
Acid and Bases Formula Derivation

ChemieLearn

Immanuel Rava

Dissociation of a Weak Monoprotic Acid/Base in Water

When an acid was dissolved in water it will dissociate to give hydronium ion (H^+) and conjugate ion (A^-). However, there are still other co-existent components such as the hydroxide anion (OH^-) and the leftover acid that co-exist in equilibrium. To calculate the amount of hydronium ion present in the solution, we shall write the necessary equations and equilibrium constant.

[1] Equilibrium Constant Expression

For a simple monoprotic acid, the acid dissociation constant is given by,

$$K_a = \frac{[H^+]_{eq}[A^-]_{eq}}{[HA]_{eq}}$$

The subscript “eq” denotes the amount of each respective compound in equilibrium concentration.

[2] Mass Balance

The mass of the initial monoprotic acid should be conserved,

$$[HA]_0 = [HA]_{eq} + [A^-]_{eq}$$

[3] Charge Balance

As the solution is neutral, the amount of negative and positive charge present in the solution must be equal,

$$[H^+]_{eq} = [OH^-]_{eq} + [A^-]_{eq}$$

Using the algebraic substitution, we can reduce the number of unknown variable in equilibrium constant expression,

$$\begin{aligned} K_a &= \frac{[H^+]_{eq}[A^-]_{eq}}{[HA]_0 - [A^-]_{eq}} \\ &= \frac{[H^+]_{eq}([H^+]_{eq} - [OH^-]_{eq})}{[HA]_0 - ([H^+]_{eq} - [OH^-]_{eq})} \end{aligned}$$

The latter equation can be simplified by using water equilibrium constant (K_w),

$$\begin{aligned} K_a &= \frac{[H^+]_{eq}^2 - [H^+]_{eq}[OH^-]_{eq}}{[HA]_0 - [H^+]_{eq} + [OH^-]_{eq}} \\ [H^+]_{eq}^2 - [H^+]_{eq}[OH^-]_{eq} &= K_a[HA]_0 - K_a[H^+]_{eq} + K_a[OH^-]_{eq} \\ [H^+]_{eq}^2 - K_w &= K_a[HA]_0 - K_a[H^+]_{eq} + \frac{K_a K_w}{[H^+]_{eq}} \end{aligned}$$

Rearrange the polynomial,

$$[H^+]_{eq}^3 + K_a[H^+]_{eq}^2 - (K_w + K_a[HA]_0)[H^+]_{eq} - K_a K_w = 0$$

For most practical applications, we can make approximations that eliminate the need to solve a cubic equation.

Assumption 1. Neglecting the population of hydroxide anion (hydronium ion)

The amount of hydroxide anion present in acidic solution can be neglected unless the acid is very weak or the solution is extremely dilute. In case of neglect of hydroxide anion in the solution, the water equilibrium constant term (K_w) diminished, enabling us to simplify the cubic expression into quadratic expression.

$$\begin{aligned} [\text{H}^+]_{\text{eq}}^3 + K_a [\text{H}^+]_{\text{eq}}^2 - K_a [\text{HA}]_0 [\text{H}^+]_{\text{eq}} &= 0 \\ [\text{H}^+]_{\text{eq}} ([\text{H}^+]_{\text{eq}}^2 + K_a [\text{H}^+]_{\text{eq}} - K_a [\text{HA}]_0) &= 0 \end{aligned}$$

Thus, the concentration of hydronium ion is given by,

$$[\text{H}^+]_{\text{eq}} = \frac{-K_a + \sqrt{K_a^2 + 4K_a[\text{HA}]_0}}{2}$$

Assumption 2. Concentrated Acid

If the acid is fairly concentrated (usually more than 10^{-3} M), a further simplification can frequently be achieved by making the assumption that $[\text{H}^+]_{\text{eq}} \ll [\text{HA}]_0$. This is justified when most of the acid remains in its protonated form, so that relatively little hydronium ion is produced.

$$\begin{aligned} [\text{H}^+]_{\text{eq}}^2 - K_a ([\text{H}^+]_{\text{eq}} - [\text{HA}]_0) &= 0 \xrightarrow{[\text{H}^+]_{\text{eq}} \ll [\text{HA}]_0} [\text{H}^+]_{\text{eq}}^2 - K_a [\text{HA}]_0 = 0 \\ [\text{H}^+]_{\text{eq}} &\approx \sqrt{K_a [\text{HA}]_0} \end{aligned}$$

