

Acids and Bases

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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.

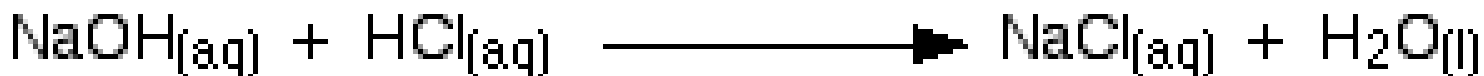
Neutralisation happens because hydrogen ions and hydroxide ions react to produce water.



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.

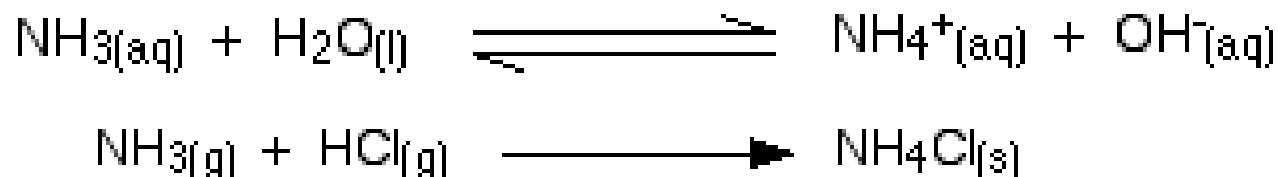
These are clearly very similar reactions. The full equations are:



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!

You can get around this by saying that the ammonia reacts with the water it is dissolved in to produce ammonium ions and hydroxide ions:



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 we can squeeze this into the Arrhenius theory.

However, 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 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.

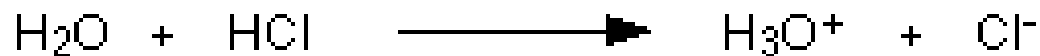
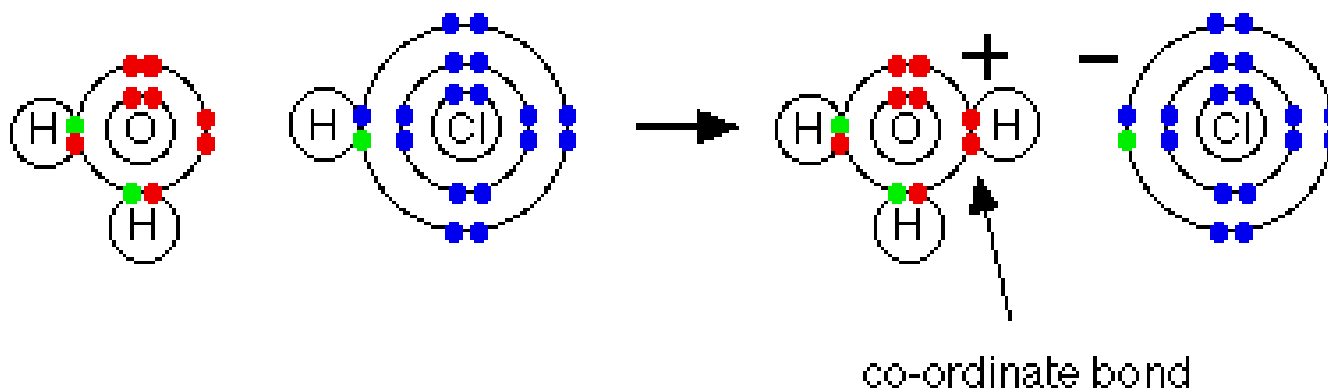
The relationship between the Bronsted-Lowry theory and the Arrhenius theory

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

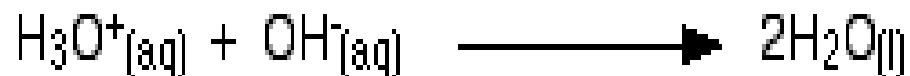
Hydroxide ions are still bases because they accept hydrogen ions from acids and form water.

