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HYDROLYSIS OF SALTS OF DISTINCT NATURE

ГИДРОЛИЗ СОЛЕЙ РАЗЛИЧНОЙ ПРИРОДЫ

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Abstract. The ionization theory attributes this phenomena to the interaction of water ions with the ions of dissolved salts, resulting the formation of an excess of hydrogen or hydroxyl ions. The concentration of hydrogen or hydroxyl ions in water is very low, they are in equilibrium with an immense number of unionized water molecules. When one of them is bound by the ions of the salt, the equilibrium is disturbed, causing new water molecules to ionize, which leads to accumulation an excess of quantities of the other ion, making the solution react acid or alkaline.

Any salt can be obtained by neutralization of acids by bases. It is natural to assume, therefore, that solutions, at least those witch are products of complete displacement of hydrogen in acids by metals, must react neutral. However, this assumption holds only for salts of strong acids and strong bases. Salts of weak acids and strong bases, or vice versa, of strong acids and weak bases, do not react neutral when dissolved in water.

The methods handbook covers the basic material on the subject ”Hydrolysis of salts of distinct nature” that may reasonably be required from Ordinary Level university standard for the trade 18.03.01 “Engineering chemistry”, in particular, when making a study in Ufa State Petroleum Technological University.

Аннотация. Теория ионизации объясняет явление гидролиза взаимодействием ионов воды с ионами растворенных солей, что приводит к образованию избытка ионов водорода или гидроксильных ионов. Концентрация водородных и гидроксильных ионов в воде очень невелика; они находятся в равновесии с огромным количеством неионизированных молекул воды. Когда один из них связывается с ионом соли, то равновесие нарушается, вызывая ионизацию новых молекул воды, что приводит к накоплению значительных количеств других ионов, что приводит либо к кислой, либо щелочной реакции среды.

Любую соль можно рассматривать как продукт реакции нейтрализации соответствующих кислоты и основания. Поэтому естественно предположить, что растворы, по крайней мере, в случае полного замещения водорода в кислотах ионами металла, должны иметь нейтральную среду. Однако это верно только для растворов солей, образованных сильными кислотами и сильными основаниями. А в растворах солей, образованных слабыми кислотами и сильными основаниями или слабыми кислотами и сильными основаниями среда не является нейтральной.

Данная работа представляет основной материал по теме «Гидролиз солей», содержащейся в государственном образовательном стандарте по направлению 18.03.01 «Химическая технология» для обучающихся, в частности, в Уфимском государственном нефтяном техническом университете.

Key words: hydrolysis, salt, water, equilibrium, displacement, acid, alkali

Ключевые слова: гидролиз, соль, вода, равновесие, смещение, кислотность, основность.

1 Definition of hydrolysis

When various substances are dissolved in water a chemical reaction of an exchange nature often occurs. Such processes are grouped under the heading of *hydrolysis*.

Hydrolysis* is, in general, any interaction between a substance and water in witch the constituent parts of substance exchange with composite parts of water. As an illustration, interaction of an ester with water leads to formation of corresponding acid and alcohol:

$$\underset{\text{methylethanoate}}{CH_3COOCH_3} + HOH \Leftrightarrow \underset{\text{ethanoate (acetic) acid}}{CH_3COOH} + \underset{\text{methanol}}{CH_3OH}$$

Another example – phosphorus trichloride PCl_3 reacts with water to form phosphorous and hydrochloric acids

$$PCl_3 + 3HOH \Leftrightarrow H_3PO_3 + 3HCl$$

In practice we especially often have to do with hydrolysis of salts.

2 Hydrolysis of salts

Hydrolysis of salts disturbs the ionic equilibrium of water that causes change in concentration of hydrogen and hydroxyl ions and leads to acidic or alkaline reaction of a solution.

As it is known, water is a weak electrolyte, ionizing slightly and reversibly as

$$HOH \Leftrightarrow H^+ + OH^- \quad **$$

If water is absolutely pure, the concentrations of hydrogen and hydroxyl ions are equal to each other and equal to 10^{-7} mole/l at temperature of 25 °C. The product of these concentrations is named ***the ion product for water Kw***

$$Kw = C_{(H^+)} \cdot C_{(OH^-)} = 10^{-14}$$

* The word "hydrolysis" means literally " decomposition by water".
** Actually the H+ is hydrated, forming chiefly H3O+ ion. But for convenience in writing we ignore the hydration of H+, just as we ignore the hydration of all the metal ions in the equations below.

To determine the acidity-alkalinity of a medium ***the hydrogen ion index pH*** and ***the hydroxyl ion index pOH*** are used

$$pH = -\lg C_{(H+)}$$

$$pOH = -\lg C_{(OH^-)}$$

It is easy to deduce from the above equations:

- neutral solution pH = 7;
- acidic solution pH < 7 (the higher acidity, the smaller it is);
- alkaline solution pH > 7 (the higher alkalinity, the larger it is).

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acidic medium pH=7
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pH=7 alkaline medium

It is obvious that $pH + pOH = 14$

There are various methods of measuring pH values. Qualitatively the reaction of a solution can be determined by means of special reagents called indicators, which change colour depending on concentration of hydrogen ion[*].

The most widely used indicators are litmus, phenolphthalein and methyl orange.

Table 1. Colours of indicators

Indicator	Reaction of solution		
	acid	neutral	alkaline
Methyl orange	red	orange	yellow
Phenolphthalein	colourless	pale crimson	crimson
Litmus	red	violet	blue

Any salt can be obtained by neutralization of acids by bases. It is natural to assume, therefore, that solutions, at least those witch are products of complete

[*] The hydrogen ion concentration is of great importance in very many cases. It has to be taken into account not only in chemical investigations, but also in a great variety of industrial processes as well as in study of phenomena in live organisms (see chapter 5).

displacement of hydrogen in acids by metals, must react neutral. However, this assumption holds only for salts of strong acids and strong bases. Salts of weak acids and strong bases, or vice versa, of strong acids and weak bases, do not react neutral when dissolved in water. As an example, a solution of zinc chloride $ZnCl_2$ reacts acid, indicating an excess of hydrogen ions as compared to hydroxyl ions $C_{(H^+)} > C_{(OH^-)}$.

In contrast to the previous example, a solution of potassium fluoride KF reacts alkaline which is characteristic of hydroxyl ion and the ratio of hydrogen and hydroxyl ions is $C_{(H^+)} < C_{(OH^-)}$.

The ionization theory attributes this phenomena to the interaction of water ions with the ions of dissolved salts, resulting the formation of an excess of hydrogen or hydroxyl ions. Although the concentration of hydrogen or hydroxyl ions is very low in water, they are in equilibrium with an immense number of unionized water molecules. When one of them is bound by the ions of the salt, the equilibrium is disturbed, causing new water molecules to ionize, which may lead to accumulation of considerable quantities of the other ion, making the solution react acid or alkaline.

Any reaction between the ions of a salt and the ions of water, attended with a change in the concentration of the latter, is called hydrolysis of the salt.

The chief cause of hydrolysis is the formation of slightly ionized substances (ions or molecules).

As it has been intimated above, hydrolysis proceed differently, depending on the strength (weakness) of the acid or base which went to form the salt.

The typical cases of hydrolysis are considered below.