Exercise

- [a] Write an expression to calculate the concentration of hydronium ion for a weak diprotic acid (H_2A) provided that it has two dissociation constant $K_{a,1}$ and $K_{a,2}$.

$$[\text{H}^+]_{\text{eq}} = \frac{K_{a,2} [\text{H}_2\text{A}]_0 ([\text{H}^+]_{\text{eq}} + 2K_{a,2})}{[\text{H}^+]_{\text{eq}}^2 + K_{a,1} [\text{H}^+]_{\text{eq}} + K_{a,1} K_{a,2}}$$

- [b] Explain what happen to the expression in part [a] if $K_{a,1} \gg K_{a,2}$.

The expression in part [a] would be similar to the formula to calculate the concentration of hydronium ion from the dissociation of weak monoprotic acid.

Salt Hydrolysis

Salt hydrolysis refers to the chemical reaction between a salt and water, resulting in the formation of an acidic or basic solution. This reaction occurs due to the dissociation of the salt into its constituent ions in water and subsequent interaction with water molecules. When a salt is dissolved in water, it breaks down into its component cations (positively charged ions) and anions (negatively charged ions). The nature of these ions determines the outcome of the hydrolysis reaction.

There are three possible scenarios for salt hydrolysis:

1. Neutral Salt

Some salts do not undergo hydrolysis because they consist of the cation and anion of a strong acid and a strong base, respectively. These salts do not affect the pH of the solution. Examples include sodium chloride, potassium nitrate, and calcium chloride.

2. Acidic Salt

When a salt is derived from a weak acid and a strong base, it hydrolyzes to produce an acidic solution. The cation of the salt acts as a weak acid by donating a proton to water, increasing the concentration of ions and lowering the pH. An example of an acidic salt is ammonium chloride.

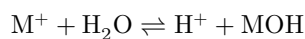


The ammonium ion (NH_4^+) reacts with water to produce hydronium ions and ammonium hydroxide, increasing the acidity of the solution.

3. Alkaline Salt

When a salt is derived from a strong acid and a weak base, it hydrolyzes to produce a basic solution. The anion of the salt acts as a weak base by accepting a proton from water, increasing the concentration of hydroxide anions and raising the pH. An example of a basic salt is sodium acetate.

The concentration of hydronium ion in the solution is dependent on the type salt, for simplicity we shall only derive the hydrolysis of acidic salt that is generated from the reaction between strong acid and weak base. Consider the reaction between a strong reactive cation (conjugate acid) with water,



Equilibrium constant expression for the reaction above is given by,

$$K'_a = \frac{[\text{MOH}]_{\text{eq}}[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}[\text{H}_2\text{O}]_{\text{eq}}}$$

We assume that the reaction occur in water medium, hence,

$$K'_a = \frac{[\text{MOH}]_{\text{eq}}[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}}$$

The equivalent of K'_a can be expressed by considering the weak base dissociation constant,

$$\begin{aligned}
K'_a &= \frac{[\text{MOH}]_{\text{eq}}[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}} \cdot \frac{[\text{OH}^-]_{\text{eq}}}{[\text{OH}^-]_{\text{eq}}} \\
&= \frac{[\text{MOH}]_{\text{eq}}}{\underbrace{[\text{M}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}_{K_b^{-1}}} \cdot K_w
\end{aligned}$$

Again, we construct the mass balance and charge balance of the reaction,

[1] Mass Balance

The mass of the initial conjugate acid should be conserved,

$$[\text{M}^+]_0 = [\text{M}^+]_{\text{eq}} + [\text{MOH}]_{\text{eq}}$$

[2] Charge Balance

As the solution is neutral, the amount of negative and positive charge present in the solution must be equal,

$$[\text{H}^+]_{\text{eq}} + [\text{M}^+]_{\text{eq}} = [\text{OH}^-]_{\text{eq}} + [\text{X}^-]_0$$

The negative X^- anion is the counter anion of the strong conjugate acid (M^+).

