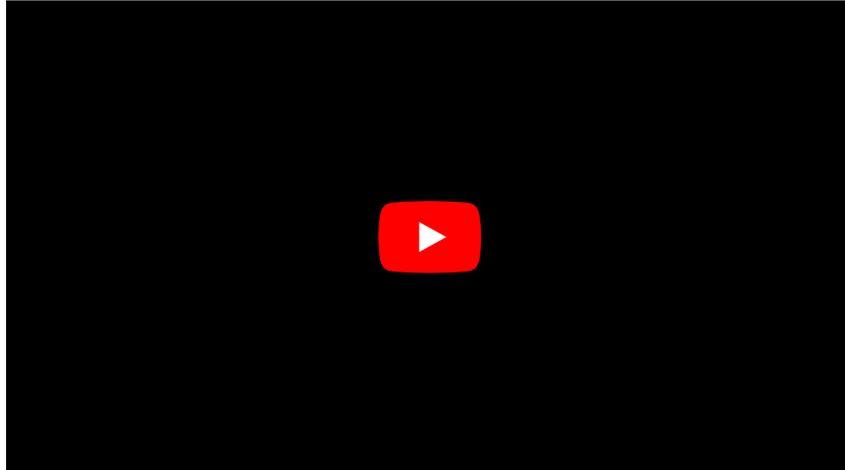


# pH

## pH significance:



'environmental pH' is the activity of its oxonium cations expressed on a negative logarithmic scale. It is thus defined as:

$$\text{pH} = -\log_{10} a_{\text{H}_3\text{O}^+}$$

Since the activity is very dependent on concentration,  $a = \gamma_c \cdot c$  and outside very concentrated solutions, it is possible to consider the activity coefficient  $\gamma_c \approx 1$ , i.e.  $a \approx c$ , can be written:

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+],$$

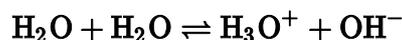
where  $[\text{H}_3\text{O}^+]$  is in  $\text{mol} \cdot \text{dm}^{-3}$  and pH is then dimensionless.

In an aqueous environment, oxonium cations are de facto hydrated hydrogen cations, hydrons, i.e. particles identical to protons, so pH is often stated as

$$\text{pH} = -\log_{10} [\text{H}^+].$$

## pH scale in aqueous environment

In almost all real situations, only the pH of the aqueous environment is considered. Water undergoes autoprotolysis according to the equilibrium reaction



with the equilibrium constant

$$K = \frac{[\text{H}_3\text{O}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]^2}.$$

The concentration of water in usual systems can be considered practically constant, so it is advantageous to work with the ionic product of water  $K_w = K \cdot [\text{H}_2\text{O}]^2$ . From the above equation, the relationship for it follows

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

The ionic product of water  $K_w$  is proportional to the equilibrium constant and therefore, like it, strongly depends on temperature. So the pH scale will be different at different temperatures. At 25 °C, laboratory temperature,  $K_w$  corresponds to  $1.008 \cdot 10^{-14}$ , so the pH scale will have a center, the so-called neutral pH, almost exactly 7. This is because

$$-\log [\text{H}_3\text{O}^+] = -\log [\text{OH}^-] = -\log \sqrt{K_w} = 7.$$

At other temperatures, the center of the scale is different (0 °C corresponds to 7.47; 10 °C 7.27; 20 °C 7.08; 30 °C 6.92; 40 °C 6.77; 50 °C 6.63; 100 °C 6.14)<sup>[1]</sup>. The pH can take on an infinite number of values, at 25 °C it can even be negative with the use of very strong acids, and under suitable conditions it can even exceed the value of 14.

## Reason for introduction of pH

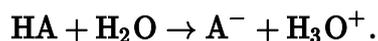
The concentration of oxonium ions takes on values in the range of many orders of magnitude, most commonly from  $10^{-1}$  to  $10^{-14}$ . When specifying such numbers, it is advantageous to specify only the exponent, which is why a logarithmic scale was introduced, since  $\log 10^{-n} = -n \cdot \log 10 = -n$  applies. At the same time, using logarithms converts multiplication to addition and division to subtraction ( $\log(A \cdot B) = \log A + \log B$ , which is a direct consequence of the fact that  $x^a \cdot x^b = x^{a+b}$ ). This fact was of general importance mainly at a time when computers and calculators were not commonly available and technical calculations were performed using a logarithmic ruler.

## pH of strong acids and bases

When calculating pH, it is always necessary to consider what is the source of oxonium cations in a given environment.