First case. Salts of a weak acid and a strong base

Example – sodium acetate CH_3COONa. When dissolved in water, this salt, like all typical salts, ionizes completely into Na^+ and CH_3COO^- ions. Theoretically these ions could combine with the ions of water to form equivalent quantities of sodium hydroxide and acetic acid; but since sodium hydroxide is a strong base, sodium ion doesn't combine with the hydroxyl of water. On the other hand, acetic acid is a very weak electrolyte (weak acid) and, therefore, when CH_3COO^- ion encounters the hydrogen ion of water it immediately begins to combine with it to form CH_3COOH molecules. The decrease in the quantity of hydrogen ion in solution disturbs the equilibrium between the molecules of water and its ions, causing further ionization of water; fresh quantities of hydrogen ions form, which in their turn combine with CH_3COO^- ions into CH_3COOH molecules, etc.; at the same time, the amount of hydroxyl ions increases.

However, the reaction does not go very far in this direction. Since the ion product for water

$$K_{H_2O} = C_{(H^+)} \cdot C_{(OH^-)} = 10^{-14} \qquad (t=25^0C)$$

is a constant, the concentration of hydrogen ion decreases as hydroxyl ion accumulates, and is soon so low that they can no longer associate. The new equilibriums are established between water molecules and their ions, on the one hand, and between the CH_3COOH molecules and H^+ and CH_3COO^- ions, on the other, and the accumulation of hydroxyl ions ceases.

Thus, when sodium acetate interacts with water, the following reaction takes place

$$CH_3COO^- + HOH \Leftrightarrow CH_3COOH + OH^-$$

or in the molecular form

$$CH_3COONa + HOH \Leftrightarrow CH_3COOH + NaOH$$

Although the equilibrium of this reaction is greatly displaced to the left, the ionic equation shows that the reaction gives rise to a certain excess of hydroxyl ion in the solution, so that a solution reacts alkaline.

The reaction described involves hydrolysis of the salt of a weak unibasic acids. When salts formed by weak polybasic acids hydrolyze, the result is usually not the free acids, but acid salts, or more precisely, acid salt anions.

For instance, if sodium hydrocarbonate Na_2CO_3 is dissolved in water, the CO_3^{2-} ion, like the CH_3COO^- ion, combines with the hydrogen ion of water; however, the result is not molecules of weak carbonic acid H_2CO_3, but

HCO_3^- ion. The formation of predominantly HCO_3^- ion is due to the fact that it ionizes much less readily than H_2CO_3 molecules (see chapter 4 and appendix)

$$CO_3^{2-} + HOH \Leftrightarrow HCO_3^- + OH^-$$

or, in the molecular form

$$Na_2CO_3 + HOH \Leftrightarrow \underset{\text{acidic salt}}{NaHCO_3} + NaOH$$

As a result of this reaction an excess of hydroxyl ion appears in the solution; therefore, a solution of soda also reacts alkaline.

Thus, salts of a weak acid and a strong base:

- hydrolyze
- the anions of the salts react with water
- a solution is alkaline (pH > 7)

The other representative salts of this type are sodium sulfide Na_2S, potassium cyanide KCN, potassium fluoride KF, barium acetate $Ba(CH_3COOH)_2$ ...

Second case. Salt of a strong acid and a weak base

This case is analogous to the previous one, with the soul difference that there the cations of the salts combine with the hydroxyl ion of water, while anions remain free. The hydrolysis product is usually a basic salt or a basic salt cations. As a case in point, when cupric chloride $CuCl_2$, salt of the weak base $Cu(OH)_2$ is dissolved in water, Cu^{2+} ion, combining with hydroxyl ion, may form either $CuOH^+$ ions or $Cu(OH)_2$ molecules. Since the former ionize less readily than $Cu(OH)_2$ molecules, it predominates among the hydrolysis products of $CuCl_2$.

The reaction that takes place is represented by the equation

$$Cu^{2+} + HOH \Leftrightarrow CuOH^+ + H^+$$

or, in the molecular form

$$CuCl_2 + HOH \Leftrightarrow \underset{\text{basic salt}}{CuOHCl} + HCl$$

Thus, salts of a weak base and a strong acid:

- hydrolyze

- the cations of the salts react with water
- a solution is acid (pH<7)

The other representative salts of this type are iron sulfate $FeSO_4$, ammonia chloride NH_4Cl, zinc nitrate $Zn(NO_3)_2$ …

Third case. Salt of a weak acid and a weak base

In this case both the anion and the cation of the salt react with water. For instance, when ammonia fluorine NH_4F is dissolved in water, the following reactions ensue:

$$NH_4^+ + HOH \Leftrightarrow NH_4OH + H^+$$

$$F^- + HOH \Leftrightarrow HF + OH^-,$$

or, in the molecular form

$$NH_4F + HOH \Leftrightarrow NH_4OH + HF$$

As to reaction of solution of such salts, it depends on the relative strength (weakness) of the acids and bases the salts result from and usually is slightly acid or slightly basic. In this example, ionization constants are close in values: $K_{(NH_4OH)} = 1{,}74 \cdot 10^{-5}$; $K_{(HF)} = 6{,}76 \cdot 10^{-4}$ (see appendix), but ammonia hydroxide is weaker as electrolyte, consequently, the solution of this salt reacts slightly basic.

Thus, salts of a weak acid and a weak base:

- hydrolyze;
- both ions react with water;
- a medium is close to neutral ($pH \approx 7$).

The other typical salts of this type: ammonia cyanide NH_4CN, ammonia acetate CH_3COONH_4, aluminium acetate $Al\,(CH_3COO)_3$ …

And what about salts whose ions come from a strong acid and a strong base? Will the hydrolysis occur? If add a salt of this type to water, it does not affect the pH, because neither the Na^+ ion nor the Cl^- ion can react with H^+ ion or OH- ion of water. Sodium hydroxide and hydrochloric acid alike are strong electrolytes, they are completely ionized.

Let us try to set up the hydrolysis equation

$$NaCl + HOH \Leftrightarrow NaOH + HCl$$

in the ionic form

$$Na^{+} + Cl^{-} + HOH \Leftrightarrow Na^{+} + OH^{-} + H^{+} + Cl^{-}.$$

Sodium and chloride ions remained the same, and canceling the symbols of these ions, we get:

$$HOH \Leftrightarrow H^{+} + OH^{-},$$

the ionic equilibrium of water is not disturbed, the reaction of the solution is neutral.

Thus, salts of strong acids and strong bases

- do not hydrolyze
- a medium remain neutral (pH=7)

The other representative salts of this type are sodium nitrate $NaNO_3$, potassium bromide KBr, calcium chloride $CaCl_2$, …

It can be easily seen from the above equations that hydrolysis is the reverse of neutralization. This means that when solutions containing equivalent amounts of an acid and a base are mixed, the reaction is complete only if both interacting substances are strong electrolytes. If an acid or a base is weak, there will always be a certain amount of unionized acid or base molecules left in the solution after reactants are mixed, so that the solution will not react neutral.

Acid salts hydrolyze as well. In this case it must be taken into account that two simultaneous processes – hydrolysis and ionization of the salt proceed. By way of illustration, a solution of sodium hydrocarbonate $NaHCO_3$:

$$HCO_3^{-} + HOH \Leftrightarrow H_2CO_3 + OH^{-} \qquad \text{(hydrolysis)}$$

$$HCO_3^{-} \Leftrightarrow H^{+} + CO_3^{2-} \qquad \text{(ionization)}$$

It follows that reaction of the solution will be alkaline in the event that hydrolysis prevails, otherwise it is acid (see also chapter 3).