Using the algebraic substitution, we can reduce the number of unknown variable in equilibrium constant expression,

$$\begin{aligned}
K'_a &= \frac{([\text{M}^+]_0 - [\text{M}^+]_{\text{eq}})[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}} \\
&= \frac{([\text{M}^+]_0 + [\text{H}^+]_{\text{eq}} - [\text{OH}^-]_{\text{eq}} - [\text{X}^-]_0)[\text{H}^+]_{\text{eq}}}{[\text{OH}^-]_{\text{eq}} + [\text{X}^-]_0 - [\text{H}^+]_{\text{eq}}}
\end{aligned}$$

In the initial condition, $[\text{M}^+]_0 = [\text{X}^-]_0$, thus,

$$K'_a = \frac{([\text{H}^+]_{\text{eq}} - [\text{OH}^-]_{\text{eq}})[\text{H}^+]_{\text{eq}}}{[\text{OH}^-]_{\text{eq}} + [\text{M}^+]_0 - [\text{H}^+]_{\text{eq}}}$$

The latter equation can be simplified by using water equilibrium constant (K_w),

$$\frac{K'_a K_w}{[\text{H}^+]_{\text{eq}}} + K'_a [\text{M}^+]_0 - K'_a [\text{H}^+]_{\text{eq}} = [\text{H}^+]_{\text{eq}}^2 - K_w$$

Rearranging the expression,

$$[\text{H}^+]_{\text{eq}}^3 + K'_a [\text{H}^+]_{\text{eq}}^2 - (K_w + K'_a [\text{M}^+]_0) [\text{H}^+]_{\text{eq}} - K'_a K_w = 0$$

For most practical applications, we can make approximations that eliminate the need to solve a cubic equation.

Assumption 1. Neglecting the population of hydroxide anion (hydronium ion)

The amount of hydroxide anion present in acidic solution can be neglected similar to the weak acid case. In case of neglect of hydroxide anion in the solution, the water equilibrium constant term (K_w) diminished, enabling us to simplify the cubic expression into quadratic expression.

$$[\text{H}^+]_{\text{eq}}^3 + K'_a [\text{H}^+]_{\text{eq}}^2 - K'_a [\text{M}^+]_0 [\text{H}^+]_{\text{eq}} = 0$$

$$[\text{H}^+]_{\text{eq}}([\text{H}^+]_{\text{eq}}^2 + K'_a[\text{H}^+]_{\text{eq}} - K'_a[\text{M}^+]_0) = 0$$

Thus, the concentration of hydronium ion is given by,

$$[\text{H}^+]_{\text{eq}} = \frac{-K'_a + \sqrt{(K'_a)^2 + 4K'_a[\text{M}^+]_0}}{2}$$

Assumption 2. High Concentration of Conjugate Acid/Base

If the concentration of the conjugate acid/base is sufficiently high, we can assume that $[\text{M}^+]_0 \gg [\text{H}^+]_{\text{eq}}$,

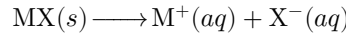
$$[\text{H}^+]_{\text{eq}}^2 + K'_a[\text{H}^+]_{\text{eq}} - K'_a[\text{M}^+]_0 = 0 \xrightarrow{[\text{M}^+]_0 \gg [\text{H}^+]_{\text{eq}}} [\text{H}^+]_{\text{eq}}^2 - K'_a[\text{M}^+]_0 = 0$$

Hence,

$$\begin{aligned} [\text{H}^+]_{\text{eq}} &\approx \sqrt{K'_a[\text{M}^+]_0} \\ &\approx \sqrt{\frac{K_w}{K_b}[\text{M}^+]_0} \end{aligned}$$

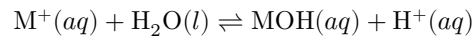
Where K_b is the equilibrium constant for the dissociation of the source of the conjugate acid (weak base).

We have discussed the derivation for the acidic and alkaline salt in which only one of its component able to hydrolyze the water. Suppose we have a salt that is result of reaction between weak acid and weak base (i.e. $\text{CH}_3\text{CO}_2\text{NH}_4$), the nature of the salt is dependent on the competition of cation and the anion of the salt to hydrolyze the water. The dissociation of the salt is given by,

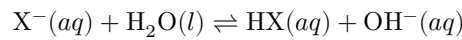


The cation (M^+) will react with water to produce hydronium ion, in contrast to the anion which will produce hydroxide ion.

