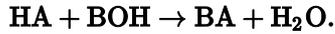


PH of salts

When we talk about the pH of salts, we mean the pH of aqueous solutions of soluble salts. Such salts dissociate in solution according to Eq



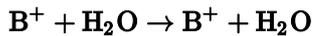
Where **BA** is a salt of an acid **HA** and a base **B(OH)**, which arises, for example, by neutralisation according to the equation



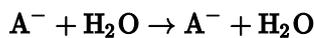
pH of salts of strong acids and strong bases

In the case of a salt of a strong acid and a strong base, we consider that

- Cation B^+ — because it is strong — it will remain dissociated:



- Anion A^- — because it is strong — it will also remain dissociated:



Therefore, not one of the salt ions will react with the water molecules and the only source H_3O^+ and OH^- will be the autoprotolysis of water itself. I mean

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [\text{OH}^-] = -\log \sqrt{K_w} = \frac{1}{2}\text{p}K_w$$

and at 25 °C the pH will be equal to 7.

pH of salts of weak acids and strong bases

In the case of a salt of a weak acid and a strong base, we consider that

- cation B^+ — because it is strong — it will remain dissociated: $\text{B}^+ + \text{H}_2\text{O} \rightarrow \text{B}^+ + \text{H}_2\text{O}$
- anion A^- — because it is weak — it will react with water, i.e. undergo so-called hydrolysis, according to the equation:
 $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$
- will hydrolyze **very few** anions, the amount of hydrolyzed anions will be negligible, i.e
- $c_{\text{BA}} - [\text{A}^-] \approx 0$, or otherwise $[\text{A}^-] \approx c_{\text{BA}}$
- the only source OH^- is the above-mentioned hydrolysis reaction, we neglect other sources of hydroxide anions and oxonium cations, i.e. the amount **HA** and OH^- will be the same according to her equation.

The above hydrolysis reaction has an equilibrium constant

$$K = \frac{[\text{HA}] \cdot [\text{OH}^-]}{[\text{A}^-] \cdot [\text{H}_2\text{O}]}$$

We will consider the concentration of water in water as constant and introduce a new constant, the so-called hydrolytic constant:

$$K_{h,A} = [\text{H}_2\text{O}] \cdot K = \frac{[\text{HA}] \cdot [\text{OH}^-]}{[\text{A}^-]}$$

If we adjust the (slightly imprecise) notation of water in chemical equations, it will be easier to see that the hydrolysis equation is de facto just the opposite equation to dissociation:

- dissociation: $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$,
- hydrolysis: $\text{A}^- + \text{H}^+ \rightarrow \text{HA}$.

It is therefore natural that the hydrolytic constant $K_{h,A}$ and the dissociation constant K_A they will be related:

$$K_{h,A} \cdot K_A = \frac{[\text{HA}] \cdot [\text{OH}^-]}{[\text{A}^-]} \cdot \frac{[\text{A}^-] \cdot [\text{H}_3\text{O}^+]}{[\text{HA}]} = [\text{OH}^-] \cdot [\text{H}_3\text{O}^+] = K_w$$

For a constant $K_{h,A}$ so we get the formula

$$K_{h,A} = \frac{K_w}{K_A}$$

If to the definition of the hydrolytic constant $K_{h,A}$ we substitute for $[\text{HA}]$ according to our assumptions $[\text{OH}^-]$, and c_{BA} for $[\text{A}^-]$ we will get

$$K_{h,A} \cdot [\text{A}^-] = K_{h,A} \cdot c_{\text{BA}} = [\text{OH}^-]^2.$$

When we express the dependence of the concentration of oxonium cations on the concentration of hydroxide anions from the definition of the ionic product of water K_w , we obtain

$$[\text{H}_3\text{O}^+]^2 = \frac{K_w^2}{[\text{OH}^-]^2} = \frac{K_w^2}{K_{h,A} \cdot c_{\text{BA}}} = \frac{K_w^2}{\frac{K_w}{K_A} \cdot c_{\text{BA}}} = \frac{K_w^2 \cdot K_A}{K_w \cdot c_{\text{BA}}} = \frac{K_w \cdot K_A}{c_{\text{BA}}}$$

