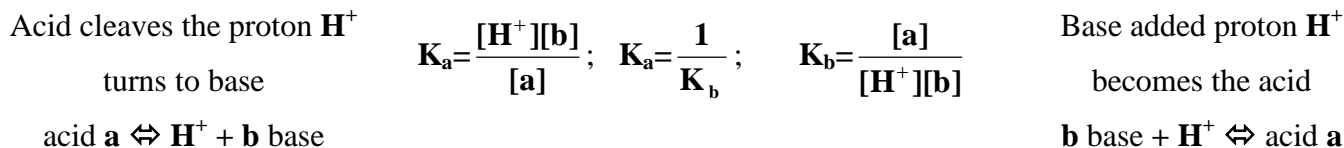


#### IV. DISSOCIATION OF WATER. pH HYDROGEN [H<sup>+</sup>] EXPONENT FUNCTION.

Brensted protolytic concept of acid and base 1923

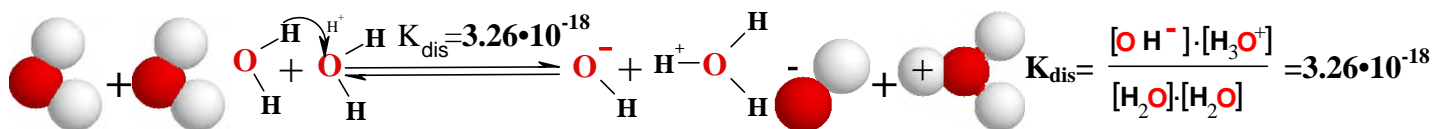


If acid **a** is weak coupled base **b** is strong ;

If base **b** is weak coupled acid **a** is strong.

Water weak acid **a<sub>1</sub>** and weak base **b<sub>2</sub>** instantly **OH<sup>-</sup>** strong base **b<sub>1</sub>** react with **H<sub>3</sub>O<sup>+</sup>** strong acid **a<sub>2</sub>** forming practically non dissociated water molecules as non electrolytes constant is small positive number  $K_{dis}=3.26 \cdot 10^{-18}$ .

**Water** is a very weak electrolyte, but still it dissociates and a dissociation equilibrium  $H_2O \rightleftharpoons OH^- + H^+$  can be written for it. To be more precise, the process in **water** is protolytical acid **H<sub>2</sub>O** cleaves the proton **H<sup>+</sup>** and add to base **H<sub>2</sub>O**, as reaction forms the strong base hydroxide **OH<sup>-</sup>** ions and strong acid hydroxonium **H<sub>3</sub>O<sup>+</sup>** ions  $H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$  looks like ionization instead dissociation but mathematically we will have the same results. An ionization (dissociation) constant expression for the dissociation of **water** is therefore:



As the numerical value of the dissociation constant of **water** is so small, the concentration of non dissociated **water** is equal to the concentration of **water** at  $T=298.15$  K and concentration is constant number **55.3 M**, which can be found as 1 liter mass  $m = 996.68$  g divided by  $M=18$  g/mol is **water** molar mass count in one liter:

$$[H_2O] = \frac{m}{M_{H_2O}} = \frac{997}{18} = 55.3 \frac{\text{mol}}{l}; \quad [H_2O]^2 = 3065.96 M^2$$

Doing two times the concentration of **water** with constant  $K_{dis}$ , we have got the **water** constant  $K_w$

$$K_w = [H^+] \cdot [OH^-] = 55,37^2 \cdot 3.26 \cdot 10^{-18} = 10^{-14} = 0.00000000000001 \quad (4.4)$$

This last equation has a very important meaning:  $pK_w = -\log K_w = 14$  as **water** constant value  $pK_w$ .

It means, that in pure **water**, as well as in all **water** solutions the product of **H<sup>+</sup>** and **OH<sup>-</sup>** concentrations is constant and it is  $10^{-14}$ . This means, that none of these two concentrations can be changed alone - if, for example, an acid is added and  $[H^+]$  increased,  $[OH^-]$  must decrease to maintain the product of concentrations constant

$$[H^+] \cdot [OH^-] = K_w = 10^{-14} = 10^{-pK_w} \quad \text{and} \quad pK_w = 14 = pH + pOH.$$

It also means that in pure **water** or any other neutral environment, which is equal acidic and equal basic, both concentrations of  $[H^+]$  and  $[OH^-]$  are equal and each of them can be calculated as

$$[H^+] = [OH^-] = \sqrt{K_w} = \sqrt{10^{-14}} = 10^{-7} \frac{\text{mol}}{l} \quad (M) = 0.0000001 \frac{\text{mol}}{l} \quad (M)$$

Scale of pH with the corresponding values of pOH and [H<sup>+</sup>] in acidic and basic medium

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
pOH	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
[H <sup>+</sup> ]	1	0.1	10 <sup>-2</sup>	10 <sup>-3</sup>	10 <sup>-4</sup>	10 <sup>-5</sup>	10 <sup>-6</sup>	10 <sup>-7</sup>	10 <sup>-8</sup>	10 <sup>-9</sup>	10 <sup>-10</sup>	10 <sup>-11</sup>	10 <sup>-12</sup>	10 <sup>-13</sup>	10 <sup>-14</sup>
	<i>acidic</i>				<i>slightly acidic</i>			<i>neutral</i>	<i>slightly basic</i>			<i>alkaline</i>			

pH of human **blood** is 7.36 - slightly basic, because it must have a reserve of alkalinity to fight the acidic products of metabolism.

Values 0 and 14 at the ends of pH scale mean:

*pH = 0 means a 1 molar solution of H<sup>+</sup> ions (1 molar strong univalent acid),*

*pH = 14 means, that pOH = 14 - pH = 0 - it is a 1 molar solution of a strong univalent base.*

pH of some well-known liquids is given in figure 4.2.