- Reaction of M^+ with water



- Reaction of X^- with water



Again, we will write the equilibrium expression for each hydrolysis reaction,

$$\begin{aligned} K'_a &= \frac{[\text{MOH}]_{\text{eq}}[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}} = \frac{K_w}{K_{b,\text{MOH}}} \\ K'_b &= \frac{[\text{HX}]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{X}^-]_{\text{eq}}} = \frac{K_w}{K_{a,\text{HX}}} \end{aligned}$$

Construct the mass balance and charge balance equation,

[1] Mass Balance

The mass of the initial conjugate acid and conjugate base should be conserved,

$$\begin{aligned}[\text{M}^+]_0 &= [\text{M}^+]_{\text{eq}} + [\text{MOH}]_{\text{eq}} \\ [\text{X}^-]_0 &= [\text{X}^-]_{\text{eq}} + [\text{HX}]_{\text{eq}}\end{aligned}$$

[2] Charge Balance

As the solution is neutral, the amount of negative and positive charge present in the solution must be equal,

$$[\text{H}^+]_{\text{eq}} + [\text{M}^+]_{\text{eq}} = [\text{OH}^-]_{\text{eq}} + [\text{X}^-]_{\text{eq}}$$

Using the algebraic substitution, we can reduce the number of unknown variable in equilibrium constant expression.

$$\begin{aligned}K'_a &= \frac{([\text{M}^+]_0 - [\text{M}^+]_{\text{eq}})[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}} \\ K'_b &= \frac{([\text{X}^-]_0 - [\text{X}^-]_{\text{eq}})[\text{OH}^-]_{\text{eq}}}{[\text{X}^-]_{\text{eq}}}\end{aligned}$$

We need to find the expression of $[\text{M}^+]_{\text{eq}}$ and $[\text{X}^-]_{\text{eq}}$ as a function of its respective equilibrium constant.

$$\begin{aligned}[\text{M}^+]_{\text{eq}} &= \frac{[\text{M}^+]_0[\text{H}^+]_{\text{eq}}}{K'_a + [\text{H}^+]_{\text{eq}}} \\ [\text{X}^-]_{\text{eq}} &= \frac{[\text{X}^-]_0[\text{OH}^-]_{\text{eq}}}{K'_b + [\text{OH}^-]_{\text{eq}}}\end{aligned}$$

Substitute the expression of $[\text{M}^+]_{\text{eq}}$ and $[\text{X}^-]_{\text{eq}}$ into the charge balance equation,

$$\begin{aligned}[\text{H}^+]_{\text{eq}} + \frac{[\text{M}^+]_0[\text{H}^+]_{\text{eq}}}{K'_a + [\text{H}^+]_{\text{eq}}} &= [\text{OH}^-]_{\text{eq}} + \frac{[\text{X}^-]_0[\text{OH}^-]_{\text{eq}}}{K'_b + [\text{OH}^-]_{\text{eq}}} \\ [\text{H}^+]_{\text{eq}} \left(1 + \frac{[\text{M}^+]_0}{K'_a + [\text{H}^+]_{\text{eq}}} \right) &= [\text{OH}^-]_{\text{eq}} \left(1 + \frac{[\text{X}^-]_0}{K'_b + [\text{OH}^-]_{\text{eq}}} \right)\end{aligned}$$

In most cases, the following approximation holds true,

$$\frac{[\text{M}^+]_0}{K'_a + [\text{H}^+]_{\text{eq}}} \gg 1 \text{ and } \frac{[\text{X}^-]_0}{K'_b + [\text{OH}^-]_{\text{eq}}} \gg 1$$

Using the approximation above, the expression can be simplified into,

$$\begin{aligned}\frac{[\text{H}^+]_{\text{eq}}[\text{M}^+]_0}{K'_a + [\text{H}^+]_{\text{eq}}} &= \frac{[\text{OH}^-]_{\text{eq}}[\text{X}^-]_0}{K'_b + [\text{OH}^-]_{\text{eq}}} \\ [\text{M}^+]_0([\text{H}^+]_{\text{eq}}K'_b + K_w) &= [\text{X}^-]_0 \left(\frac{K'_aK_w}{[\text{H}^+]_{\text{eq}}} + K_w \right) \\ K'_b[\text{M}^+]_0[\text{H}^+]_{\text{eq}}^2 + K_w[\text{M}^+]_0[\text{H}^+]_{\text{eq}} &= K'_aK_w[\text{X}^-]_0 + K_w[\text{X}^-]_0[\text{H}^+]_{\text{eq}} \\ K'_b[\text{M}^+]_0[\text{H}^+]_{\text{eq}}^2 + K_w([\text{M}^+]_0 - [\text{X}^-]_0)[\text{H}^+]_{\text{eq}} - K'_aK_w[\text{X}^-]_0 &= 0\end{aligned}$$

