Inorganic Chemistry Department
General and Inorganic Chemistry

Hydrolysis of Salts

In specialty 226 Pharmacy, industry pharmacy

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Plan

1. **The mechanism of hydrolysis**
2. **Four possible types of salts**
3. **The Degree of Hydrolysis and the Hydrolysis Constant**
4. **Ostwald's dilution low**
5. **Hydrolysis of Acidic Salts**
6. **Co-hydrolysis**
7. **Hydrolysis of Compounds with Covalent Bonds**

Actuality of theme

The process of interaction of salts with water, which is accompanied by the formation of a low soluble electrolyte, is an important topic for studying the behavior of drugs in an aqueous solution, as well as the conditions for their storage.

Aim: Acquaint students with the behavior of salts in aqueous solution, which leads to a change in pH of the medium.

Specific goals:

- Classify electrolytes by degree of dissociation.
- Use tabular data of Kh and pH of the salts medium.
- Displacement of the equilibrium of hydrolysis.

Hydrolysis of simple substances, esters, carbohydrates and proteins.

Bibliographical Guidance

General and inorganic chemistry: Textbook for students of higher schools Ye.Ya.Levitin, I.O.Vedernikova.– Kharkiv:Publishing House of NUPH :Golden Pages, 2009. – 360 p.

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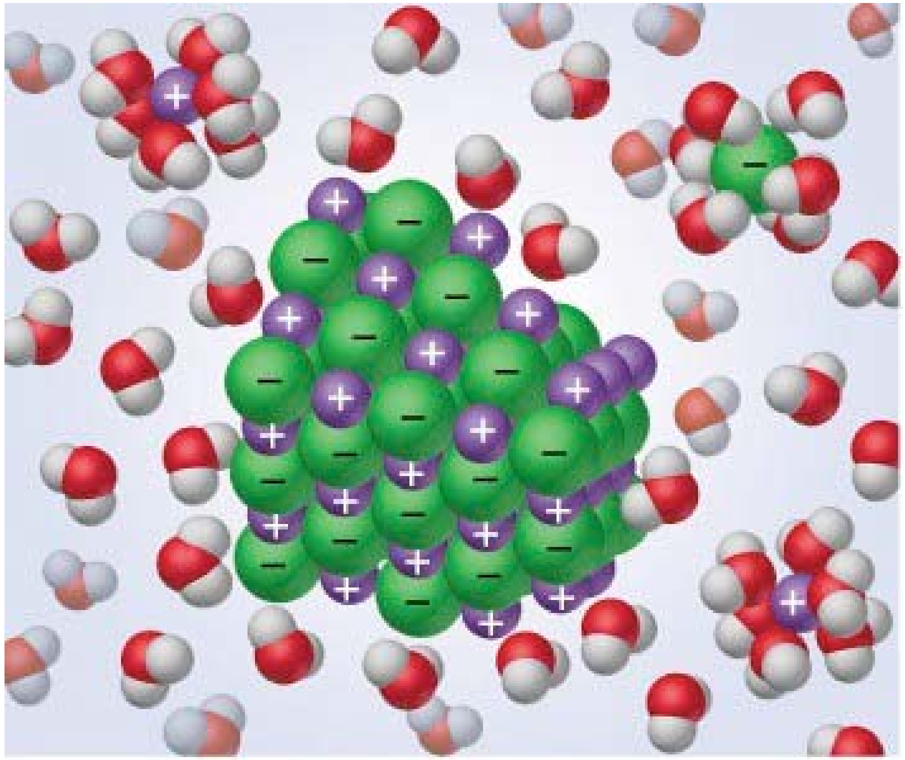
Lecture № Date

Hydrolysis of Salts

The hydrolysis is the reaction of ions exchange of a salt with water molecules, which leads to the formation of a weak electrolyte and change the pH of the solution.