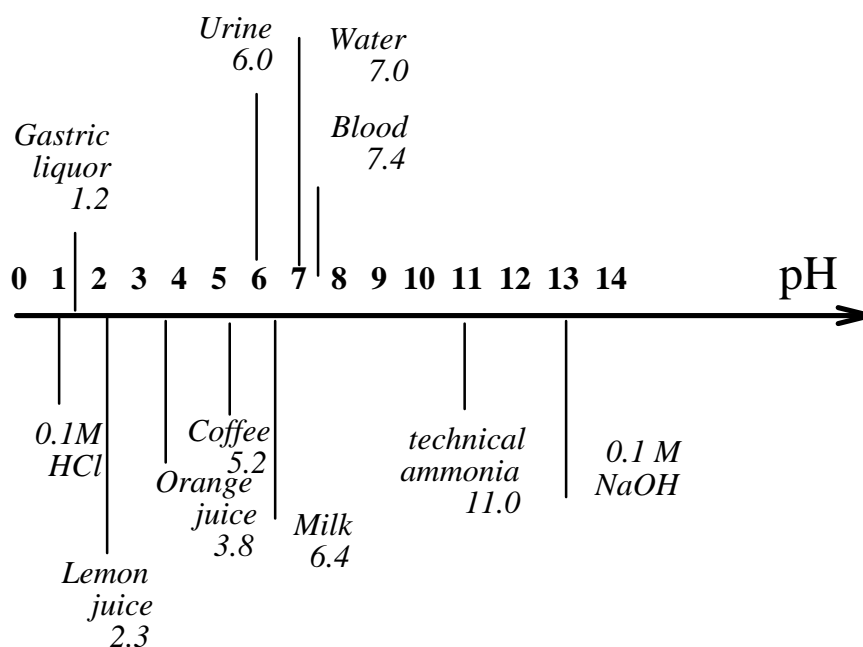


Fig.4.2. pH values of some well-known liquids

Biological medium	pH	Biological medium name	pH
plasma of <b>blood</b>	7.4	Urine	4.80÷6.85
extract of <b>blood</b>	7.35÷7.45	Juice from surrounding of Skin tissues	6.20÷7.50
		Skin surface antibacterial defense pH	5.5
Saliva	6.35÷6.85	Gland juice behind of stomach	7.80÷8.00
poor gastric liquor	0.90÷1.50	Lemon juice	2.3
pH of stomach	1.20÷3.00	Tomatoes juice	4.3

Water solubility **DISSOCIATION THERMODYNAMICS OF ELECTROLYTES** strong, weak electrolytes

A process of dissociation of ionic **crystalline**  $\text{Na}^+\text{Cl}^- \rightleftharpoons \text{Na}^+ + \text{Cl}^-$  electrolyte **solution** in **water** (4.1)

can be treated as a sum of two processes:

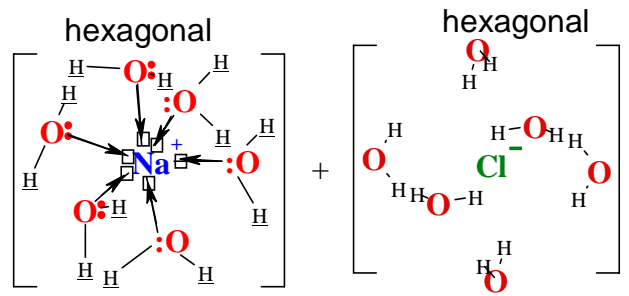
1) the **separation crystalline** sodium chloride  $\text{Na}^+\text{Cl}^-$  into positive cations  $\text{Na}^+$  and into negative  $\text{Cl}^-$  anions,

2) When tetramers dismissed the **hydration** with six water molecules coordinated ions  $[\text{Na}(\text{H}_2\text{O})_6]^+$ ,  $[\text{Cl}(\text{H}_2\text{O})_6]^-$ .

**Crystalline** sodium chloride dissolves in water:



Overall dissociation process free energy change  $\Delta G$  is:



$$\Delta G_r = \Delta H_r - T\Delta S_r; \quad \text{exoergic} \quad \Delta G_r = 3.82 \cdot 1000 - 298.15 \cdot 43.5 = -9150 \text{ J/mol} = -9.15 \text{ kJ/mol}$$

$$\text{endothermic} \quad \Delta H_r = -240.1 - 167.2 + 411.12 = +3.82 \text{ kJ/mol};$$

$$\Delta S_{\text{dispers}} = -\Delta H_r/T = -1000 \cdot 3.82/298.15 = -12.812 \text{ J/(mol K)}; \quad \Delta S_{\text{hydratation}} = +59 + 56.5 - (72) = +43.5 \text{ J/(mol K)}$$

$$\text{total entropy change in dissociation process is } \Delta S_{\text{total}} = \Delta S_{\text{dispers}} + \Delta S_{\text{hydratation}} = -12.812 + 43.5 = +30.688 \text{ J/(mol K)}$$

$$\text{crystalline } \text{Na}^+\text{Cl}^- \quad \Delta H^\circ = -411.12 \text{ kJ/mol}; \quad \Delta S^\circ = 72 \text{ J/(mol K)}$$

$$\text{H}_2\text{O} \quad \Delta H^\circ = -286 \text{ kJ/mol}; \quad \Delta S^\circ = 69.956 \text{ J/(mol K)} \quad \Delta G = -286 \text{ kJ/mol}$$

$$\text{Na}^+_{\text{aqua}} \quad \Delta H^\circ = -240.1 \text{ kJ/mol}; \quad \Delta S^\circ = 59 \text{ J/(mol K)} \quad [\text{Na}(\text{H}_2\text{O})_6]^+ \text{ evident as aqua}$$

$$\text{Cl}^-_{\text{aqua}} \quad \Delta H^\circ = -167.2 \text{ kJ/mol}; \quad \Delta S^\circ = 56.5 \text{ J/(mol K)} \quad [\text{Cl}(\text{H}_2\text{O})_6]^- \text{ evident as aqua.}$$