### Strong monosaturated acids

For **strong monosaturated acids** the dissociation follows the equation



For the calculation we assume:

- the substance quantity of  $\text{H}_3\text{O}^+$  according to the above equation will be the same as  $\text{A}^-$ , which, given an identical volume, is also true for the concentration, i.e.  $[\text{H}_3\text{O}^+] = [\text{A}^-]$ ;
- all acid - because it is a strong acid - is converted into  $\text{A}^-$  a  $\text{H}_3\text{O}^+$ , therefore we will mark  $[\text{A}^-]$  its concentration, i.e.  $[\text{A}^-] = c_{\text{HA}}$

Let's deduce:

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [\text{A}^-] = -\log c_{\text{HA}},$$

and to calculate the pH we get the formula

$$\text{pH} = -\log c_{\text{HA}}.$$

### Strong monosaturated bases

For **strong monosaturated bases** the dissociation follows the equation



We assume, as in the case of strong monosaturates, that:

- the amount, or concentration, of hydroxide ions and the resulting  $\text{B}^+$  is the same according to the above chemical equation, i.e.  $[\text{OH}^-] = [\text{B}^+]$ ;
- dissociation occurs completely, i.e.  $[\text{B}^+] = c_{\text{BOH}}$ .

The calculation is therefore analogous, we just have to remember that unlike acids, the base is not a source of oxonium cations, but takes oxonium cations from the environment (see the theory of acids and bases), so we add from the equation for the ionic product of water:

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

and from these assumptions, we deduce

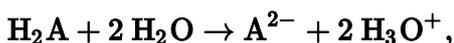
$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = \log [\text{OH}^-] - \log K_w = \log [\text{B}^+] - \log K_w = \log c_{\text{BOH}} - \log K_w.$$

Calculate the pH at 25 °C using the formula

$$\text{pH} = 14 + \log c_{\text{BOH}}.$$

### Strong dibasic acids

**Strong dibasic acids** dissociate according to the equation



we assume, then:

- complete dissociation, i.e.  $c_{\text{H}_2\text{A}} = [\text{A}^{2-}]$ ;
- however, the amount of oxonium cations and the amount of formed  $\text{A}^{2-}$  is - in contrast to monosaturated acids - in a ratio of 1:2, i.e.  $[\text{H}_3\text{O}^+] = 2 \cdot c_{\text{H}_2\text{A}}$ .

From this we derive  $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [\text{A}^{2-}] = -\log(2 \cdot c_{\text{H}_2\text{A}}) = -\log 2 - \log c_{\text{H}_2\text{A}}$

and the pH is calculated according to the formula

$$\text{pH} = -\log c_{\text{H}_2\text{A}} - \log 2.$$

## Strong dibasic bases

**Strong dibasic bases** dissociate according to the equation



as we assume for monosaturated bases and dibasic acids:

- complete dissociation, i.e.  $c_{\text{B}(\text{OH})_2} = [\text{B}^{2+}]$ ;
- concentration of the formed  $\text{B}^{2+}$  and the concentration of hydroxide anions is in the ratio 1:2, i.e.  $[\text{OH}^-] = 2 \cdot [\text{B}^{2+}]$ , in addition, according to the previous assumption  $[\text{OH}^-] = 2 \cdot c_{\text{B}(\text{OH})_2}$
- hydroxide anions drain oxonium cations from the environment,  $[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$ .

Then we derive

$$-\log[\text{H}_3\text{O}^+] = -\log \frac{K_w}{[\text{OH}^-]} = \log [\text{OH}^-] - \log K_w = \log(2 \cdot c_{\text{B}(\text{OH})_2}) - \log K_w = \log 2 + \log c_{\text{B}(\text{OH})_2} - \log K_w$$

and the pH at 25 °C is calculated according to the formula

$$\text{pH} = 14 + \log 2 + \log c_{\text{B}(\text{OH})_2}.$$

## pH of weak acids and bases

PH of weak acids and bases

## pH of medium strength acids and bases

Moderately strong acids and bases defy both assumptions from the previous models - complete dissociation cannot be assumed, but the amount of undissociated acid or base cannot be completely neglected either. If we use any of the previous procedures, which are in themselves idealized, i.e. burdened with a certain error, we will move even further away from the real situation, so it is necessary to realize that the error will be several times larger.

## Links

### Related Articles

- pH-metry
- PH measurement
- pH of buffers
- Urine pH
- pH of salts

### References

1. CLARK, Jim. *The ionic product of water* [online]. ©2002. [cit. 2009-12-15]. <<http://www.chemguide.co.uk/physical/acidbaseeqia/kw.html>>.

### References

- BERKA, Antonín - FETL, Ladislav, et al. *Practitioner's Guide to Quantitative Analytical Chemistry*. 1. edition. Bratislava : SNTL, 1985. 228 pp. pp. 56-66.

## External links

- [PH \(Czech Wikipedia\)](#)
- [PH \(disambiguation\) \(English Wikipedia\)](#)
- [Acidity \(Czech Wikipedia\)](#)
- [pH \(disambiguation\) \(English Wikipedia\)](#)
- [Practicing pH calculations \(http://chemicke-vypocty.cz/Vypocet-pH.html\)](http://chemicke-vypocty.cz/Vypocet-pH.html)