$NaCN_{(s)} \rightarrow Na^{+}_{(aq)} + CN^{-}_{(aq)}$

The mechanism of hydrolysis

Note that water is polar, causing O to be slightly negative and H to be slightly positive. The positively charged of sodium ion is attracted to the O in water and the negatively charged cyanide ion is attracted to the H in water.

In aqueous solution, cations and anions are in the form of hydrated ions.

There are four possible types of salts:

1. If the salt is formed from a *strong* base and *strong* acid, then the salt solution is neutral, pH = 7. Cations of strong bases and anions of strong acids cannot polarize the water molecule.

KCl, KNO_3, Na_2SO_4, KI, $Ca(NO_3)_2$

2. If the salt is formed from a *strong* acid and *weak* base, the bonds in the salt solution will break apart and becomes **acidic**. NH_4Cl, $CuSO_4$, $ZnCl_2$, $FeSO_4$, $SnCl_2$, $Al_2(SO_4)_3$, $CrCl_3$

$$K_h = K_W/K_b$$

Salt hydrolyzes by cation, pH < 7.

When NH_4Cl is added to water, the pH falls below 7. This means that $[H^+]$ in the solution increases and $[OH^-]$ decreases. Cl^- cannot act as an acid. However, as we have already seen, a reaction does occur between NH_4^+ and H_2O.

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

$$NH_4^+ + HOH \leftrightarrows NH_3 \cdot H_2O + H^+$$

$$NH_4Cl + H_2O \leftrightarrows NH_3 \cdot H_2O + HCl,$$

pH < 7, acidic reaction

<u>Conclusion:</u> hydrolysis of such salts goes on cation of the weak basis, and reaction of a water solution of salt – acid.

3. The salt is formed from a *strong* base and *weak* acid, the salt solution is **basic**, pH > 7. Cations of strong bases cannot polarize the water molecule.

$NaCH_3COO$, KCN, Na_2CO_3

$NaCH_3COO \rightarrow Na^+ + CH_3COO^-$

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

$NaCH_3COO + H_2O \leftrightarrows CH_3COOH + NaOH$

pH > 7, basic reaction

4. If the salt is formed from a *weak* base and *weak* acid, will hydrolyze, but the acidity or basicity depends on the equilibrium constants of K_a and K_b. If the K_a value is greater than the K_b value, the resulting solution will be acidic and vice versa.

$$CH_3COONH_4,\ NH_4CN,\ (NH_4)_2S,\ Al_2S_3,\ (NH_4)_2SiO_3$$

Salt hydrolyzes by anion and on anion. They are most hydrolyzed, pH ~ 7.

$$K_h = \frac{K_w}{K_a \cdot K_b}$$

<u>Salts of the weak bases and weak acids.</u>

$$NH_4CH_3COO \rightarrow NH_4^+ + CH_3COO^-$$

$$NH_4^+ + HOH \leftrightarrows NH_3 \cdot H_2O + H^+$$

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

$$NH_4CH_3COO + H_2O \leftrightarrows NH_3 \cdot H_2O + HCl$$

<u>Conclusion:</u> Such salts are exposed to hydrolysis both on cation, and on anion, and reaction of a water solution of salt is neutral, because $K_a(CH_3COOH) = K_b(NH_3 \cdot H_2O)$

The Degree of Hydrolysis and the Hydrolysis Constant

Quantitative characteristics of the salt hydrolysis are ***the degree of hydrolysis h*** and ***hydrolysis constant K_h***.

The degree of hydrolysis h is calculated as the ratio of the molar concentration of salt hydrolysed C_M hydr. to its total concentration in solution C_M:

$$h = \frac{\text{number of molecules which have undergone to hydrolysis}}{\text{the general number of molecules of salt in a solution}}$$

$$h = \frac{C_{M\ hydr.}}{C_M}$$

h from 0 to 1

$$h = \frac{C_{M\ hydr.}}{C_M} \cdot 100\%$$

h = from 0 to 100%

The value of h depends on:

– nature of the salt;

– concentration of the salt;

– temperature.

