

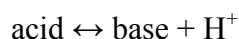
# BUILDING CHEMISTRY

## LAB 3

### SALT HYDROLYSIS AND pH DETERMINATION OF SUBSTANCES

#### THEORETICAL BACKGROUND

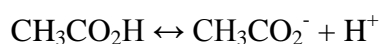
An acid is a molecule or an ion capable of donating a hydron (proton or hydrogen ion  $H^+$ ). Bases are the substances capable of binding hydrons. The definition of acids and bases can also be presented with the following equation:



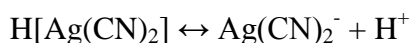
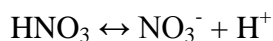
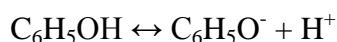
This is also known as an acid-base pair.

E.g.:

Acetic acid corresponds to the base of an acetate ion:



Similar phenomenon occurs in oxygen acids and complex acids:

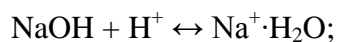


Ammonium ion is an acid that corresponds to the ammonia base.



Numerous organic substances that contain  $\equiv N$ ,  $=O$ ,  $=S$  etc. are bases, because they can bond with protons.

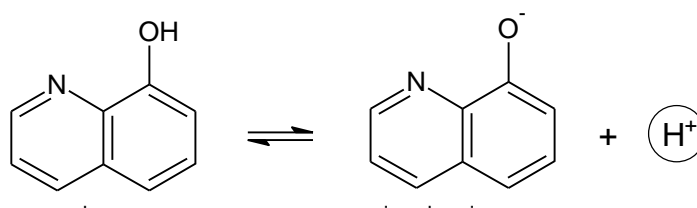
An example of such base is sodium hydroxide and it corresponds to the acid of hydrated sodium cation.



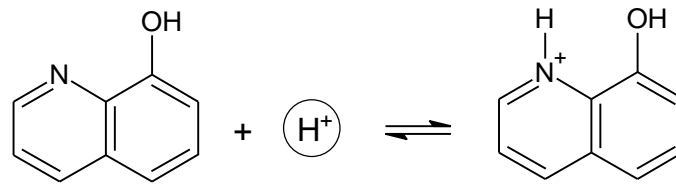
Many cations act like acids in the presence of water:



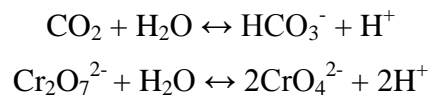
8-Hydroxyquinoline is an acid due to the presence of phenols.



At the same time, it is also a base due to the presence of the nitrogen atom, which can bond with a proton.



In aqueous solutions, some substances have acid-like behavior:



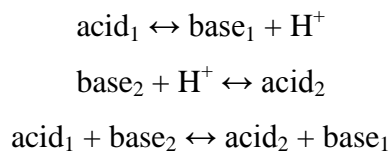
Solvent molecules can be acids or bases, therefore water in the equation can be treated as a base:



$\text{H}^+$  is a proton;  $\text{H}_3\text{O}^+$  is a symbol of a solvated proton or solvated hydrogen ion; usually it is called hydrogen ion and it is presented as  $\text{H}^+$ .

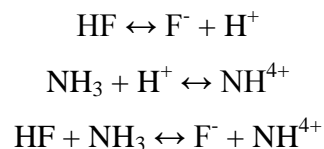
### Acids – bases reactions

Free protons practically do not exist. For protons to be released from acids, it is necessary for the base present to be able to bond with them. When acid<sub>1</sub> reacts with base<sub>2</sub> two complexes of acid-base are formed:



The balance between the two acid-base complexes establishes.

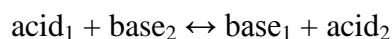
E.g.:



Here, the exchange of protons can be observed.

Chemical reaction prediction (strength of acids and bases)

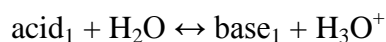
Let us consider the following reaction:





If the balance is moved to the right, it means that acid<sub>1</sub> reacts with base<sub>2</sub>, not vice versa. In such instance, we say that acid<sub>1</sub> is stronger than acid<sub>2</sub>. At the same time, we can also say that base<sub>2</sub> affects acid<sub>1</sub> but not that base<sub>1</sub> affects acid<sub>2</sub>, therefore base<sub>2</sub> is stronger than base<sub>1</sub>. Stronger acids always correspond to weaker bases.

