

## 14.4: Molecular Definitions of Acids and Bases

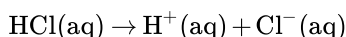
### Learning Objectives

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

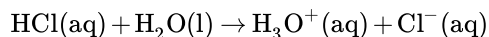
There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces  $\text{H}^+$  in solution and a base produces  $\text{OH}^-$ . Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; the [Lewis theory](#) is discussed elsewhere.

### The Arrhenius Theory of Acids and Bases

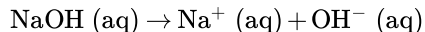
In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that **increases the concentration of  $\text{H}^+$  ions** that are present when added to water. These  $\text{H}^+$  ions form the [hydronium](#) ion ( $\text{H}_3\text{O}^+$ ) when they combine with water molecules. This process is represented in a chemical equation by adding  $\text{H}_2\text{O}$  to the reactants side.



In this reaction, hydrochloric acid ( $\text{HCl}$ ) dissociates completely into hydrogen ( $\text{H}^+$ ) and chlorine ( $\text{Cl}^-$ ) ions when dissolved in water, thereby releasing  $\text{H}^+$  ions into solution. Formation of the hydronium ion equation:



An **Arrhenius base** is a compound that **increases the concentration of  $\text{OH}^-$  ions** that are present when added to water. The dissociation is represented by the following equation:



In this reaction, sodium hydroxide ( $\text{NaOH}$ ) dissociates into sodium ( $\text{Na}^+$ ) and hydroxide ( $\text{OH}^-$ ) ions when dissolved in water, thereby releasing  $\text{OH}^-$  ions into solution.

*Arrhenius acids are substances which produce hydrogen ions in solution and Arrhenius bases are substances which produce hydroxide ions in solution.*

### Limitations to the Arrhenius Theory

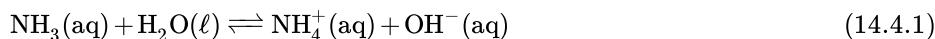
The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia ( $\text{NH}_3$ ), which in the presence of water, releases hydroxide ions into solution, but does not contain  $\text{OH}^-$  itself. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

### The Brønsted-Lowry Theory of Acids and Bases

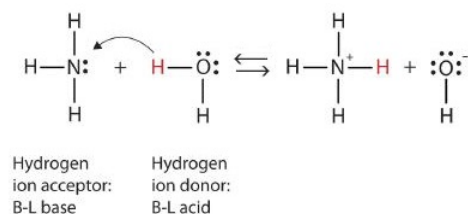
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton ( $\text{H}^+$ ) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a **Brønsted-Lowry acid** is a **proton donor (PD)**, while a **Brønsted-Lowry base** is a **proton acceptor (PA)**.

*A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.*

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:



What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:

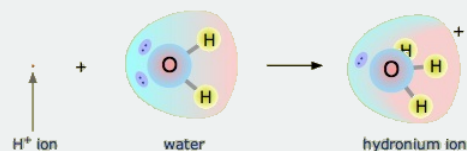


Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

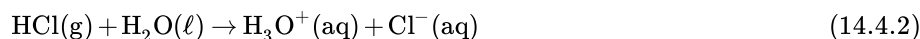
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the  $\text{H}^+$  ion attaches itself to  $\text{H}_2\text{O}$  to make  $\text{H}_3\text{O}^+$ , which is called the *hydronium ion*. For most purposes,  $\text{H}^+$  and  $\text{H}_3\text{O}^+$  represent the same species, but writing  $\text{H}_3\text{O}^+$  instead of  $\text{H}^+$  shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

### 📌 The Hydronium Ion

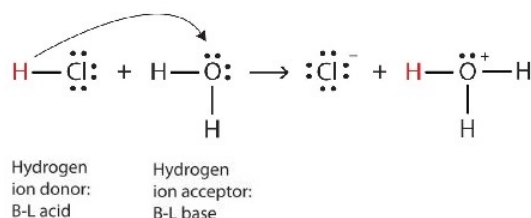
A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like  $\text{H}_5\text{O}_2^+$  or  $\text{H}_9\text{O}_4^+$  rather than  $\text{H}_3\text{O}^+$ . It is simpler, however, to use  $\text{H}_3\text{O}^+$  to represent the [hydronium ion](#).



With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in  $\text{H}_2\text{O}$ :



We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the  $\text{H}_2\text{O}$  molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor,  $\text{H}_2\text{O}$  is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense, but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions,  $\text{H}_2\text{O}$  is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled  $\text{H}_2\text{O}$  a base in this circumstance.