Hydrolysis constant is equal to the quotient of the ionic product of water to the dissociation constant of a weak electrolyte is formed by hydrolysis:

$$K_h = \frac{K_w}{Ki}$$

The weaker the acid (or base), that is less than its dissociation constant, the more hydrolysis constant its salts will be.

A value of hydrolysis constant characterizes the ability of the salts hydrolyse: the more constant of hydrolysis, the greater hydrolysis occurs (at the same temperature and salt concentration).

Task 1. Write the ionic and molecular equations of salts hydrolysis a) ammonium nitrate NH_4NO_3;
b) chromium (III) chloride $CrCl_3$.

Solution:

a) $NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$

$NH_4^+ + HOH \leftrightarrows NH_3 \cdot H_2O + H^+$

$NH_4NO_3 + H_2O \leftrightarrows NH_3 \cdot H_2O + HNO_3$

pH < 7, acidic solution

b) $CrCl_3 \rightarrow Cr^{3+} + 3Cl^-$

$Cr^{3+} + HOH \leftrightarrows CrOH^{2+} + H^+$

$CrCl_3 + H_2O \rightarrow CrOHCl_2 + HCl$

pH < 7, acidic solution

Task 2. Write the ionic and molecular equations of salts hydrolysis and expression of their hydrolysis constants K_h:

a) potassium cyanide KCN; b) sodium carbonate Na_2CO_3.

Solution:

a)

$$KCN \rightarrow K^+ + CN^-$$

$$CN^- + HOH \leftrightarrows HCN + OH^-$$

In molecular form:

$$KCN + HOH \leftrightarrows HCN + KOH$$

$$K_h = \frac{K_w}{K_a HCN}$$

b)

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$

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

In molecular form:

$$Na_2CO_3 + HOH \leftrightarrows NaHCO_3 + NaOH$$

$$K_h = \frac{K_w}{K_{a2} H_2CO_3}$$

Task 3. Calculate the constant of hydrolysis of ammonium chloride NH_4Cl. $K_b(NH_4OH) = 1.75\times10^{-5}$

Solution:

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

$$NH_4^+ + HOH \leftrightarrows NH_3 \cdot H_2O + H^+$$

$$NH_4Cl + H_2O \leftrightarrows NH_3 \cdot H_2O + HCl,$$

$pH < 7$, acidic reaction

$$K_h = \frac{K_W}{K_a of\ weak\ base} = \frac{10^{-14}}{1.75\times10^{-5}} = 5.71x10^{-9}$$

Ostwald's dilution law

Ostwald's dilution law (relationship between K_h and h) is also valid for the case of hydrolysis:

$$K_h = \frac{Ch^2}{1-h}$$

When h is much less than unity, the equation K_h is:

$K_h = Ch^2$ or $$h = \sqrt{\frac{K_h}{C_M}}$$

Consequences of the law Ostwald dilution:

- the lower salt concentration, the more hydrolysed salt;
- the weaker the acid or base, which formed the salt, the greater the degree of hydrolysis.

Task 4. Calculate the degree of hydrolysis and pH of 0.001N solution of CH_3COOK. K_a $CH_3COOH = 1.75\times10^{-5}$

Solution: $CH_3COOK \leftrightarrows K^+ + CH_3COO^-$

$$\underset{C_M}{CH_3COO^-} + HOH \leftrightarrows CH_3COOH + \underset{C_M \cdot h}{OH^-}$$

Step 1: $h = \sqrt{\dfrac{K_h}{C_M}}$ $\qquad K_h = \dfrac{K_w}{K_a}$

$$h = \sqrt{\frac{K_w}{K_a \cdot C_M}} = \sqrt{\frac{1\times10^{-14}}{1.75\times10^{-5}\times0.001}} = 7.55\times10^{-4}$$

$$C_{OH^-} = C_M \cdot h = 0.001\times7.55\times10^{-4} = 7.55\times10^{-7}\ \text{mol/L}$$

$$C_{OH^-} = \sqrt{K_h \cdot C_M} = \sqrt{\frac{1\times10^{-14}\times0.001}{1.75\times10^{-5}}} = 7.55\times10^{-7}\ \text{mol/L}$$