We take the square root (concentrations are always positive), logarithmize and multiply by -1 :

$$-\log[\text{H}_3\text{O}^+] = -\log \sqrt{\frac{K_w \cdot K_A}{c_{\text{BA}}}} = -\log \frac{K_w^{\frac{1}{2}} \cdot K_A^{\frac{1}{2}}}{c_{\text{BA}}^{\frac{1}{2}}} = \frac{1}{2} \log c_{\text{BA}} - \frac{1}{2} \log K_w - \frac{1}{2} \log K_A = \frac{1}{2} \log c_{\text{BA}} + \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_A$$

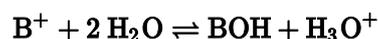
At 25 °C we get the formula $\text{pH} = 7 + \frac{1}{2} \log c_{\text{BA}} + \frac{1}{2} \text{p}K_A$

The resulting **pH will be alkaline**. This is due to the fact that the anion of the acid draws hydrons from the system.

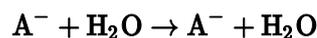
The pH of a salt of a strong acid and a weak base

In the case of a salt of a strong acid and a weak base, we consider that

- cation B^+ —because it is weak — it will hydrolyse according to the reaction



- anion A^- — because it is strong — it will not hydrolyse, that is



- will hydrolyze **very few** cations, and the amount of hydrolyzed cations will thus be negligible, i.e.
- $c_{\text{BA}} - [\text{B}^+] \approx 0$, or not $c_{\text{BA}} \approx [\text{B}^+]$
- hydrolysis of cations is the only source of oxonium cations, we neglect other sources, so according to the hydrolysis equation $[\text{H}_3\text{O}^+] = [\text{BOH}]$

For hydrolysis, we introduce a hydrolytic constant $K_{h,B} = K \cdot [\text{H}_2\text{O}]^2$ like

$$K_{h,B} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{BOH}]}{[\text{B}^+]},$$

for which it can again be proved to hold $K_{h,B} \cdot K_B = K_w$.

According to the assumptions, we substitute in the hydrolytic constant c_{BA} za B^+ and $[\text{H}_3\text{O}^+]$ for $[\text{BOH}]$:

$$[\text{B}^+] \cdot K_{h,B} = c_{\text{BA}} \cdot K_{h,B} = [\text{H}_3\text{O}^+]^2$$

We take the square root (concentrations are always positive numbers), logarithmize and multiply by -1 :

$$-\log [\text{H}_3\text{O}^+] = \frac{1}{2} (-\log c_{\text{BA}} - \log K_{h,B}) = \frac{1}{2} \left(-\log c_{\text{BA}} - \log \frac{K_w}{K_B} \right)$$

$$-\log [\text{H}_3\text{O}^+] = \frac{1}{2} (-\log c_{\text{BA}} + \log K_B - \log K_w) = \frac{1}{2} (\text{p}K_w - \text{p}K_B - \log c_{\text{BA}})$$

So at 25 °C we get the formula:

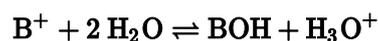
$$\text{pH} = 7 - \frac{1}{2} \text{p}K_B - \frac{1}{2} \log c_{\text{BA}}$$

The resulting **pH will be acidic**. This is because the base cation adds hydrons to the system.

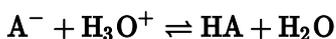
pH of salts of weak acids and weak bases

In the case of a salt of a weak acid and a weak base, we consider that

- Cation B^+ will hydrolyse according to Eq



- anion A^- will react with the resulting oxonium cations and then possibly further hydrolyse according to the equation



