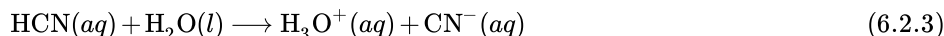
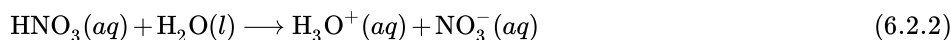
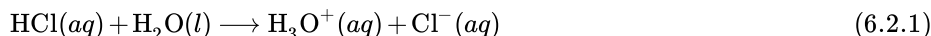


6.2: Polyprotic Acids

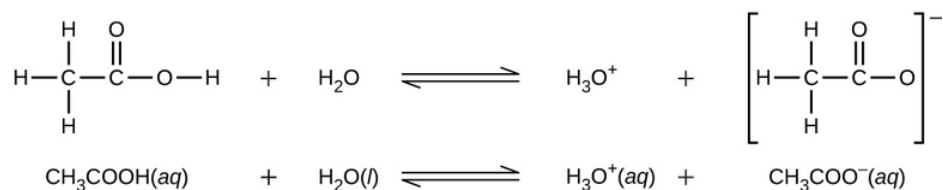
Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton
- Predict whether amphoteric species will act as acids or bases in solution and calculate the pH of a solution

We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl , HNO_3 , and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:



Even though it contains four hydrogen atoms, acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\text{COOH}$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

6.2.1: Diprotic Acids

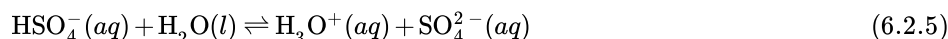
Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- The first ionization is**



with $K_{a1} > 10^2$; *complete dissociation*.

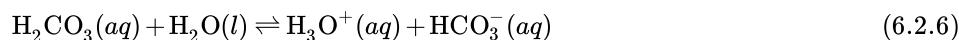
- The second ionization is**



with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, H_2CO_3 , is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- First Ionization**

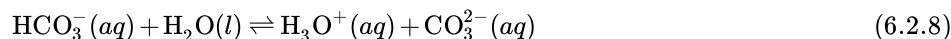


with

$$K_{\text{H}_2\text{CO}_3} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.3 \times 10^{-7} \quad (6.2.7)$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- Second Ionization**



with

$$K_{\text{HCO}_3^-} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11} \quad (6.2.9)$$

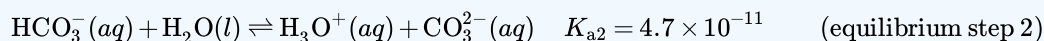
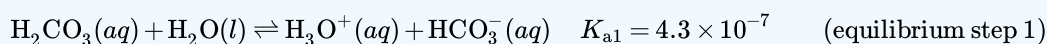
$K_{\text{H}_2\text{CO}_3}$ is larger than $K_{\text{HCO}_3^-}$ by a factor of 10^4 , so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3 .

The sequential K_a values for a polyprotic acid are labeled K_{a1} , K_{a2} , K_{a3} , etc., and refer respectively to the acid ionization constant for the proton that ionizes first, the proton that ionizes next, and so on.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, 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 H_3O^+ 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.

✓ Example 6.2.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3 . What are $[\text{H}_3\text{O}^+]$, $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ in a saturated solution of CO_2 with an initial $[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$?

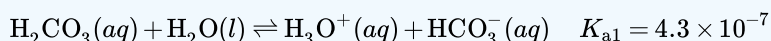


Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^- , so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. First Ionization: Determine the concentrations of H_3O^+ and HCO_3^- .

Since [equilibrium step 1](#) has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for [equilibrium step 2](#), we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).



An abbreviated table of changes and concentrations shows:

ICE Table	$\text{H}_2\text{CO}_3(aq)$	$\text{H}_2\text{O}(l)$	$\text{H}_3\text{O}^+(aq)$	$\text{HCO}_3^-(aq)$
Initial (M)	0.033 M	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033 \text{ M} - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{\text{H}_2\text{CO}_3} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

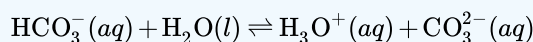
Thus:

$$[\text{H}_2\text{CO}_3] = 0.033 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 1.2 \times 10^{-4} \text{ M}$$

2. *Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.*

Since the [equilibrium step 1](#) has a much bigger K_a than [equilibrium step 2](#), we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the [equilibrium step 2](#):



ICE Table	$\text{HCO}_3^-(aq)$	$\text{H}_2\text{O}(l)$	$\text{H}_3\text{O}^+(aq)$	$\text{CO}_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4} \text{ M}$	-	$1.2 \times 10^{-4} \text{ M}$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4} \text{ M} - y$	-	$1.2 \times 10^{-4} \text{ M} + y$	y

$$K_{\text{HCO}_3^-} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$= \frac{(1.2 \times 10^{-4} \text{ M} + y)(y)}{(1.2 \times 10^{-4} \text{ M} - y)}$$

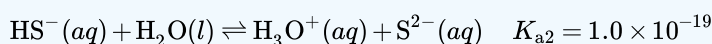
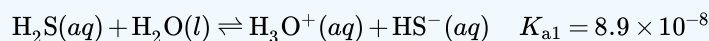
We can assume $y \ll 1.2 \times 10^{-4} \text{ M}$ so

$$K_{\text{HCO}_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4} \text{ M})(y)}{(1.2 \times 10^{-4} \text{ M})}$$

$$[\text{CO}_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

? Exercise 6.2.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[\text{H}_3\text{O}^+]$, $[\text{HS}^-]$, and $[\text{S}^{2-}]$ in the solution:



Answer

$$[\text{H}_2\text{S}] = 0.1 \text{ M}, [\text{H}_3\text{O}^+] = [\text{HS}^-] = 0.0001 \text{ M}, [\text{S}^{2-}] = 1 \times 10^{-19} \text{ M}$$

We note that the concentration of the sulfide ion is the same as K_{a2} . This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

6.2.2: Triprotic Acids

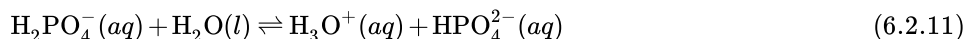
A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**



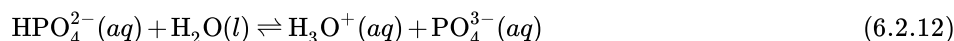
with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**



with $K_{a2} = 6.2 \times 10^{-8}$.