5<sup>th</sup> page : <http://aris.gusc.lv/BioThermodynamics/CO2O2Thermodynamic15A.pdf>

The entropy change in such a process is positive, as a more chaotic state (two ions) is obtained from a more ordered state (two ions). The overall  $\Delta H$  change make two parts:

$$\Delta H = \Delta H^{\text{separation}} + \Delta H^{\text{hydration}} = 3.82 \text{ kJ/mol endothermic reaction,}$$

where  $\Delta H^{\text{separation}} > 0$  is positive heat, that has to be supplied for separation of positive and negative ions from each other. As this process requires energy,  $\Delta H^{\text{separation}} > 0$  is positive value, but  $\Delta H^{\text{hydration}}$  is the heat of **hydration** process. As hydration of ions is an **exothermic** process,  $\Delta H^{\text{hydration}} < 0$ , that's negative value.

Salt reaction with **water** is **endothermic**  $\Delta H = 3.82 \text{ kJ/mol}$  as salt mixed with melting ice decreases temperature up to  $-12^\circ \text{C}$ . Freezing suggests positive value  $0 < 3.82 \text{ kJ/mol} = \Delta H = \Delta H^{\text{separation}} + \Delta H^{\text{hydration}}$

as positive :  $\Delta H^{\text{separation}} > \Delta H^{\text{hydration}}$  negative.

Determining the sign of  $\Delta G$ , one has to compare the sum of negative values ( $-T\Delta S$  and  $\Delta H^{\text{hydration}}$ ) to positive value ( $\Delta H^{\text{separation}}$ ). If  $|\Delta H^{\text{hydration}} - T\Delta S| > |\Delta H^{\text{separation}}|$ ,

$\Delta G < 0 = -9.15 \text{ kJ/mol}$  is negative and dissociation is a spontaneous process.

In the opposite case  $\Delta G = +9.15 \text{ kJ/mol} > 0$  is positive and dissociation is thermodynamically forbidden process. Evaporation of **water**  $12\text{H}_2\text{O} \uparrow$  as adding heat can make back process to **crystalline**  $\text{Na}^+\text{Cl}^-$  salt.

If the heats of processes here play the most important role, if ions are well hydrated and not very much energy is required for their separation, dissociation occurs spontaneously. That refers to **water** soluble salts.

If the ions are weakly hydrated and great energy is required for their separation, dissociation is thermodynamically forbidden process.

$$\text{Equilibrium constant for equation expressed as : } K_{\text{dis}} = \frac{[\text{Na}^+] \cdot [\text{Cl}^-]}{[\text{Na}^+\text{Cl}^-]_{\text{nondis}}}, \quad (4.2)$$

where  $[\text{Na}^+]$  and  $[\text{Cl}^-]$  are the concentrations of ions and  $[\text{Na}^+\text{Cl}^-]_{\text{nondis}}$  is the concentration of non-dissociated molecules.

$$\text{Dissociation constant, as all the equilibrium constants, can be expressed as: } K_{\text{dis}} = e^{-\Delta G/RT}. \quad (4.3)$$

If  $\Delta G < 0$  is negative for dissociation process, then  $K_{\text{dis}} \gg 1$  (as e is taken into **positive** power  $e^{+\text{positive}}$ ). In this case the product of ionic concentrations is much greater than the concentration of non-dissociated molecules (see (4.2)). In this case electrolyte is called strong electrolyte.

If  $\Delta G$  is positive, e is taken into a negative power  $e^{-\text{negative}}$  in calculation of  $K_{\text{dis}}$ , therefore  $K_{\text{dis}}$  much smaller than 1 ( $0 < K_{\text{dis}} \ll 1$ ) and never reach the zero 0. In this case the electrolyte is weak.

## CALCULATION OF pH IN SOLUTIONS OF ACIDS AND BASES

In this chapter the formulae for pH calculation will be derived for the 4 most important cases in nature: weak and strong acid and base. **pH IN A SOLUTION OF STRONG ACID.**

In a solution of strong acid the concentration of  $H^+$  ions can be calculated as  $[H^+] = zC_{dis}$ , where  $z$  is the number of  $H^+$  ions in one molecule of acid,  $C_{dis}$  is the concentration of *dissociated* molecules.

As  $C_{dis} = \alpha \cdot C_M$ , the concentration of  $H^+$  ions is  $[H^+] = C_M \cdot \alpha \cdot z$  or,  $C_M \cdot z = C_N$ ,  $[H^+] = C_N \cdot \alpha$

Taking logarithm from both sides and changing signs we obtain:  $pH = -\log [H^+] = -\log C_M \cdot \alpha \cdot z$   
or  $pH = -\log C_N \cdot \alpha$ .