Thus, the concentration of the hydronium ion is given by,

$$[\text{H}^+]_{\text{eq}} = \frac{-K_w([\text{M}^+]_0 - [\text{X}^-]_0) + \sqrt{K_w^2([\text{M}^+]_0 - [\text{X}^-]_0)^2 + 4K'_aK'_bK_w[\text{M}^+]_0[\text{X}^-]_0}}{2K'_b[\text{M}^+]_0}$$

We can assume that the amount of M^+ ion and X^- ion is equal as they dissociated from single MX salt,

$$\begin{aligned} [H^+]_{eq} &= \frac{\sqrt{4K'_a K'_b K_w [M^+]_0^2}}{2K'_b [M^+]_0} \\ &= \sqrt{\frac{K'_a K_w}{K'_b}} \\ &= \sqrt{\frac{K_{a,HX} K_w}{K_{b,MOH}}} \end{aligned}$$

From the expression of $[H^+]_{eq}$, we can deduce that the nature of salt that is produced by reacting weak acid (HX) and weak base (MOH) could be predicted by finding the ratio of $K_{a,HX}$ with respect to $K_{b,MOH}$.

- $K_{a,HX} > K_{b,MOH} \implies$ Acidic Salt
- $K_{a,HX} = K_{b,MOH} \implies$ Neutral Salt
- $K_{a,HX} < K_{b,MOH} \implies$ Alkaline Salt

Buffer Solution

A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added to it. It consists of a mixture of a weak acid and its conjugate base (or a weak base and its conjugate acid) in approximately equal concentrations. The pH of a buffer solution can be calculated by considering the existing conjugate ion species and the remaining acid or base.

For simplicity, we shall discuss the acidic buffer as the derivation for the alkaline buffer would be similar to deriving the acidic buffer. Considering the dissociation of weak acid HX with initial concentration $[HX]_0$ and dissociation of MX salt with concentration $[MX]_0$. We write the dissociation constant for acid HX as follows,

$$K_a = \frac{[H^+]_{eq}[X^-]_{eq}}{[HX]_{eq}}$$

We write the mass balance and charge balance equation,

[1] Mass Balance

- Cation M^+

$$[MX]_0 = [M^+]_0$$

- Anion X^-

$$[HX]_0 + [MX]_0 = [X^-]_{eq} + [HX]_{eq}$$

[2] Charge Balance

The solution is neutral in the first place, therefore,

$$[M^+]_0 + [H^+]_{eq} = [X^-]_{eq} + [OH^-]_{eq}$$

Using substitution, the expression for the equilibrium constant can be modified as follows,

$$K_a = \frac{[H^+]_{eq}[X^-]_{eq}}{[HX]_0 + [MX]_0 - [X^-]_{eq}}$$

We further utilize the charge balance to substitute $[X^-]_{eq}$,

$$\begin{aligned} K_a &= \frac{[H^+]_{eq}([M^+]_0 + [H^+]_{eq} - [OH^-]_{eq})}{[HX]_0 + [M^+]_0 - ([M^+]_0 + [H^+]_{eq} - [OH^-]_{eq})} \\ &= \frac{[H^+]_{eq}([M^+]_0 + [H^+]_{eq} - [OH^-]_{eq})}{[HX]_0 - [H^+]_{eq} + [OH^-]_{eq}} \\ &= \frac{[H^+]_{eq}^3 + [M^+]_0[H^+]_{eq}^2 - K_w[H^+]_{eq}}{-[H^+]_{eq}^2 + [HX]_0[H^+]_{eq} + K_w} \end{aligned}$$

Rearrange the terms,

$$[H^+]_{eq}^3 + ([M^+]_0 + K_a)[H^+]_{eq}^2 - (K_w + K_a[HX]_0)[H^+]_{eq} + K_a K_w = 0$$

For most practical applications, we can make approximations that eliminate the need to solve a cubic equation.