Step 2:

$$pH = 14 - \lg[OH^-] = 14 - \lg 7.55\times10^{-7} = 7.88$$

Hydrolysis of Acidic Salts

Task 5. Explain why a reaction of sodium hydrogen carbonate solution is alkaline, and a reaction of sodium hydrogen sulphite solution is acidic.

Solution: $K_{a1_{H_2CO_3}} = 4.5\times10^{-7}$; $K_{a2_{H_2CO_3}} = 4.7\times10^{-11}$;

$K_{a1_{H_2SO_3}} = 1.6\times10^{-2}$; $K_{a2_{H_2SO_3}} = 6.3\times10^{-8}$

For an estimation pH solution of acidic salts (in which hydroanion of an acid simultaneously is exposed to hydrolysis and dissociates) it is necessary to compare K_h of salt and K_a a weak acid on the appropriate step:

a) $NaHCO_3 \rightarrow Na^+ + HCO_3^-$

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

$H_2CO_3 \leftrightarrows H^+ + HCO_3^-$ $K_{a1} = 4.5\times10^{-7}$

$HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$ $K_{a2} = 4.7\times10^{-11}$

$$K_h = \frac{K_w}{K_{a_1}} = \frac{1\times10^{-14}}{4.5\times10^{-7}} = 2.2\times10^{-8}$$

$$HCO_3^- \leftrightarrows H^+ + CO_3^{2-}$$

$$K_{a2} = 4.7\times10^{-11}$$

$K_h > K_{a2}$ means pH > 7 (basic solution)

b)

$$NaHSO_3 \rightarrow Na^+ + HSO_3^-$$

$$HSO_3^- + HOH \leftrightarrows H_2SO_3 + OH^-$$

$$K_h = \frac{K_w}{K_{a_1}} = \frac{1\times10^{-14}}{1.6\times10^{-2}} = 6.25\times10^{-13}$$

$$HSO_3^- \leftrightarrows H^+ + SO_3^{2-}$$

$$K_{a2} = 6.3\times10^{-8}$$

$K_h << K_{a2}$, pH < 7 (acidic solution)

Task 6. Calculate hydrolysis constant of sodium hydrogen phosphate (Na_2HPO_4) and indicate the reaction of an aqueous solution of salt.

K_{a1} H_3PO_4 = 7.1×10^{-3}, K_{a2} H_3PO_4 = 6.3×10^{-8}, K_{a3} H_3PO_4 = 1.3×10^{-12}

Solution:

$$Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{2-}$$

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

$$H_3PO_4 \leftrightarrows H^+ + H_2PO_4^- \qquad K_{a1}$$

$$H_2PO_4^- \leftrightarrows H^+ + HPO_4^{2-} \qquad K_{a2}$$

$$HPO_4^{2-} \leftrightarrows H^+ + PO_4^{3-} \qquad K_{a3}$$

$$K_h = \frac{K_w}{K_{a_2}} = \frac{1\times10^{-14}}{6.3\times10^{-8}} = 1.59\times10^{-7}$$

The Simultaneous Hydrolysis of two Salts (Co-hydrolysis)

The interaction in solution of two salts, one of which is formed by a weak base and a strong acid, and the second is formed by a strong base and a weak acid, leads to the formation of a precipitate of weak base and weak dissociate acid.