The other representative salts of this type are sodium hydrosulfide NaHS, potassium hydrophosphate K_2HPO_4, potassium dihydrophosphate KH_2PO_4 …

Special cases of hydrolysis

If an acid and a base, whose ions come to form a salt, are very weak, volatile or hard soluble, hydrolysis can be complete, i.e., the salt may decompose entirely. As a case in point, this happens, when aluminium sulfide interacts with water

$$Al_2S_3 + 6HOH \Leftrightarrow 2Al(OH)_3\downarrow + 3H_2S\uparrow$$

precipitate gas

Another example – interaction of aluminium chloride with sodium carbonate:

$$2AlCl_3 + 3Na_2CO_3 + 3HOH \Leftrightarrow 2Al(OH)_3\downarrow + 3CO_2 + 6NaCl$$

or, in the ionic form

$$2Al^{3+} + 3CO_3^{2-} + 3HOH \Leftrightarrow 2Al(OH)_3\downarrow + 3CO_2\uparrow$$

Other typical salts of this kind are, for example, zinc silicate $ZnSiO_3$, zinc sulfide ZnS, chromium sulfide Cr_2S_3, aluminium cyanide $Al(CN)_3$ The hydrolysis of all of them proceeds *irreversibly*. The products leave the reaction area, i.e. *the salts are nonexistent in aqueous solution.*

Irreversible process takes place as well, if some halogenides of amphoteric metals are subject to hydrolysis. Oxidation state of a metal in these compounds must be the highest and the type of chemical bond – covalent polar; for example, $SnCl_4$, PbF_4, $TiCl_4$ and others. Oxides of metals or oxyacids are generated:

$$SnCl_4 + 3HOH = H_2SnO_3\downarrow + 4HCl$$

$$TiCl_4 + 2HOH = TiO_2\downarrow + 4HCl$$

Some other groups of compounds – carbides, nitrides, phosphides, hydrides also react with water irreversibly:

$$CaC_2 + 2HOH = Ca(OH)_2\downarrow + C_2H_2$$

$$Al_4C_3 + 12HOH = 4Al(OH)_3\downarrow + 3CH_4$$

$$Mg_3N_2 + 6HOH = 3Mg(OH)_2\downarrow + 2NH_3$$

$$Ca_3P_2 + 6HOH = 3Ca(OH)_2\downarrow + 2PH_3$$

$$NaH + HOH = NaOH + H_2\uparrow$$

3 Quantitative characteristics of hydrolysis. Factors, effecting the hydrolysis

The degree of hydrolysis (**h**) – the ratio between the quantity of a salt hydrolyzed and the total quantity of the salt in the solution.

Values of **h** are different for distinct salt. As a case of illustration, the degrees of hydrolysis for the following salts in 0,1N solution at temperature of 25 °C are

Sodium acetate CH_3COONa……..0,08 per cent

Borax $Na_2B_4O_7$…………………...0,5 %

Potassium cyanide KCN…........… 1,2 %

Sodium carbonate Na_2CO_3 ……. 2,9 %

The difference depends on chemical nature of products of hydrolysis: the weaker electrolyte(s) (ion or molecule) formed as a product(s) the higher value of h.

The degree of hydrolysis of most salts is very low. That is the reason, in particular, why basic salts produced as the result of hydrolysis, though practically insoluble in water, nevertheless, usually remain in solution due to their insignificant concentration.

The hydrolysis constant (**Kh**). Any hydrolysis reaction is a reversible process, it is always at equilibrium, with extremely rapid formation of products and initial molecules of a salt and water. Therefore, the principles of chemical equilibrium apply, and we can write the equilibrium constant expression.

Let us demonstrate it by hydrolysis of potassium fluoride KF. It is the salt of the weak acid HF and the strong base KOH, and the proper chemical equation must be the following:

$$F^- + HOH \Leftrightarrow HF + OH^-$$

$$\text{and} \quad Keq = \frac{[HF][OH^-]}{[F^-][HOH]}$$

If we consider concentration of water to remain constant, we have

$$\text{Keq}\,[HOH] = \frac{[HF][OH^-]}{[F^-]} = \text{Kh}$$

Kh is called the hydrolysis constant. Unlike ionization constants, which are tabulated in extensive tables, values of Kh are never tabulated because they are easily calculated from values of ionization constants Ki. For instance, if we take the product of the expressions for Ki and Kh for hydrofluoric acid and fluoride ion, we get

$$\text{Ki} \cdot \text{Kh} = \frac{[H^+][F^-]}{[HF]} \cdot \frac{[HF][OH^-]}{[F^-]} = [H^+] \cdot [OH^-] = \text{Kw} = 10^{-14}$$

from which we may solve for Kh

$$\text{Kh} = \frac{Kw}{Ki}$$

The equation is a general expression, in which Ki is the ionization constant for the weak acid or weak base that is formed on hydrolysis:

for the hydrolysis of the fluorine ion F^- ($Ki_{HF} = 6{,}76 \cdot 10^{-4}$, see appendix) we get

$$\text{Kh} = \frac{Kw}{Ki} = 10^{-14}/(6{,}76 \cdot 10^{-4}) = 1{,}48 \cdot 10^{-11};$$

for the hydrolysis of the ammonium ion ($Ki_{NH_4OH} = 1{,}74 \cdot 10^{-5}$) we get

$$NH_4^+ + HOH \Leftrightarrow NH_4OH + H^+$$

$$\text{Kh} = \frac{Kw}{Ki} = 10^{-14}/(1{,}74 \cdot 10^{-5}) = 5{,}75 \cdot 10^{-10}$$

and so on.

It is obvious: the less value of Ki, that is the weaker an acid or a base, the higher value of Kh, the deeper hydrolysis proceeds.

We may use the hydrolysis constant to compute the pH of a salt solution, as illustrated in the following problems.

Problem: Calculate the pH of 0,05 M acetic acid CH_3COOH solution.

Solution: Write the chemical equation

$$\underset{0{,}05-x}{CH_3COO^-} + HOH \Leftrightarrow \underset{x}{CH_3COOH} + \underset{x}{OH^-}$$

Let us represent the small unknown concentration of OH^- by x. Since CH_3COOH is formed simultaneously with OH^- ion and in equal amounts, its concentration also is x. The unhydrolyzed concentration of CH_3COO^- is 0,05-x. Substitution of these values into Kh expression gives

$$Kh = \frac{Kw}{Ki} = 10^{-14}/(1,74 \cdot 10^{-5}) = 5,75 \cdot 10^{-10} = x^2/(0,05-x)$$

Neglecting x compared to 0,05, we have

$$x^2/0,05 = 5,75 \cdot 10^{-10}$$

$$x = [OH^-] = 5,36 \cdot 10^{-6} \text{ mole/l}$$

$$[H^+] = 10^{-14}/(5,36 \cdot 10^{-6}) = 1,86 \cdot 10^{-9} \text{ mole/l}$$

$$pH = -\lg(1,86 \cdot 10^{-9}) = 8,73$$

or

$$pOH = -\lg(5,36 \cdot 10^{-6}) = 5,27$$

$$pH = 14 - 5,27 = 8,73$$

Problem: If 10 ml of 0,25 M CH_3COOH are added to 40 ml of 0,0625 M NaOH, what is the pH of the resulting solution?

Solution:

$$CH_3COOH + NaOH \Leftrightarrow CH_3COONa + HOH$$

We must first find the number of moles of acid and base used, in order to determine whether there is an excess of either one.

Moles of NaOH edded = 0,01(l) · 0,25(mole/l) = 0,0025 mole

Moles of CH_3COOH edded = 0,04(l) · 0,0625(mole/l) = 0,0025 mole

Because equal numbers of moles of acid and base are added, only the salt is present; 0,0025 mole of CH_3COONa in 0,05 liter to give

$$[CH_3COO^-] = \frac{0,0025}{0,05} = 0,05 \text{ mole/l}$$

Presence of a salt as the only substance in solution reduces the problem to the hydrolysis equilibrium

$$CH_3COO^- + HOH \Leftrightarrow CH_3COOH + OH^-$$

just as the last problem. Solving in the same manner gives pH = 8,79.