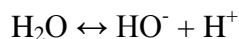
In aqueous solutions acids react with water, which can be treated like a base:



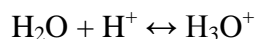
This is how the strength of various acid-base complexes can be compared to the H<sub>3</sub>O<sup>+</sup>/H<sub>2</sub>O complex.

### Aqueous solutions

Water can act like an acid:



or a base:



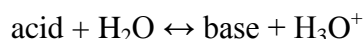
hence:



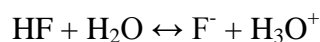
In aqueous solutions, this phenomenon distinguishes proton exchange from electron exchange.

### Hydrolysis

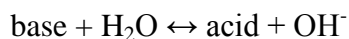
After the addition of an acid into water, the acid releases its protons which are then bonded with water. The chemical balance is reached.



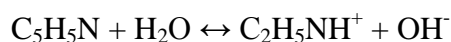
E.g.:



After the addition of a base into water, the base can bond the protons because water can release them:



e.g. pyridine:



Such behavior of water is called hydrolysis. It can be performed with acids, as well as with bases. More precisely, the balance depends on the acid-base pair.

According to the mass-action law:



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$$\frac{[\text{base}][\text{H}_3\text{O}^+]}{[\text{acid}][\text{H}_2\text{O}]} = K$$

Water concentration is very high and practically constant in diluted solutions, hence:

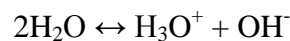
$$\frac{[\text{base}][\text{H}_3\text{O}^+]}{[\text{acid}]} = K_a$$

Where  $K_a$  is called acid constant of an acid-base pair (or an acid dissociation constant). It is more precise to use  $\text{p}K_a = -\log K_a$ , which is called *acid strength index*.

Based on the equation  $[\text{base} + \text{H}_2\text{O} \leftrightarrow \text{acid} + \text{OH}^-]$  the base dissociation constant can be determined.

$$\frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = K_b$$

Those two balance equations are not independent from one another, they are connected by the following equation:



hence:

$$K_a K_b = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

To simplify the notation, only the  $K_a$  constant shall be used.

The stronger the acid, the more the balance  $[\text{acid} + \text{H}_2\text{O} \leftrightarrow \text{base} + \text{H}_3\text{O}^+]$  is moved to the right, i.e. the greater the  $K_a$  constant is (or the smaller the  $\text{p}K_a$  is).

The stronger the base, the more vigorously it bonds with the protons, i.e. the more on the left it is.

The  $K_a$  constant determines the strength of the acid-base pair well. The stronger the acid, the weaker the base.

For example, HCN (hydrogen cyanide) is a weak acid ( $\text{p}K_a = 9,3$ ), whereas  $\text{CN}^-$  is a relatively strong base.

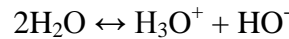
Similarly, ammonium ion  $\text{NH}_4^+$ , is an acid of a more or less the same strength:  $\text{p}K_a=9,2$ , and the corresponding base  $\text{NH}_3$  base is almost equal to  $\text{CN}^-$  base.

The HF acid (hydrofluoric acid) is stronger ( $\text{p}K_a = 3,2$ ).  $\text{F}^-$  is a very weak base.



### Hydrogen index

The more protons are bonded to water, the more acidic is the solution –  $[H_3O^+]$  is more concentrated.



Therefore, in accordance with the mass-action law:

$$\frac{[H_3O^+][OH^-]}{[H_2O]^2} = K$$

The K value is determined for given temperature. The concentration of the dissociated part of a solution is usually very low in relation to the general number of water molecules in a diluted solution. It can be assumed that the content of  $[H_2O]^2$  is relatively constant.

Therefore:

$$[H_3O^+][OH^-] = KH_2O$$

The value of the  $KH_2O$  constant is very low - 10-13,98 in 25 °C, 10-14,2 in 18 °C.

