Acids and Bases

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December 4, 2017

1 Introduction

This paper describes the different theories regarding acids and bases, and explains the relationships between them, It also explains the theory of conjugate pairs.

2 Theory

The Arrhenius Theory of Acids and Bases:

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:

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

Limitations of the Theory:

Hydrochloric acid is neutralised by both sodium hydroxide solution and ammonia solution. These are clearly very similar reactions. The full equations are:

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

and:

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

However, in the ammonia case, there doesn'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:

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

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 as 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.

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

This same reaction also happens between ammonia gas and hydrogen chloride gas. In this case, there aren't any hydrogen ions or hydroxide ions in solution because there isn't any solution. The Arrhenius theory would not 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.

The Bronsted-Lowry Theory of Acids and Bases:

The Bronsted-Lowry Theory of Acids and Bases states that an acid is a proton (hydrogen ion) donor. And that a base is a proton (hydrogen ion) acceptor. 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.

$$H_2O_{(l)} + HCl_{(g)} \longrightarrow H_3O^+_{(aq)} + Cl_{(aq)}$$

A co-ordinate (dative covalent) bond is formed between one of the lone pairs on the oxygen and the hydrogen from the $\mathrm{HCl}_{(g)}$. Hydroxonium ions, $\mathrm{H_3O^+}_{(aq)}$, 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.

$$H_3O^{+}_{(aq)} + OH^{-}_{(aq)} \longrightarrow 2H_2O_{(l)}$$

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 Bronsted-Lowry Theory does not have the same pitfalls as the Arrhenius Theory because 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:

$$\mathrm{NH_{3(aq)}\,+\,H_{3}O^{+}}_{(aq)}\quad \longrightarrow\quad \mathrm{NH_{4}}^{+}{}_{(aq)}\,+\,H_{2}O_{(l)}$$

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

$$\mathrm{NH_{3(g)}\,+\,HCl_{(g)}}\quad\longrightarrow\quad\mathrm{NH_4}^+{}_{(l)}\,+\,\mathrm{Cl}^-{}_{(s)}$$

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:

$$H_2O_{(1)} + HCl \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

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:

$$HA + H_2O \Longrightarrow H_3O^+ + A^-$$

Thinking about the forward reaction, HA is an acid because it is donating a proton (hydrogen ion) to the water, and water is a base because it is accepting a proton from the HA. 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 refoms 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.

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

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

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 as 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. You may possibly have noticed 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.