General Chemistry
Conjugated acids and bases. Hydrolysis of salts.

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The difference between Arrhenius, Bronsted-Lowry and Lewis theories can be better understood by taking into account the difference between the approaches they are based upon.

The first theory, Arrhenius theory, was proposed before the structure of atoms was discovered. The theory was a part of the electrolytic dissociation theory, i.e., on the idea that many compounds (electrolytes) dissociate in aqueous solution, and the products of this dissociation are charged particles, or ions. By the moment this theory was proposed, nobody knew what these ions are composed of, and what the mechanisms of their interaction are. The only thing that was possible to detect (and to discuss) was the very fact of dissociation. As a result, the Arrhenius theory used a *composition based* approach that can be formulatted as follows:

> *According to Arrhenius, if a molecule contains a precoursor of H^+ (and can dissociate upon H^+ and something else in aqueous solutions), it is an acid; if it contains a precoursor of OH^-, it is a base.*

Bronsted and Lowry proposed their theory later, when more information was collected about interaction between acids and bases. Their theory summarizes these interactions, and their approach can be characterized as a *functional approach*:

> *According to Bronsted, if a molecule accepts an H^+ from another molecule, it is a base, and the molecule that donates H^+ is an acid.*

Lewis, who proposed his theory concurrently with Bronsted and Lowry, was one of the authors of the covalent bond theory: for example, so called Lewis formulas were proposed by him. It is not a surprise that due to his deep understanding of structural theory he asked himself: what are the common structural features of all acids and all bases? This approach, which can be called a *structural approach*, allowed him to define acids and bases from the point of view of their electronic structure:

> *According to Lewis, an acid is a species that has a vacant orbital capable of accepting an electron pair. A molecule (or an ion) that has such an electron pair and can donate it is called a base.*

As we can see, the difference between these theories are actually the differences in the approaches. Obviously, these theories are not contradicting and not mutually exclusive, they all can be used, depending on a situation.

1 Acids and their conjugated bases

One of the most important components of the Bronsted-Lowry theory is the concept of *conjugated acids and bases*. To understand it let's look again at the dissociation reaction of some acid, for example, of hydrogen fluoride. It can be written as:

$$HF \longrightarrow H^+ + F^- \tag{1}$$

In this reaction, the HF molecule generates a hydrogen ion, and therefore behaves as an acid. However, we know this reaction never goes to completion: some amount of HF is always present in the HF solution. That means the opposite reaction always occurs:

$$H^+ + F^- \longrightarrow HF \tag{2}$$

In this reaction, a fluoride ion *accepts* a hydrogen ion, and, therefore it behaves as a base. Clearly, the HF and F^- species relate to each other, and this relationship can be described as follows.

> **When some acid HX dissociates onto a hydrogen ion and a particle X, the latter behaves as a base, and, accordingly, it is called a *conjugated base of an acid HX*.**

In other words, the general equation of any reaction of dissociation of an acid can be written as:

$$Acid \rightleftharpoons H^+ + ConjugatedBase \tag{3}$$

Depending on a situation, a conjugated base can be an anion or a neutral particle. For example, when HF, HCl, or H_2SO_4 dissociate, their conjugated bases are charged negatively. However, when an ammonium ion dissociates, the products are neutral ammonia and H^+.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \tag{4}$$

In this reaction, ammonia (NH_3) is a conjugated base of the ammonium ion, which, in this reaction, plays a role of an acid.

1.1 Are conjugated bases a separate class of bases?

To answer this question, consider two reactions. First, the reaction of dissociation of water:

$$H^+ \rightleftharpoons H^+ + OH^- \tag{5}$$

In this reaction, a hydroxide ion is a conjugated base of water. The second reaction is a reation of precipitation of $Fe(OH)_2$:

$$Fe^{2+} + 2\,OH^- \rightleftharpoons Fe(OH)_2 \tag{6}$$

Obviously, in this reaction, OH^- plays a role of a typical base.

This, as well as many other examples demonstrate that conjugated bases are not a separate type of bases. Any molecule can be considered as a conjugated base of some acid. This formalism is needed to make our life easier, and we will see it soon.

1.2   Strengths of acids and their conjugated bases

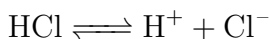HF is a moderate strength acid, so in the reaction:

$$HF \rightleftharpoons H^+ + F^-$$
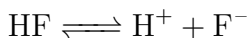
the equilibrium is shifted to the left side. If we rewrite this equation as:

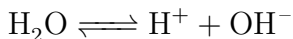$$H^+ + F^- \rightleftharpoons HF$$
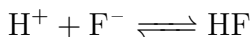
it looks like a neutralization reaction, and this equilibrium is shifted to the right side, which suggests F^- is a rather strong base.