$Al_2(SO_4)_3 + Na_2CO_3 + H_2O =$

If to mix solutions of two salts, one of which is formed by the weak basis and a strong acid, and another is formed by weak acid and the strong basis, then joint hydrolysis reaction proceeds up to the end:

$CO_3^{2-} + H_2O \leftrightarrows HCO_3^- + OH^-$ **$HCO_3^- + H_2O \leftrightarrows H_2CO_3 + OH^-$**	**$Al^{3+} + HOH \leftrightarrows AlOH^{2+} + H^+$** **$AlOH^{2+} + H_2O \leftrightarrows Al(OH)_2^+ + H^+$** **$Al(OH)_2^+ + H_2O \leftrightarrows Al(OH)_3 + H^+$**

$$3Na_2CO_3 + Al_2(SO_4)_3 + 3H_2O \rightarrow 3CO_{2(g)} + 2Al(OH)_{3(s)} + 3Na_2SO_4$$

$$3CO_3^{2-} + 2Al^{3+} + 3H_2O \rightarrow 3CO_{2(g)} + 2Al(OH)_{3(s)}$$

<u>Conclusion</u>: the ions H^+ formed at hydrolysis of $Al_2(SO_4)_3$, will neutralize ions OH^- which are formed at hydrolysis of Na_2CO_3, and reaction proceeds up to the end.

Peculiar cases of hydrolysis

Hydrolysis of salts of antimony (III), bismuth (III) and other proceeds on the cation in two steps with the formation of precipitation of oxosalts.

In water solution of antimony (III) and bismuth (III) salts the hydrolysis reaction proceeds up to the end is easy not only on the first, but also on the second step:

$$BiCl_3 \rightarrow Bi^{3+} + 3Cl^-$$

$$Bi^{3+} + H_2O \leftrightarrows BiOH^{2+} + H^+$$

$$BiOHCl_2 + H_2O \leftrightarrows Bi(OH)_2Cl + HCl$$

$$Bi(OH)_2Cl \leftrightarrows BiOCl_{(s)} + H_2O$$

At acidifying sediment dissolves:

$$BiOCl_{(s)} + 2HCl_{(aq)} \leftrightarrows BiCl_{3(aq)} + H_2O$$

Hydrolysis of sodium silicate leads to the formation of dimetasilikate-ion.

The hydrolysis of sodium silicate, unlike other similar salts, is occurred with formation of dimetasilicate-ion:

$$Na_2SiO_3 \rightarrow 2Na^+ + SiO_3^{2-}$$

$$SiO_3^{2-} + HOH \leftrightarrows HSiO_3^- + OH^-$$

$$2HSiO_3^- \leftrightarrows Si_2O_5^{2-} + H_2O$$

Total reaction equation of hydrolysis is:

$$2Na_2SiO_3 + HOH \leftrightarrows Na_2Si_2O_5 + 2NaOH$$

Hydrolysis of Compounds with Covalent Bonds

$$Na_3N + 3H_2O = 3NaOH + NH_{3(g)}$$

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_{2(g)}$$

$$Al_4C_3 + 12H_2O = 4Al(OH)_{3(s)} + 3CH_{4(g)}$$

$$SiCl_4 + 3H_2O = H_2SiO_{3(s)} + 4HCl$$

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl$$

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl$$

$$SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

Shift the Equilibrium in the Hydrolysis

Task 7. Specify what factors will increase the hydrolysis of sodium carbonate.

Solution:

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \leftrightarrows HCO_3^- + OH^-$$

