

IV. DISSOCIATION OF WATER. pH HYDROGEN [H⁺] EXPONENT FUNCTION.

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Brensted protolytic concept of acid and base 1923

Acid cleaves the proton H⁺
turns to base
acid **a** ⇌ H⁺ + **b** base

$$K_a = \frac{[H^+][b]}{[a]}; K_a = \frac{1}{K_b}; K_b = \frac{[a]}{[H^+][b]}$$

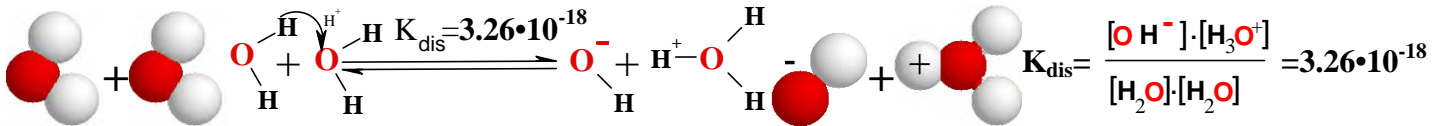
Base added proton H⁺
becomes the acid
b base + H⁺ ⇌ acid **a**

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

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

Water weak acid **a**₁ and weak base **b**₂ instantly OH⁻ strong base **b**₁ react with H₃O⁺ strong acid **a**₂ forming practically non dissociated water molecules as non electrolytes constant is small positive number K_{dis}=3.26•10⁻¹⁸.

Water is a very weak electrolyte, but still it dissociates and a dissociation equilibrium H₂O ⇌ OH⁻ + H⁺ can be written for it. To be more precise, the process in **water** is protolytical acid H₂O cleaves the proton H⁺ and add to base H₂O, as reaction forms the strong base hydroxide OH⁻ ions and strong acid hydroxonium H₃O⁺ ions H₂O + H₂O ⇌ OH⁻ + H₃O⁺ 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:

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

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

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

This last equation has a very important meaning: pK_w = -logK_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⁺ and OH⁻ 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⁺][OH⁻] = 10⁻¹⁴ and pK_w = 14.

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

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

Finally, this K_w expression can be used for calculation of [H⁺] ions concentrations, if [OH⁻] is known and vice versa. As these calculations are connected with dividing of values, having negative powers, this has seemed inconvenient to the investigators, therefore the so-called hydrogen exponent pH was invented.

$$[H^+] = 10^{-pH} \text{ M (mol/L)}, \quad \text{where } pH = -\log([H^+]) \text{ and}$$

$$[OH^-] = 10^{-pOH} \text{ M (mol/L)}, \quad \text{where } pOH = -\log([OH^-]) \text{ and}$$

$$K_w = 10^{-Kw}, \quad \text{where } pK_w = -\log(K_w).$$

If we take a logarithm of both sides of (4.4), we have:

$$\log([H^+][OH^-]) = \log 10^{-14}; \quad \text{or} \quad \log [H^+] + \log [OH^-] = -14,$$

or, changing the signs of both sides -log [H⁺] - log [OH⁻] = 14

Value -log [H⁺] was called pH (hydrogen exponent), value -log [OH⁻] was called pOH (hydroxyl exponent), therefore the last equation can be rewritten as; pH + pOH = 14

Using this equation it is very easy to find pH, if pOH is known and vice versa.

pH scale is normally used from 0 to 14. The pH of a neutral solution is 7 (as in a neutral solution [H⁺]=10⁻⁷ moles/l). In acidic solutions pH values are below 7, in basic environment - over 7:

Scale of pH with the corresponding values of pOH and [H⁺] 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 ⁺]	1	0.1	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻⁵	10 ⁻⁶	10 ⁻⁷	10 ⁻⁸	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	10 ⁻¹²	10 ⁻¹³	10 ⁻¹⁴
	<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⁺ 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.