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

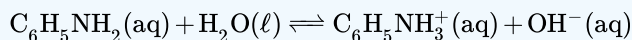
- All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

#### ✓ Example 14.4.1

Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

#### Solution

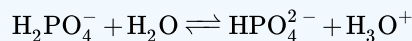
$\text{C}_6\text{H}_5\text{NH}_2$  and  $\text{H}_2\text{O}$  are the reactants. When  $\text{C}_6\text{H}_5\text{NH}_2$  accepts a proton from  $\text{H}_2\text{O}$ , it gains an extra H and a positive charge and leaves an  $\text{OH}^-$  ion behind. The reaction is as follows:



Because  $\text{C}_6\text{H}_5\text{NH}_2$  accepts a proton, it is the Brønsted-Lowry base. The  $\text{H}_2\text{O}$  molecule, because it donates a proton, is the Brønsted-Lowry acid.

#### ? Exercise 14.4.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.



#### Answer

Brønsted-Lowry acid:  $\text{H}_2\text{PO}_4^-$ ; Brønsted-Lowry base:  $\text{H}_2\text{O}$

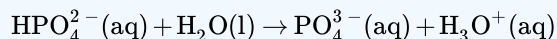
#### ? Exercise 14.4.2

Which of the following compounds is a Brønsted-Lowry base?

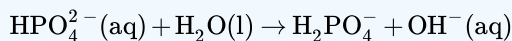
- $\text{HCl}$
- $\text{HPO}_4^{2-}$
- $\text{H}_3\text{PO}_4$
- $\text{NH}_4^+$
- $\text{CH}_3\text{NH}_3^+$

#### Answer

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an  $\text{H}^+$ . This eliminates  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{NH}_4^+$  and  $\text{CH}_3\text{NH}_3^+$  because they are Brønsted-Lowry acids. They all give away protons. In the case of  $\text{HPO}_4^{2-}$ , consider the following equation:



Here, it is clear that  $\text{HPO}_4^{2-}$  is the acid since it donates a proton to water to make  $\text{H}_3\text{O}^+$  and  $\text{PO}_4^{3-}$ . Now consider the following equation:

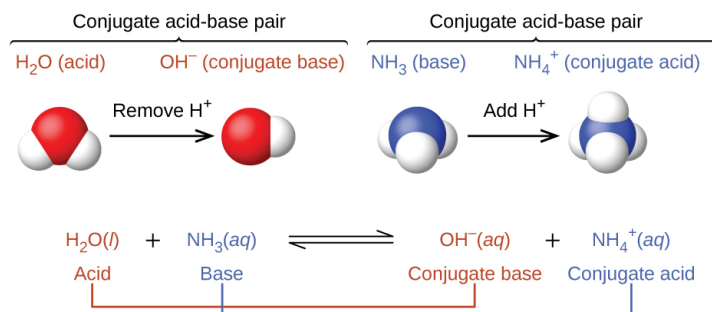


In this case,  $\text{HPO}_4^{2-}$  is the base since it accepts a proton from water to form  $\text{H}_2\text{PO}_4^-$  and  $\text{OH}^-$ . Thus,  $\text{HPO}_4^{2-}$  is an acid and base together, making it amphoteric.

Since  $\text{HPO}_4^{2-}$  is the only compound from the options that can act as a base, the answer is **(b)  $\text{HPO}_4^{2-}$** .

## Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water,  $\text{OH}^-$ , and the conjugate acid of ammonia,  $\text{NH}_4^+$ :



This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of  $\text{H}_2\text{O}$  is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label " $\text{H}_2\text{O}$  (acid)" in purple. An arrow points right, which is labeled "Remove  $\text{H}^+$ ." To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, " $\text{OH}^-$  (conjugate base)." Above both of these red and white models is an upward pointing bracket that is labeled "Conjugate acid-base pair." To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads " $\text{NH}_3$  (base)." An arrow labeled "Add  $\text{H}^+$ " points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads " $\text{NH}_4^+$  (conjugate acid)." Above both of these blue and white models is an upward pointing bracket that is labeled "Conjugate acid-base pair." The second row of the figure shows the chemical reaction,  $\text{H}_2\text{O(l)} + \text{NH}_3\text{(aq)} \rightleftharpoons \text{OH}^-\text{(aq)} + \text{NH}_4^+\text{(aq)}$ . The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are  $\text{NH}_4^+/\text{NH}_3$  and  $\text{H}_2\text{O}/\text{OH}^-$ .