The problem emphasizes the point that there is only the salt present (no excess acid or base), and the pH of the solution will be determined entirely by the hydrolysis of that salt.

Problem: The hydrolysis degree of ammonia nitrate NH_4NO_3 with concentration of 0,001 M is equal to $7{,}5 \cdot 10^{-4}$. Work out the pH of the solution.

Solution: For the reasons just given, the proper chemical equation to consider is

$$NH_4^+ + HOH \Leftrightarrow H^+ + NH_4OH$$

The equation states that one mole of ammonia ion reacted gives one mole of hydrogen ion H^+. Taking into account that quantity of ammonia ion hydrolyzed equals $C \cdot h$, we have

$$C \cdot h = [H^+] = 0{,}001 \cdot 7{,}5 \cdot 10^{-4} = 7{,}5 \cdot 10^{-7}\ M$$

and $$pH = -\lg(7{,}5 \cdot 10^{-7}) = 6{,}13$$

A definite relation exists between the hydrolysis constant and the degree of hydrolysis of a salt, making it possible to express either of these values in terms of the other. If *C* is the initial molar concentration of a salt and its degree of hydrolysis in a given solution is *h*, the concentration of each of the products at equilibrium will be $C \cdot h$ and the concentration of unhydrolyzed molecules $C - C \cdot h$.

As a case in point, the hydrolysis of potassium cyanide KCN (the salt of the weak hydrocyanic acid and the strong potassium hydroxide KOH):

$$\begin{array}{ccccccc} C-Ch & & & & Ch & & Ch \\ CN^- & + & HOH & \Leftrightarrow & HCN & + & OH^- \end{array}$$

Then the equation of the hydrolysis constant

$$Kh = \frac{[HCN][OH^-]}{[CN^-]}$$

will be $$Kh = \frac{Ch \cdot Ch}{C - Ch} = Ch^2/(1-h)$$

Neglecting h compared to 1, we have

$$Kh = Ch^2$$

and $$h = \sqrt{\frac{Kh}{C}}$$

On the other hand, $Kh = \frac{Kw}{Kiacid}$

and $h = \sqrt{\frac{Kw}{Kiacid \cdot C}}$

As for salts of weak bases and strong acids, the equations are analogous:

$$Kh = \frac{Kw}{Kibase}$$

$$h = \sqrt{\frac{Kw}{Kibase \cdot C}}$$

It can be concluded from the above equations:

1) the smaller values of ionization constants of an acid or a base (i.e., the weaker an acid or a base formed a salt), the grater a hydrolysis constant.

2) the lower concentration of a salt, the higher value of h. In other words, ***dilution of solutions of salts leads to more complete hydrolysis***, i.e., dilution shifts the equilibrium of hydrolysis to the right, towards decomposition of an initial salt in accordance with the Law of mass action.

As a case in point, the dependence between the degree of hydrolysis and the concentration for the reaction

$$Na_2CO_3 + HOH \Leftrightarrow NaHCO_3 + NaOH$$

at 25 °C is

c, mole/l	0,2	0,1	0,05	0,01	0,005	0,001
h, %	1,7	2,9	4,5	11,3	16	34

Let us describe quantitatively the hydrolysis of a salt formed by both weak electrolytes (an acid and a base) and deduce the relation between the hydrolysis constant and the degree of hydrolysis. For instance, the hydrolysis of ammonia acetate CH_3COONH_4. The hydrolysis equation in the ionic form is the following:

$$CH_3COO^- + NH_4^+ + HOH \Leftrightarrow CH_3COOH + NH_4OH$$

In accordance to the Law of mass action the equilibrium constant must be expressed

$$Keq = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+][H_2O]}$$

As it was mentioned above, the concentration of water may considered remain a constant, then

$$Kh = Keq \cdot [H_2O] = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

Let us multiply the numerator and denominator by the ion product of water:

$$Kh = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \frac{[H^+][OH^-]}{[H^+][OH^-]}$$

It should be taken into account that

$$\frac{[CH_3COOH]}{[CH_3COO^-][H^+]} = \frac{1}{Kiacid}$$

and $$\frac{[NH_4OH]}{[NH_4^+][OH^-]} = \frac{1}{Kibase},$$

Ki acid – ionization constant for acetic acid CH_3COOH

Ki base – ionization constant for ammonia hydroxide NH_4OH,

then $$Kh = \frac{Kw}{Kiacid \cdot Kibase}$$

According to this equation the hydrolysis of salts of weak acids and weak bases is the most clearly defined, because the hydrolysis constant depends inversely on *the product* of ionization constants of an acid and a base, therefore, its value is particularly high. Let us consider the reactions of the ions of ammonia acetate CH_3COONH_4 singly:

$$CH_3COO^- + HOH \Leftrightarrow CH_3COOH + OH^-$$

$$NH_4^+ + HOH \Leftrightarrow NH_4OH + H^+$$

The hydroxyl and hydrogen ions can not go together in large quantities. They combine to give water molecules, and it causes the shift of both equilibriums to the right. In other words, the two simultaneous processes strengthen each other.

Influence of temperature on hydrolysis. The effect of temperature upon the degree of hydrolysis can be explained in the following way: the degree of ionization of water (and evidently the ion product of water Kw) increases sharply with rising temperature (whereas for most other electrolytes it changes only slightly):

t, °C	10	18	25	30	40	50	100
Kw, 10^{-14}	0,36	0,74	1,00	1,47	2,92	5,60	74

Therefore, if solution is heated, the concentration of H^+ and OH^- ions increases substantially, and this raises the number of their collisions with ions of a salt and, consequently, the probability of formation of resultants, again in accordance with the Law of mass action. Thus, ***heating of a solution greatly increases the degree of hydrolysis***, i.e., shifts the equilibrium of hydrolysis to the right.

As an illustration, in the case of hydrolysis of chromium chloride $CrCl_3$

$$CrCl_3 + HOH \Leftrightarrow CrOHCl_2 + HCl$$

at C = 0,01 mole/l, the temperature dependence of the degree of hydrolysis is

t, °C	0	25	50	75	100
h, %	4,6	9,4	17	28	40

In addition, the effect of temperature and dilution of a solution upon the degree of hydrolysis follows from the Le Chatelier' Principle. Neutralization reaction is exothermic (gives out the heat to the surroundings), and hydrolysis, accordingly, is endothermic reaction (heat is taken into the system). Since a yield of endothermic process grows as the temperature elevates, the hydrolysis degree increases too. Dilution of a solution means increase in concentration of one of the initial substances; it always shifts the equilibrium to the right, towards the expenditure of them.

Hence, we get following general rules concerning the displacement of hydrolytic equilibrium. If it is desired to shift the equilibrium towards the maximum possible decomposition of a salt, dilute solutions should be used at high temperatures. Conversely, if the minimum possible hydrolysis is desired, strong solutions should be used at low temperatures. In the latter case, it is also very useful to add an excess of one of the hydrolysis products (acid or alkaline) to the solution. These directions are often found useful in chemical practice.

4 Stepwise hydrolysis

In the course of hydrolysis under the normal conditions molecules (ions) of a salt and water interact, in general, in the ratio of one per one. It is named the first step of hydrolysis. But if a salt is of a polybasic acid or a polyacid base, there is the next steps of hydrolysis are possible.