### pH in strong base solution

$$pH = 14 - pOH = 14 + \log C_M \cdot \alpha \cdot z$$

In strong base solutions  $[OH^-]$  expression has the same form, as  $[H^+]$  expression for strong acid:

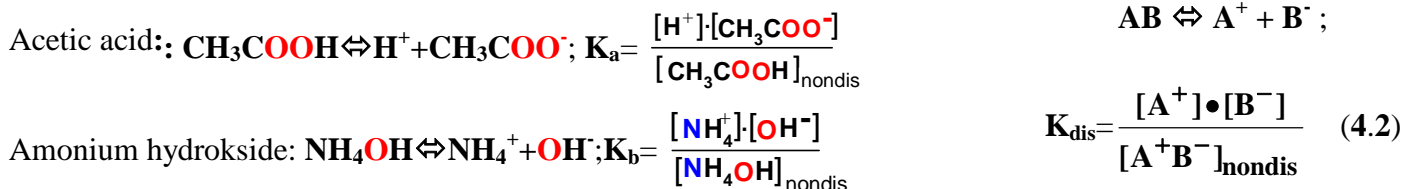
$[OH^-] = z \cdot C_{dis} = \alpha \cdot z \cdot C_M = \alpha \cdot C_N$ . **pOH expression as  $-\log[OH^-]$** , give for us: **pOH =  $-\log C_M \cdot \alpha \cdot z = -\log C_N \cdot \alpha$**   
or: **pH =  $14 - pOH = 14 + \log C_M \cdot \alpha \cdot z$**

## DISSOCIATION OF A WEAK ELECTROLYTE *Ostwald's dilution law*

There are two different characteristics for the dissociation of an electrolyte - the dissociation constant  $K_{dis}$  and the dissociation degree  $\alpha$ , which is expressed as :  $\alpha = n_{dis} / n_{total} = C_{dis} / C_{total}$ ;  $K_{dis} = [A^+][B^-] / [AB]_{nondissoc}$ .

For calculations of ionic concentrations  $\alpha$  is much more convenient to use, than  $K_{dis}$ , because ionic concentration can always be found as  $\alpha$  product of  $\alpha$  and the total concentration of molecules. Unfortunately,  $\alpha$  is not a constant value at different concentrations: the lower is the concentration of solution, the more easily ions escape from each other and the lower is the probability, that they meet to form back a molecule. For this reason, the lower is concentration, the greater is  $\alpha$ . As it is impossible to make tables of  $\alpha$  for all concentrations and all electrolytes, normally a dissociation constant of a weak electrolyte can be found in chemical tables and  $\alpha$  has to be calculated from it for a given concentration.

Dissociation constant, as all equilibrium constants, is not dependent on ionic concentrations, thus there is just one value of dissociation constant of a given electrolyte at a given temperature join  $K$  un  $\alpha$ , expressing:



The concentrations of ions and non-dissociated molecules through  $\alpha$  and the total concentration of electrolyte and insert the results into (4.2). As the concentrations of both ions are equal and they are at the same time equal to the concentration of dissociated molecules, we have

$$\text{total } C = [AB]_{nondis} + [A^+] \text{ or } [B^-] \text{ dissociated } [A^+] = [B^-] = C_{dis} = \alpha C,$$

where  $C$  is the total concentration of electrolyte.

Concentration of non-dissociated molecules is equal to the difference between total the concentration of electrolyte and the concentration of dissociated molecules:  $[AB]_{nondis} = C - C_{dis} = C - \alpha C$

Inserting all these results into (4.2) we have:  $K_{dis} = \frac{\alpha^2 C}{C - \alpha C}$  = Ostwald's dilution law (4.4)

Expression (4.3) in its present form allows the calculation of  $K_{dis}$ , when  $\alpha$  is known. The opposite case - calculation of  $\alpha$  from known  $K_{dis}$  is more common, therefore let us express  $\alpha$  through  $K_{dis}$ .

(3). As we are dealing with a weak electrolyte,  $\alpha \ll 1$  and  $(1 - \alpha) \approx 1$  at the same time, therefore  $K_{dis} = \alpha^2 C$

and, solving it for  $\alpha$ , we have 
$$\alpha = \sqrt{\frac{K_{dis}}{C}} \quad (4.4a)$$

In (4.4a) it is seen mathematically, that the greater is the concentration of solution, the smaller is  $\alpha$  and vice versa. Calculating the concentration of ions, we get:  $[A^+] = [B^-] = C_{dis} = \alpha C = C \cdot \sqrt{\frac{K}{C}} = \sqrt{K \cdot C}$

Weak acid:  $[H^+] = \sqrt{K_a \cdot C} = 10^{-pH}$  Molarity. Weak base:  $[OH^-] = \sqrt{K_b \cdot C} = 10^{-pOH}$  Molarity.

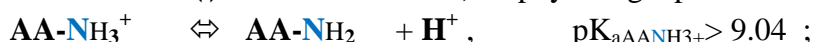
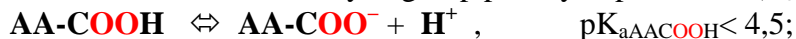
In protein molecule work parallel protolytic equilibria. The average parallel equilibria  $pK_a$  constant value one calculates adding given N-terminus  $pK_{a-NH_3^+}$  value, adding C-terminus  $pK_{a-COOH^-}$  value and summing amino acids said chains  $\Sigma pK_{aRgroup}$  values in total sum dividing with total count number  $NpK_a$  of functional groups :

$$pK_a = IEP = (\Sigma pK_{aRgroup} + pK_{aNterminus} + pK_{aCterminus}) / NpK_a, \text{ where } pK_a \text{ average}$$

is protein isoelectric point IEP as medium pH value having zero net charge of whole molecule.

