

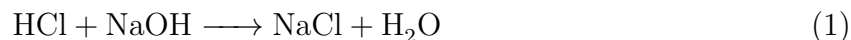
# GENERAL CHEMISTRY

Acid-base reactions. Arrhenius, Bronsted-Lowry and Lewis acids and bases.

January 7, 2018

## 1 Acid-base reactions

We already know many examples of acid-base reactions. One of a typical examples is the reaction between HCl and NaOH :



A short ionic equation of this reaction is even more simple:



Importantly, exactly the same equation describes *all* reactions between all acids and bases that we have studied by now, and the process behind all these acid-base reactions is the same: a hydrogen cation binds to a hydroxide anion, and other ions are just spectator ions.

From that, we can deduce a definition of an acid and a base:

**Acids are the compounds that can dissociate onto a hydrogen cation and some anion.**

And, accordingly:

**Bases are the compounds that dissociate onto a hydroxide ion and some cation.**

This definition was proposed by a Swedish chemist Svante Arrhenius, the same person who developed the electrolytic dissociation theory. We can call it a *definition number 3*<sup>1</sup>. This definition was proposed at the very beginning of XX century, it is consistent with modern theories, but is it comprehensive? Let's see.

---

<sup>1</sup>As you can see, we continue our attempts to propose a universal definition for acids, the work we started one year ago.

## 1.1 Non-hydroxide bases

Ammonia is a compound that is a very close analog of water. Its formula is  $\text{NH}_3$ , and it can be considered a *hydrogen nitride* (by analogy with *hydrogen oxide*, a formal chemical name of water). It is a gas with an unpleasant odour, and it is extremely soluble in water (several hundreds of volumes of  $\text{NH}_3$  gas dissolve in one volume of water). Judging by its formula, it is hard to tell if it is an acid, a base, or a neutral compound. Surprisingly, ammonia vigorously reacts with  $\text{HCl}$  and other acids, and the products of this reaction are nearly neutral salt like compounds:



A short ionic equation of this reaction is, obviously:



The ion that forms in this reaction ( $\text{NH}_4^+$ ) is called an *ammonium* ion, and its properties are close to those of a potassium or sodium ions ( $\text{K}^+$  or  $\text{Na}^+$ ).

In other words, ammonia behaves as a base (it binds to a hydrogen cation to form a new species), but no water form in this reaction. Many other examples of bases are known that do not form a hydroxide ion upon dissociation, or even do not dissociate at all. That suggest the ability to form an  $\text{OH}^-$  upon dissociation is not a universal trait of a base. The person who realized that, a Swedish chemist Bronsted, proposed a modified version of the Arrhenius' definition, and this is a universally accepted definition is as follows:

**Acids are the compounds that can donate a hydrogen cation to some other molecule.**

And, accordingly:

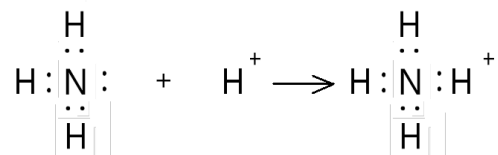
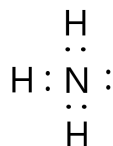
**Bases are the compounds that accept  $\text{H}^+$ .**

This definition is called a Bronsted definition (or Bronsted-Lowry definition), and the acids and bases that fit this definition are called "Bronsted acids" and "Bronsted bases" accordingly.

These two terms are widely accepted now, but even more comprehensive vision of the acidity/basicity phenomenon was proposed later, and it deserves a separate section.

## 1.2 Lewis acids and bases

How does the ammonium ion form? In this ion, a nitrogen atom is connected to four hydrogen atoms, which sounds counterintuitive, because nitrogen has 5 electrons on its outer shell, so it can share just 3 electrons to get a full (eight electron) shell. In ammonia ( $\text{NH}_3$ ) the outer shell of nitrogen is always full, so the mechanism responsible for keeping the 4th hydrogen in ammonium seems not obvious. To understand that, let's take a look at the electronic formula of ammonia. If we denote each electron occupying each orbitals a dot, the formula of ammonia looks like that:



This way to draw molecular formulas is called “Lewis formulas”. It is convenient for understanding many aspects of structure and behaviour of molecules, and it is especially useful for understanding the acidity/basicity phenomenon.

What happens when an ammonia molecule meets a hydrogen cation? The process is shown at the next picture.

When we look at their Lewis structures, we see ammonia has four orbitals each of which is occupied with a pair of electrons, three of them participate in covalent bond formation, and the last one is not involved in any covalent bond. Such a pair is called *a lone pair*. Obviously, we are talking only about the electrons at the outer shell of each atom, because the electrons that occupy inner shells (nitrogen has two such electrons) are bound to the nucleus too tightly, so we can safely ignore them.

Let’s take a look at the hydrogen ion now. It has no electrons, but it would love to get some. What happens when an ammonia molecule (which has a orbital that contains two electrons not shared with any other atom) meets a hydrogen atom (which has an empty orbital)? Obviously, these two species try to collaborate: ammonia donates its electron pair, and two atoms, hydrogen and nitrogen, form a covalent bond. Since both electrons that form this bond come from one atom, this bond is called *a dative bond*.

