

4.8: Day 34- Acid-Base Reactions

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Day 34: Acid-Base Reactions

D34.1 Polyprotic Acids

We can classify acids by the number of protons per molecule that they can donate in an acid-base reaction. *Acids that contain one ionizable hydrogen atom per molecule* are called **monoprotic acids**. Examples are HCl, HNO₃, CH₃COOH, and HCN.

Even though it contains four hydrogen atoms, acetic acid is also monoprotic because only the hydrogen atom from the carboxyl group (-COOH) reacts with bases:



The three hydrogen atoms in the methyl group are not reactive (the C–H bonds are similar those in alkanes, which are unreactive).

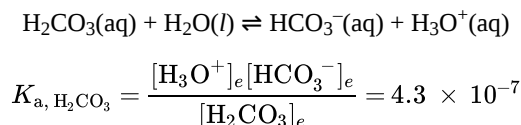
In the same vein, **monoprotic bases** are *bases that accept a single proton*.

Diprotic acids contain two ionizable hydrogen atoms per molecule. The dissociation of the first H⁺ always takes place to a greater extent than the dissociation of the second H⁺. For example, sulfuric acid ionizes in two steps:

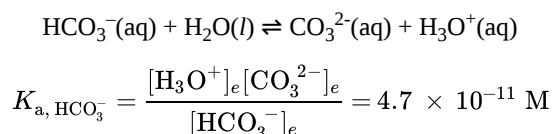
$\text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{HSO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	$K_{a,1} > 10^2$
$\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$	$K_{a,2} = 1.1 \times 10^{-2}$

This *stepwise ionization* occurs for all polyprotic acids.

A solution of a weak diprotic acid contains a mixture of acids. For example, when carbonic acid loses one H⁺, it yields hydronium ions and bicarbonate ions in small quantities:



The bicarbonate ion can lose an H⁺ to form hydronium ions and carbonate ions in even smaller quantities:

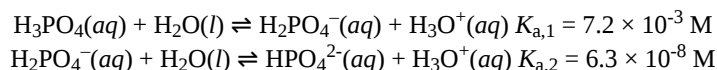


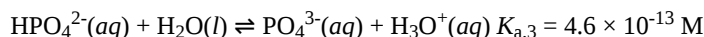
$K_a(\text{H}_2\text{CO}_3)$ is larger than $K_a(\text{HCO}_3^-)$ by about four orders of magnitude (10^4 times larger), so H₂CO₃ is the dominant producer of H₃O⁺ in the solution. This means that the concentrations of H₃O⁺ and HCO₃[−] are practically equal in a pure aqueous solution of H₂CO₃.

If $K_{a,1}$ of a weak diprotic acid at least 20 times larger than $K_{a,2}$, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H₃O⁺ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Activity 1: Ionization of a Diprotic Acid

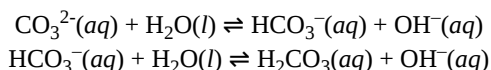
A **triprotic acid** is an acid that has *three protons that undergo stepwise ionization*: Phosphoric acid is an example:





Again, the differences in the ionization constants of these reactions tell us that the degree of ionization is significantly weaker in each successive step. This is a general characteristic of polyprotic acids. Here, because the successive ionization constants differ by a factor of 10^5 - 10^6 , the calculations of equilibrium concentrations in a solution of H_3PO_4 can be broken down into a series of parts, similar to activity 1.

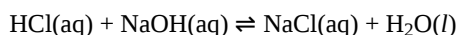
Polyprotic bases can accept more than one H^+ . The carbonate ion is an example of a **diprotic base**, because it can accept up to two protons. Solutions of alkali metal carbonates (e.g. K_2CO_3) are quite alkaline, due to the reactions:



D34.2 Acid-Base Reactions

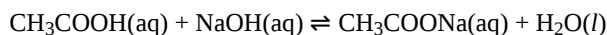
Mixing a solution of an acid with a solution of a base results in an acid-base neutralization reaction that produces a salt and water. The thermodynamics of an acid-base reaction dictates that the side with the weaker acid and weaker base is favored. In other words, if the weaker acid and weaker base are on the left side of an equilibrium reaction, the reaction is reactant-favored at equilibrium; if the weaker acid and weaker base are on the right side, the reaction is product-favored at equilibrium. Strengths of acids and bases are quantitatively comparable by their K_{a} and K_{b} values, which can be obtained from a [reference table](#).