Assumption 1. Neglecting the population of hydroxide anion (hydronium ion)

The amount of hydroxide anion present in acidic solution can be neglected similar to the weak acid case. In case of neglection of hydroxide anion in the solution, the water equilibrium constant term (K_w) diminished, enabling us to simplify the cubic expression into quadratic expression.

$$[\text{H}^+]_{\text{eq}}^3 + ([\text{M}^+]_0 + K_a)[\text{H}^+]_{\text{eq}}^2 - K_a[\text{HX}]_0[\text{H}^+]_{\text{eq}} = 0$$

$$[\text{H}^+]_{\text{eq}}([\text{H}^+]_{\text{eq}}^2 + ([\text{M}^+]_0 + K_a)[\text{H}^+]_{\text{eq}} - K_a[\text{HX}]_0) = 0$$

Thus, the concentration of hydronium ion is given by,

$$[\text{H}^+]_{\text{eq}} = \frac{-[\text{M}^+]_0 - K_a + \sqrt{([\text{M}^+]_0 + K_a)^2 + 4K_a[\text{HX}]_0}}{2}$$

Assumption 2. High Concentration of Conjugate Acid/Base and Weak Acid/Base

If the concentration of both the conjugate acid/base and the weak acid/base is sufficiently high, we can assume the following,

[1] Assumption that $[\text{HX}]_0 \gg [\text{H}^+]_{\text{eq}}$

$$[\text{H}^+]_{\text{eq}}^2 + [\text{M}^+]_0[\text{H}^+]_{\text{eq}} + K_a[\text{H}^+]_{\text{eq}} - K_a[\text{HX}]_0 = 0$$

$$[\text{H}^+]_{\text{eq}}^2 + [\text{M}^+]_0[\text{H}^+]_{\text{eq}} + K_a([\text{H}^+]_{\text{eq}} - [\text{HX}]_0) = 0 \xrightarrow{[\text{HX}]_0 \gg [\text{H}^+]_{\text{eq}}} [\text{H}^+]_{\text{eq}}^2 + [\text{M}^+]_0[\text{H}^+]_{\text{eq}} - K_a[\text{HX}]_0 = 0$$

[2] Assumption that $[\text{MX}]_0 \gg [\text{H}^+]_{\text{eq}}$

$$[\text{H}^+]_{\text{eq}}^2 + [\text{M}^+]_0[\text{H}^+]_{\text{eq}} - K_a[\text{HX}]_0 = 0$$

$$([\text{H}^+]_{\text{eq}} + [\text{M}^+]_0)[\text{H}^+]_{\text{eq}} - K_a[\text{HX}]_0 = 0 \xrightarrow{[\text{MX}]_0 \gg [\text{H}^+]_{\text{eq}}} [\text{M}^+]_0[\text{H}^+]_{\text{eq}} - K_a[\text{HX}]_0 = 0$$

Rearranging the equation,

$$[\text{M}^+]_0[\text{H}^+]_{\text{eq}} = K_a[\text{HX}]_0$$

$$[\text{H}^+]_{\text{eq}} = K_a \frac{[\text{HX}]_0}{[\text{M}^+]_0}$$

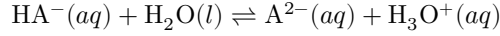
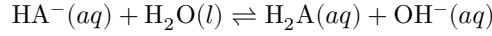
The $[\text{M}^+]_0$ is equivalent with $[\text{MX}]_0$,

$$[\text{H}^+]_{\text{eq}} = K_a \frac{[\text{HX}]_0}{[\text{MX}]_0}$$

With this assumption, the Henderson-Hasselbalch equation has been derived.

Amphiprotic Species

Amphiprotic species are molecules or ions that can act as both acids and bases by donating or accepting protons depending on the reaction conditions. The pH of amphiprotic solution is determined by two equilibrium process. Assume we have an amphiprotic species HA^- (result of dissociation M^+HA^- salt) that could react with water as either acid or base.