In a room-temperature, this value equals:

$$[H_3O^+][OH^-] = 10^{-14}$$

In clear water, the amount of the  $H_3O^+$  ions is equal to the amount of the  $HO^-$  ions, hence:

$$[H_3O^+] = [OH^-] = 10^{-7}$$

The environment is called *acidic* when the excess of  $H_3O^+$  ions is present,  $[H_3O^+] > 10^{-7}$ . The environment is called neutral, when  $[H_3O^+] = 10^{-7}$ , and it is called basic (or alkali) when  $[H_3O^+] < 10^{-7}$ .

To determine the acidity of a solution, it is more convenient to use the pH value instead of the  $H_3O^+$  ions activity, where:

$$pH = -\log[H_3O^+]$$

pH of clear water equals 7. For acids,  $pH < 7$ , up to -1. For bases  $pH > 7$ , up to 15.

If we confine ourselves to exclusively considering solutions that are not highly concentrated, we can consider the pH value to be between 0 and 14.

In the balance reaction:



the stronger the acid, the more acidic the solution, hence:

$$\frac{[\text{base}][H_3O^+]}{[\text{acid}]} = K_a$$

or:

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

Chemical reaction prediction

Consider the acid<sub>1</sub>–base<sub>1</sub> pair:

$$pH_1 = pK_1 + \log \frac{[base_1]}{[acid_1]}$$

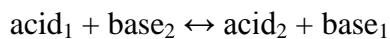
For the acid<sub>2</sub>–base<sub>2</sub> pair:

$$pH_2 = pK_2 + \log \frac{[base_2]}{[acid_2]}$$

After mixing the solutions, the ratio:

$$\frac{[base_1]}{[acid_1]} \quad \text{and} \quad \frac{[base_2]}{[acid_2]}$$

will change as the effect of the proton exchange:



until the common value of  $[H_3O^+]$  or pH is determined.

If solution<sub>1</sub> is more acidic than solution<sub>2</sub> ( $pH_1 < pH_2$ ), acid<sub>1</sub> will react with base<sub>2</sub>, the ratio base<sub>1</sub>/acid<sub>1</sub> will increase, and the ratio base<sub>2</sub>/acid<sub>2</sub> will decrease, until  $pH_1 = pH_2$ . Then, the proton exchange will cease. Hence, the equilibrium constant value is determined as:

$$K = \frac{[base_1][acid_2]}{[acid_1][base_2]} = \frac{K_1}{K_2}$$

The following formula:

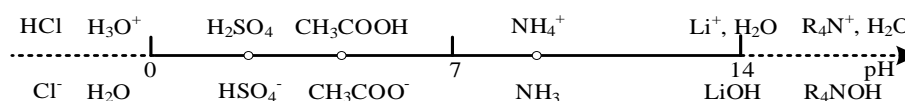
$$pH = pK_1 + \log \frac{[base_1]}{[acid_1]} = pK_2 + \log \frac{[base_2]}{[acid_2]}$$

results in:

$$pK = pK_1 - pK_2.$$

The pH scale

On the pH scale, all the acid-base pairs can be presented with the use of a proper value of the pK<sub>a</sub> constant: when  $[acid] = [base]$ , the pK<sub>a</sub> constant is equal to the pH value.



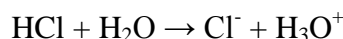


Every acid on the left side can react with every base on the right side of the graph. The pK value is determined as the distance between the points which represent the acid-base pairs.

### Limitation of the pH determination

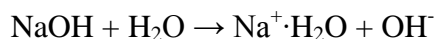
Some acids are very strong, even stronger than the  $\text{H}_3\text{O}^+$ . They release protons to be bonded with the water molecules, with a practically quantitative  $\text{H}_3\text{O}^+$  formation. As one liter of a diluted solution contains 55 moles of  $\text{H}_2\text{O}$ , the acids disappear completely. The balance acid +  $\text{H}_2\text{O}$  = base +  $\text{H}_3\text{O}^+$  is completely moved to the right side.

Acids stronger than  $\text{H}_3\text{O}^+$ , that cannot exist in aqueous solution ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ) are called *strong acids*.



