

Defining pH

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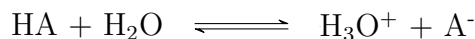
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1 Introduction

This paper will discuss the concept of measuring acidity or alkalinity numerically.

2 Strong Acids

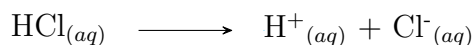
When an acid dissolves in water, a proton (hydrogen ion) is transferred to a water molecule to produce a hydroxonium ion and a negative ion depending on what acid you are starting from:



These reactions are all reversible, but in some cases, the acid is so good at giving away hydrogen ions that we can think of the reaction as being one-way. The acid is virtually 100% ionised:



At any one time, virtually 100% of the hydrogen chloride will have reacted to produce hydroxonium ions and chloride ions. Hydrogen chloride is described as a strong acid. A strong acid is one which is virtually 100% ionised in solution. Other common strong acids include sulphuric acid and nitric acid.



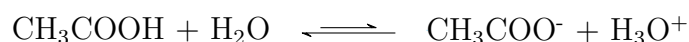
This version is often used in this work just to make things look easier. If you use it, remember that the water is actually involved, and that when you write $\text{H}^+_{(aq)}$ what you really mean is a hydroxonium ion, $\text{H}_3\text{O}^+_{(aq)}$. The concept of pH is that it is a measure of the concentration of hydrogen ions in a solution. Strong acids like hydrochloric acid at the sort of concentrations you normally use in the lab have a pH of around 0 to 1. The lower the pH, the higher the concentration of hydrogen ions in the solution. The value of pH can be easily calculated using the following formula:

$$pH = -\log_{10}[\text{H}^+] \quad (1)$$

Where $[\text{H}^+]$ is the concentration of the hydrogen ions in mol dm^{-3} . Suppose you had to work out the pH of 0.1 mol dm^{-3} hydrochloric acid. All you have to do is work out the concentration of the hydrogen ions in the solution, and then use your calculator to convert it to a pH. With strong acids this is easy. Hydrochloric acid is a strong acid and is virtually 100% ionised. Each mole of HCl reacts with the water to give 1 mole of hydrogen ions and 1 mole of chloride ions. That means that if the concentration of the acid is 0.1 mol dm^{-3} , then the concentration of hydrogen ions is also 0.1 mol dm^{-3} . By using equation (1) to calculate the value of pH, you should arrive at the value of 1.

3 Weak Acids

A weak acid is one which doesn't ionise fully when it is dissolved in water. Ethanoic acid is a typical weak acid. It reacts with water to produce hydroxonium ions and ethanoate ions, but the back reaction is more successful than the forward one. The ions react very easily to reform the acid and the water:



At any one time, only about 1% of the ethanoic acid molecules have converted into ions. The rest remain as simple ethanoic acid molecules. Most organic acids are weak. Hydrogen fluoride (dissolving in water to produce hydrofluoric acid) is a weak inorganic acid that you may come across elsewhere. You can get a measure of the position of an equilibrium by writing an equilibrium constant for the reaction. The lower the value for the constant, the more the equilibrium lies to the left. The dissociation (ionisation) of an acid is an example of a homogeneous reaction. Everything is present in the same phase as in this case, in a solution of water. You can therefore write a simple expression for the equilibrium constant, K_c for the following equation:



And you might expect the equilibrium constant to be written as:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \quad (2)$$

However, since the value of $[\text{H}_2\text{O}]$ is so large in comparison to all the other values present in the expression, and the fact that the acid barely dissociates, we can safely assume the value of $[\text{H}_2\text{O}]$ to be a constant. In that case, there isn't a lot of point in including it in the expression as if it were a variable. Instead, a new equilibrium constant is defined which leaves it out. This new equilibrium constant is called K_a and is the acid dissociation constant:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (3)$$

To take a specific common example, the equilibrium for the dissociation of ethanoic acid is properly written as:



The K_a expression is:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \quad (4)$$

The table shows some values of K_a for some simple acids:

Acid	K_a (mol dm ⁻³)
Hydrofluoric Acid	5.6E -4
Methanoic Acid	1.6E -4
Ethanoic Acid	1.7E -5
Hydrogen Sulphide	8.9E -8

These are all weak acids because the values for K_a are very small. They are listed in order of decreasing acid strength, and the K_a values get smaller as you go down the table. However the notation of K_a is such that it is difficult to easily differentiate between different values of K_a due to confusion caused by the exponent value. To avoid this, the numbers are often converted into a new, easier form, called pK_a . pK_a bears exactly the same relationship to K_a as pH does to the hydrogen ion concentration:

$$pK_a = -\log_{10}K_a \quad (5)$$

If you use your calculator on all the K_a values in the table above and convert them into pK_a values, you get:

Acid	K_a (mol dm ⁻³)	pK_a
Hydrofluoric Acid	5.6E -4	3.3
Methanoic Acid	1.6E -4	3.8
Ethanoic Acid	1.7E -5	4.8
Hydrogen Sulphide	8.9E -8	7.1

Notice that the weaker the acid, the larger the value of pK_a . It is now easy to see the trend towards weaker acids as you go down the table.