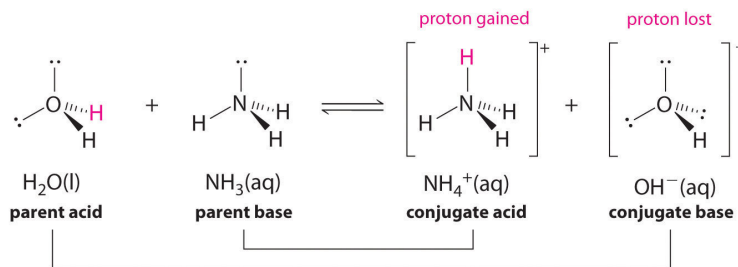


Figure 14.4.1. The pairing of parent acids and bases with conjugate acids and bases.

ACID		BASE	
negligible	$\text{OH}^-$	$\text{O}^{2-}$	strong
	$\text{HS}^-$	$\text{S}^{2-}$	
weak	$\text{H}_2\text{O}$	$\text{OH}^-$	weak
	$\text{HPO}_4^{2-}$	$\text{PO}_4^{3-}$	
	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	
	$\text{NH}_4^+$	$\text{NH}_3$	
	$\text{HCN}$	$\text{CN}^-$	
	$\text{H}_2\text{PO}_4^-$	$\text{HPO}_4^{2-}$	
	$\text{HSO}_3^-$	$\text{SO}_3^{2-}$	
	$\text{H}_2\text{S}$	$\text{HS}^-$	
	$\text{H}_2\text{CO}_3$	$\text{HCO}_3^-$	
	$\text{C}_5\text{H}_5\text{NH}^+$	$\text{C}_5\text{H}_5\text{N}$	
	$\text{CH}_3\text{CO}_2\text{H}$	$\text{CH}_3\text{CO}_2^-$	
	$\text{HF}$	$\text{F}^-$	
	$\text{H}_3\text{PO}_4$	$\text{H}_2\text{PO}_4^-$	
	$\text{H}_2\text{SO}_3$	$\text{HSO}_3^-$	
strong	$\text{HSO}_4^-$	$\text{SO}_4^{2-}$	negligible
	$\text{H}_3\text{O}^+$	$\text{H}_2\text{O}$	
	$\text{HNO}_3$	$\text{NO}_3^-$	
	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	
	$\text{HCl}$	$\text{Cl}^-$	
	$\text{HBr}$	$\text{Br}^-$	

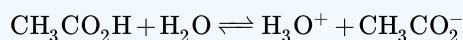
← Relative acid strength increasing

Relative base strength increasing →

Figure 14.4.1: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

### ✓ Example 14.4.2

Identify the conjugate acid-base pairs in this equilibrium.

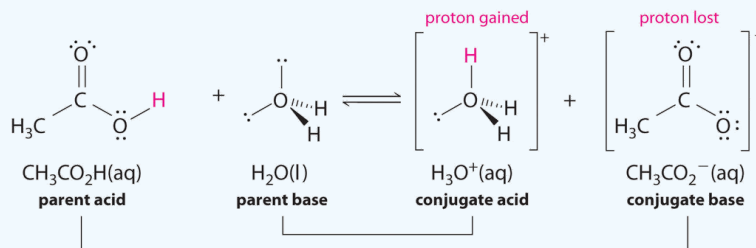


### Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction,  $\text{H}_3\text{O}^+$  is the acid that donates a proton to the acetate ion, which acts as the base.

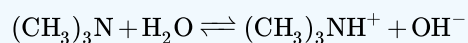
Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ( $\text{CH}_3\text{CO}_2\text{H} / \text{CH}_3\text{CO}_2^-$ ) and
- the parent base and its conjugate acid ( $\text{H}_3\text{O}^+ / \text{H}_2\text{O}$ ).



## ✓ Example 14.4.3

Identify the conjugate acid-base pairs in this equilibrium.

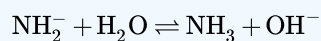
**Solution**

One pair is  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , where  $\text{H}_2\text{O}$  has one more  $\text{H}^+$  and is the conjugate acid, while  $\text{OH}^-$  has one less  $\text{H}^+$  and is the conjugate base.

The other pair consists of  $(\text{CH}_3)_3\text{N}$  and  $(\text{CH}_3)_3\text{NH}^+$ , where  $(\text{CH}_3)_3\text{NH}^+$  is the conjugate acid (it has an additional proton) and  $(\text{CH}_3)_3\text{N}$  is the conjugate base.

## ? Exercise 14.4.3

Identify the conjugate acid-base pairs in this equilibrium.

**Answer**

$\text{H}_2\text{O}$  (acid) and  $\text{OH}^-$  (base);  $\text{NH}_2^-$  (base) and  $\text{NH}_3$  (acid)

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