Amino acids **AA** have two types functional groups the carboxyl and the amino:

Amino acid **AA** carboxylic group protolytic pair acid **a**( $H_3CCOOH$ ) and conjugated base-salt **b**( $H_3CCOO^-$ )



Protolytic pair acid **a**( $AA-NH_3^+$ ) protonated **N** and conjugated deprotonated **N** base **b**  $AA-NH_2$

14<sup>th</sup> page: [http://aris.gusc.lv/BioThermodynamics/Data\\_bookSpring2015CT.pdf](http://aris.gusc.lv/BioThermodynamics/Data_bookSpring2015CT.pdf)

$$K_{aCOOH} = \frac{[AA-COO^-] \cdot [H^+]}{[AA-COOH]_{nondis}} = 10^{-pK_a}; \quad K_{aNH3^+} = \frac{[AA-NH_2] \cdot [H^+]}{[AA-NH_3^+]_{protonated}} = 10^{-pK_a};$$

Like hemoglobin **Hb** proteins are long chain polypeptides of amino acids with four type protolytic acid groups:

Amino Acid  $pK_{aCOOH}$   $pK_{aNH3^+}$   $pK_{aRgroup}$

Isoleucine 2.36 9.68

Valine 2.32 9.62

Leucine 2.36 9.60

Phenylalanine 1.83 9.13

Cysteine 1.96 10.28 8.18

Methionine 2.28 9.21

Alanine 2.34 9.69

Proline 1.99 10.96

Glycine 2.34 9.60

Threonine 2.11 9.62

Serine 2.21 9.15

Tryptophan 2.38 9.39

Tyrosine 2.20 9.11 10.07

Histidine 1.82 9.17 6.00

Aspartate 1.88 9.60 3.65

Glutamate 2.19 9.67 4.25

Asparagine 2.02 8.80

Glutamine 2.17 9.13

Lysine 2.18 8.95 10.53

Arginine 2.17 9.04 12.48

**-COO<sup>-</sup>** deprotonated carboxyl negative anion salt groups,  
protonated positive charged ammonium groups **-NH<sub>3</sub><sup>+</sup>**,  
neutral phenolic acid **-OH** and **-SH** neutral sulfhydryl groups.

In physiologic medium  $pH=7,36 \pm 0.01$

Carbonic acid groups deprotonated negative charged **-COO<sup>-</sup>** and amino groups **R-NH<sub>3</sub><sup>+</sup>** protonated positive charged.

Table given maximal  $pK_{a-COOH^-}$  value smaller about 7,36:

$$pK_{a-COOH^-} = 4.25 < 7,36 \text{ and}$$

given smallest  $pK_{a-NH_3^+}$  value greater about 7,36 < 9,04 =  $pK_{a-NH_3^+}$

20 amino acids have four protolytic  $pK_a$  equilibria in 47 groups:

1. **R-COOH**  $\Leftrightarrow$  **R-COO<sup>-</sup>** + **H<sup>+</sup>**, 22 groups of 47
2. **R-NH<sub>3</sub><sup>+</sup>**  $\Leftrightarrow$  **R-NH<sub>2</sub>** + **H<sup>+</sup>** 22+1 group of 47
3. **Tyrosine-phenol-OH**  $\Leftrightarrow$  **Tyrosine-phenolate-O<sup>-</sup>** + **H<sup>+</sup>** one group,
4. **Cysteine-SH**  $\Leftrightarrow$  **Cysteine-S<sup>-</sup>** + **H<sup>+</sup>** one group .

$NpK_a$  number of parallel protolytic equilibria average  $pK_a$  value is calculated as  $pK_a = (\Sigma pK_{aRgroup} + pK_{a-NH_3^+} + pK_{a-COOH}) / NpK_a$

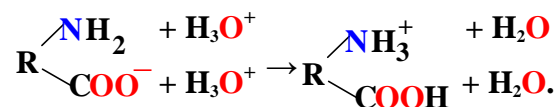
In *Ostwald's dilution law* calculates one the pH of solution at

$$\text{concentration } C \text{ logarithm: } pH = \frac{pK_a - \log C}{2} = \dots$$

If strong acid solution add to hemoglobin **Hb** like protein solution, than

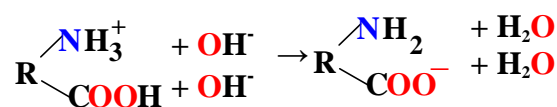
hydrogen **H<sub>3</sub>O<sup>+</sup>** ions react with weak base amino group and basic karboxylate anion negative charged group.

Strong acid **H<sub>3</sub>O<sup>+</sup>** converts to water, to weak base **H<sub>2</sub>O** .



If strong base add to protein solution, than hydroxyl **OH<sup>-</sup>** ions react with acidic ammonium group and weak acid carboxyl group.

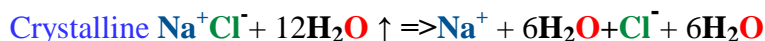
Strong base **OH<sup>-</sup>** converts to water, to weak acid **H<sub>2</sub>O** .





## STRONG ELECTROLYTES *ionic strength* $\mu$

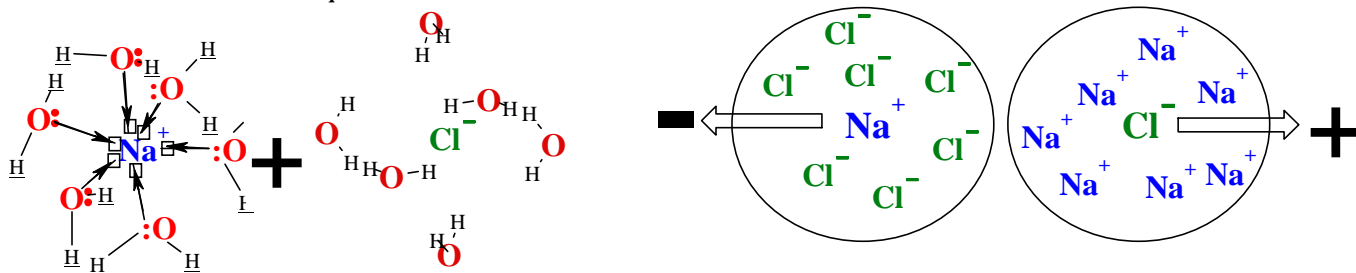
Many of the strong electrolytes (all water soluble salts, for instance) exist in an ionic crystalline already before dissolution. When they are dissolved in **water**, no dissociation is required - just ions are transferred from the crystalline into solution. From these considerations it is clear, that  $\alpha = 1$  in the solutions of strong electrolytes.