Consider another example, a dissociation of HCl, which is a very strong acid:

$$HCl \rightleftharpoons H^+ + Cl^-$$

In this reaction, the equilibrium is shifted to the right side, which means Cl^- is a weak base.

The next example is dissociation of water:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Clearly, water dissociates only slightly, and there is almost to H^+ and OH^- in pure water. Accordingly, OH^-, which is water's conjugated base, is a very strong base (which we know from our previous experience).

The last example is dissociation of the ammonium ion (NH_4): $NH_4 \rightleftharpoons H^+ + NH_3$

Ammonium ion is *very* stable, it dissociates even less actively than water. That makes ammonia solution basic (we will talk about that in more details later)

Based on that, we can draw the following rule:

> **Strengths of acids and their conjugated bases are inversely correlated. Conjugated bases of strong acids are weak bases, and conjugated bases of weak acids are strong.**

2   Bases and their conjugated acids

If some particle can be considered a conjugated base, what about acids? Do conjugated acids exist? Sure. According to Bronsted, any particle capable of donating H^+ is an acid. When H^+ and F^- associate (equation 2), product of this reaction is a molecule capable of donating a proton, i.e., an acid. This acid is just a hydrofluoric acid, but it can also be considered as a conjugated acid of the fluoride ion.

This can be summarized as follows: In any dissociation reaction, the particle A that donates a hydrogen ion is considered an acid, and by donating a hydrohed ion it becomes a conjugated base of the particle A (usually, to A^-). Accordingly, a particle B that accepts a hydrogen ion behaves as a base, and it transforms to a conjugated acid of the base B (usually to the ion BH^+).

2.1 Water

To understand that concept better, let's take a look at water. We already know that water is a Janus molecule (it is neither an acid nor a base, but it is both an acid and a base). Now, in addition to that, we have to learn one more secret of water: *textbfhydrogen cations do not exist in water solution!* What does it mean? Does it mean acids do not dissociate, and water does not dissociate?

Actually, dissociation of water or acids is not a real dissociation, but a transfer of H^+. The real process can be described by the exuation

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \tag{7}$$
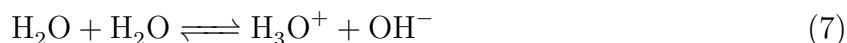
The ion H_3O^+ is called *oxonium* [1] Its structure is similar to the structure of the ammonium ion, except it has just three hydrogen atoms and the central atom is oxygen, not nitrogen. However, the electronic structure of oxonium is totally identical to that of ammonium. The major difference is stability: an oxonium ion is much less stable than ammonium, so the squilibrium of this reaction is shifted to the left side (oxonium easily donates its extra proton to hydrogen, and two water molecule form as a result)

Accordingly, the coreect way to writhe an equation of the reaction of dissociation of any acid is as follows (using HCl as an example):

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- \tag{8}$$

Why don't we do that? The answer is trivial: for simplicity. We chemists know that all H^+ ions exist in a form of H_3O^+ ions in aqueous solution, but to save time prefer not to draw H_3O^+ explicitly. However, we always keep that fact in mind, and we remember about that when it is needed. And now it is a good time to remember about that. If we look at the equation 8, we will see that any dissociation reaction of an acid is actually not a dissociation of an acid, but a *transfer* of a proton from one molecule to another. In the equation 8, the HCl molecule plays a role of an acid (it donates a proton), whereas a water molecule acts as a base (it accepts a proton). Duting this process, HCl converts into its conjugated base, a Cl^- ion, and water becomes an oxonium ion H_3O^+, i.e. a conjugated acid of water. Interestingly, if we look again at the dissociation of water (equation 7), we will see that two molecules of water play a role of an acid and a base, accordingly, and a conjugated base and conjugated acid of water form as a result. That is the most convinsing demonstration of a dual nature of water.

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[1] In school textbook it is also called *hydronium* by analogy with ammonium NH_4.

3   General equation of reactions between Bronsted-Lawry acids and bases

If we denote a Bronsted acid as AH and base as B, the equation can be written as:

$$AH + B \rightleftharpoons BH + A \tag{9}$$

where BH is a conjugated acid of the base B, and A is a conjugated base of an acid A. This is the equation of an acid-base reaction[2] in the most general form.

