Electrolytes.
Buffer solutions.

Electrolytes

- Electrolytes are substances, being dissolved in water, decompose into cations (plus-charged ions) and anions (minus-charged ions). These solutions conduct electricity due to mobility of the positive and negative ions. Electrolytes conduct electricity only when molten or in aqueous solutions.
- There are two classes of electrolytes: **strong electrolytes** and **weak electrolytes.**

STRONG ELECTROLYTES

- A strong electrolyte is a solute that completely, or almost completely (→100%), ionizes or dissociates in a solution. Originally, a "strong electrolyte" was defined as a chemical (in the aqueous solution) and is a good electricity conductor. For strong electrolytes, a single arrow reaction shows that the reaction occurs completely in one direction, in contrast to the weak electrolytes dissociation, which both ionize and re-bond in significant quantities.

Strong electrolyte (aq) → Cation+ (aq) + Anion– (aq)

- Virtually all salts belong to strong electrolytes. Among the most important acids and bases, the following are strong electrolytes: HNO_3, $HClO_4$, HCl, HBr, HI, KOH, NaOH, $Ba(OH)_2$, $Ca(OH)_2$.

THE ACTIVITY

- The ions state in a solution is assessed with the aid of a quantity called the activity a. The ion activity means its effect, conditional concentration and its activity in chemical reactions. The ion a activity is equal to its concentration c multiplied by the activity coefficient f:

$$a = f \cdot c$$

- The activity coefficients of various ions are different. In addition, they are changed upon the conditions, particularly by changes of the solution’s concentration.
- The activity coefficient is usually less than unity for concentrated solutions, and it approaches unity in very dilute solutions.

THE IONIC STRENGTH

- We can state approximately that the activity coefficient of a given ion depends only on its charge and on the ionic strength I of the relevant solution.
- The latter is defined as the half-sum of the concentrations (mol/L) products of all the ions in the solution and the square of their charge:
- $\mathbf{I = 1/2\,(C_1 \cdot Z_1^{\,2} + C_2 \cdot Z_2^{\,2} + \ldots + C_n \cdot Z_n^{\,2})}$
- The activity coefficient close to unity points to the ions weak interaction. In dilute solutions, the nature of ions slightly affects the values of their activity coefficients.

$$\lg f_i = (-0{,}5\ z_i^2 \sqrt{I_c}) / (1 + \sqrt{I_c})$$

WEAK ELECTROLYTES

- Small fractions of weak electrolytes molecules are ionized, being dissolved in water. Some neutral molecules are present in their solutions. For example, ammonia, NH_4OH, carbonic acid, H_2CO_3, acetic acid, CH_3COOH, and most organic acids and bases are weak electrolytes. The following ionization is not completed,

$$\mathbf{HNO_{2\,(aq)} = H^{+}{}_{(aq)} + NO_2{}^{-}{}_{(aq)}}$$

- there are HNO_2 molecules and ions in the solution. Ionization can be viewed as

$$\mathbf{K = [H^{+}]\cdot[NO_2^{-}] / [HNO_2]}$$

THE DEGREE OF DISSOCIATION

By the electrolyte the degree of dissociation shows the ratio of the molecules number that have been broken up into ions in the given solution (X) to the total number of its molecules in the solution (C):

$$\alpha = X / C \text{ or } \alpha = [X / C] \cdot 100\%$$

W. OSTWALD'S DILUTION LAW

- If we denote the concentration of an electrolyte dissociating by c, and the degree of its dissociation in the given solution by α, then the concentration of each of the ions will be c·α, and the concentration of the undissociated molecules will be c·(1– α). Hence, the equation of the dissociation constant gets the form of:

$$\mathbf{K = (c\cdot\alpha)^2 / c\cdot(1-\alpha) \quad or \quad K = c\cdot\alpha^2 / 1-\alpha}$$

- This equation expresses **W. Ostwald's dilution law**. Using this equation we can also calculate the dissociation constant of an electrolyte knowing its degree of dissociation and the concentration.

$$\mathbf{K = c\cdot\alpha^2}$$

- This equation shows the relationship existing between the concentration of a weak electrolyte and the degree of its dissociation: the degree of dissociation increases upon dilution of the solution.