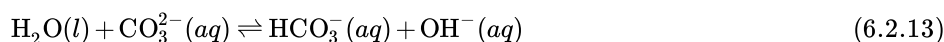
- **The third ionization is**



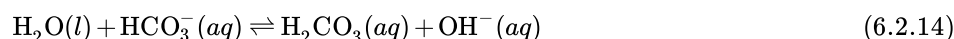
with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6 . This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6 , the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

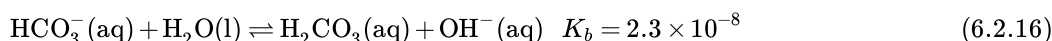
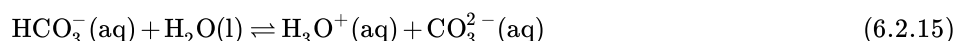


and



6.2.3: Polyprotic Acids Contain Amphoteric Species

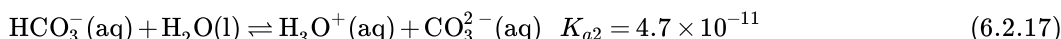
Because polyprotic acids contain more than one ionizable proton, the conjugate bases of polyprotic acids are amphoteric species - species that can either accept or donate a proton. When an amphoteric species exists in solution, it has the ability to act as either an acid or a base. For example, bicarbonate participates in the following equilibria:



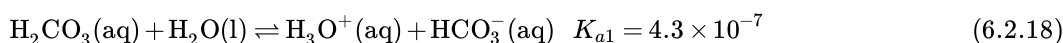
Which of these equilibrium reactions dominates the pH of the solution depends on the relative magnitudes of the K_a and K_b values.

Typically we are only given the K_a values for the ionizable protons of the polyprotic acid. We can use the K_a for the ionization of the proton in question to determine the K_b for the base reaction.

The acid equilibrium reaction here represents the ionization of the second proton from H_2CO_3 , thus the acid ionization constant is K_{a2} .



The base equilibrium reaction here represents re-association of the first proton from H_2CO_3 . To calculate the K_b for this reaction, we will use K_{a1} :



$$K_b = \frac{K_w}{K_{a1}} = \frac{1 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8} \quad (6.2.19)$$

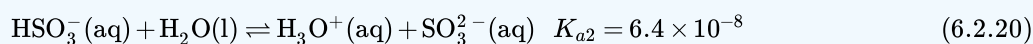
In this case, K_b (2.3×10^{-8}) is much larger than K_a (4.7×10^{-11}) so the bicarbonate will act as a base in solution.

✓ Example 6.2.2 pH of a solution with an amphoteric species

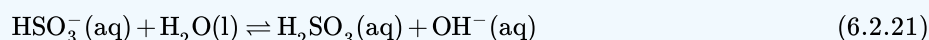
What is the pH of a solution that contains 0.20 M NaHSO_3 ?

Solution

In this solution, the Na^+ is pH neutral. The HSO_3^- can act as either an acid or a base. The acid equilibrium reaction and K_a value are:



The base equilibrium reaction is:



To determine the K_b , we can use the K_a for sulfurous acid, $K_{a1} = 1.7 \times 10^{-2}$.

$$K_b = \frac{K_w}{K_{a1}} = \frac{1 \times 10^{-14}}{1.7 \times 10^{-2}} = 5.9 \times 10^{-13} \quad (6.2.22)$$

The acid equilibrium reaction will dominate the pH of the solution.

	$\text{HSO}_3^-(\text{aq}) +$	$\text{H}_2\text{O}(\text{l}) \rightleftharpoons$	$\text{H}_3\text{O}^+(\text{aq}) +$	$\text{SO}_3^{2-}(\text{aq})$
Initial	0.20 M	excess	~ 0	0
Change	-x	-x	+x	+x
Equilibrium	(0.20 - x)	excess	x	x

Solving for x,

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 6.4 \times 10^{-8} \quad (6.2.23)$$

$$K_a = \frac{(x)(x)}{(0.20 - x)} = 6.4 \times 10^{-8} \quad (6.2.24)$$

$$x = [\text{H}_3\text{O}^+] = 1.1 \times 10^{-4} \quad (6.2.25)$$

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) = -\log(1.1 \times 10^{-4}) = 3.95 \quad (6.2.26)$$

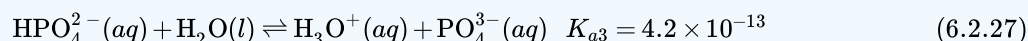
? Exercise 6.2.3

What is the pH of a solution that contains 0.100 M K_2HPO_4 ? (K_a values are provided above.)

Answer

The K^+ ion is pH neutral, so we need only to focus on the equilibrium reactions for HPO_4^{2-} .

The HPO_4^{2-} ion can act as an acid as follows:



The HPO_4^{2-} ion can act as a base as follows:



The K_b for this reaction is calculated using K_{a2} :

$$K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7} \quad (6.2.29)$$

In this case, K_b is much larger than K_a and the species predominately acts as a base.

pH = 10.10

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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