A strong acid reacts with a strong base to form a neutral solution (containing equal concentrations of H_3O^+ and OH^-) provided that *stoichiometrically equivalent quantities* of acid and base are mixed. For example:×

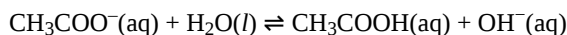


The salt formed, $\text{NaCl}(\text{aq})$, consists of $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$, each of which has negligible acid or base strength. Hence, this equilibrium heavily favors the product side and goes essentially to completion. (Note that any soluble salt consists of aqueous ions, so the formula $\text{NaCl}(\text{aq})$ represents an aqueous solution consisting of the same number of $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions.) If the mixture has an excess of one of the reactants, then the concentration of leftover acid (HCl) or base (NaOH) determines the pH of the solution.

A weak acid reacts with a strong base to form a salt that contains the conjugate base of the weak acid, which is usually a weak base. For example, the reaction of acetic acid with sodium hydroxide forms sodium acetate:

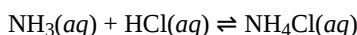


The equilibrium of this reaction favors the product side, and the reaction can be approximated as going to completion. Mixing stoichiometrically equivalent amounts of reactants gives a solution containing $\text{Na}^+(\text{aq})$, which has no effect on the pH of the solution, and $\text{CH}_3\text{COO}^-(\text{aq})$, the conjugate base of acetic acid. Because the acetate anion is a weak base, the solution pH is >7 after acetic acid reacts stoichiometrically with a strong base. The weak-base reaction is:

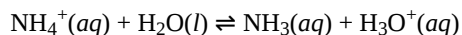


The equilibrium constant for this reaction is the ionization constant, K_{b} , for the acetate anion. (Some reference tables only report ionization constants for acids; K_{b} can be calculated from K_{w} and K_{a} of the conjugate acid—acetic acid in this case.) Generalizing this example, when a strong base reacts stoichiometrically with a weak acid, the solution that results is basic.

A strong acid reacting with a weak base forms a salt containing the conjugate acid of the weak base, which is usually a weak acid. For example, the reaction of HCl with ammonia forms ammonium chloride:



The equilibrium of this reaction favors the product side, and the reaction can be approximated as going to completion. Mixing stoichiometrically equivalent amounts of reactants gives a solution that contains $\text{Cl}^-(\text{aq})$, which is the conjugate base of a strong acid and has no effect on the pH of the solution, and $\text{NH}_4^+(\text{aq})$, the conjugate acid of ammonia. Because the ammonium ion is a weak acid, the solution pH would be <7 after ammonia reacts stoichiometrically with a strong acid. The reaction is:



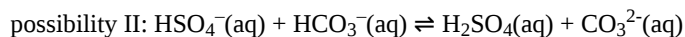
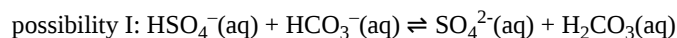
The equilibrium constant for this reaction is the ionization constant, K_{a} , for the acid NH_4^+ . Generalizing this example, when a weak base reacts stoichiometrically with a strong acid, the solution that results is acidic.

Activity 2: pH of an Ammonium Salt

To predict the pH of a solution resulting from the reaction between a **weak acid and a weak base**, we must know both the K_a of the weak acid and the K_b of the weak base. If $K_a > K_b$, the solution is acidic; if $K_b > K_a$, the solution is basic.

D34.3 Reaction Between Amphiprotic Species

Acid-base reactions can also occur between two amphiprotic species. For example, mixing a solution containing hydrogen sulfate ions (HSO_4^-) and a solution containing hydrogen carbonate ions (HCO_3^-) results in an acid-base reaction. However, if both reactants can act as either an acid or a base, which reactant is the acid and which is the base? In the example mixture, there are two possibilities:

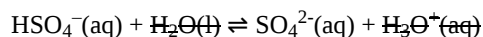


Qualitatively, a product-favored acid-base reaction involves a stronger acid reacting with a stronger base to form a weaker acid and a weaker base. Acid and base strengths are comparable by K_a and K_b values.

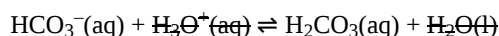
In possibility I the acids are HSO_4^- ($K_a = 1.1 \times 10^{-2}$) and H_2CO_3 ($K_a = 4.3 \times 10^{-7}$) and the bases are HCO_3^- ($K_b = 2.3 \times 10^{-8}$) and SO_4^{2-} ($K_b = 9.1 \times 10^{-13}$). The stronger acid and the stronger base are on the left side of the equation so this reaction is product-favored.

On the other hand, possibility II is reactant-favored because it produces H_2SO_4 , a strong acid, and CO_3^{2-} , a weak base with a relatively large $K_b = 2.1 \times 10^{-4}$ (significantly larger than the K_b for HSO_4^-).