- both ions will hydrolyse in negligible amounts, ie

$$c_{\text{BA}} \approx [\text{B}^+] \approx [\text{A}^-]$$

- there is no other source of hydroxide anions and oxonium cations in the system, therefore
 - oxonium cations **formed** by hydrolysis of the base cation B^+ we mark $[\text{H}_3\text{O}^+]_{\text{B}}$ and according to the chemical equation of hydrolysis it applies to them $[\text{H}_3\text{O}^+]_{\text{B}} = [\text{BOH}]$.
 - oxonium cations **destroyed** by acid anion hydrolysis $[\text{A}^-]$ we mark $[\text{H}_3\text{O}^+]_{\text{A}}$ and according to the chemical equation of hydrolysis it applies to them $[\text{H}_3\text{O}^+]_{\text{A}} = [\text{HA}]$
- the equilibrium concentration of oxonium cations is calculated as the difference between the concentration of oxonium cations formed by the hydrolysis of the base cation and the concentration of oxonium cations consumed by the hydrolysis of the acid anion**, i.e.

$$[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_{\text{B}} - [\text{H}_3\text{O}^+]_{\text{A}}$$

For the hydrolysis of the cation, we have the hydrolysis constant: $K_{h,\text{B}} = \frac{K_w}{K_B} = \frac{[\text{H}_3\text{O}^+] \cdot [\text{BOH}]}{[\text{B}^]}$

and for the hydrolysis of the anion it is better to express the concentration of oxonium cations using another constant describing the equilibrium, namely the dissociation constant:

$$K_A = \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{[\text{HA}]}$$

By adding the penultimate assumption to the last assumption, we get

$$[\text{H}_3\text{O}^+] = [\text{BOH}] - [\text{HA}].$$

We express $[\text{BOH}]$ and $[\text{HA}]$ from the equations for the equilibrium constants:

$$[\text{H}_3\text{O}^+] = \frac{K_w \cdot [\text{B}^+]}{K_B \cdot [\text{H}_3\text{O}^+]} - \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{K_A}$$

We will edit:

$$[\text{H}_3\text{O}^+] + \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{K_A} = [\text{H}_3\text{O}^+] \left(1 + \frac{[\text{A}^-]}{K_A} \right) = \frac{K_w \cdot [\text{B}^+]}{K_B \cdot [\text{H}_3\text{O}^+]}$$

We express the concentration of oxonium cations:

$$[\text{H}_3\text{O}^+]^2 = \frac{\frac{K_w \cdot [\text{B}^+]}{K_B}}{1 + \frac{[\text{A}^-]}{K_A}} = \frac{\frac{K_w \cdot [\text{B}^+]}{K_B}}{\frac{K_A + [\text{A}^-]}{K_A}} = \frac{K_w \cdot [\text{B}^+] \cdot K_A}{K_B \cdot (K_A + [\text{A}^-])}$$

Because it is $[\text{A}^-] \gg K_A$, we can K_A neglect the denominator and approximate the formula to

$$[\text{H}_3\text{O}^+]^2 = \frac{K_w \cdot [\text{B}^+] \cdot K_A}{K_B \cdot [\text{A}^-]}$$

By supplementing c_{BA} by assumptions we get

$$[\text{H}_3\text{O}^+]^2 = \frac{K_w \cdot c_{\text{BA}} \cdot K_A}{K_B \cdot c_{\text{BA}}} = \frac{K_w \cdot K_A}{K_B}$$

We take the square root (these are positive constants), take the logarithm, multiply by -1 and get

$$-\log [\text{H}_3\text{O}^+] = -\frac{1}{2} \log K_w - \frac{1}{2} \log K_A + \frac{1}{2} \log K_B = \frac{1}{2} (\text{p}K_w + \text{p}K_A - \text{p}K_B)$$

Thus, the pH of the salt of a weak acid and a weak base (after approximation) does not depend on the concentration of the salt.

At 25 °C we get

$$\text{pH} = 7 + \frac{1}{2} \text{p}K_A - \frac{1}{2} \text{p}K_B$$

Links

related articles

- pH
- pH of strong acids and bases
- pH of weak acids and bases
- pH-metry
- pH measurement
- pH of buffers
- Urine pH

related articles

References

- BERKA, Antonín – FETL, Ladislav – NĚMEC, Ivan. *Practitioner's Guide to Quantitative Analytical Chemistry*. 1. edition. SNTL, 1985. 228 pp. pp. 56-66.

recommended literature