For example, the hydrolysis of sodium carbonate Na_2CO_3:

the first step in the ionic form

$$CO_3^{2-} + HOH \Leftrightarrow HCO_3^- + OH^-$$

or, in the molecular form

$$Na_2CO_3 + HOH \Leftrightarrow NaHCO_3 + NaOH$$

the second step in the ionic form

$$HCO_3^- + HOH \Leftrightarrow H_2CO_3 + OH^-$$

or, in the molecular form

$$NaHCO_3 + HOH \Leftrightarrow H_2CO_3 + NaOH$$

The proper equations for the hydrolysis constants are

$$Kh_1 = \frac{Kw}{Kiacid_2}$$

$$Kh_2 = \frac{Kw}{Kiacid_1}$$

Pay attention (**!**), there are namely $Ki\,acid_2$ and $K\,acid_1$ must be accordingly used in equations for the hydrolysis constants for *the first* Kh_1 and *the second* Kh_2 steps.

As a value of the first ionization constant for any electrolyte is always much higher then that of the next one, the first hydrolysis constant is always greater than that of the second one ($Kh_1 > Kh_2$), i.e., *the first step of hydrolysis is always more pronounced*. Moreover, the ions formed at the first step (in the example in hand – hydroxyl ions) promote displacement of the equilibrium to the left, that is to say, inhibit the second step of hydrolysis.

The hydrolysis of aluminium chloride $AlCl_3$ can theoretically proceed on *three* steps:

the first step $Al^{3+} + HOH \Leftrightarrow AlOH^{2+} + H^+$

$AlCl_3 + HOH \Leftrightarrow AlOHCl_2 + HCl$

the second step $AlOH^{2+} + HOH \Leftrightarrow Al(OH)_2^+ + H^+$

$AlOHCl_2 + HOH \Leftrightarrow Al(OH)_2Cl + HCl$

the third step $Al(OH)_2^+ + HOH \Leftrightarrow Al(OH)_3 + H^+$

$Al(OH)_2Cl + HOH \Leftrightarrow Al(OH)_3 + HCl$

The proper expressions for the hydrolysis constants on steps:

$$Kh_1 = \frac{Kw}{Kibase_3} \qquad Kh_2 = \frac{Kw}{Kibase_2} \qquad Kh_3 = \frac{Kw}{Kibase_1}$$

Problem: Calculate the degree of hydrolysis (h) and the pH of 0,1M solution of potassium phosphate K_3PO_4.

Solution: For this salt three steps of the hydrolysis are theoretically possible, so that the process corresponds to the ionic equations:

the first step $PO_4^{3-} + HOH \Leftrightarrow HPO_4^{2-} + OH^-$

the second step $HPO_4^{2-} + HOH \Leftrightarrow H_2PO_4^- + OH^-$

the third step $H_2PO_4^- + HOH \Leftrightarrow H_3PO_4 + OH^-$

The ionization constants for phosphorous acid H_3PO_4 (see appendix)

$Ki_1 = 5{,}89 \cdot 10^{-3}$ $Ki_2 = 6{,}17 \cdot 10^{-8}$ $Ki_3 = 4{,}79 \cdot 10^{-13}$

The degree of hydrolysis for the third and the second steps are negligible quantity. Then the magnitudes found are calculated from the equations

$$Kh = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = \frac{Kw}{Ki_3} = \frac{10^{-14}}{4{,}79 \cdot 10^{-13}}. = 0{,}021$$

$$h = \sqrt{\frac{Kw}{Ki_3 \cdot C}} = \sqrt{\frac{10^{-14}}{4{,}79 \cdot 10^{-13} \cdot 0{,}1}} = 0{,}457 \ (45{,}7\ \%)$$

It follows that $[OH^-] = C \cdot h = 0{,}1 \cdot 0{,}457 = 4{,}57 \cdot 10^{-2}$

$pOH = -\lg [OH^-] = -\lg (4{,}57 \cdot 10^{-2}) = 1{,}48$

$$pH = 14 - 1{,}48 = 12{,}52$$

Problem: What is the reaction of a solution of the acid salt: a) sodium hydrocarbonate $NaHCO_3$; b) sodium hydrosulfite $NaHSO_3$? Assume the concentrations of the salts to be equal.

Solution:

a) It needs to be taken into account the two simultaneous processes

$$HCO_3^- + HOH \Leftrightarrow H_2CO_3 + OH^- \quad \text{(hydrolysis)}$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad \text{(ionization)}$$

The reaction of the solution depends on the ratio of the hydrolysis constant of the salt and the corresponding ionization constant.

$$Kh = \frac{Kw}{Ki_1} = \frac{10^{-14}}{4{,}5 \cdot 10^{-7}} = 2{,}22 \cdot 10^{-8}$$

(we must use namely the first ionization constant)

$Ki_2 = 4{,}68 \cdot 10^{-11}$ (see appendix)

The hydrolysis constant of hydrocarbonate ion HCO_3^- is an excess of the ionization constant, therefore, the solution reacts slightly alkaline;

b) Solving in the same way, we get

$$HSO_3^- + HOH \Leftrightarrow H_2SO_3 + OH^- \quad \text{(hydrolysis)}$$

$$HSO_3^- \Leftrightarrow H^+ + SO_3^{2-} \quad \text{(ionization)}$$

$$Kh = \frac{Kw}{Ki_1} = \frac{10^{-14}}{1{,}74 \cdot 10^{-2}} = 5{,}75 \cdot 10^{-13}$$

$Ki_2 = 6{,}17 \cdot 10^{-8}$ (see appendix)

In contrast to the previous case, $Ki_2 > Kh$, therefore, the solution reacts slightly acid.

Table 2. Ionization constants at 25 ºC

Electrolyte		Ki
Weak acids:		
Acetic acid	CH_3COOH	$1,74\cdot10^{-5}$
Boric acid	H_3BO_3	K_1 $5,89\cdot10^{-10}$
Carbonic acid	H_2CO_3	K_1 $4,50\cdot10^{-7}$ K_2 $4,68\cdot10^{-11}$
Formic acid	HCOOH	$1,7\cdot10^{-4}$
Hydrocyanic acid	HCN	$6,31\cdot10^{-10}$
Hydrofluoric	HF	$6,76\cdot10^{-4}$
Hydrosulfuric acid	H_2S	K_1 $1,00\cdot10^{-7}$ K_2 $1,20\cdot10^{-13}$
Nitrous acid	HNO_2	$5,13.10^{-4}$
Oxalic acid	$H_2C_2O_4$	K_1 $5,62\cdot10^{-2}$ K_2 $5,25\cdot10^{-5}$
Phosphoric acid	H_3PO_4	K_1 $5,89\cdot10^{-3}$ K_2 $6,17\cdot10^{-8}$ K_3 $4,79\cdot10^{-13}$
Phosphorous acid	H_3PO_3	K_1 $1,00\cdot10^{-2}$
Silicic acid	H_2SiO_3	K_1 $2,2.10^{-2}$ K_2 $1,6\cdot10^{-12}$
Sulfurous acid	H_2SO_3	K_1 $1,74\cdot10^{-2}$ K_2 $6,17\cdot10^{-8}$
Weak bases:		
Ammonia	NH_4OH	$1,74\cdot10^{-5}$
Methylamine	CH_3NH_2	$4,59\cdot10^{-4}$
Ethylamine	$C_2H_5NH_2$	$5,00\cdot10^{-4}$
Dimethylamine	$(CH_3)_2NH$	$5,81\cdot10^{-4}$
Trimethylamine	$(CH_3)_3N$	$6,11\cdot10^{-5}$
Aniline	$C_6H_5NH_2$	$4,17\cdot10^{-10}$
Pyridine	C_5H_5N	$1,48\cdot10^{-9}$

5 Importance of hydrolysis in nature

Besides its purely chemical and industrial applications, hydrolysis is a wide spread and of great importance in animate nature. Hydrolysis of proteins, fats, hydrocarbons is indispensable step to take up the nutritive materials by living organisms. Hydrolysis of adenosinetriphosphate (ATP) is the source of energy in living cells.

