

Acid-Base Equilibria

What you should know already.

From **GCSE Combined Science** and earlier schooling, you will be aware;

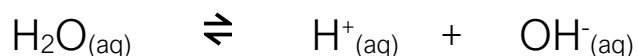
1. we quantify acidity and alkalinity using the pH scale
2. the pH scale covers the range 1-14; 7 being considered neutral
3. there are families of bases including hydroxides, oxides and carbonates

From **GCSE Chemistry**, you will be aware of statements 1-3 plus;

4. acids are chemicals that release hydrogen ions, H^+ , in aqueous solution
5. pH is related quantitatively to the concentrations of H^+ ions
6. if the concentration of H^+ ions is expressed as $10^{-x} \text{ mol dm}^{-3}$, then the pH has the value, **x**.
7. strength of acids is a measure of the extent of dissociation of the acid molecules in water
8. alkalis are water soluble bases that release hydroxide ions, OH^- , in aqueous solution
9. bases are chemicals that neutralise acids to produce salt and water

Calculation of pH

Water molecules naturally dissociate in water. This happens according to the following simplified equation:



This equation represents how **Arrhenius** considered acid molecules to behave.

Arrhenius definition of acids:

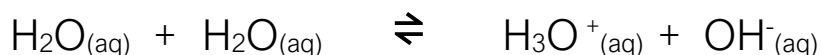
Acids are chemicals that **release hydrogen ions** in solution.
Alkalis are chemicals that **release hydroxide ions** in solution.



This definition won Arrhenius the Nobel Prize in 1903!

However, it was limited in its scope and the definition had to be redefined to explain a far greater number of situations for which, the **Arrhenius** definition didn't work.

It is known that there are no 'free' $\text{H}^+_{(\text{aq})}$ ions in solution. In fact, the dissociation is the result of a collision and reaction between 2 water molecules. This is known as autoionization.



This equation represents how Lowry and Brønsted (separately but around the same period) considered acids to behave.

H_3O^+ is known variously as hydroxonium ion, oxonium ion and hydronium ion. Make sure that you know what your exam board call it.

Lowry-Brønsted definition of acids and bases:

Acids are chemicals that **donate hydrogen ions** in solution.

Bases are chemicals that **accept hydrogen ions** in solution



In the second equation you can see that the water molecule doesn't simply release a hydrogen ion into solution, it only does it by **donation to something else**. In this case, the 'something else' is simply a dissolved water molecule. Be clear though, it is donating to another reactant (also a water molecule). If the molecule was dissolved in liquid ammonia, then it would protonate the ammonia molecules. Ammonia molecules would be the base in this situation because they accept the proton that water molecules are donating.

Can you see that an acid is only an acid if something is prepared to accept its proton? It's a 2-way process. By analogy, Mr Burns (Simpsons) could not describe himself as charitable or philanthropic if the only time he goes to the *Springfield Charity Shop* is when it is closed. You must actually **donate** the money **to something**. This is what Lowry and Brønsted realised. I consider it essential that you understand this, trivial as it seems. It is the foundation to acid-base reactions.

Now that I've said that the hydrogen ions are actually bonded to a water molecule in the form of the hydroxonium ion, I will go further to say that we will generally write H^+ rather than H_3O^+ because it's easier.

Going back to the dissociation of water, the amount of dissociation has been worked out. The concentration of both H_3O^+ and OH^- ions is $1.00 \times 10^{-7} \text{ mol dm}^{-3}$

$$\text{@ } 25^\circ\text{C; } [H_3O^+_{(aq)}] = [OH^-_{(aq)}] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$$

Specifying the temperature is essential as the values of the **concentrations are dependent on temperature** as we will see pretty soon.

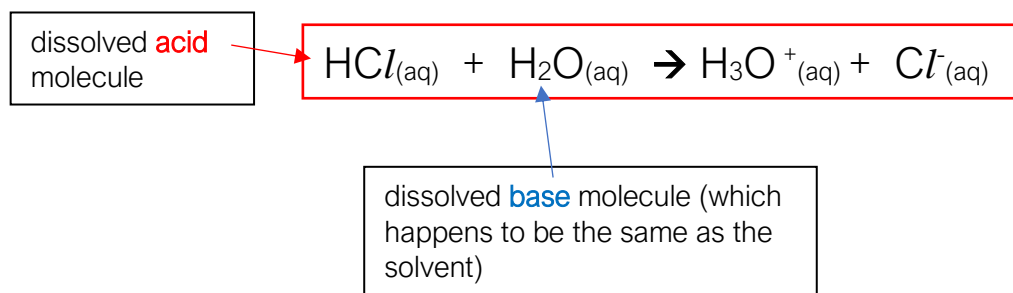
Note that the $[H_3O^+]$ and $[OH^-]$ are both very small.