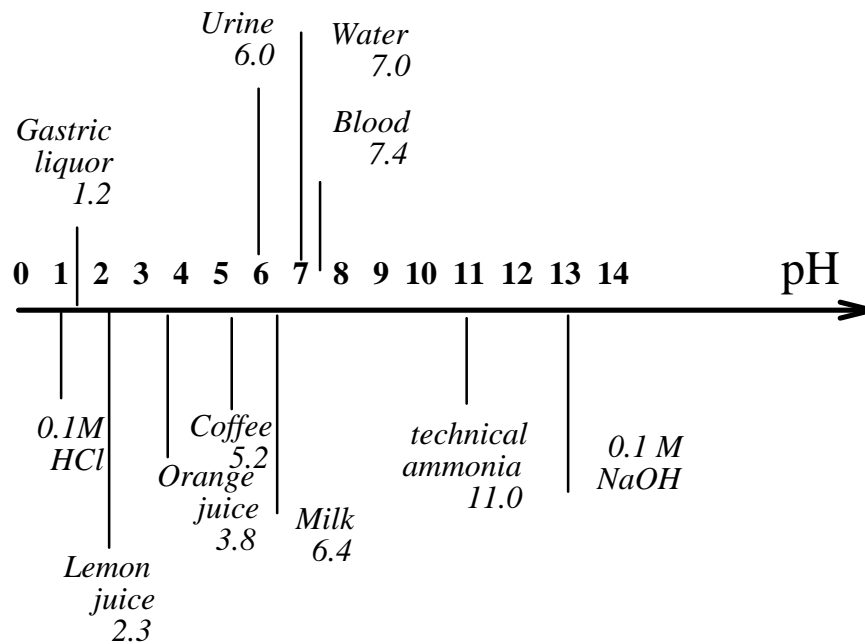


Fig.4.2. pH values of some well-known liquids

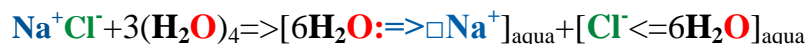
Biological medium	pH	Biological medium name	pH
plasma of blood	7.4	Urine	4.80÷6.85
extract of blood	7.35÷7.45	Juice from surrounding of Skin tissues	6.20÷7.50
Saliva	6.35÷6.85	Skin surface antibacterial defense pH	5.5
poor gastric liquor	0.90÷1.50	Gland juice behind of stomach	7.80÷8.00
pH of stomach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

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

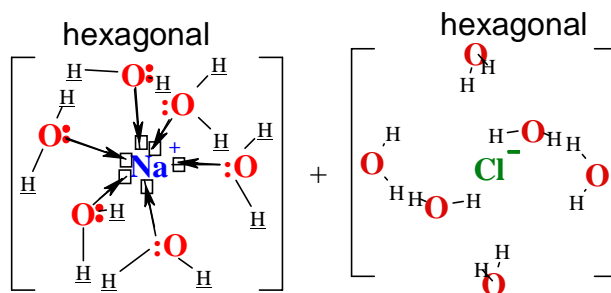
A process of dissociation of ionic **crystalline** $\text{Na}^+\text{Cl}^- \rightleftharpoons \text{Na}^+ + \text{Cl}^-$ electrolyte **solution** in **water** (4.1)

can be treated as a sum of two processes:

- 1) the **separation crystalline** sodium chloride Na^+Cl^- into positive cations Na^+ and into negative 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 disolutes in water:



Overall dissociation process free energy change ΔG is:



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

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

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

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

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

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

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

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

5th 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 ΔH 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°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 ΔG , 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** Na^+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 ΔG is positive, e is taken into a negative power $e^{-\text{negative}}$ in calculation of K_{dis} , therefore K_{dis} much smaller than 1 ($0 < K_{\text{dis}} \ll 1$) and never reach the zero 0. In this case the electrolyte is weak.

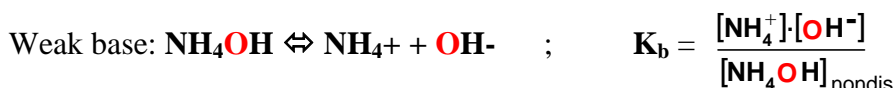
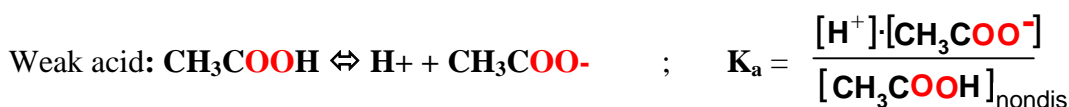
DISSOCIATION OF A WEAK ELECTROLYTE *Ostwald's dilution law*

There are two different characteristics for the dissociation of an electrolyte - the dissociation constant (see (4.2)) and the dissociation degree α , which is expressed as

$$\alpha = n_{\text{dis}} / n_{\text{total}} = C_{\text{dis}} / C_{\text{total}}$$

For calculations of ionic concentrations α is much more convenient to use, than K_{dis} , because ionic concentration can always be found as α product of α and the total concentration of molecules. Unfortunately, α 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 (see (4.1)). For this reason, the lower is concentration, the greater is α . As it is impossible to make tables of α for all concentrations and all electrolytes, normally a dissociation constant of a weak electrolyte can be found in chemical tables and α 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.



