THEORIES OF ACIDS AND BASES

The Arrhenius Theory of acids and bases

The theory

- Acids are substances which produce hydrogen ions in solution.
- Bases are substances which produce hydroxide ions in solution.

Neutralisation happens because hydrogen ions and hydroxide ions react to produce water.

H⁺(aq) + OHī(aq) → H₂O(I)

Limitations of the theory

Hydrochloric acid is neutralised by both sodium hydroxide solution and ammonia solution. In both cases, you get a colourless solution which you can crystallise to get a white salt either sodium chloride or ammonium chloride.

These are clearly very similar reactions. The full equations are:

 $NaOH_{(aq)} + HCI_{(aq)} \longrightarrow NaCI_{(aq)} + H_2O_{(I)}$

NH_{3(aq)} + HCl_(aq) → NH₄Cl_(aq)

In the sodium hydroxide case, hydrogen ions from the acid are reacting with hydroxide ions from the sodium hydroxide - in line with the Arrhenius theory.

However, in the ammonia case, there don't appear to be any hydroxide ions!

But if you look at the equations carefully, the ammonia is in solution - $NH_{3(aq)}$. Ammonia reacts with water like this:

 $NH_{3(aq)} + H_2O_{(l)} \longrightarrow NH_4^+(aq) + OH^-(aq)$

This is a reversible reaction, and in a typical dilute ammonia solution, about 99% of the ammonia remains as ammonia

molecules. Nevertheless, there are hydroxide ions there and those react with hydrogen ions in just the same way as hydroxide ions from sodium hydroxide.

So you can just about justify ammonia as being a base on the Arrhenius definition - it does produce hydroxide ions in solution. But most of the reaction is going to be a direct reaction between ammonia molecules and hydrogen ions - which doesn't fit the Arrhenius definition.

This same reaction also happens between ammonia gas and hydrogen chloride gas.

 $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$

In this case, there aren't any hydrogen ions or hydroxide ions in solution - because there isn't any solution. The Arrhenius theory wouldn't count this as an acid-base reaction, despite the fact that it is producing the same product as when the two substances were in solution. That's silly!

The Bronsted-Lowry Theory of acids and bases

The theory

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

The relationship between the Bronsted-Lowry theory and the Arrhenius theory

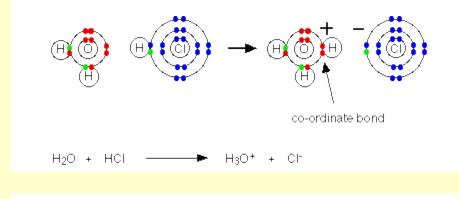
The Bronsted-Lowry theory doesn't go against the Arrhenius theory in any way - it just adds to it.

Hydroxide ions are still bases because they accept hydrogen ions from acids and form water.

An acid produces hydrogen ions in solution because it reacts with the water molecules by giving a proton to them.

When hydrogen chloride gas dissolves in water to produce

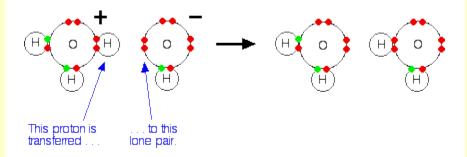
hydrochloric acid, the hydrogen chloride molecule gives a proton (a hydrogen ion) to a water molecule. A co-ordinate (dative covalent) bond is formed between one of the lone pairs on the oxygen and the hydrogen from the HCl. Hydroxonium ions, H_3O^+ , are produced.



When an acid in solution reacts with a base, what is actually functioning as the acid is the hydroxonium ion. For example, a proton is transferred from a hydroxonium ion to a hydroxide ion to make water.

H₃O⁺(aq) + OH⁻(aq) → 2H₂O(I)

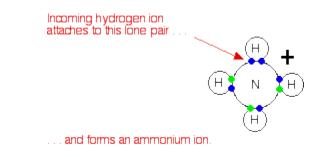
Showing the electrons, but leaving out the inner ones:



It is important to realise that whenever you talk about hydrogen ions in solution, $H^+_{(aq)}$, what you are actually talking about are hydroxonium ions.

The hydrogen chloride / ammonia problem

This is no longer a problem using the Bronsted-Lowry theory. Whether you are talking about the reaction in solution or in the gas state, ammonia is a base because it accepts a proton (a hydrogen ion). The hydrogen becomes attached to the lone pair on the nitrogen of the ammonia via a co-ordinate bond.



If it is in solution, the ammonia accepts a proton from a hydroxonium ion:

NH_{3(aq)} + H₃O⁺_(aq) ----- NH₄⁺_(aq) + H₂O_(I)

If the reaction is happening in the gas state, the ammonia accepts a proton directly from the hydrogen chloride:

 $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_{4^{+}(s)} + Cl_{(s)}$

Either way, the ammonia acts as a base by accepting a hydrogen ion from an acid.

Conjugate pairs

When hydrogen chloride dissolves in water, almost 100% of it reacts with the water to produce hydroxonium ions and chloride ions. Hydrogen chloride is a strong acid, and we tend to write this as a one-way reaction:



In fact, the reaction between HCl and water is reversible, but only to a very minor extent. In order to generalise, consider an acid HA, and think of the reaction as being reversible.

HA + H₂O _____ H₃O⁺ + A⁻

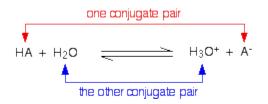
Thinking about the forward reaction:

- The HA is an acid because it is donating a proton (hydrogen ion) to the water.
- The water is a base because it is accepting a proton from the HA.

But there is also a *back reaction* between the hydroxonium ion and the A^{-} ion:

- The H₃O⁺ is an acid because it is donating a proton (hydrogen ion) to the A⁻ ion.
- The A⁻ ion is a base because it is accepting a proton from the H_3O^+ .

The reversible reaction contains *two* acids and *two* bases. We think of them in pairs, called *conjugate pairs*.



When the acid, HA, loses a proton it forms a base, A⁻. When the base, A⁻, accepts a proton back again, it obviously reforms the acid, HA. These two are a conjugate pair.

Members of a conjugate pair differ from each other by the presence or absence of the transferable hydrogen ion.

If you are thinking about HA as the acid, then A^{-} is its conjugate base.

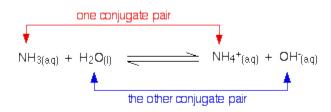
If you are thinking about A^{-} as the base, then HA is its conjugate acid.

The water and the hydroxonium ion are also a conjugate pair. Thinking of the water as a base, the hydroxonium ion is its conjugate acid because it has the extra hydrogen ion which it can give away again.

Thinking about the hydroxonium ion as an acid, then water is its conjugate base. The water can accept a hydrogen ion back again to reform the hydroxonium ion.

A second example of conjugate pairs

This is the reaction between ammonia and water that we looked at earlier:



Think first about the forward reaction. Ammonia is a base because it is accepting hydrogen ions from the water. The ammonium ion is its conjugate acid - it can release that hydrogen ion again to reform the ammonia.

The water is acting as an acid, and its conjugate base is the hydroxide ion. The hydroxide ion can accept a hydrogen ion to reform the water.

Looking at it from the other side, the ammonium ion is an acid, and ammonia is its conjugate base. The hydroxide ion is a base and water is its conjugate acid.

Amphoteric substances

You may possibly have noticed (although probably not!) that in one of the last two examples, water was acting as a base, whereas in the other one it was acting as an acid.

A substance which can act as either an acid or a base is described as being *amphoteric*.

