

2. Dissociation, dissociation degree, pH

If we are given an ionic compound (salt, acid, base), we can observe its dissociation in polar solvents (like water), respectively:

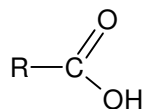
salt, e.g. $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

acid, e.g. $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$ see ¹

base, e.g. $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$

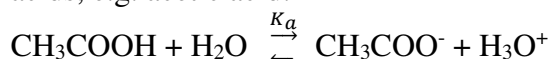
Almost all salts dissociate in water fully (at 100% level), so their α (dissociation degree) is equal to 1. Similar behavior is observed for strong acids and strong bases. All those systems are assumed to have dissociation degree $\alpha = 1$, usually regardless of their concentration (in quite wide concentration range; that does not apply to very concentrated systems, for instance at few moles per liter concentration).

Weak acids and weak bases systems are the issue here, as depending on their concentration in the solution they exhibit different dissociation degrees. The weak acids are for instance all organic acids, of the general formula R-COOH , where R- is: H- or a hydrocarbon chain. Acid radical of organic acid is as follows:

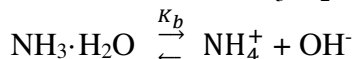


Weak acids/bases dissociate according to the equilibria presented below:

acids, e.g. acetic acid:



ammonium base $\text{NH}_3 \cdot \text{H}_2\text{O}$:



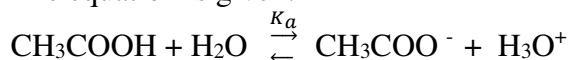
Each dissociation constant, depending on whether it refers to acid or base, can be represented by K_a or K_b , respectively. K_a or K_b constants always refer to acid-base systems.

K_a constant – is an acidity constant (a for acid); for easier memorizing – if you have this constant then in the dissociation equation H_3O^+ ion has to occur on the right side.

K_b constant – is a basicity constant (b for basic); for easier memorizing – if you have this constant then in the dissociation equation OH^- ion has to occur on the right side.

How do we write down equilibrium constants?

The equation is given:



K_a constant is obtained through the division of concentrations of products (right side of the equation) with concentrations of substrates (left side of the equation):

$$K_a = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}] \cdot [\text{H}_2\text{O}]}$$

¹ Here we could write equation in a form of $\text{HCl} \leftrightarrow \text{H}^+ + \text{Cl}^-$, but such form would not be in concert with reality. Hydrogen ion „H⁺“ is extremely small, thus per its Surface the concentration of the positive charge is extremely high. As a result, in a fraction of second, in the water solution we can observe formation of H_3O^+ ion. It is an ion, in which to the free electron pair of H_2O molecule H^+ is attached through an association process. This is why one needs to take into account water molecule in the dissociation equation.

[H₂O] is a pure substance, given in excess (environment of the process) and thus, its activity can be considered as 1, as its relative concentration would not change due to the process.

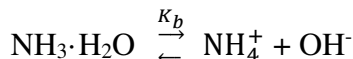
Therefore, formula can be simplified to the following form:

$$K_a = \frac{[\text{CH}_3\text{COO}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

Every constant in chemistry is constant at the given temperature. Usually (unless it is specified otherwise) all data in tables or references are provided for 25°C.

Constant K_a is often given in the $-\log K_a$ (or $\text{p}K_a$) form. Due to that, it is very important to take into account the form in which given constant is provided.²

In the case of ammonium base, if:



then constant K_b is given as:

$$K_b = \frac{[\text{OH}^-] \cdot [\text{NH}_4^+]}{[\text{NH}_3 \cdot \text{H}_2\text{O}]}$$

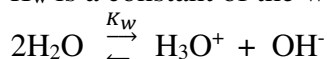
Concentration of ions is equal to the product of acid or base concentration and its dissociation constant ($c_{\text{HA}} \cdot \alpha$ or $c_{\text{BOH}} \cdot \alpha$). Numerator in such equation is thus $c^2 \alpha^2$ and denominator is $c(1-\alpha)$, as concentration of undissociated acid or base is total concentration (c) minus its dissociated part (ions) – therefore $c - c\alpha = c(1-\alpha)$. K_a constant can be associated with dissociation degree in the following way:

$$K_a = \frac{c_{\text{HA}} \cdot \alpha^2}{1 - \alpha}$$

In this equation it is important to substitute c_{HA} with total concentration of the weak acid (all of what has been added to the system). In the same manner one can calculate dissociation degree of weak bases, using in the respective places K_b and C_{BOH} .

$$K_b = \frac{c_{\text{BOH}} \cdot \alpha^2}{1 - \alpha}$$

K_w is a constant of the water autodissociation, according to the equation:



