Acid and Bases Formula Sheet
Studium

Imanuel 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 unkown variable in equilibrium constant expression,

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

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

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

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**

The amount of hydroxide anion present in acidic solution can be neglected unless the acid is very weak or the solution is extermely dilute. 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.

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

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.

$$[\text{H}^+]_{\text{eq}}^2 - K_a([\text{H}^+]_{\text{eq}} - [\text{HA}]_0) = 0 \xrightarrow{\;[\text{H}^+]_{\text{eq}} \ll [\text{HA}]_0\;} [\text{H}^+]_{\text{eq}}^2 - K_a[\text{HA}]_0 = 0$$

$$[\text{H}^+]_{\text{eq}} \approx \sqrt{K_a[\text{HA}]_0}$$

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

[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.
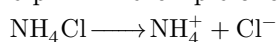
There are three possible scenarios for salt hydrolysis:

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.
 $$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
   The ammonium ion (NH_4^+) reacts with water to produce hydronium ions and ammonium hydroxide, increasing the acidity of the solution.

3. Basic 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,

$$M^+ + H_2O \rightleftharpoons H^+ + MOH$$
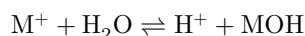
Equilibrium constant expression for the reaction above is given by,

$$K_a' = \frac{[MOH]_{eq}[H^+]_{eq}}{[M^+]_{eq}[H_2O]_{eq}}$$

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

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

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

$$K_a' = \frac{[\text{MOH}]_{\text{eq}}[\text{H}^+]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}} \cdot \frac{[\text{OH}^-]_{\text{eq}}}{[\text{OH}^-]_{\text{eq}}}$$

$$= \underbrace{\frac{[\text{MOH}]_{\text{eq}}}{[\text{M}^+]_{\text{eq}}[\text{OH}^-]_{\text{eq}}}}_{K_b^{-1}} \cdot K_w$$

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 unkown variable in equilibrium constant expression,

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

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

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),

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

Rearranging the expression,

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

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

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.

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

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

Thus, the concentration of hydronium ion is given by,

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