However, if  $\alpha$  is measured experimentally (from the measurements of freezing point depression, boiling point raise, osmotic pressure or electrical conductivity of solution), the measured values of  $\alpha$  are smaller than **1** - they often are around  $\alpha = 0.8-0.9$ . As the true dissociation degree for the strong electrolytes is **1**, a conclusion has to be done, that only a part of ions is active, or, in other words, only a part (**0.8-0.9**) of ions express themselves in the properties of solution.

The reason of this is easily understood, if one considers the measurements of electrical conductivity. When electrodes are immersed into solution and a potential difference between them exists, positive ions should move towards the negative electrode and vice versa. Any positive ion is surrounded by negative ions, that make a *ionic atmosphere* around it. Forces of the electrical attraction from the side of ionic atmosphere work against motion of the ion towards the electrode, therefore the motion of ion in the electrical field is slower, than it could be, if ion was alone and the result of the conductivity measurement is lowered. For this reason, value of  $\alpha$ , that is calculated from conductivity measurements, is lower than **1**.

It is easy to understand, that, the more dense is the ionic atmosphere, the smaller will be the measured  $\alpha$ , which will be further called imaginary  $\alpha$  (as the real  $\alpha$  is equal to **1**).



**Fig.4.1.** *Ionic atmosphere around ions.*

The active concentration or *activity* of solute can be calculated from the total concentration of solute as

$$a = \gamma C, \text{ where } \gamma \text{ is the activity coefficient, } 0 < \gamma < 1.$$

Values of the activity coefficients can be calculated precisely from the expressions of *Debye - Hückels'* theory of strong electrolytes, but, as these expressions are very complicated, a more common case is to find of activity coefficients in tables.

As it can be understood from the previous material, the activity coefficient must be dependent on the density of ionic atmosphere - the more dense is the ionic atmosphere, the lower must be the activity coefficient. To characterize the density of ionic atmosphere a parameter, called *ionic strength*  $\mu$  of solution is invented:

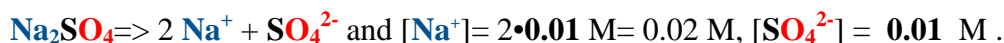
$$\mu = 1/2 \sum C_i z_i^2,$$

where  $C_i$  and  $z_i$  are the concentration and charge half sum  $1/2 \sum$  of each ion respectively.

Values of the activity coefficients are given in chemical tables for each given value of ionic strength.

Activity coefficient of a given ion depends on its charge, too. From fig.4.1 it is easy to understand, that the greater is the charge of anion, the more it will be attracted by ionic atmosphere. For example, in a **0.01 M** solution of **Na<sub>2</sub>SO<sub>4</sub>** activity coefficients are  $\gamma_{\text{Na}^+} = 0.85$  for **Na<sup>+</sup>** ion and  $\gamma_{\text{SO}_4^{2-}} = 0.45$  for **SO<sub>4</sub><sup>2-</sup>** ion.

$2 \cdot 0.01 \text{ M} + 0.01 \text{ M} = 0.03 \text{ Molarity}$  is total concentration of ions for **[Na<sub>2</sub>SO<sub>4</sub>] = 0.01 M**.

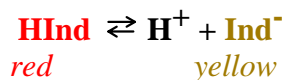


Electrolyte **Na<sub>2</sub>SO<sub>4</sub>** ionic strength is:

$$\mu = \frac{1}{2}(1^2 \cdot 0.02 + 2^2 \cdot 0.01) = \frac{1}{2}(1 \cdot 0.02 + 4 \cdot 0.01) = \frac{1}{2}(0.02 + 0.04) = \frac{1}{2}(0.06) = 0.03 \text{ Molarity}$$

## THEORY OF pH INDICATORS

Indicators are compounds, which change their color according to the concentration of  $\text{H}^+$  ions in the solution. All the **pH** indicators themselves are weak acids or weak bases, the molecular form of which has a different color from the ionic form. Let us discuss indicator theory for a case, when the indicator is a weak acid (all conclusions will be the same in the opposite case, too **pOH value**). If we assign a symbol **HInd** to indicator, its dissociation process will be expressed by equilibrium, for example, to methyl orange:



Let us take as an example, that the **molecular form** of the indicator methyl orange has a **color red**, but the **ionic form** is **yellow**.

If the indicator is added to an acidic solution, the  $\text{H}^+$  ions of that solution will be involved in the equilibrium of indicator's dissociation and they will shift the equilibrium to the left. For this reason, the color of the molecular form will prevail and we shall see the solution in **red color**.

If the same indicator will be added to a basic solution, the  $\text{OH}^-$  ions from the solution will react with  $\text{H}^+$  ions from indicators equilibrium, the concentration of  $\text{H}^+$  will decrease and this will shift the equilibrium to the right. As a result, the ionic form of indicator will prevail in solution and we shall see the **solution yellow**.