The solution would be alkaline if the first equilibrium predominates. However, if the second reaction predominates the first reaction, the solution would be acidic. The relative magnitudes of the equilibrium constants for these processes determine whether a solution of HA^- is acidic or basic.

$$K'_b = \frac{[\text{H}_2\text{A}]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}{[\text{HA}^-]_{\text{eq}}} = \frac{K_w}{K_{a,1}}$$

$$K_{a,2} = \frac{[\text{A}^{2-}]_{\text{eq}}[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}^-]_{\text{eq}}}$$

We write the mass balance and charge balance equation,

[1] Mass Balance

$$[\text{HA}^-]_0 = [\text{HA}^-]_{\text{eq}} + [\text{H}_2\text{A}]_{\text{eq}} + [\text{A}^{2-}]_{\text{eq}}$$

[2] Charge Balance

$$[\text{H}^+]_{\text{eq}} + [\text{M}^+]_0 = [\text{HA}^-]_{\text{eq}} + 2[\text{A}^{2-}]_{\text{eq}} + [\text{OH}^-]$$

By elimination process between charge balance equation and mass balance equation,

$$[\text{H}^+]_{\text{eq}} + ([\text{M}^+]_0 - [\text{HA}^-]_0) = [\text{A}^{2-}]_{\text{eq}} + [\text{OH}^-] - [\text{H}_2\text{A}]_{\text{eq}}$$

Since $[\text{M}^+]_0$ and $[\text{HA}^-]_0$ came from M^+HA^- salt, their initial concentration must be equal to each other, hence we can simplify the expression above into,

$$[\text{H}^+]_{\text{eq}} = [\text{A}^{2-}]_{\text{eq}} + [\text{OH}^-] - [\text{H}_2\text{A}]_{\text{eq}}$$

Using K_a and K_b , we will substitute $[\text{A}^{2-}]$ and $[\text{H}_2\text{A}]_{\text{eq}}$ variable such that it will be expressed as $[\text{HA}^-]_{\text{eq}}$.

$$[\text{H}^+]_{\text{eq}} = \frac{K_{a,2}[\text{HA}^-]_{\text{eq}}}{[\text{H}^+]_{\text{eq}}} + \frac{K_w}{[\text{H}^+]_{\text{eq}}} - \frac{K'_b[\text{HA}^-]_{\text{eq}}[\text{H}^+]_{\text{eq}}}{K_w}$$

$$[\text{H}^+]_{\text{eq}}^2 = K_{a,2}[\text{HA}^-]_{\text{eq}} + K_w - \frac{K'_b[\text{HA}^-]_{\text{eq}}[\text{H}^+]_{\text{eq}}^2}{K_w}$$

$$\left(\frac{K'_b[\text{HA}^-]_{\text{eq}}}{K_w} + 1 \right) [\text{H}^+]_{\text{eq}}^2 = K_{a,2}[\text{HA}^-]_{\text{eq}} + K_w$$

Thus, the expression of hydronium ion in the system is given by,

$$[\text{H}^+]_{\text{eq}} = \sqrt{\frac{K_{a,2}K_w[\text{HA}^-]_{\text{eq}} + K_w^2}{K'_b[\text{HA}^-]_{\text{eq}} + K_w}}$$

This expression can be further simplified by substituting $K'_b = K_w K_{a,1}^{-1}$,

$$[\text{H}^+]_{\text{eq}} = \sqrt{\frac{K_{a,2}[\text{HA}^-]_{\text{eq}} + K_w}{K_{a,1}^{-1}[\text{HA}^-]_{\text{eq}} + 1}}$$

In most cases the ratio of the equilibrium concentration of HA^- with the first dissociation constant of acid H_2A is sufficiently larger than 1.

$$\frac{[\text{HA}^-]_{\text{eq}}}{K_{a,1}} \gg 1$$

Hence,

$$[\text{H}^+]_{\text{eq}} = \sqrt{\frac{K_{a,2}[\text{HA}^-]_{\text{eq}} + K_w}{K_{a,1}^{-1}[\text{HA}^-]_{\text{eq}}}}$$

Further simplification of the expression for $[\text{H}^+]_{\text{eq}}$ can be achieved by assuming that $K_{a,2}[\text{HA}^-] \gg K_w$, giving the simplest expression of $[\text{H}^+]_{\text{eq}}$ for amphiprotic species.

$$[\text{H}^+]_{\text{eq}} = \sqrt{K_{a,1}K_{a,2}}$$