$$\Delta H > 0 \text{ (endotermic reaction)}$$

a. Na_2CO_3 is added to the system ←

b. NaOH is added to the system ←

c. heating ←

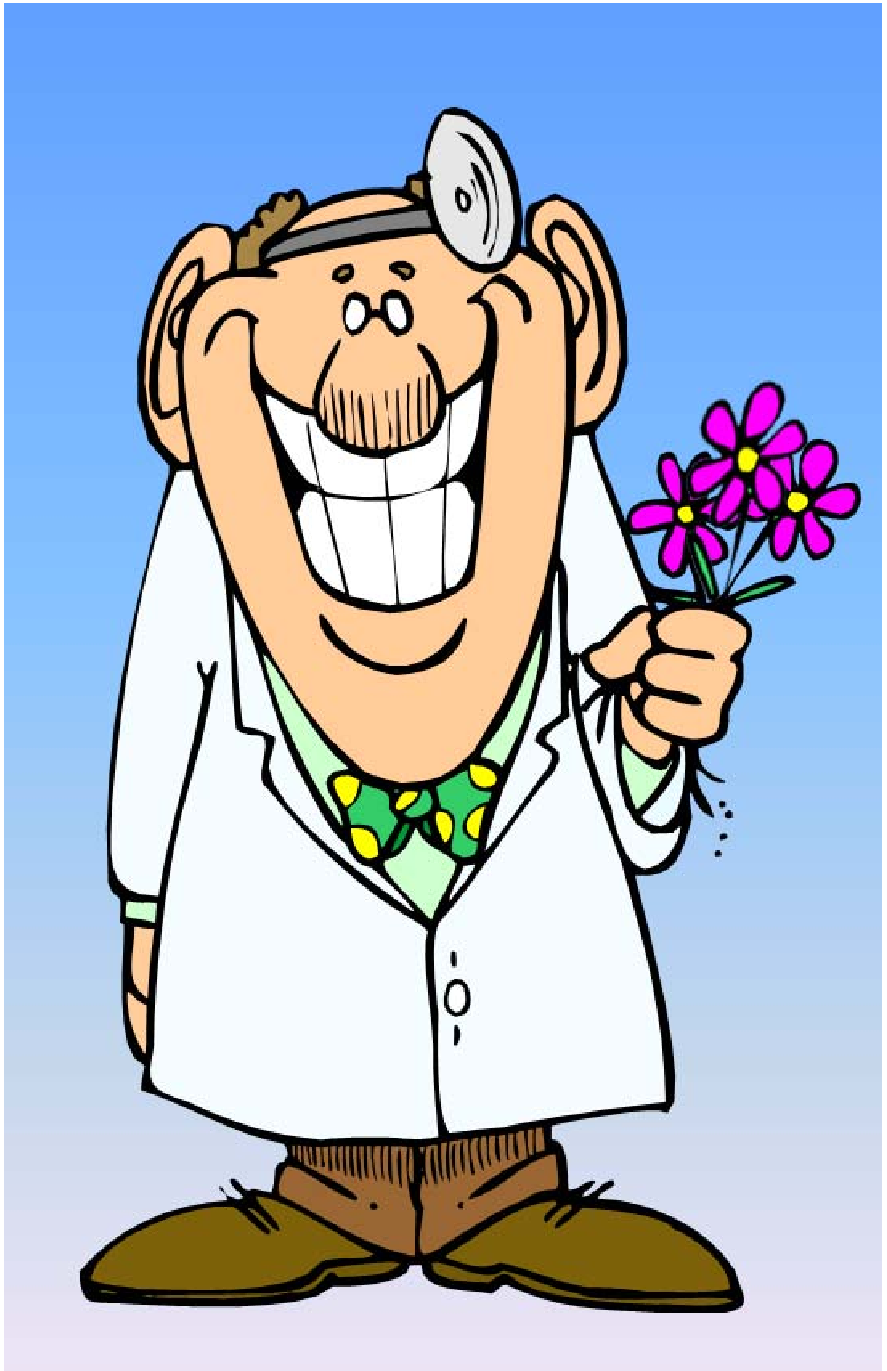
d. H_2O is added to the system →

f. HCl is added to the system →

Not only salts undergo hydrolysis. Proteins, fats, carbohydrates and many other compounds are hydrolysed.

Hydrolysis is widely used for the production of valuable products such as glucose, starch, soap, glycerine, alcohol, food organic acids etc.

Understanding of hydrolysis allows the pharmacist to cook and store liquid pharmaceutical forms, as well as to synthesize biologically active substances required for the creation of new groups of pharmaceuticals.



Thank you for attention!