If B is a water molecule, the equation 9 becomes an equation of dissociation of an acid (see the equation 8 as an example). The same can be said about the dissociation of a base: if AH is a water molecule (and A is OH^-) this equation becomes an equation of dissociation of a base, for example:

$$H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+ \tag{10}$$
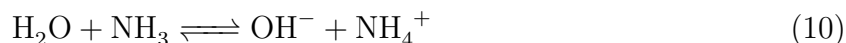
One of important conclusions from that is:

> *Reactions of dissociation of acids or bases in aqueous solutions are actually acid-base reactions, the only difference from "true" acid-base reactions is that the role a base (or an acid) in these reactions is played by water.*

Now we are ready to understand more complex phenomenae related to the behavior of salts in solutions.

4   Hydrolysis of salts

What practical consequences can all of that have? Consider a solution of NaCl, a salt fromed in a reaction between a strong acid (HCl) and a strong base (NaOH). Since HCl is a strong acid, its conjugated base, Cl^- is a *weak* base. That means dissociation of NaCl:

$$NaCl \longrightarrow Na^+ + Cl^- \tag{11}$$

produces a weak base (Cl^- and a sodium ion that interacts with water realtively weakly, so we can say it displays no acidic or basic properties. That means the presence of Na^+ in water cannot affect the retion between H^+ and OH^- ions. The same can be said about Cl^-: the reaction:

$$Cl^- + H_3O^+ \longrightarrow HCl + H_2O \tag{12}$$

is virtually impossible, because HCl is a *very* strong acid, so Cl^- is a really weak base. That means the presence of a chloride ion does not affect the concentration of H_3O^+ (or, as we called it previously, H^+). That meance the presence of equal amounts of Na^+ and Cl^- ions in solution does not make the solution basic or acidic: the solution of NaCl is *neutral*. The same can be said about all other salts formed by strong acids and strong bases.

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[2]A reaction between Bronsted-Lawry acids and bases

A situation changes when we consider a salt of a weak (or moderate) acid and a strong base, for example, sodium fluoride. It is a salt of a moderate acid (HF) and a strong base, NaOH. That means, after dissociation of this salt generates two type ions, a sodium ion, Na^+ and a fluoride ion, F^-.

$$NaF \rightleftharpoons Na^+ + F^- \tag{13}$$

The former does not interact with water (see above).

In contrast, fluoride ion is moderate bases, which means they will bind hydrogen ions to form neutral molecules, HF. That means a standard water equilibrium becomes perturbed, and to maintain a water product $K_w=[H^+][OH^-]$ constant, water starts to dissociate more actively, and the concentration of hydroxide ions increases. This can be summarized in the equation:

$$F^- + H_3O^+ \rightleftharpoons HF + H_2O \tag{14}$$

That means the presence of a significant amount of F^- in aqueous solution leads to a decrease of H_3O^+ concentration. Taking into account that the latter forms in the process described by the equation 15:

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \tag{15}$$

that leads to constant removal of H_3O^+ from a solution whereas the formation of OH^- is not affected. As a result, the solution becomes basic.

The combination of the processes described by equations 13, 14, and water gives the equation 16

$$Na^+ + F^- + H_2O \rightleftharpoons Na^+ + HF + OH^- \tag{16}$$
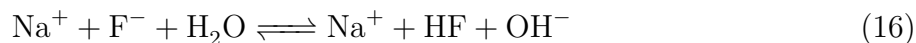
The equation can be summarised as follows:

1. Water molecule dissociate upon H_3O^+ and OH^-, which occurs spantaneously, and both species from in equal amount. That is why pure water is neutral.

2. Fluoride ion forms in large amounts when NaF dissolves in water and dissociates.

3. Fluoride ions bind H_3O^+ and neutralize it by converting it into HF (moderately weak acid) and water, whereas the process of formation of OH^- is not suppressed, which results in an excess of OH^-, and the solution becomes basic.

This process is called **hydrolysis of salts**.

When a salt formed by a strong base and a weak acid dissolves in water, the pH of that solution is greater than 7. This phenomenon is called *hydrolysis of salts*.

The same effect works for the salts formed by weak *bases* and strong acids. In that case, pH of the solution will be (.... guess by yourself, and explain why).

Homework

1. Draw formulas of conjugated bases of: (i) sulfuric acid, (ii) hydrogen sulfide, (iii) hypochlorous acid;

2. Hypochlorous acid and hydrogen selenide are weak acids. Draw the equation of hydrolysis of their sodium salts. Use the equation 16 as an example.

3. Ammonia is a weak base. Draw the equation of hydrolysis of ammonium chloride (NH_4Cl). Will the solution be acidic, basic or neutral

If you have any questions, feel free to ask.
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