The reason of color change is now clear, but it is necessary to know, at what value of **pH** each particular indicator will change its color. To find the **pH** interval of color change, we have to write an equation of equilibrium constant for indicator's dissociation and solve that equation against  $[\text{H}^+]$ :

$$K_{\text{Ind}} = \frac{[\text{H}^+] \times [\text{Ind}^-]}{[\text{HInd}]}$$

Expressing the concentration of hydrogen ions from the previous equation, we get:

$$[\text{H}^+] = K_{\text{Ind}} \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

and **pH** is obtained taking **log** from both sides of the equation using minus sign:

$$\text{pH} = -\log[\text{H}^+] = -\log K_{\text{Ind}} \frac{[\text{HInd}]}{[\text{Ind}^-]} = -\log K_{\text{Ind}} - \log \frac{[\text{HInd}]}{[\text{Ind}^-]}$$

Taking into account, that  $-\log K = \text{p}K$  and changing sign of the second part of the equation, **pH** becomes:

$$\text{pH} = \text{p}K_{\text{Ind}} + \log \frac{[\text{Ind}^-]}{[\text{HInd}]}$$

If the concentrations of both forms of indicator in the solution are equal, then

$$\text{pH} = \text{p}K_{\text{Ind}} + \log 1 = \text{p}K_{\text{Ind}} + 0 = \text{p}K_{\text{Ind}}$$

The **pH** value, which is equal to  $\text{p}K_{\text{Ind}}$  of indicator is called the *color change point* of the indicator, as at this **pH** both forms are in equal amounts, but shifting **pH** to any side will cause domination of one form.

Visually indicator solution at  $\text{pH} = \text{p}K_{\text{Ind}}$  has an intermediate color (in our example - **orange color**).

The properties of the human eye are such, that it is possible to indicate visually the domination of one form, if its concentration is **10** times greater, than the concentration of the other form.

Thus, we will see the color of ionic form **yellow**, if the ratio  $\frac{[\text{Ind}^-]}{[\text{HInd}]} \geq 10$

$$\frac{[\text{Ind}^-]}{[\text{HInd}]} \leq \frac{1}{10}$$

and the color of molecular form **red**, if

Inserting the values **10** and **1/10** into the equation of **pH** we get the *color change interval* of the indicator:

$$\text{pH} = \text{p}K_{\text{Ind}} \pm 1$$

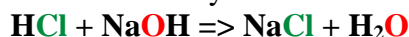
(as  $\log 10 = 1$  and  $\log 1/10 = -1$ )

This means, that, using only one indicator, we can only say, whether **pH** is greater than  $\text{p}K_{\text{Ind}} + 1$  (indicator will have the color of **ionic form** then) or it is below  $\text{p}K_{\text{Ind}} - 1$  (indicator will have the color of **molecular form** then). Inside of the interval the indicator has an intermediate color and it is impossible to detect visually the dominance of any form.

## CHOICE OF INDICATORS FOR ACID-BASE TITRATION

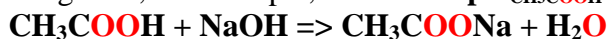
(see next chapter about hydrolysis if these questions are not clear)

At acid-base titration **pH** indicators are used to indicate the endpoint of titration. If a strong acid is titrated by a strong base (or vice versa), for example **HCl** is titrated by **NaOH**:



At the endpoint of titration only **NaCl** and **water** are present in the solution. As **NaCl** is a salt of a strong acid and a strong base, it is not hydrolyzed and the solution is neutral, i.e. its **pH = 7**. For this case of titration an indicator with **pK<sub>Ind</sub>** value close to **7** will be required.

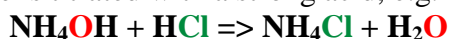
When a weak acid is titrated by a strong base, for example, acetic acid **pK<sub>CH<sub>3</sub>COOH</sub> = 4,76** is titrated by **NaOH**:



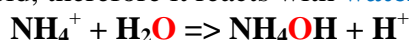
As sodium acetate is a salt of a weak acid, the anion **CH<sub>3</sub>COO<sup>-</sup>** is a rather strong base, therefore it is hydrolyzed as **pK<sub>CH<sub>3</sub>COOH</sub> = 4,76**: **CH<sub>3</sub>COO<sup>-</sup> + H<sub>2</sub>O ⇌ CH<sub>3</sub>COOH + OH<sup>-</sup>**

As **OH<sup>-</sup>** ions are formed in this equilibrium, the environment is basic and an indicator, having **pK<sub>Ind</sub>** value greater than **7** approximately **8** is required, because **8 = pH<sub>hydrolyze</sub> = 14 - 4,76 - logC<sub>CH<sub>3</sub>COONa</sub>**, if **C<sub>CH<sub>3</sub>COONa</sub> = 0,056 M**.

When a weak base is titrated with a strong acid, e.g. **NH<sub>4</sub>OH** is titrated by **HCl**:



As **NH<sub>4</sub>OH** is a weak base, ion is an acid, therefore it reacts with **water** (it is hydrolyzed):



**H<sup>+</sup>** ions are a product of this equilibrium, therefore the environment is acidic and an indicator, having **pK<sub>Ind</sub>** below **7** approximately **6** is required, because **6 = pH<sub>hydrolyze</sub> = 4,76 + logC<sub>NH<sub>4</sub>Cl</sub>**, if **C<sub>NH<sub>4</sub>Cl</sub> = 0,056 M**.

### VIII. HYDROLYSIS OF SALTS

Sam salt and **water** can be considered to be produced in a reaction between an acid and a base. As both of these two compounds can be strong or weak, there are **4** groups of salts:

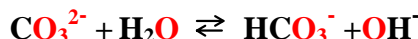
#### 1) SALT OF A STRONG ACID AND A STRONG BASE.

Salts of this group are not hydrolyzed, because anion of a strong acid is very weak base and metal ion of a strong base is a very weak acid.

Thus, for instance, **Na<sub>2</sub>SO<sub>4</sub>** is not hydrolyzed, as **SO<sub>4</sub><sup>2-</sup>** ion is a very weak base and **Na<sup>+</sup>** ion is a very weak acid.