The equation, that connects K and α is called *Ostwald's dilution law*. To obtain the expression, connecting α and K we have to express the concentrations of ions and non-dissociated molecules through α 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

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

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: $[AB]_{\text{nondis}} = C - C_{\text{dis}} = C - \alpha C$

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

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

$$K_{\text{dis}} = \alpha^2 C$$

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

In (4.3a) it is seen mathematically, that the greater is the concentration of solution, the smaller is α and vice versa. Calculating the concentration of ions, we get:

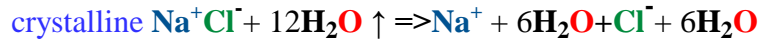
$$[A^+] = [B^-] = C_{\text{dis}} = \alpha C = C \cdot \sqrt{\frac{K}{C}} = \sqrt{K \cdot C}$$

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

$$\text{Weak base: } [OH^-] = \sqrt{K_b \cdot C} = 10^{-\text{pOH}} \text{ Molarity.}$$

STRONG ELECTROLYTES *ionic strength* μ

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 α is measured experimentally (from the measurements of freezing point depression, boiling point raise, osmotic pressure or electrical conductivity of solution), the measured values of α 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 α , 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 α , which will be further called imaginary α (as the real α is equal to 1).

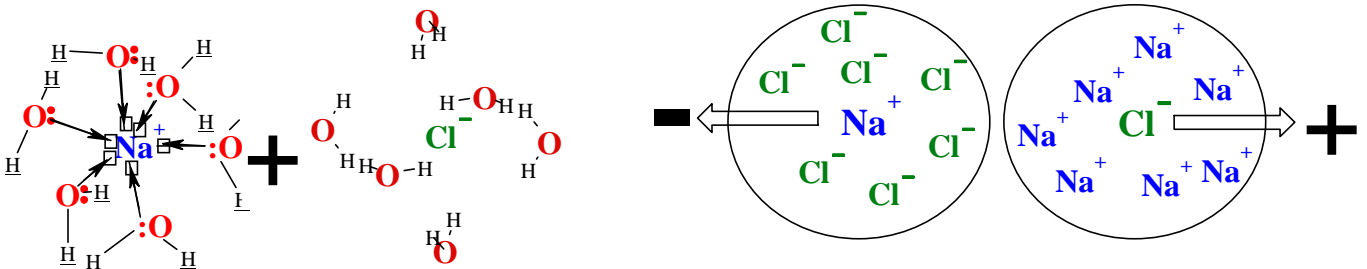


Fig.4.1. *Ionic atmosphere around ions.*

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 - Huckels'* 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* μ of solution is invented:

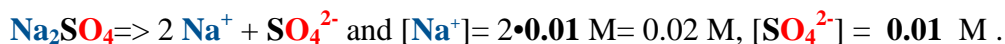
$$\mu = 1/2 \sum C_i z_i^2,$$

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 an ion, the more it will be attracted by ionic atmosphere. For example, in a 0.01 M solution of Na_2SO_4 activity coefficients are $\gamma_{\text{Na}^+} = 0.85$ for Na^+ ion and $\gamma_{\text{SO}_4^{2-}} = 0.45$ for SO_4^{2-} ion.

$2 \cdot 0.01 \text{ M} + 0.01 \text{ M} = 0.03 \text{ Molarity}$ is total concentration of ions for $[\text{Na}_2\text{SO}_4] = 0.01 \text{ M}$.



Electrolyte Na_2SO_4 ionic strength is:

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

V. 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.

V.1. pH IN A SOLUTION OF STRONG ACID.

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

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

Taking logarithm from both sides and changing signs we obtain:

$$\text{pH} = -\log [\text{H}^+] = -\log C_M \times \alpha \times z \text{ or } \text{pH} = -\log C_N \times \alpha.$$

V.2. pH IN A SOLUTION OF WEAK ACID.

In a solution of a weak acid the concentration of H^+ ions can be found as $[\text{H}^+] = \sqrt{K_a \cdot C}$ (see page 53).

Taking a logarithm from both sides, we have $\log[\text{H}^+] = \log \sqrt{K_a \cdot C} = \frac{\log K_a C}{2} = \frac{\text{p}K_a + \log C}{2}$

$$\text{After changing signs: } \text{pH} = -\log[\text{H}^+] = \frac{\text{p}K_a - \log C}{2}$$

A symbol $\text{p}K_a$ is assigned to $-\log K_a$, therefore the final pH equation looks like: $\text{pH} = \frac{\text{p}K_a - \log C}{2}$

V.3. pH SOLUTION OF A STRONG BASE.

In a solution of a strong base the expression of $[\text{OH}^-]$ has the same form, as the expression for $[\text{H}^+]$ in a strong acid: $[\text{OH}^-] = z \times C_{\text{dis}} = \alpha \times z \times C_M = \alpha \times C_N$

Expressing pOH as $-\log [\text{OH}^-]$, we have: $\text{pOH} = -\log C_M \alpha z = -\log C_N \alpha$ or: $\text{pH} = 14 - \text{pOH} = 14 + \log C_M \alpha z$

V.4. pH SOLUTION OF A WEAK BASE.