The biological role of certain salts in blood (sodium hydrocarbonate $NaHCO_3$ and sodium hydrophosphate Na_2HPO_4) chiefly consists in maintaining a definite concentration of hydrogen ions. This is accomplished by a shift in hydrolysis equilibrium according to the equations:

$$HCO_3^- + HOH \Leftrightarrow H_2CO_3 + OH^-$$

$$HPO_4^{2-} + HOH \Leftrightarrow H_2PO_4^- + OH^-$$

If an excess of H^+ ions occurs in the blood for some reason or other these ions are bound by hydroxyl ions, and the above equilibria shift to the right, while if there is an excess of hydroxyl ions, the equilibria shift to the left. Owing to this, the pH of the blood in a normal person fluctuates only slightly about the mean value of 7.4, which is essential for normal functioning of the organism.

The biological effect of the hydrogen ion concentration also extends to plant organisms. For most successful growth, each variety of land plant requires a definite concentration of hydrogen ions in the soil. As a case in point, potatoes grow best of all on slightly acid soils (pH = 5), lucerne – on slightly alkaline soils (pH = 8), and wheat - on the neutral soils (pH = 7). Marine plants are more handicapped in this respect, since the concentration of hydrogen ions in sea water is maintained at an approximately constant level of pH = 7.9 – 8.4, due to the hydrolysis of carbonates.

6 Tasks and exercises

1. In which of the solutions phenolphthalein becomes crimson?

The solutions given: a) $(NH_4)_2SO_4$; b) $ZnSO_4$; c) KF; d) NaBr.

Set up the proper equations in the ionic and in the molecular form. Estimate the pH of the solutions.

2. In which of the solutions litmus is red?

The solutions given: a) $Bi(NO_3)_3$; b) $Ca(NO_3)_2$; c) $NaHSO_3$

Is the pH of this solution more or less than seven?

Set up the proper equations in the ionic and in the molecular form.

3. In which of the solutions methyl orange is red?

The solutions given: a) $CoCl_2$; b) $SrSO_4$; c) NaCN; d) $LiClO_4$

Set up the proper equations in the ionic and in the molecular form.

Is the pH of this solution more or less than seven?

4. In which of the solutions litmus is blue?

The solutions given: a) $FeCl_3$; b) MgI_2; c) K_3PO_4; d) BaI_2

Set up the proper equations in the ionic and in the molecular form.

Is the pH of this solution more or less than seven?

5. The medium will be alkaline in the following solutions:

a) LiBr; b) K_2S; c) KCl d) $Fe(NO_3)_2$; c) KI d) CH_3COONa

Write the equations in the ionic and in the molecular form.

6. The highest concentration of hydrogen ion H^+ is in a solution of the salt:

a) NaI; b) $Ca(NO_3)_2$; c) K_2CO_3; d) $CuSO_4$.

7. The hydrolysis of the salt leads to the acidic medium:

a) CH_3COOK; b) KCN; c) $BaBr_2$ d) $Cr_2(SO_4)_3$; e) Na_3PO_4

Write the equations in the ionic and in the molecular form.

8. Which of the salts hydrolyze: a) LiCl; b) $NaNO_3$; c) KNO_2; d) MgI_2 ?

Write the equations in the ionic and in the molecular form.

Which of the solution has the pH more than seven?

9. Compare the pH of the solutions without calculations:

a) CH_3COONa and HCOONa; b) Na_2CO_3 and Na_2SO_3;

c) HCOONa and $HCOONH_4$.

Explain your answer. Set up the proper equations.

10. Compare the pH of the solutions without calculations:

a) $NaClO_4$ and NaClO; b) K_2S and K_2Se; c) Na_2CO_3 and $NaHCO_3$.

Prove your answer. Set up the proper equations.

11. Compare the pH of the solutions of Na_3PO_4 and NaH_2PO_4 without calculations.

Explain your answer with the help of the proper chemical equations.

12. Compare the pH of the solutions without calculations: a) $(NH_4)_2SO_4$ and $(NH_4)_2SO_3$; b) $AlCl_3$ and $AlOHCl_2$; c) $CoCl_2$ and CoOHCl.

Prove your answer. Set up the proper equations.

13. Compare the pH of the solutions without calculations:

a) $ZnCl_2$ and $MgCl_2$; b) NaI and NaF; c) $(NH_4)_2SO_4$ and $HCOONH_4$.

Set up the proper equations in the ionic and in the molecular form.

14. Which of the salt causes the most alkaline medium?

The solutions given: a) K_2CO_3; b) KCN; c) CH_3COONa

Prove your reasoning.

15. Which of the salt causes the most alkaline medium?

The solutions given: a) $NaNO_3$; b) $Mg(NO_3)_2$; c) $Fe(NO_3)_2$

Prove your answer. Set up the proper equations.

16. Complete the equations in the ionic and the molecular form:

a) $FeCl_3 + (NH_4)_2S + HOH \Leftrightarrow$

b) $AlCl_3 + Na_2CO_3 + HOH \Leftrightarrow$

17. Complete the equations in the ionic and the molecular form:

a) $Cr_2(SO_4)_3 + K_2S + HOH \Leftrightarrow$

b) $Na_2SiO_3 + NH_4Cl + HOH \Leftrightarrow$

18. Complete the equations in the ionic and the molecular form:

a) $CuSO_4 + Na_2CO_3 + HOH \Leftrightarrow [Cu(OH)]_2CO_3 + \ldots$

b) $AlCl_3 + CH_3COONa + HOH \Leftrightarrow Al(OH)(CH_3COO)_2 + \ldots$

19. When solutions of $Cr(NO_3)_3$ and Na_2S are mixed a precipitate occurs and a gas liberates.

Set up the hydrolysis equations in the ionic and in the molecular form.

20. When solutions of $Al_2(SO_4)_3$ and $(NH_4)_2S$ are mixed a precipitate falls down and gases give off.

Set up the hydrolysis equations in the ionic and in the molecular form.

21. What needs to be done to shift the equilibriums to the right?

a) CO_3^{2-} + HOH ⇔ HCO_3^- + OH^-

b) Cu^{2+} + HOH ⇔ $CuOH^+$ + H^+

Explain your answer.

22. Why the iron hydroxide, but not iron carbonate is formed, if a solution of soda is added to a solution of iron chloride. Explain your answer by the proper chemical reactions.

23. What one can go about to shift the equilibriums to the right?

a) Fe^{2+} + HOH ⇔ $FeOH^+$ + H^+

b) Se^{2-} + HOH ⇔ HSe^- + OH^-

Explain your answer.

24. Give all possible ways to shift an equilibrium of hydrolysis

a) to the right; b) to the left

Provide support for your answer.

25. In what direction the equilibrium of the hydrolysis of NaCN will be displaced, if the following substance is added to the solution:

a) an alkali; b) an acid; c) ammonia chloride ?

Provide support for your answer.

26. In what direction the equilibrium of the hydrolysis of NH_4Cl will be shifted, if the following substance is added to the solution:

a) an alkali; b) an acid; c) potassium fluoride?

Provide support for your answer.

27. Is an acid or a base must be added to a solution of the following salt to repress the hydrolysis:

a) Na_2S; b) HCOOLi; c) $Fe(NO_3)_3$?

Provide support for your answer.