IONIZATION OF WATER

$$H_2O \leftrightarrow H^+ + OH^-$$

Applying the law of mass action to the ionization of water at 298K, we may write
:

$$K_{eq} = \frac{[H^+]\cdot[OH^-]}{[H_2O]} = 1.82\cdot 10^{-16}$$

$$[H^+]\cdot[OH^-] = [H_2O]\cdot K_{eq}$$

$$[H^+]\cdot[OH^-] = K_W = 10^{-14}$$

This constant is called the **ionic product of water.**

THE HYDROGEN ION INDEX

$$pH = -\log[H^+]$$

$$pOH = -\log[OH^-]$$

$$pH + pOH = 14$$

Buffer solutions

- **Buffer solutions** are solutions in which the pH remains relatively constant when small amounts of strong acid or strong base are added.

There are **four types of buffer solutions**:

- 1) ***Acid buffer*** is a mixture of a weak acid and its salt with strong base.

For example: acetic acid- acetate ion CH_3COOH/ CH_3COO^-,

carbonic acid- bicarbonate ion H_2CO_3/ HCO_3^-,

- 2) ***Base buffer*** is a solution of a weak base and its salt with strong acid.

For example: ammonium ion- ammonia NH_4^+/ NH_3.

- 3) ***Mixture of acid salt and normal salt or two acid salts***:

dihydrophosphate ion-monohydrogen phosphate ion $H_2PO_4^-/ HPO_4^{-2}$,

carbonate ion-bicarbonate ion CO_3^{2-} / HCO_3^-.

- 4) ***Ions or molecules of ampholytes***.

Mechanism of buffer solutions action

Acetic acid and sodium acetate in the solution are dissociated:

$CH_3COOH \leftrightarrow CH_3COO^–$

$CH_3COONa \leftrightarrow CH_3COO^- + Na^+$

The acetic acid/ acetate ion buffer is a solution of acetic acid and acetate ion.

When an acid, a source of hydrogen ions, is added to the solution, the acetate ions act as a “proton sponge” to mop up these hydrogen ions. Recall that acetic acid does not dissociate extensively in water. Therefore, most of the acetate ion becomes acetic acid, and the pH does not appreciably change:

$CH_3COO^-_{(aq)} \quad + \quad H^+_{(aq)} \quad \leftrightarrow \quad CH_3COOH_{(aq)}$

Acetate ion hydrogen ion acetic acid

When a base, a source of hydroxide ions, is added to the solution, the acetic acid and the base react to produce neutral water:

$CH_3COOH_{(aq)} \quad + \quad OH^-_{(aq)} \quad \leftrightarrow \quad CH_3COO^-_{(aq)} \quad + \quad H_2O_{(l)}$

acetic acid hydrogen ion acetate ion water

The acetate ion is not a strong enough base to accept hydrogen ions from water extensively, and again, the pH changes very little.

The calculation of pH of buffer system containing a weak acid and its salt

$$CH_3COONa \rightarrow Na^+ + CH_3COO^-$$

$$CH_3COOH + H_2O = H_3O^+ + CH_3COO^-$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$[H_3O^+] = K_a \frac{c(CH_3COOH)}{c(CH_3COONa)}.$$

$$pH = pK_a + \lg \frac{C_{salt}}{C_{acid}}$$

The calculation of pH of buffer system containing a weak base and its salt

$$NH_3 \cdot H_2O + NH_4Cl$$

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

$$NH_3 + H_2O = NH_3 \cdot H_2O = NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad [OH^-] = K_b \frac{[NH_3]}{[NH_4^+]}.$$

$$pH = 14 - pK_b - \log \frac{C_{salt}}{C_{base}}$$

Buffer capacity

- The **capacity of a buffer** is the amount of a strong acid or base it can handle before the pH of the solution changes drastically.
- ***Acidic buffer capacity*** (mole/L):

$$B_{acid} = \frac{n(\frac{1}{z}\,acid)}{|\,pH_1 - pH_2\,| \cdot V_{buffer}} = \frac{C(\frac{1}{z}\,acid) \cdot V_{acid}}{|\,pH_1 - pH_2\,| \cdot V_{buffer}}$$

- *Basic buffer capacity* (mole/L):

