like proton donors, HPO_4^{2-} ions – recipient of protons and ions of the base, e.g. Na^+.
Adding acid to that system will cause the following reaction:

$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$

Meanwhile, adding base:

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

There are several buffer systems in the body fluids of living organisms. E.g. in the blood of mammals there are: carbonate buffer (based on carbonic acid formed by the presence of CO_2, phosphate buffer and protein buffers (based on plasma proteins. In the laboratory mainly single buffers are used for experiments. There are a lot of them, because each one is characterized by different properties. Primarily they have different pH and buffer capacity.

pH of the buffer depends on its components: buffers based on acids have lower pH than buffers based on bases. The proportions of components are also relevant, what have been already discussed above. In addition, the relative proportions of the ingredients and their concentration affects the ability of binding by buffer acids and bases, it means the ability of a given amount of a buffer to bind a given quantity of hydrogen ions or hydroxyl without significant change of the pH. This property is called the buffer capacity (β), which is the number of moles of strong acid or strong base which must be added to 1 dm^3 of the buffer to cause a change in the pH by one unit:

$$\beta = \frac{\Delta B}{\Delta pH}$$

where: Δ B means the number of moles of strong acid or base, and Δ pH – change of pH. Buffer capacity decreases with the dilution, because buffer compounds are diluted too.