28. The hydrolysis is more pronounced in a solution of the salt:

a) NaCN or CH_3COONa; b) $MgCl_2$ or $ZnCl_2$; c) K_2CO_3 or K_2SO_3 ?

Compare the pH in each pair of the solutions.

Prove your answer. Set up the proper equations.

29. Why the reaction of a solution of NaH_2PO_4 is weak acid, and that of Na_3PO_4 is strong alkaline?

Explain the fact; set up the proper equations.

30. Why the reaction of a solution of $NaHCO_3$ is weak alkaline, and that of $NaHSO_3$ is weak acid?

Explain the fact; set up the proper equations.

31. Estimate the reaction (pH) of the following aqueous solutions of salts:

a) Na_3PO_4; b) Na_2HPO_4 c) NaH_2PO_4

Set up the proper equations.

32. Calculate the hydrolysis constant Kh, the ionization degree, the pH of a solution of CH_3COONa with concentration of 0,1 M.

33. Calculate the hydrolysis constant Kh, the ionization degree, the pH of a solution of K_2S with concentration of 0,01 M.

34. The hydrolysis degree for ammonia nitrate in a solution with concentration of 0,001 M is equal to $7{,}5 \cdot 10^{-4}$. Find the pH of the solution (when solving, do not use a tabulated value for the ionization constant).

35. The hydrolysis degree for sodium carbonate in a solution with concentration of 0,1 N is equal to $3 \cdot 10^{-2}$. Calculate the pH (when solving, do not use a tabulated value for the ionization constant).

36. What is the pH of a solution of sodium sulfite with concentration of 10^{-2} M?

37. Calculate the pH of a solution of ammonia chloride with concentration of 0,05 M.

38. Find the pH of a solution of potassium fluoride with concentration of 0,02 M.

39. Calculate the hydrolysis constant for sodium sulfide, the hydrolysis degree for the salt in a solution with concentration of 0,2 N. What is the pH of the solution?

40. Calculate the hydrolysis constant, the hydrolysis degree for potassium phosphate in solutions with concentration of: a) 2,4 M; b) 0,1 N. Find the pH of the solutions.

41. The hydrolysis degree for a solution of sodium cyanide equals 0,01; the pH equals 11. Compute the molarity of the solution (when solving, do not use a tabulated value for the ionization constant.)

42. Calculate the concentration of sodium $C_6H_5NH_3Cl$ in a solution, whose pH is equal to 10 and the degree of hydrolysis equals $7{,}5 \cdot 10^{-4}$ (when solving, do not use a tabulated value for the ionization constant).

43. The pH of a solution of potassium fluoride equals 7,74. Calculate the concentration of the salt.

44. The pH of a solution of ammonia chloride equals 5,28. What is the molarity of the solution?

45. The pH of the following solutions is determined experimentally by pH meter or colour comparison with indicators. Calculate the concentration of the salt:

a) CH_3NH_3Cl has the pH of 5,83

b) HCOOK has the pH of 8,38

46. The pH of the following solutions is determined experimentally by pH meter or colour comparison with indicators. Calculate the concentration of the salt:

a) C_5H_5NHCl has the pH of 3,58

b) HCOOLi has the pH of 7,89

47. By pH meter or by colour comparison with indicators, the solutions are found to have the pH values given. Calculate the concentration of the salt:

a) KCN has the pH of 10,59

b) $(CH_3)_2NH_2Cl$ has the pH of 6,38

48. By pH meter or by colour comparison with indicators, the solutions are found to have the pH values given. Calculate the concentration of the salt:

a) $C_6H_5NH_3Cl$ has the pH of 2,81

b) CH_3COONa has the pH of 8,88

49. Calculate the pH of the solutions resulting from the following solutions mixed together:

a) 35 ml of 0,2 M HCN + 140 ml of 0,05 M LiOH

b) 30 ml of 0,1 M CH_3COOH + 10 ml of 0,3 M NaOH

50. Calculate the pH of the solutions resulting from the following solutions mixed together:

a) 40 ml of 0,1 M HCOOH + 20 ml of 0,2 M KOH

b) 25 ml of 0,1 M HCl + 50 ml of 0,05 M NH_3

51. Calculate the pH of the solutions resulting from the following solutions mixed together:

a) 20 ml of 0,25 M H_3BO_3 + 10 ml of 0,5 M KOH

b) 50 ml of 0,2 M HCN + 40 ml of 0,25 M LiOH

52. Calculate the hydrolysis constant Kh, the ionization degree, the pH of a solution of K_2S with concentration of 0,01 M. Assume that hydrolysis practically proceeds on the first step only.

53. Find the pH of a solution of K_3PO_4 with concentration of 0,1 M. Assume that hydrolysis practically proceeds on the first step only.

54. Find the pH of a solution of Na_2SO_3 with concentration of 0,1 M. Assume that hydrolysis practically proceeds on the first step only.

55. Calculate the hydrolysis constant Kh, the ionization degree, the pH of a solution of Na_2CO_3 with concentration of 0,01 M. Assume that hydrolysis practically proceeds on the first step only.

56. Calculate the concentration of K_3PO_4 in a solution, if the pH of the solution is 12, 52. Assume that hydrolysis practically proceeds on the first step only.

57. If a sample of zinc is added to a solution of iron chloride, release of a gas can be observed. Explain the phenomenon. Provide support for your reasoning by the proper chemical equations.

58. If a sample of aluminium is added to a solution of copper sulfate, liberation of a gas occurs. Explain the phenomenon. Provide support for your reasoning by the proper chemical equations.

59. If a sample of beryllium is added to a solution of sodium phosphate, release of a gas can be observed. Explain the phenomenon. Provide support for your reasoning by the proper chemical equations.

60. If a sample of tin is added to a solution of potassium cyanide, release of a gas can be observed. Explain the phenomenon. Provide support for your reasoning by the proper chemical equations.

61. Do the hydrolysis of aluminium acetate and aluminium chloride differ from each other? Substantiate your answer by the proper equations.

62. Do the hydrolysis of aluminium chloride and aluminium fluoride differ from each other? Provide support for you view.

63. Which of the solutions reacts more acid: $SnCl_2$ or $SnCl_4$? Lay the question to rest on a basis of comparison between oxidation states of tin.

64. Which of the salts hydrolysis irreversible: PbF_2 or PbF_4? Tackle the question on a basis of comparison between oxidation states of plumbum.

Table 3. Homework

Variant	Number of task			
1	1	17	33	49
2	2	18	34	50
3	3	19	35	51
4	4	20	36	52
5	5	21	37	53
6	6	22	38	54
7	7	23	39	55
8	8	24	40	56
9	9	25	41	57
10	10	26	42	58
11	11	27	43	59
12	12	28	44	60
13	13	29	45	61
14	14	30	46	62
15	15	31	47	63
16	16	32	48	64