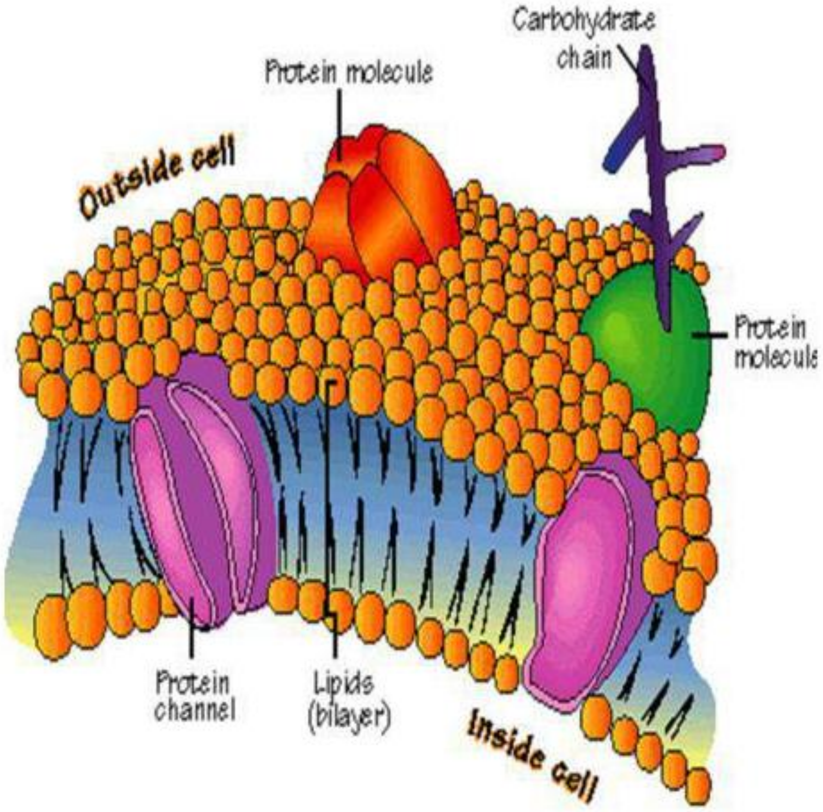
$$B_{base} = \frac{n(\frac{1}{z}\,base)}{|\,pH_1 - pH_2\,| \cdot V_{buffer}} = \frac{C(\frac{1}{z}\,base) \cdot V_{base}}{|\,pH_1 - pH_2\,| \cdot V_{buffer}}$$

HOMEOSTASIS

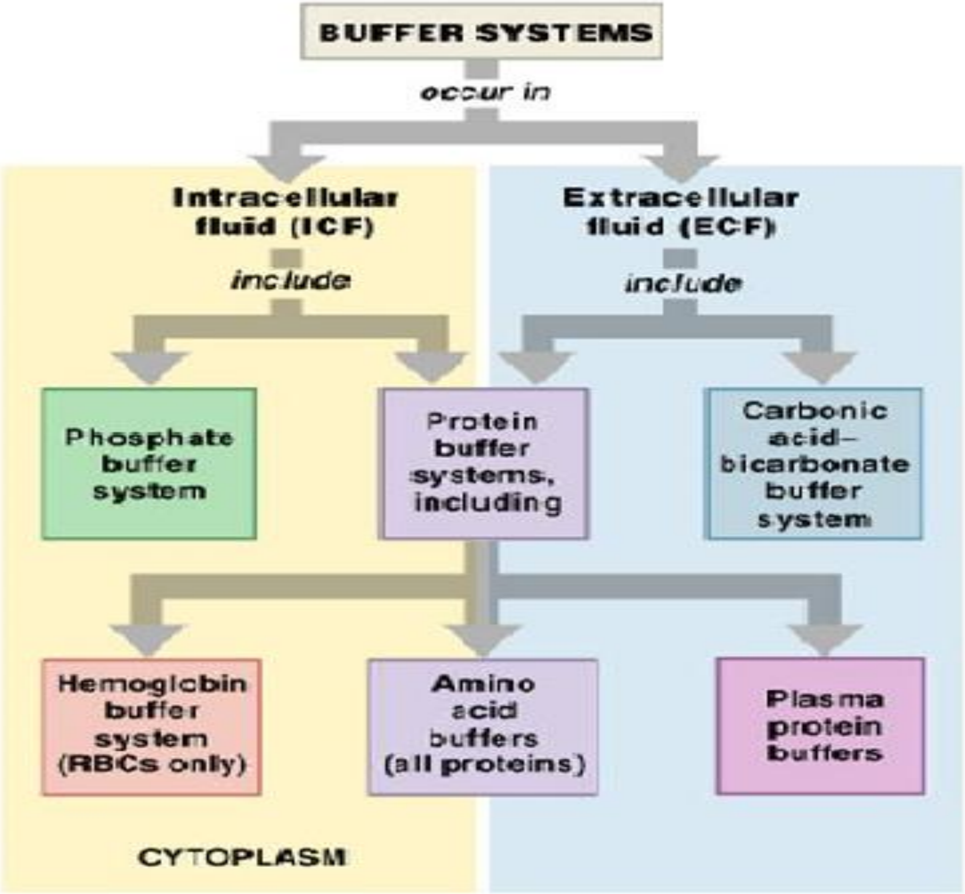
- **Homeostasis is the ability of living systems to maintain a steady and uniform internal environment to allow the normal functioning of the systems.**
- It is the tendency to achieve equilibrium against various natural and environmental factors.
- Homeostasis results in a dynamic equilibrium, where continuous changes keep on taking place, and yet steady conditions are maintained.
- Homeostasis is mainly involved in managing various internal variables of the living system like body temperature, pH of various fluids, the concentration of different ions, and the body sugar level.
- A number of regulatory mechanisms are employed to resist changes in the body against environmental and bodily factors.
- Homeostasis can be maintained by separate organs or by the entire body at once.