Thus, K_w constant can be written as a ionic concentration product of water:

$$K_w = [\text{H}_3\text{O}^+] \cdot [\text{OH}^-]$$

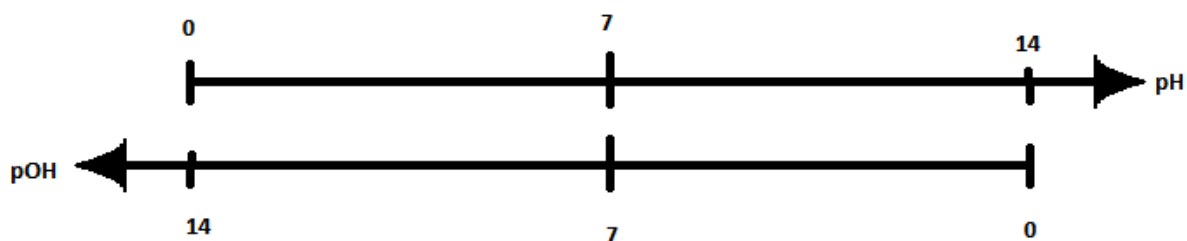
This constant at room temperature is 10^{-14} , so $\text{p}K_w = 14$.

Neutral solution is such one that H_3O^+ ions concentration is equal to OH^- ions concentration.

pH scale is defined in reference to H_3O^+ ions concentration.

pH is calculated as $-\log[\text{H}_3\text{O}^+]$

pH and pOH scales are visualized below:



From the above illustration it can be concluded that between pH and pOH scales there is a following dependence: $\text{pH} + \text{pOH} = \text{p}K_w$

Verification: in the neutral environment $\text{pH} = \text{pOH} = 7$, thus $\text{pH} + \text{pOH} = 7 + 7 = 14$

² If the constant is given in the $\text{p}K_a$ form then in order to obtain K_a one need to calculate $10^{-(\text{p}K_a)} = K_a$.

So it can be concluded that concentration of both is $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$

Example 1. What pH has a solution with $\text{pOH} = 3$?

Answer: $\text{pH} = 14 - 3 = 11$

Attention! All equilibrium constants are given for the specific temperature (usually 25°C). If the temperature is different than that, it has to be specified. For all calculations one needs to use constants determined/calculated for the same temperature. Taking constants for different temperatures can lead to significant errors. Constant K_w value is 10^{-14} , but only at 25°C . In other temperatures it may have completely different values (for instance, at 60°C $K_w = 10^{-13}$). It seems logical, as the higher temperature, the higher energy of particles. Therefore, the dissociation degree will be higher as well. This is why at 60°C ionic concentration will increase to $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 3.16 \cdot 10^{-7} \text{ M}$. One also needs to remember that the charge neutrality condition has to be satisfied in whole solution regardless of the temperature.

Task 2.1

Calculate pH of the 0.1M acetic acid solution ($\text{CH}_3\text{COOH} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$). What will be the dissociation degree of acetic acid solution at such concentration? How will the dissociation degree change after diluting the solution 10-fold? $\text{p}K_a = 4.76$, $\text{p}K_w = 14$

Solution:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{c_{\text{CH}_3\text{COOH}} \cdot \alpha \cdot c_{\text{CH}_3\text{COOH}} \cdot \alpha}{c_{\text{CH}_3\text{COOH}} (1 - \alpha)} = c_{\text{CH}_3\text{COOH}} \frac{\alpha^2}{(1 - \alpha)}$$

$$c_{\text{CH}_3\text{COOH}} = 0.1$$

$$K_a = 10^{-4.76} \approx 0.00001738$$

$$0.00001738 = 0.1 \cdot \alpha^2 / (1 - \alpha)$$

$$0.0001738 = \alpha^2 / (1 - \alpha)$$

$$0.0001738 - 0.0001738 \alpha = \alpha^2$$

$$\alpha^2 + 0.0001738 \alpha - 0.0001738 = 0$$

$$\Delta = 3.02 \cdot 10^{-8} + 0.0006952$$

$$\Delta^{1/2} = 0.02636$$

$$\alpha_1 = (-0.0001738 + 0.02636)/2 = 0.0262/2 \approx 0.013$$

α_2 has negative value, so without physical meaning.

The same method applies to calculation of dissociation degree for other concentrations and K_a values.

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) = -\log(c_{\text{CH}_3\text{COOH}} \cdot \alpha) = -\log(0.1 \cdot 0.013) = -\log(0.0013) \approx -2.89$$

Answer: $\text{pH} = 2.89$ $\alpha_1 \approx 0.013$ after the dilution: $\alpha_2 \approx 0.041$.

Task 2.2

Calculate the theoretical hydrochloric acid solution concentration at $\text{pH}=3$.

Answer: 10^{-3} M

Task 2.3

Calculate the $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution concentration of that base at $\text{pH}=12$. $\text{p}K_b = 4.7$

Answer: Approximately 0.2 M , more precisely $10^{-0.7} \text{ M}$

Task 2.4

What is the dissociation degree of the 0.1M solution of the ammonium base?

Answer: $\alpha = 0.014$