Quantitatively, we can make use of the ionization constants to determine which reaction occurs. In possibility I,



$$K_1 = K_{a, \text{HSO}_4^-} = 1.1 \times 10^{-2}$$



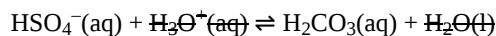
$$K_2 = \frac{1}{K_{a, \text{H}_2\text{CO}_3}} = \frac{1}{4.3 \times 10^{-7}}$$

The sum of these two equilibria gives the overall reaction for possibility I: $\text{HSO}_4^-(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{CO}_3(\text{aq})$, and the total equilibrium constant is:

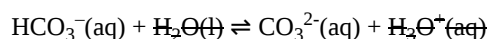
$$K_{\text{total, possibility I}} = K_1 \times K_2 = \frac{1.1 \times 10^{-2}}{4.3 \times 10^{-7}} = 2.6 \times 10^4$$

Clearly possibility I is product-favored at equilibrium because the equilibrium constant is much greater than 1.

In possibility II,



$$K_1 = \frac{1}{K_{a, \text{H}_2\text{SO}_4}} \leq \frac{1}{20}$$



$$K_2 = K_{a, \text{HCO}_3^-} = 4.7 \times 10^{-11}$$

(K_a for H_2SO_4 is too large to measure in aqueous solution but is greater than K_a for HNO_3 , which is ≈ 20 , so the value 20 is a minimum for K_a for H_2SO_4 .) The sum of these two equilibria gives the overall reaction for possibility II: $\text{HSO}_4^-(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$, and the total equilibrium constant is:

$$K_{\text{total, possibility II}} = K_1 \times K_2 = \frac{4.7 \times 10^{-11}}{20} = 2 \times 10^{-12}$$

Possibility II is heavily reactant-favored at equilibrium. Therefore, of the two possibilities, the reaction that proceeds (and produces products) is possibility I, where HSO_4^- acts as an acid and HCO_3^- acts as a base.

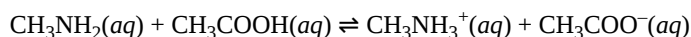
D34.4 Amino Acids

Amino acids are amphoteric because each amino acid molecule contains a carboxylic acid group that can donate a proton and an amine group that can accept a proton. Carboxylic acids are moderately acidic, many with K_a of $\sim 10^{-5}$. Organic amines are somewhat basic, many with K_b of $\sim 10^{-4}$. This combination creates an interesting situation, where an acid-base reaction is possible within a single amino acid molecule:



The carboxylic acid group, with $K_a = \sim 10^{-5}$, is a stronger acid than the protonated amine group, with $K_a = K_w/K_b(\text{amine}) = 10^{-14}/10^{-4} = \sim 10^{-10}$. The amine group ($K_b = \sim 10^{-4}$) is a stronger base than the carboxylate anion ($K_b = \sim 10^{-9}$). The stronger acid and stronger base are on the left side so this reaction is product-favored at $\text{pH} = \sim 7$. Hence, at the pH of a typical living organism, the amino acid is a **zwitterion** (German for “double ion”). A zwitterion is a species with no overall electrical charge but with separate parts that are positively and negatively charged.

The formation of a zwitterion is analogous to the acid-base reaction between methylamine ($K_b = 4.4 \times 10^{-4}$) and acetic acid ($K_a = 1.8 \times 10^{-5}$):



where the equilibrium favors products because:

$$K_{\text{total}} = \frac{1.8 \times 10^{-5}}{2.3 \times 10^{-11}} = 7.8 \times 10^5$$

Increasing the pH of an amino acid solution by adding hydroxide ions can remove the hydrogen ion from the $-\text{NH}_3^+$ group:



The product molecule is no longer a zwitterion. Instead, it is an anion with an overall charge of -1.

Similarly, decreasing the pH by adding strong acid to an amino acid solution protonates the $-\text{COO}^-$ part of the zwitterion:



Again, the product molecule is not a zwitterion, but a cation with an overall charge of +1.

Podia Question

Write a clear, concise explanation in scientifically appropriate language for each of these correct statements.

1. When a polyprotic acid donates a hydrogen ion, the species that remains is usually a much weaker acid than was the original polyprotic acid.
2. When trichloroacetic acid reacts with hydrogen carbonate ion the equilibrium is significantly more product-favored than when acetic acid reacts with hydrogen carbonate ion.
3. When a strong base reacts with a weak acid in stoichiometrically equivalent quantity, the pH of the solution is above 7.

Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

Comments. If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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