

pKa and Ka

The Ka value is a value used to describe the tendency of compounds or ions to dissociate and is also called the dissociation constant, the ionisation constant and the acid constant.

The pKa value is a value related to the Ka value in a logic manner. pKa values are easier to remember than Ka values and pKa values are in many cases easier to use for fast approximations of concentrations of compounds and ions in equilibriums than Ka values.

Definition of pKa and Ka

The definition of Ka is: $\frac{[H^+] \cdot [B]}{[HB]}$, where B is the conjugate base of the acid HB.

The pKa value is defined from Ka and can be calculated from the Ka value and from the equation

$$pKa = -\text{Log}_{10}(Ka)$$

Example on how pKa and Ka values are used

An easy about ammonium and ammonia example on how Ka and pKa values are used for calculating equilibriums is given below. The Ka value of NH_4^+ is $5.75 \cdot 10^{-10}$ under ideal conditions at 25 degrees Celsius.

This Ka value is used to determine how much of the NH_4^+ is dissociated into its conjugate base NH_3 by the reaction $NH_4^+ \rightarrow NH_3 + H^+$.

Do also notice that the reaction $NH_4^+ \leftrightarrow NH_3 + H^+$ can go either way depending on conditions.

By introducing the parameter TAN (Total Ammonium Nitrogen) which is ($[NH_4^+] + [NH_3]$) it can be calculated how much of the TAN is on the form NH_4^+ and NH_3 at any given pH.

The calculations allowing this is a bit complicated, but once you have been through them once it's really simple:

$$TAN = [NH_4^+] + [NH_3] = [NH_3] \cdot \left(1 + \frac{NH_4^+}{NH_3}\right)$$

By removing the second part of the above equation only:

$$TAN = [NH_3] \cdot \left(1 + \frac{NH_4^+}{NH_3}\right)$$

remains. This equation can be rearranged to:

$$[\text{NH}_3] = \frac{\text{TAN}}{\left(1 + \frac{[\text{NH}_4^+]}{[\text{NH}_3]}\right)}$$

By multiplying the denominator in the last part of the above equation with $[\text{H}^+]$ one gets:

$$[\text{NH}_3] = \frac{\text{TAN}}{\left(1 + \frac{[\text{H}^+] \cdot [\text{NH}_4^+]}{[\text{NH}_3] \cdot [\text{H}^+]}\right)} \quad (*)$$

The definition of K_a said that $K_a = \frac{[\text{H}^+] \cdot [\text{B}]}{[\text{HB}]}$. Written in the context of the above

example K_a of ammonium or NH_4^+ is: $\frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}$

This is not enough for a smooth substitution in (*) so we calculate $\frac{1}{K_a}$ to $\frac{[\text{NH}_4^+]}{[\text{H}^+][\text{NH}_3]}$ which can be substituted into (*):

$$[\text{NH}_3] = \frac{\text{TAN}}{\left(1 + \frac{[\text{H}^+] \cdot [\text{NH}_4^+]}{[\text{NH}_3] \cdot [\text{H}^+]}\right)} \leftrightarrow [\text{NH}_3] = \frac{\text{TAN}}{\left(1 + \frac{[\text{H}^+]}{K_a}\right)} \quad (\#)$$

From this equation $[\text{NH}_3]$ can be calculated when TAN, $[\text{H}^+]$ and K_a are known.

Let's say that TAN is 0.1 M, pH is 8.24 and the K_a value is $5.75 \cdot 10^{-10}$, equivalent of a p K_a value of 9.24. If we place these values into (#) we get that:

$$[\text{NH}_3] = \frac{0.1}{\left(1 + \frac{5.75 \cdot 10^{-9}}{5.75 \cdot 10^{-10}}\right)} \approx 0.009 \text{ M}$$

The trick with using p K_a values is, that in equilibriums like the ammonium/ammonia equilibrium you can always tell, that if the pH value is 1 unit lower than the p K_a value, the concentration of ammonia $[\text{NH}_3]$ is 1/11 of the total TAN concentration because of the base 10 log relationship between K_a and p K_a . Had the pH value been 7.24 or 2 units less than the p K_a value, 1/101 of the TAN had been $[\text{NH}_3]$.

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