HOMEOSTASIS

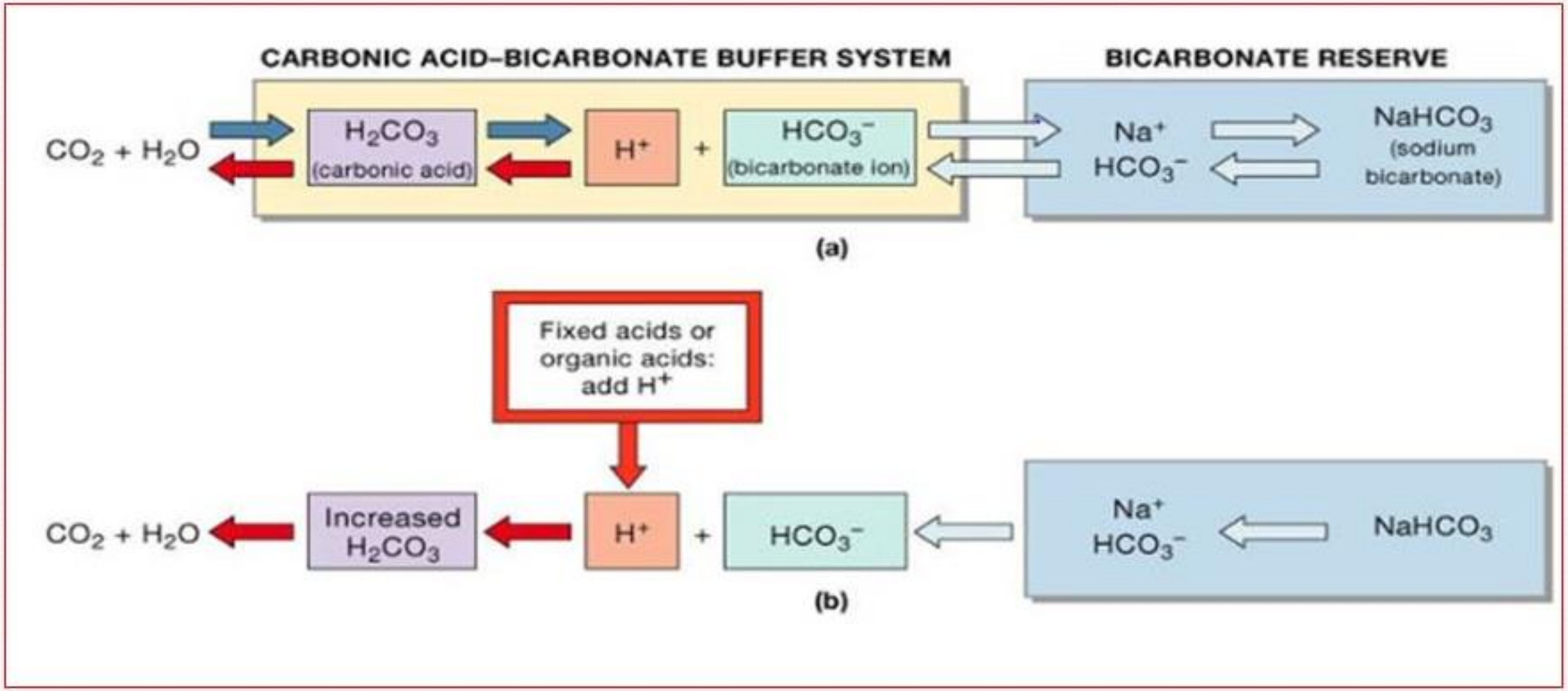
- the maintenance of a **constant internal environment** in response to changes in:
  - the changing conditions of the external environment.
  - the changing conditions of the internal environment.



