Acid-Base Equilibria

SCH 4U1

Mr. Dvorsky

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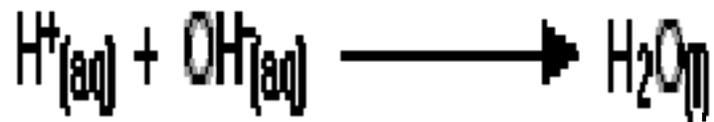
The Arrhenius Theory of acids and bases

The theory:

- Acids are substances which produce hydrogen ions in solution.

- Bases are substances which produce hydroxide ions in solution.

Neutralization 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 neutralized by both sodium hydroxide solution and ammonia solution.

These are clearly very similar reactions. The full

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

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

- 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!

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.

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Conjugate Acid-Base 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:

$$H_2O + HCl \longrightarrow H_3O^+ + Cl^-$$

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
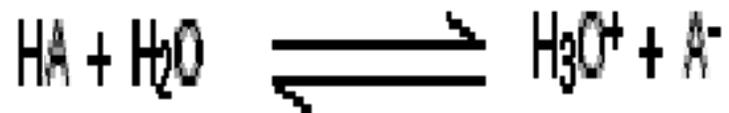
Thinking about the *forward reaction:*
- The HA is an acid because it is donating a proton (hydrogen ion) to the water.
- The water is a base because it is accepting a proton from the HA.

But there is also a *back reaction* between the hydroxonium ion and the A^- ion:
- The H_3O^+ 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**

one conjugate pair

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

the other conjugate pair
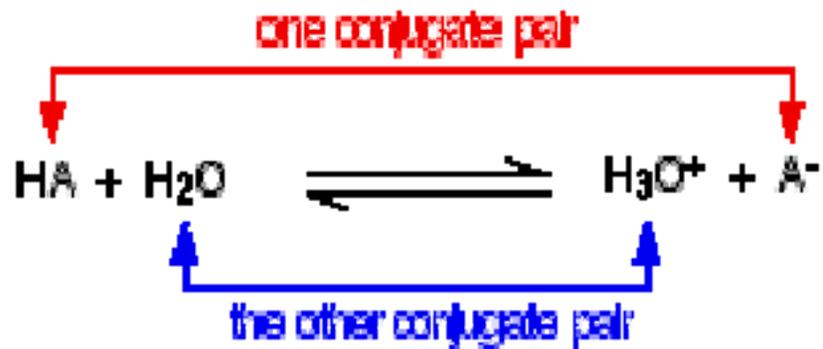
- When the acid, HA, loses a proton it forms a base, A^-. When the base, A^-, accepts a proton back again, it obviously refoms the acid, HA. These two are a conjugate pair.

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.
- 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.

The pH of pure water - Why does pure water have a pH of 7?

That question is actually misleading! In fact, pure water only has a pH of 7 at a particular temperature - the temperature at which the K_w value is 1.00×10^{-14}

This is how it comes about:

To find the pH you need first to find the hydrogen ion concentration (or hydronium ion concentration - it's the same thing). Then you convert it to pH.

In pure water at room temperature the K_w value tells you that:

$[H^+] [OH^-] = 1.00 \times 10^{-14}$

But in pure water, the hydrogen ion (hydroxonium ion) concentration must be equal to the hydroxide ion concentration. For every hydrogen ion formed, there is a hydroxide ion formed as well.

That means that you can replace the $[OH^-]$ term in the K_w expression by another $[H^+]$.

$[H^+]^2 = 1.00 \times 10^{-14}$

Taking the square root of each side gives:

$[H^+] = 1.00 \times 10^{-7}$

Converting that into pH:

$pH = - \log_{10} [H^+]$

$pH = 7$

That's where the familiar value of 7 comes from.

I ○ N A C₃ H₄ E m S T R Y

According to Le Chatelier, if you increase the temperature of the water, the equilibrium will move to lower the temperature again. It will do that by absorbing the extra heat.

That means that the forward reaction will be favoured, and more hydrogen ions and hydroxide ions will be formed. The effect of that is to increase the value of K_w as temperature increases.

The table below shows the effect of temp on K_w. For each value of K_w, a new pH has been calculated using the same method as above. It might be useful if you were to check these pH values yourself.

T (°C)	K_w	pH
0	0.114×10^{-14}	7.47
10	0.293×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.008×10^{-14}	7.00
30	1.471×10^{-14}	6.92
40	2.916×10^{-14}	6.77
50	5.476×10^{-14}	6.63
100	51.3×10^{-14}	6.14

Sometimes the concentration of hydroxide ions is very small in dilute basic solution. It becomes convenient to describe hydroxide ion concentrations in a similar way

$$pOH = -log[OH^-(aq)]$$

A solution's pOH may be used to calculate the hydroxide ion concentration:

$$[OH^-(aq)] = 10^{-pOH}$$

- The mathematics of logarithms allow us to derive a simple relationship between pH and pOH. But first I need to explain pKw

pKw = -logKw

Since Kw = 1×10^{-14} at STP.....

pKw = $-\log(1 \times 10^{-14})$

= - (-14.00) = 14.00

 or pH + pOH = pKw

So pH + pOH = 14.00