Considering acidity,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  are neutral ions. They are not able to bond with protons, therefore they cannot react with water ions.

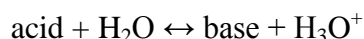
Strong bases, however, react with water in quantitative way:



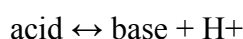
$\text{R}_4\text{N}^+$ ,  $\text{R}_4\text{M}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  etc., coming from strong bases, do not carry acids' properties and they do not change the pH of a solution.

The effect of water's influence on a proton (hydration) was earlier presented with the  $\text{H}_3\text{O}^+$  symbol. To simplify the notation, from now on, the symbol of  $\text{H}^+$  shall be used, and the hydrated proton shall be called *hydrogen ion*.

Instead of the balance equation:



the following equation shall be used:



The acid constant formula will take the form of:

$$\frac{[\text{base}][\text{H}^+]}{[\text{acid}]} = K_a$$

Normality of a solution (equivalent concentration)

In chemistry, the equivalent concentration or normality of a solution is defined as the molar concentration  $c_i$  divided by an equivalence factor  $f_{\text{eq}}$ . The unit symbol "N" is used to denote "eq/L" (equivalent per liter) which is normality. Although losing favor, medical reporting of serum concentrations in "meq/L" (= 0.001 N) still occurs.





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Normality can be used for acid-base titrations. For example, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a diprotic acid. Since only 0.5 mol of  $\text{H}_2\text{SO}_4$  are needed to neutralize 1 mol of  $\text{OH}^-$ , the equivalence factor is:

$$f_{\text{eq}}(\text{H}_2\text{SO}_4) = 0.5$$

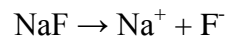
If the concentration of a sulfuric acid solution is  $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/L}$ , then its normality is 2 N. It can also be called a "2 normal" solution.

Similarly, for a solution with  $c(\text{H}_3\text{PO}_4) = 1 \text{ mol/L}$ , the normality is 3 N because phosphoric acid contains 3 acidic H atoms.

### Salt dissociation

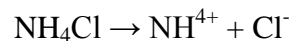
Experience shows that large amount of salts behave like an unstable complex in a solution. They practically completely dissociate.

Sodium fluoride constitutes a perfect example:



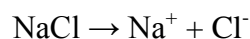
$\text{F}^-$  is a base;  $\text{Na}^+$  is a neutral ion (very weak acid).

Ammonium chloride behaves alike:



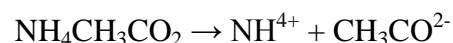
$\text{NH}_4^+$  is an acid,  $\text{Cl}^-$  is a neutral ion (very weak base).

For sodium chloride:



The solution is neutral.

For ammonium acetate:



$\text{NH}_4^+$  is an acid,  $\text{CH}_3\text{CO}_2^-$  is a base.



## PRACTICAL SESSION

### SALT HYDROLYSIS AND PH DETERMINATION OF SELECTED SUBSTANCES

Equipment: volumetric flask (100 cm<sup>3</sup>), polypropylene beaker (50 ml), pH-meter, pipette, wash bottle

Reagents: 0.1M solution of acids: hydrochloric, acetic; 0.1M solution of salts: sodium chloride, ammonium chloride, trisodium citrate

### PROCEDURE

1. Transfer 10 cm<sup>3</sup> of 0.1M HCl into the volumetric flask and add distilled water up to 100 cm<sup>3</sup>.
2. Mix thoroughly.
3. Transfer 10 cm<sup>3</sup> of 0.01M HCl from the volumetric flask into the second flask, add distilled water up to 100 cm<sup>3</sup> and mix thoroughly.
4. By analogy, prepare the solutions of HCl up to 0.000001M.
5. Transfer app. 45 ml of hydrochloric acids (0.1M – 0.000001M) into the polypropylene beakers and determine the pH of the solution.
6. Transfer app. 45 ml of the acetic acid into the polypropylene beaker and determine the pH.
7. Transfer app. 45 ml of selected salts into the polypropylene beakers and determine the pH of sodium chloride, ammonium chloride, and trisodium citrate.
8. Note the hydrolysis equations for selected salts (molecular and ionic).