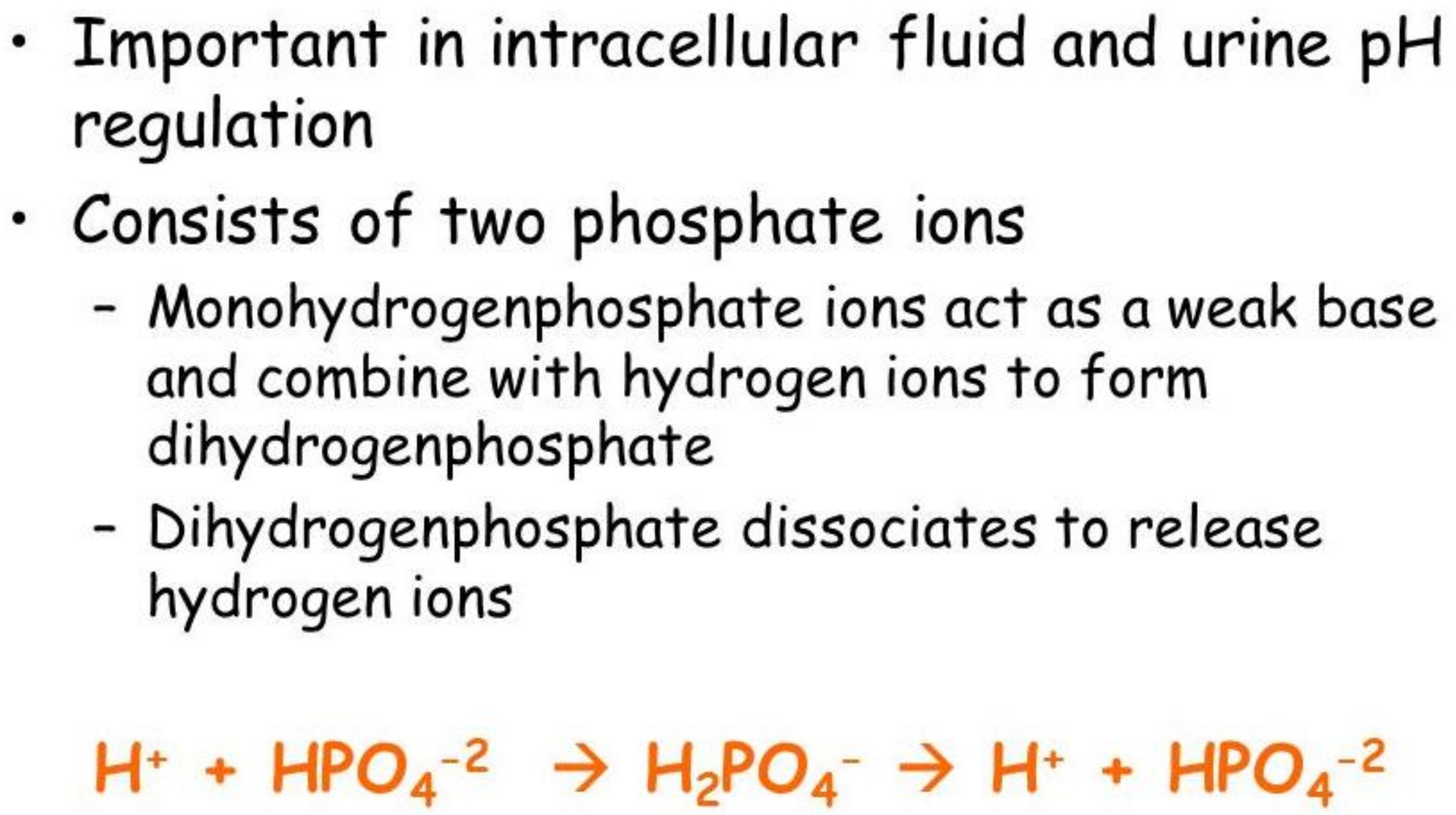
BUFFER SYSTEMS OF BLOOD



BICARBONATE BUFFER SYSTEM



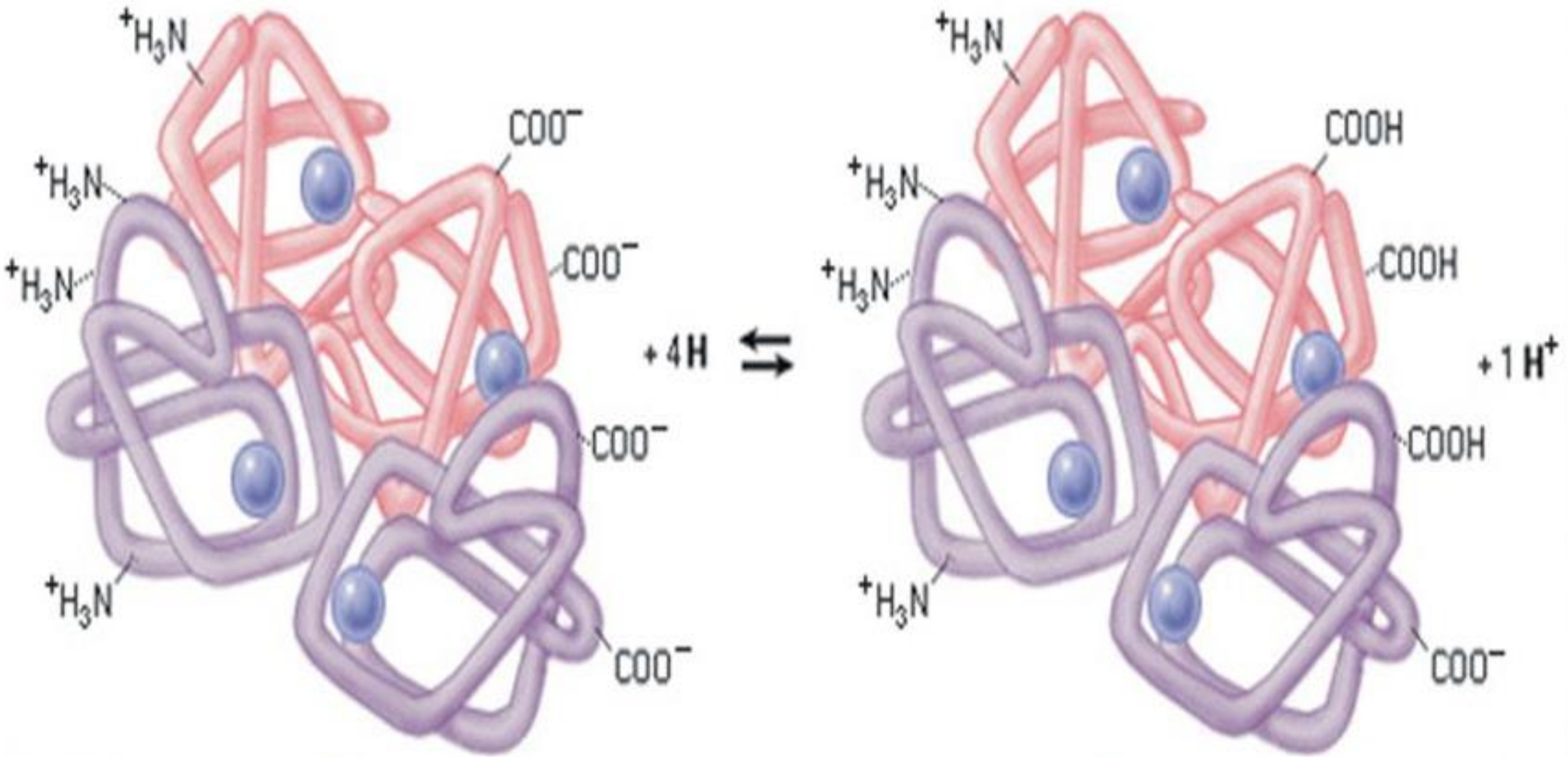
PHOSPHATE BUFFER SYSTEM



- Important in intracellular fluid and urine pH regulation
- Consists of two phosphate ions
  - Monohydrogenphosphate ions act as a weak base and combine with hydrogen ions to form dihydrogenphosphate
  - Dihydrogenphosphate dissociates to release hydrogen ions

