

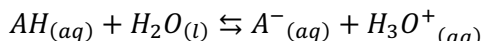
Acid/base equilibria

Note: In Brönsted's theory, the following applies only to weak acids and weak bases. Strong acids and strong bases are completely dissociated in water.

Acid constant of an acid/base couple

1. Reaction of an acid with water.

Let's consider the reaction of an acid AH with water:



This reaction can be defined by the following equilibrium constant: $K_A = \frac{[A^{-}]_{eq}[H_3O^{+}]_{eq}}{[AH]_{eq}}$

K_A is the acid constant of the couple AH/A^{-} .

2. pK_A of an acid/base couple.

The same mathematical operator ($pX = -\log(X)$) can be applied to the acid constant than has been applied to the concentration in oxonium ions to define the pH. This gives the pK_A of the couple.

$$pK_A = -\log K_A = -\log \frac{[A^{-}]_{eq}[H_3O^{+}]_{eq}}{[AH]_{eq}}$$

3. Force of an acid or a base

The lower the pK_A of a couple, the stronger the acid and the weaker its conjugated base.

The higher the pK_A of a couple, the weaker the acid and the stronger its conjugated base.

4. Relation between pK_A of a couple and pH of the solution it is found in

$$pK_A = -\log K_A = -\log \frac{[A^{-}]_{eq}[H_3O^{+}]_{eq}}{[AH]_{eq}} = -\log \frac{[A^{-}]_{eq}}{[AH]_{eq}} - \log[H_3O^{+}]_{eq}$$

$$\Rightarrow pH = pK_A + \log \frac{[A^{-}]_{eq}}{[AH]_{eq}}$$

5. Prevalence diagram of an acid/base couple.

Based on the previous expression, we can establish the pH ranges where the species of an acid-base pair predominate. Indeed:

- If $pH = pK_A$, then $\log \frac{[A^{-}]_{eq}}{[AH]_{eq}} = 0 \Rightarrow \frac{[A^{-}]_{eq}}{[AH]_{eq}} = 1$
The acid and its conjugated base have the same concentration.
- If $pH > pK_A$, then $\log \frac{[A^{-}]_{eq}}{[AH]_{eq}} > 0 \Rightarrow \frac{[A^{-}]_{eq}}{[AH]_{eq}} > 1$
The basic form, A^{-}_{aq} , predominates.

Note: Generally, the basic form is considered to predominate when $pH > pK_A + 1$.

The concentration of the basic form is then 10 times higher than the concentration of the acidic form..

- If $pH < pK_A$, then $\log \frac{[A^{-}]_{eq}}{[AH]_{eq}} < 0 \Rightarrow \frac{[A^{-}]_{eq}}{[AH]_{eq}} < 1$

The acidic form, AH_{aq} , predominates.

Note: Generally, the acidic form is considered to predominate when $pH < pK_A - 1$.

The concentration of the acidic form is then 10 times higher than the concentration of the basic form..

A prevalence diagram can then be drawn:



Note: This is a prevalence diagram, not a presence diagram. Both forms are present, but the concentration of one form might be higher than the concentration of the other.

Acid	Base
perchloric acid hydrofluoric acid hydrogen iodide hydrogen bromide hydrogen chloride nitric acid hydrobromic acid hydrogen sulfide ion phosphoric acid hydrogen fluoride nitrous acid acetic acid carbonic acid hydrogen sulfide cyanosulfonic acid hydrogen cyanide hydrogen carbonate ion water hydrogen sulfide ion ethanol ammonia hydrogen methane	ClO_4^{-} HF I^{-} Br^{-} Cl^{-} NO_3^{-} H_2O HS^{-} $H_2PO_4^{-}$ HF NO_2^{-} CH_3COO^{-} H_2CO_3 HS^{-} HCN CO_3^{2-} OH^{-} C_2H_5OH NH_3 H_2 CH_4

6. Ionic product of water.

Water is an amphoteric molecule, participating in two acid/base couples. An acid constant can be defined for each of these couples:

- H_3O^+/H_2O : $K_A(H_3O^+/H_2O) = \frac{[H_3O^+]_{eq}}{[H_3O^+]_{eq}} = 1 \Rightarrow pK_A(H_3O^+/H_2O) = 0$

Note: pK_A of a strong acid is negative.

- H_2O/HO^- : $K_A(H_2O/HO^-) = [H_3O^+]_{eq}[HO^-]_{eq}$

This peculiar acid constant is the ionic product of water, K_w .

$$K_w = [H_3O^+]_{eq}[HO^-]_{eq}$$

At ambient temperature, $K_w = 10^{-14} \Rightarrow pK_w = pK_A(H_2O/HO^-) = 14$

Notes: pK_A of a strong base is higher than 14.

It is the value of K_w that explains the pH scale.

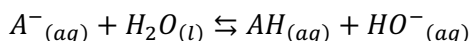
Indeed, when a solution is neutral, it does not contain no oxonium ions and hydroxide ions, but contains AS MANY oxonium ions than hydroxide ions.

$$[H_3O^+]_{eq} = [HO^-]_{eq} \Rightarrow K_w = [H_3O^+]_{eq}^2 \Rightarrow [H_3O^+]_{eq} = \sqrt{pH} = 10^{-7} \text{ mol. L}^{-1} \Rightarrow pH = 7$$

Equilibrium constant of an acid/base reaction

1. Equilibrium constant of the reaction of a base with water.

The reaction of a base A^- with water can be written



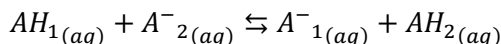
The equilibrium constant of this reaction is:

$$K = \frac{[AH]_{eq}[HO^-]_{eq}}{[A^-]_{eq}} = \frac{[AH]_{eq}[HO^-]_{eq}}{[A^-]_{eq}} \times \frac{[H_3O^+]_{eq}}{[H_3O^+]_{eq}} = \frac{[HO^-]_{eq}[H_3O^+]_{eq}}{\frac{[A^-]_{eq}[H_3O^+]_{eq}}{[AH]_{eq}}} = \frac{K_w}{K_A}$$

Note: This constant is defined as the base constant of the couple, K_b .

2. Equilibrium constant of the reaction between two acid/base couples.

The equation of the reaction between an acid AH_1 and a base A^-_2 can be written



The equilibrium constant of this reaction is:

$$K = \frac{[A^-_1]_{eq}[AH_2]_{eq}}{[AH_1]_{eq}[A^-_2]_{eq}} = \frac{[A^-_1]_{eq}[AH_2]_{eq}}{[AH_1]_{eq}[A^-_2]_{eq}} \times \frac{[H_3O^+]_{eq}}{[H_3O^+]_{eq}} = \frac{\frac{[A^-_1]_{eq}[H_3O^+]_{eq}}{[AH_1]_{eq}}}{\frac{[A^-_2]_{eq}[H_3O^+]_{eq}}{[AH_2]_{eq}}} = \frac{K_{A1}}{K_{A2}}$$

3. Quantitative approach of the reaction between two acid/base couples.

The expression of the equilibrium constant, combined with the construction of a progress table, makes it possible to determine the concentrations of the chemical species involved in the reaction between two acid/base pairs. To do this, it is sufficient to know the following quantities:

- the acidity constant of each of the pairs involved.
- either the pH of the solution at equilibrium, or the final progress x_f , or the final progress rate τ_ϕ , or the concentrations of the reactants, etc.