Here the equation for OH^- concentration has the same form as the equation for the H^+ concentration in a weak acid: $[\text{OH}^-] = \sqrt{K_b \cdot C}$,

where K is the dissociation constant of the base. Logarithming both sides, we have:

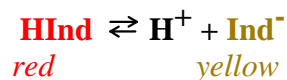
$$\log[\text{OH}^-] = \log \sqrt{K_b \cdot C} = \frac{\log K_b C}{2} = \frac{\text{p}K_b + \log C}{2}$$

After changing signs: $\text{pOH} = -\log[\text{OH}^-] = \frac{\text{p}K_b - \log C}{2}$

$$\text{or: } \text{pH} = 14 - \text{pOH} = 14 - \frac{\text{p}K_b - \log C}{2}$$

VI. THEORY OF pH INDICATORS

Indicators are compounds, which change their color according to the concentration of 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 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 OH^- ions from the solution will react with H^+ ions from indicators equilibrium, the concentration of 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:

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

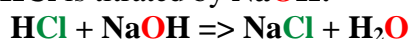
(as $\log 10 = 1$ and $\log 1/10 = -1$)

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.

VII. CHOICE OF INDICATORS FOR ACID-BASE TITRATION

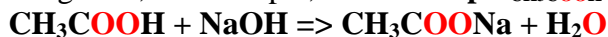
(see next chapter about hydrolysis if these questions are not clear)

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**:



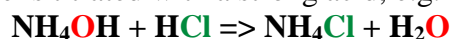
At the endpoint of titration only **NaCl** and **water** are present in the solution. As **NaCl** is a salt of a strong acid and a strong base, it is not hydrolyzed and the solution is neutral, i.e. its **pH = 7**. For this case of titration an indicator with **pK_{Ind}** value close to **7** will be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

When a weak acid is titrated by a strong base, for example, acetic acid **pK_{CH₃COOH} = 4,76** is titrated by **NaOH**:

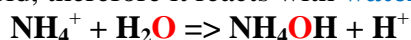


As sodium acetate is a salt of a weak acid, the anion **CH₃COO⁻** is a rather strong base, therefore it is hydrolyzed as **pK_{CH₃COOH} = 4,76**: $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$

As **OH⁻** ions are formed in this equilibrium, the environment is basic and an indicator, having **pK_{Ind}** value greater than **7** approximately **8** is required, because **8 = pH_{hydrolyze} = 14 - 4,76 - logC_{CH₃COONa}**, if **C_{CH₃COONa} = 0,056 M**. When a weak base is titrated with a strong acid, e.g. **NH₄OH** is titrated by **HCl**:



As **NH₄OH** is a weak base, ion is an acid, therefore it reacts with **water** (it is hydrolyzed):



H⁺ ions are a product of this equilibrium, therefore the environment is acidic and an indicator, having **pK_{Ind}** below **7** approximately **6** is required, because **6 = pH_{hydrolyze} = 4,76 + logC_{NH₄Cl}**, if **C_{NH₄Cl} = 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:

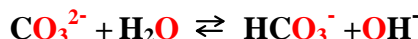
1) SALT OF A STRONG ACID AND A STRONG BASE.

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, **Na₂SO₄** is not hydrolyzed, as **SO₄²⁻** ion is a very weak base and **Na⁺** ion is a very weak acid.

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

Let us take **Na₂CO₃** as example. In this case **Na⁺** ion is not hydrolyzed, as it is a very weak acid, but **CO₃²⁻** ion (as an anion of a weak acid) is a rather strong base and therefore it reacts with **water**. The hydrolysis of **CO₃²⁻** ion occurs in **2** stages: *stage I*:

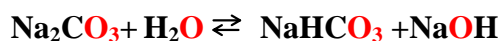


As **OH⁻** ions are products of this equilibrium reaction, the environment in a solution of a salt of weak acid and strong base is basic, hence, its **pH > 7**. *stage II*: $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$

Bicarbonate weak can be hydrolyzed further just with strong acid, as it can accept one more **H⁺** ion, therefore *stage II* dose not take a place with water: *stage II no reaction*: $\text{HCO}_3^- + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 + \text{OH}^-$

The second stage of hydrolysis, however, occurs to a very small extent. This can be explained by the following: **HCO₃⁻** 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⁻** ions from the **1st** stage in the solution. If we consider the influence of the extra **OH⁻** 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:



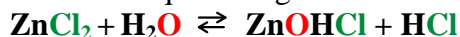
For this group of salts, the hydrolysis will be increased by adding acid to solution (consider the influence of **H⁺** on the equilibrium) and oppressed by adding base.

3) SALT OF A STRONG ACID AND A WEAK BASE, FOR EXAMPLE $ZnCl_2$.

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).



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 $Fe_2(CO_3)_3$,