Let's consider a dilute solution of a strong monobasic (or monoprotic) acid, *e.g.* hydrochloric acid.

The concentration is $0.100 \text{ mol dm}^{-3}$

Stating that hydrochloric acid is a **strong acid** is saying that it **fully dissociates in water**. The truth is that it doesn't fully dissociate but it is so close to being fully dissociated that we assume that it is to make the calculation easier. There are stronger acids than hydrochloric acid!

We can write an equation for the process.



If the acid fully dissociates, it will produce a solution that now contains a $0.100 \text{ mol dm}^{-3}$ solution of $[\text{H}_3\text{O}^+]$.

So, the $[\text{H}^+] = 0.100 \text{ mol dm}^{-3}$ which we can write as $10^{-1} \text{ mol dm}^{-3}$

If we compare $[\text{H}^+]$ in water and $[\text{H}^+]$ in $0.100 \text{ mol dm}^{-3}$ solution of hydrochloric acid, we see that the difference is enormous.

$[\text{H}^+]$ in water 10^{-7} & 10^{-1} is the $[\text{H}^+]$ in $0.100 \text{ mol dm}^{-3}$ solution of hydrochloric acid

These concentrations vary over such a huge range, we use a simple mathematical operation to make the numbers more useful. We 'take logs' of the values of the concentration.

The log (base 10) of a number, x , is the power that we raise 10 by to produce x .

For example,

$\log 100 = 2$ This is because $100 = 10^2$ so **2** is the power of 10

$\log 1\ 000 = 3$ This is because $1000 = 10^3$ so **3** is the power of 10

$\log 1\ 000\ 000 = 7$ This is because $1\ 000\ 000 = 10^7$ so **7** is the power of 10

$\log 126 = 2.10$ This is because $126 = 10^{2.10}$ so **2.10** is the power of 10

We can do this for numbers **smaller than 1**.

$\log 0.100 = -1$ This is because $0.100 = 10^{-1}$ so **-1** is the power of 10

$\log 0.00100 = -3$ This is because $0.00100 = 10^{-3}$ so **-3** is the power of 10

$\log 0.0854 = -1.07$ This is because $0.0854 = 10^{-1.07}$ so **-1.07** is the power of 10

Now we know a little about logarithms, we can **define pH**

Definition of pH $\text{pH} = -\log[\text{H}^+]$

The negative sign in the definition simply ensures that pHs have a positive value.

We can now calculate the pH of the $0.100 \text{ mol dm}^{-3}$ solution of hydrochloric acid.

$$\text{pH} = -\log[\text{H}^+] = -\log 0.100 = 1.00$$

If this $\text{HCl}_{(\text{aq})}$ was **diluted 10 times**, it would have a new concentration of $0.0100 \text{ mol dm}^{-3}$

$$\text{pH} = -\log[\text{H}^+] = -\log 0.0100 = 2.00$$

For every 10 times dilution, the pH moves up by **1.00** units. This is a useful thing to remember!

Calculating the **pH of a strong acid** is straightforward. If you know the concentration of a **monobasic acid** (releases or donates 1 proton per molecule), you can assume that the concentration of the acid is the same as the concentration of H^+ . Then you simply carry out the calculation:

$$\text{pH} = -\log[\text{H}^+]$$

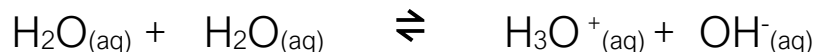
If an acid is **diprotic**, e.g. $\text{H}_2\text{SO}_{4(\text{aq})}$ you need to be a little careful. Some textbooks state that you can find $[\text{H}^+]$ by simply doubling the concentration of the sulfuric acid. This is fundamentally wrong. The first proton that disassociates is strong, so it is true to say that **sulfuric acid is a strong acid**.