7 Selftest

1. The reversible hydrolysis of salts:

a) is always attended with liberation of gases and occurrence of precipitates;

b) must occur with the transfer of electrons from one particles to others;

c) is attended with heat evolution;

d) is an exchange reaction of a salt with water;

e) proceeds without a change of oxidation states of atoms

2. The salt hydrolyzes by cation:

1) Na_2SO_3; 2) $ZnCl_2$; 3) $Ca(NO_3)_2$; 4) LiF; 5) BaI_2

3. The salt hydrolyzes by cation:

1) Na_2CrO_4; 2) $KHCO_3$; 3) $SrCl_2$; 4) $CuSO_4$; 5) CsI

4. The salt hydrolyzes by cation:

1) $FeCl_2$; 2) NaBr; 3) RbI; 4) KNO_3; 5) Li_2S

5. The salt hydrolyzes by cation:

1) Li_2SO_3; 2) K_3PO_4; 3) CH_3COONa; 4) $CaBr_2$; 5) NH_4Cl

6. The salt hydrolyzes by anion:

1) K_2CO_3; 2) $Fe(NO_3)_3$; 3) $MgCl_2$; 4) $(NH_4)_2SO_4$; 5) LiBr

7. The salt hydrolyzes by anion:

1) KBr; 2) $NaNO_3$; 3) Na_3PO_4; 4) $MgSO_4$; 5) NH_4I

8. The salt hydrolyzes by anion:

1)$AgNO_3$; 2) CH_3COOK; 3) $AlCl_3$; 4) $NaClO_4$; 5) $MnSO_4$

9. The salt hydrolyzes by anion:

1) $NiBr_2$; 2) $BeSO_4$; 3) $Cu(NO_3)_2$; 4) Na_2S; 5) KI

10. The salt doesn’t hydrolyze:

1) $FeSO_4$; 2) $CuBr_2$; 3) $Pb(NO_3)_2$; 4) $KMnO_4$; 5) $CrCl_3$

11. The salt doesn’t hydrolyze:

1) NaCl; 2) $AlCl_3$; 3) $Bi(NO_3)_3$; 4) $SnSO_4$; K_2CO_3

12. The salt doesn’t hydrolyze:

1) $BiCl_3$; 2) $FeSO_4$; 3) $Pb(NO_3)_2$; 4) $Al_2(SO_4)_3$; 5) $Ca(NO_3)_2$

13. The following group of compounds doesn’t hydrolyze

1) oxides; 2) nitrides; 3) phosphides; 4) hydrides

14. The following salts hydrolyze only by cation:

1) Na_2SO_4, $K_2Cr_2O_7$, $Ba(NO_3)_2$; 2) $CuCl_2$, NH_4Br, $Fe_2(SO_4)_3$;

3) LiI, KClO, Na_2S; 4) KF, $NaHCO_3$, $CaCl_2$; 5) $NaNO_2$, $KClO_3$, KI

15. The following salts hydrolyze only by anion:

1) Na_2SO_4, $Al_2(SO_4)_3$, KNO_3; 2) $CuCl_2$, NH_4Br, $FeSO_4$;

3) K_2CO_3, Na_2HPO_4, As_2S_3; 4) KCN, $NaHCO_3$, CH_3COOLi;

5) $KClO_4$, NaH_2PO_4, $CuSO_4$

16. The salt doesn't hydrolyze:

1) $Al_2(SO_4)_3$; 2) $Ba(NO_3)_2$; 3) Na_2SO_3; 4) NH_4Br; 5) Na_3PO_4

17. Zinc will be dissolved when added to a solution of:

1) NaCl; 2) $BaCl_2$; 3) $AlCl_3$; 4) KCl

18. Tin will be dissolved when added to a solution of:

1) KCN; 2) K_2SO_4; 3) KNO_3; 4) $KClO_4$

19. A gas is given off owing to mutual strengthening of hydrolysis at joint presence of the following salts:

1) $Fe_2(SO_4)_3$ and K_2CO_3; 2) $Cr(NO_3)_3$ and K_2SO_3; 3) Na_2SO_3 and KCl
4) K_2CO_3 and Li_2SO_4; 5) $Cu(NO_3)_3$ and K_2CO_3; 6) $AlCl_3$ and Na_2S

20. In aqueous solution of potassium sulfide concentration of ions will be the greatest

1) HS^-, 2) S^{2-}, 3) H^+, 4) OH^-

21. In aqueous solution of aluminium nitrate concentration of ions will be the greatest

1) $Al(OH)_2^+$, 2) $AlOH^{2+}$, 3) H^+, 4) OH^-, 5) Al^{3+}

22. A gas is released if solutions of chromium (3+) chloride and one of the following salt are mixed:

1) barium hydrosulfate; 2) potassium hydrosilicate;
3) sodium dihydrophosphate; 4) ammonia hydrosulfide;

23. The hydrolysis of sodium nitrite can be repressed by addition:

1) $NaNO_3$; 2) NaOH; 3) H_2O; 4) HCl; 5) Na_2SO_4

24. As a result of mutual strengthening of hydrolysis of magnesium nitrate and sodium carbonate one of the product is:

1) $Mg(OH)_2$; 2) $MgCO_3$; 3) $(MgOH)_2CO_3$; 4) MgO; 5) $NaNO_3$
(assume that the solution of sodium carbonate is added slowly)

25. To strengthen the hydrolysis of iron chloride it needs:

1) to increase a solution temperature; 2) to lower a solution temperature;

3) to add hydrochloric acid; 4) to add sodium chloride

5) to add water

8 Laboratory work “Hydrolysis of salt”

Experiment 1. Determining the pH of the solutions of acids and bases

The solutions given: HCl, CH_3COOH, NaOH, NH_4OH.

The pH is going to be determined by colour comparison with indicator.

Place some strips of universal indicator and touch each of them with one drop of the solutions studied. Compare at once the colouring in reference to scale of indicator. Which of the electrolytes are strong and which of them are weak?

Write the equations of ionization processes.

Draw a conclusion.

Experiment 2. Hydrolysis of salts of different nature.

The solutions given: $MgCl_2$, $CuSO_4$, NaCl, Na_2CO_3

Place some strips of the universal indicator and apply on one drop of the solutions studied. At once compare the colouring in reference to scale of indicator.

Set up the proper ionic and molecular equations.

Draw a conclusion.

Experiment 3. Influence of temperature on hydrolysis

Instill 5 drops of iron chloride $FeCl_3$ solution and 5 drops of acetic acid CH_3COOH solution into a test-tube. Heat the mixture to the boiling point. Observe the precipitation of mono- and dibasic acetic salts of iron. Set up the equations of hydrolysis of iron acetate $Fe(CH_3COOH)_3$.

Draw a conclusion.

Experiment 4. Effect of dilution on hydrolysis

Place 2 drops of antimony chloride $SbCl_3$ solution into a test-tube, then add 3-4 drops of water. Observe the precipitation of dibasic salt of antimony $Sb(OH)_2Cl$, which readily gives off a water molecule. Write the hydrolysis reaction resulting in chloride antimonit SbOCl as a product. (Keep the precipitate for the next experiment.)

Draw a conclusion.

Experiment 5. Reversibility of hydrolysis

1) Pour enough amount of a solution of hydrochloric acid to the solution with the precipitate of SbOCl (from the previous experiment) up to complete dissolution. Then add some drops of water. Explain the phenomena observed.

2) Instill about 10 drops of 0,5N solution of sodium acetate CH_3COONa and 1 drop of phenolphthalein into a test tube. Heat the liquid to the boiling point, then cool it. Write the hydrolysis equation. Explain the phenomena. Draw an inference.

Experiment 6. Complete hydrolysis

Instill on 5 drops of a salt of aluminium into two test tubes and add on 5 drops in each. Observe the precipitate falls down, and carbon dioxide CO_2 releases. Assure himself that the precipitate is aluminium hydroxide. Treat it with diluted hydrochloric acid in one of the test tube and with sodium hydroxide in another. Observe the dissolution of the precipitate in both test tubes. Set up the proper chemical equations.

Draw an inference.

Conclusions

Salts of a weak acid and a strong base:

- hydrolyze
- the anions of the salts react with water
- a solution is alkaline ($pH > 7$)

Salts of a weak base and a strong acid:

- hydrolyze
- the cations of the salts react with water
- a solution is acid (pH<7)

Salts of a weak acid and a weak base:

- hydrolyze;
- both ions react with water;
- a medium is close to neutral (pH$\approx$7).

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