#### 2) SALT OF A WEAK ACID AND A STRONG BASE.

Let us take **Na<sub>2</sub>CO<sub>3</sub>** as example. In this case **Na<sup>+</sup>** ion is not hydrolyzed, as it is a very weak acid, but **CO<sub>3</sub><sup>2-</sup>** ion (as an anion of a weak acid) is a rather strong base and therefore it reacts with **water**. The hydrolysis of **CO<sub>3</sub><sup>2-</sup>** ion occurs in **2** stages: *stage I*:

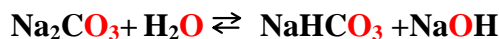


As **OH<sup>-</sup>** ions are products of this equilibrium reaction, the environment in a solution of a salt of weak acid and strong base is basic, hence, its **pH > 7**. *stage II*: **HCO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O ⇌ H<sub>2</sub>CO<sub>3</sub> + OH<sup>-</sup>**

Bicarbonate weak can be hydrolyzed further just with strong acid, as it can accept one more **H<sup>+</sup>** ion, therefore *stage II* does not take a place with water: *stage II no reaction*: **HCO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O = H<sub>2</sub>CO<sub>3</sub> + OH<sup>-</sup>**

The second stage of hydrolysis, however, occurs to a very small extent. This can be explained by the following: **HCO<sub>3</sub><sup>-</sup>** ion, which is the product of the first stage of hydrolysis, is the initial compound for the second stage. This means, that, when the **2nd** stage begins, there are already **OH<sup>-</sup>** ions from the **1st** stage in the solution. If we consider the influence of the extra **OH<sup>-</sup>** ions (from *stage I*) to the equilibrium of *stage II*, it is clear, that they shift the equilibrium to the left.

Thus, the **2nd** stage of hydrolysis is oppressed by the **1st** stage. For this reason, if we have to write the hydrolysis reaction in molecular form, we have to write it according to **1st** stage:



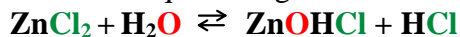
For this group of salts, the hydrolysis will be increased by adding acid to solution (consider the influence of **H<sup>+</sup>** on the equilibrium) and oppressed by adding base.



In this case the anion is not hydrolyzed, as it comes from a strong acid and, hence, is a very weak base. The cation comes from a weak base and therefore it is a rather strong acid. It reacts with **water** (in this case, as  $Zn^{2+}$  is a bivalent ion, the hydrolysis reaction will again occur in 2 stages): *stage I*:  $Zn^{2+} + H_2O \rightleftharpoons ZnOH^+ + H^+$

As hydrogen ions are formed, the reaction of a solution of a salt of a strong acid and a weak base will be acidic,  $pH < 7$ . *stage II*:  $ZnOH^+$  ion can react with another molecule of **water**:  $ZnOH^+ + H_2O \rightleftharpoons Zn(OH)_2 + H^+$

Here the 2nd stage of hydrolysis is oppressed by hydrogen ions from *stage I*, as they are already present in the solution when *stage II* begins. Thus, the molecular equation again has to be written for *stage I*:



### SPECIAL PROPERTIES OF SALTS WITH TRIVALENT METAL IONS

If the metal ion comes from a very weak trivalent base (for example,  $Bi^{3+}$ ,  $Cr^{3+}$ ,  $Sb^{3+}$ ,  $Fe^{3+}$ ), their hydrolysis really occurs up to the stage II (all together three stages could be possible in this case).

$Bi^{3+} + H_2O \rightleftharpoons BiOH^{2+} + H^+$ ;  $BiOH^{2+} + H_2O \rightleftharpoons Bi(OH)_2^+ + H^+$   
 and a molecule of  $H_2O$  is extracted from the product of *stage II*:  $Bi(OH)_2^+ \Rightarrow BiO^+ + H_2O$ .

The molecular form of the reaction has a form:  $BiCl_3 + H_2O \rightleftharpoons BiOCl + HCl$

The ions  $BiO^+$ ,  $CrO^+$ ,  $SbO^+$  and  $FeO^+$  are called *bismuthyl-*, *chromyl-*, *antimonyl-* and *ferryl-*ions respectively.

4) *salt of a weak acid and weak base*, for example  $CH_3COONH_4$  or  $(CH_3COO)_2Zn$ .

In this case both ions are hydrolyzed, because the anion of a weak acid is a strong base and the metal ion of a weak base is a rather strong acid. For instance, for ammonium acetate we have to write hydrolysis equilibriums for both ions:  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ ;  $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

In this case hydrolysis occurs to a great extent, because  $H^+$  and  $OH^-$  ions, that are formed at the same time, combine together to form **water**:  $H^+ + OH^- \Rightarrow H_2O$

As the concentration of a product of reaction drops down in both equilibriums, both equilibriums are shifted to the right.

To consider  $pH$  of the solution, one has to compare the strengths of acid and base, that have formed the salt. For example, for ammonium acetate, strength of acetic acid is equal to strength of ammonium hydroxide ( $K_{CH_3COOH} = K_{NH_4OH} = 1.8 \times 10^{-5}$ )

For this reason both acetate and ammonium ions are hydrolyzed to the same extent and the solution should be neutral,  $pH = 7$ .

For zinc acetate the situation is different:

$Zn(OH)_2$  is much weaker as a base, than acetic acid as an acid. For this reason, zinc ion is more hydrolyzed, than acetate ion and the solution must be acidic ( $pH < 7$ ).

As it was shown a little before, a salt of a weak acid and a weak base is hydrolyzed to a great extent. If it happens so, that the salt is composed from a weak acid and a weak base and the final products of hydrolysis are gaseous, then the salt is completely decomposed by **water**. Such cases are:  $Al_2S_3$ ,  $Cr_2S_3$ ,  $Al_2(CO_3)_3$ ,  $Cr_2(CO_3)_3$  and  $Fe_2(CO_3)_3$ ,