BUT, having lost one proton, the hydrogen sulfate ion (HSO_4^-) produced from the loss of the first proton, is actually a weak acid. This means that the total number of protons produced is not double the amount of sulfuric acid molecules. Make sure that you know what your exam board are expecting you to do if you get a problem like this one.

Calculating the pH of Strong Bases

We need to deal with the slightly more complicated matter of working out the **pH for strong bases**.

Let's begin by bringing back an equation from earlier:



This is clearly an equilibrium that lies well to the left. We know this because of the tiny concentration of $\text{H}_3\text{O}^+_{(\text{aq})}$ and $\text{OH}^-_{(\text{aq})}$

We can write an equilibrium expression for this in terms of concentrations.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]}$$

The value of $[\text{H}_2\text{O}]$ is very large (55.6 mol dm^{-3}) and so it is approximately **constant** in this equilibrium. That means that we can combine $[\text{H}_2\text{O}][\text{H}_2\text{O}]$ with K_c to make a new constant, K_w .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

We saw earlier that these concentrations are known at 25°C :

$$\text{@ } 25^\circ\text{C}; [\text{H}_3\text{O}^+_{(\text{aq})}] = [\text{OH}^-_{(\text{aq})}] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$$

So, we can work out the value of K_w

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-7} \times 1.00 \times 10^{-7} = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

This gives us an important relationship called the **IONIC PRODUCT of WATER**.

The value is temperature dependent because it is associated with an equilibrium constant K_w

$$\text{@}25^\circ\text{C} \quad K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

This equation tells us that $[\text{H}_3\text{O}^+_{(\text{aq})}]$ and $[\text{OH}^-_{(\text{aq})}]$ are linked.

If you change either $[\text{H}_3\text{O}^+_{(\text{aq})}]$ or $[\text{OH}^-_{(\text{aq})}]$, then the other must be change so that the value of K_w **remains** $10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

An increase in $[\text{H}_3\text{O}^+]$ must cause a decrease in $[\text{OH}^-]$ and vice versa.

However, it is not like a regular seesaw. If you increase $[\text{H}_3\text{O}^+]$ by 10 times then you must decrease $[\text{OH}^-_{(\text{aq})}]$ by 10 times. Make sure that you understand that this equation is not suggesting that the total number of ions remains constant! It is the product of the two concentrations (hence the name of the constant).

This expression will now allow us to calculate the $[\text{H}_3\text{O}^+_{(\text{aq})}]$ if we are given the $[\text{OH}^-_{(\text{aq})}]$

For example:

Q. Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of the strong base, sodium hydroxide, $\text{NaOH}_{(\text{aq})}$.

A. If it's a strong base then the solution must contain a $0.100 \text{ mol dm}^{-3}$ solution hydroxide ions

$[\text{OH}^-] = 0.100 \text{ mol dm}^{-3}$ We need to find the value of $[\text{H}^+]$ so we can calculate a pH.

Recall $K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Rearranging: $\frac{K_w}{[\text{OH}^-]} = [\text{H}^+] = \frac{1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{0.100 \text{ mol dm}^{-3}} = [\text{H}^+] = 1.00 \times 10^{-13} \text{ mol dm}^{-3}$

$$\text{pH} = -\log 1.00 \times 10^{-13} = \underline{13.0}$$

Have a go at the following:

1. Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of $\text{HNO}_{3(\text{aq})}$.

Answer_____

2. Calculate the pH of a $0.0891 \text{ mol dm}^{-3}$ solution of $\text{HCl}_{(\text{aq})}$.

Answer_____

3. Calculate the pH of a $4.51 \times 10^{-3} \text{ mol dm}^{-3}$ solution of $\text{HNO}_{3(\text{aq})}$.

Answer_____

4. Calculate the pH of a $8.24 \times 10^{-2} \text{ mol dm}^{-3}$ solution of $\text{NaOH}_{(\text{aq})}$

Answer_____

5. Calculate the pH of a $0.0424 \text{ mol dm}^{-3}$ solution of $\text{Ba}(\text{OH})_{2(\text{aq})}$ (CARE!)

Answer_____

There are many more self-marking pH questions on [CramNow](#)