From a point of view of electronic structure, there is no difference between a dative bond and a normal covalent bond. The difference is just in a way the bond is formed: whereas a usual covalent bond forms between two atoms each of which donates one electron, in a dative bond, both electrons come from one atom. When you take a look at the ammonium ion (it is possible, for example, to measure the length of each N-H bonds), you will see that all four bonds are identical, and the positive charge is evenly distributed among all four hydrogen atoms.

A second example is even simpler. When a hydrogen cation and a hydroxide anion interact, the water forms (see the equation 2), and the bond formation occurs via a dative mechanism: an electron pair comes from the  $\text{OH}^-$  ion, and  $\text{OH}^-$  donates an empty orbital. The water that forms as a result of this process is a usual water molecule, the same molecule that forms when hydrogen burns in oxygen.

That suggests that the species that donate an electron pair in a process of a dative bond formation ( $\text{NH}_3$ ,  $\text{OH}^-$ ) demonstrate basic behaviour, whereas the species that act as electron pair acceptors ( $\text{H}^+$ ) are acids. Based on this observation, American chemists Gilbert Lewis

proposed the most general definition of the terms “acid” and “base”:

**Acids are the molecules that have an empty orbital capable of accepting a pair of electrons.**

**Bases are the species that have a lone pair of electrons they can share.**

In other words, a reaction between an acid and a base is a process of donation of a lone electron pair by one molecule (a base) to another molecule (an acid).

### 1.3 Relationship between Arrhenius, Bronsted and Lewis acids and bases

According to Arrhenius, an acid is a compound that dissociates upon  $H^+$  and some anion, and a base is a compound that dissociates upon  $OH^-$  and some cation. However,  $H^+$  is a species that has an empty orbital capable of accepting a lone pair, which means  $H^+$  is just one example of a Lewis acid.

Similarly,  $OH^-$  is a species that has a lone pair (actually, three lone pairs) it can donate to any acceptor. That makes a hydroxy anion a Lewis base.

According to Bronsted and Lowry, any acceptor of  $H^+$  is a base. Since the only way  $H^+$  can form a chemical bond with any species is formation of a dative chemical bond (a proton has no electrons), any acceptor of a proton (a Bronsted base) must have a lone pair it can share with some other molecule or ion. That means any Bronsted base is actually a Lewis base too, and vice versa: any Lewis base is simultaneously a Bronsted base. With regard to Bronsted acids (actually, *the* Bronsted acid), it is always a  $H^+$ , a particle that can be considered a Lewis acid too (because it is an acceptor of an electron pair).

In summary, Arrhenius acids and bases are subsets of Bronsted-Lowry acids and bases. Bronsted-Lowry bases and Lewis bases are essentially the same compounds, whereas Bronsted acids are just a small subset of Lewis acids.

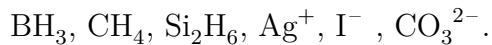
## 2 Acid-base reactions and oxidation state

When we look at the equation of Arrhenius acid-base reaction, we see that oxidation state of all atoms is preserved in this process: a proton, obviously, has an oxidation state +1 (no electrons at all), a hydroxy hydrogen has the same oxidation state (an electron pair responsible for chemical bond formation is displaced towards oxygen), and oxygen has an oxidation state of -2 (it pulls the electron pair responsible for the O-H bond, and it has extra negative charge that changes the oxidation state by -1). After the reaction, when  $H^+$  and  $OH^-$  form a water molecule, oxidation states of both hydrogens are +1 (they are connected to the oxygen atom that is more electronegative), and, for the same reason, oxidation state of oxygen is -2 (because it is connected to two hydrogens, which are *less* electronegative than oxygen).

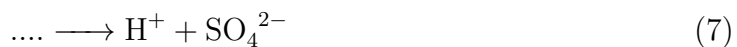
That suggests that may be a general rule: in any acid-base reaction, no change in oxidation state occurs. Oxidation state of each atom in each molecule involved in the acid-base reaction is always preserved. It is easy to demonstrate this rule works for Bronsted and Lewis acids and bases too. This is a major difference between acid-base and redox reactions.

## Homework

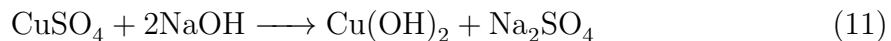
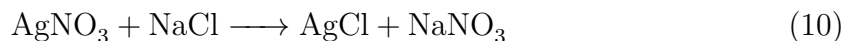
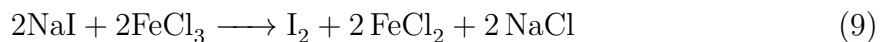
1. Write Lewis formulas for the following molecules and tell if they are acids, bases or neutral compounds:



2. In the equations shown below the left part is missing. Restore it (including coefficients).



3. Tell which equations describe acid-base reactions and which reactions are redox reactions<sup>2</sup>:



If you have any questions, feel free to ask.

My e-mail is mark.lukin@gmail.com

©Mark Lukin

---

<sup>2</sup>The best way to answer this question is to look at the oxidation state of each atom in reactants and products