

Henderson-Hasselbalch equation/derivation

This article has been translated from WikiSkripta; ready for the **editor's review**.

A buffer is a solution of a weak acid and its salt, or a weak base and its salt. Let us now assume the first option.

The weak acid HA will dissociate in solution according to the equation: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$. The equilibrium state for this reaction can be described by the acid dissociation constant K_A , while according to Guldberg and Waag's law :

$$K_A = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (1)$$

HA is a weak acid, so the given equilibrium is significantly shifted to the left. In other words, only a very small fraction of the acid is in the dissociated state. We can say that the equilibrium concentration $[\text{HA}]$ is practically equal to its theoretical initial concentration c_A :

$$[\text{HA}] \approx c_A \quad (2)$$

Let us define the theoretical initial concentration c_A as follows: imagine that we can dissolve HA acid in water in a very short time, while the dissociation of HA into H^+ and A^- takes a relatively long time. The theoretical initial concentration c_A is the concentration that HA acid would have in solution just after its complete dissolution, but before it has had time to dissociate. We can also say that in a solution of HA acid alone $c_A = [\text{HA}] + [\text{A}^-]$.

The other component of the buffer, salt, completely dissociates in aqueous solution:



Since only a very small part of the acid HA provides the anion A^- , and on the contrary, practically all molecules of the salt AB form A^- , we can claim that the equilibrium concentration of A^- is practically equal to the theoretical initial concentration of the salt AB (we denote c_B):

$$[\text{A}^-] \approx c_B \quad (3)$$

We substitute (2) and (3) into equation (1):

$$K_A = [\text{H}^+] \cdot \frac{c_B}{c_A}$$

We express $[\text{H}^+]$:

$$[\text{H}^+] = K_A \cdot \frac{c_A}{c_B},$$

and by definition we get:

$$\text{pH} = -\log\left(K_A \cdot \frac{c_A}{c_B}\right).$$

We adjust algebraically:

$$\text{pH} = \text{p}K_A - \log \frac{c_A}{c_B}$$

and finally:

$$\text{pH} = \text{p}K_A + \log \frac{c_B}{c_A}.$$

Let's summarize the assumptions under which the Henderson and Hasselbalch equation will be valid:

1. We are working with a very dilute solution whose behavior is close to an ideal solution. The activities and concentrations of the components are practically the same, the dissociation constant does not depend on the composition of the solution.
2. HA is a weak acid that dissociates very little.
3. The AB salt completely hydrolyzes in aqueous solution.