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

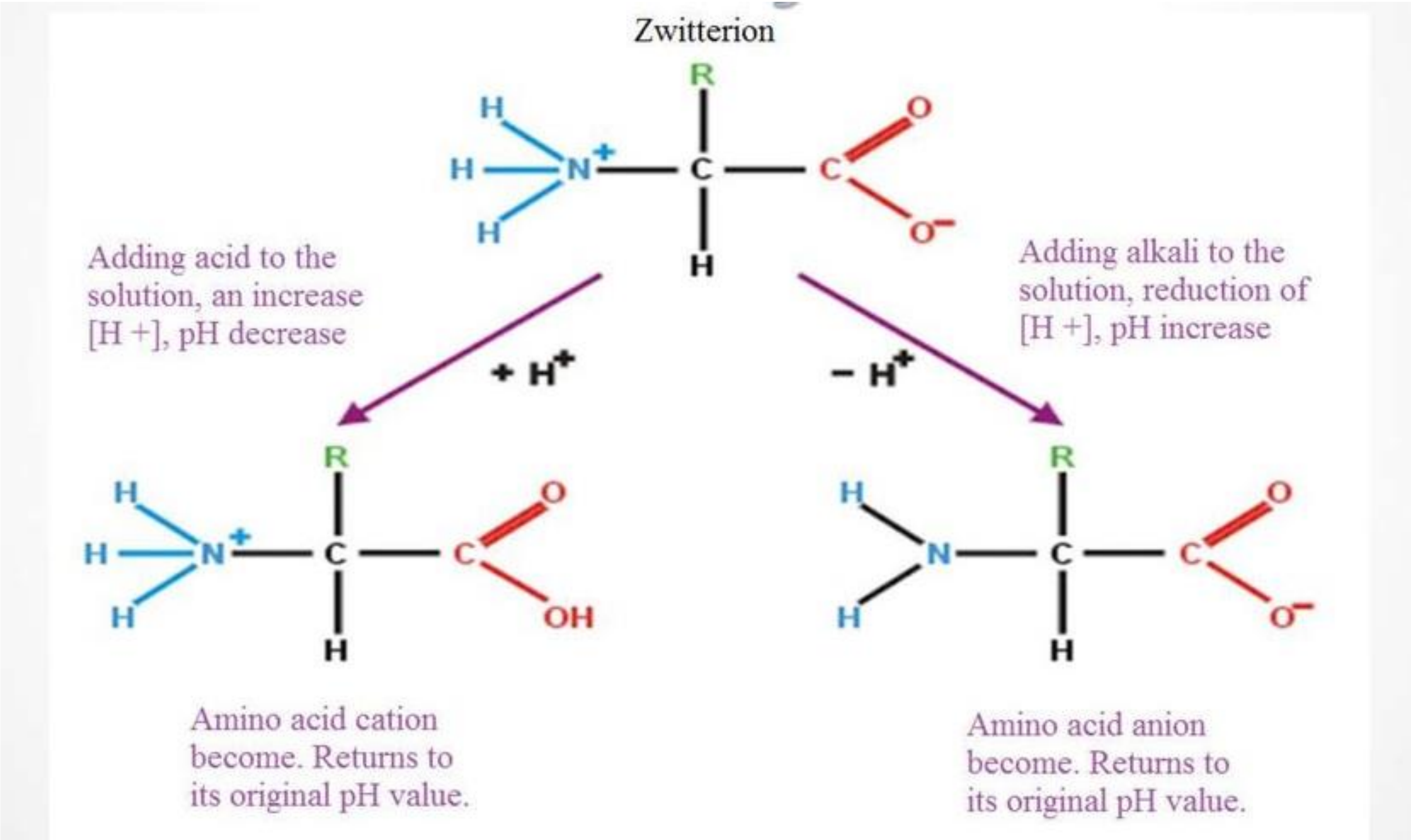
HEMOGLOBIN BUFFER SYSTEM



Isoelectric protein. The total charge = 0

Titration acid. The total charge = 3 +

PROTEIN BUFFER SYSTEM



Adding acid to the solution, an increase [H +], pH decrease

Adding alkali to the solution, reduction of [H +], pH increase

Amino acid cation become. Returns to its original pH value.

Amino acid anion become. Returns to its original pH value.