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

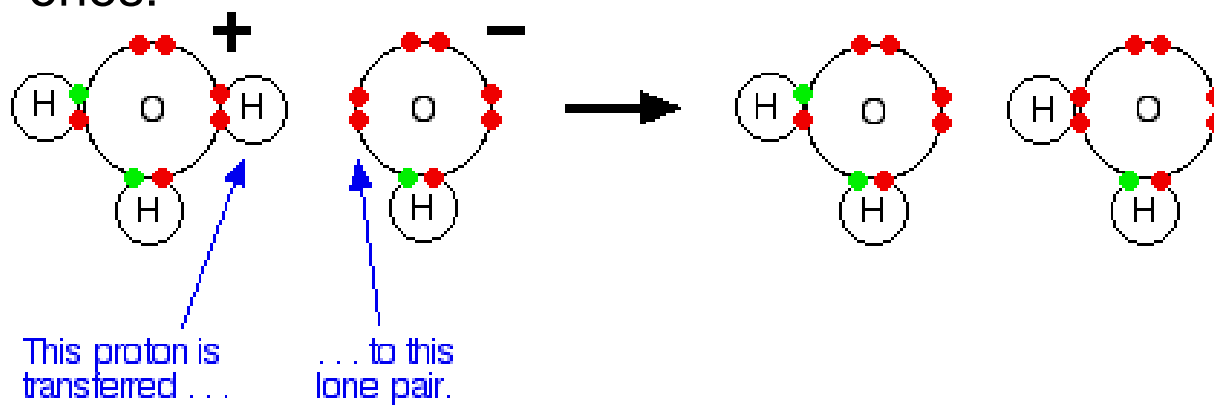
When hydrogen chloride gas dissolves in water to produce hydrochloric acid, the hydrogen chloride molecule gives a proton (a hydrogen ion) to a water molecule. A co-ordinate (dative covalent) bond is formed between one of the lone pairs on the oxygen and the hydrogen from the HCl. *Hydroxonium ions, 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.



Showing the electrons, but leaving out the inner ones:

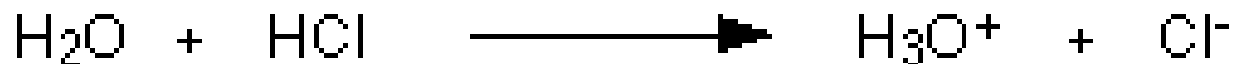


It is important to realise that whenever you talk about hydrogen ions in solution, $\text{H}^+(\text{aq})$, what you are actually talking about are hydroxonium ions.

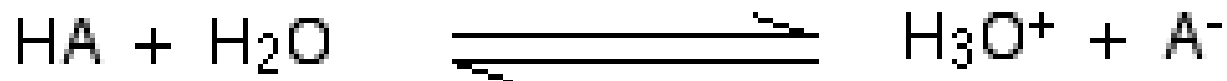
Conjugate pairs

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.



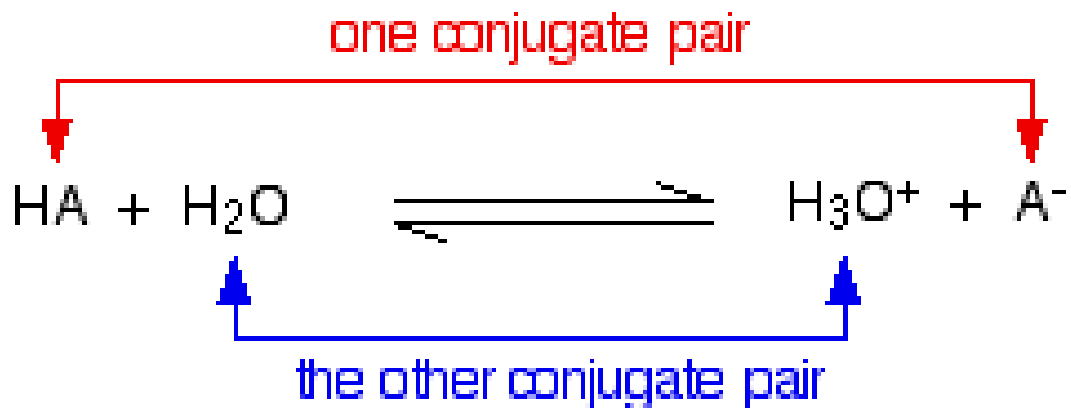
Thinking about the *forward reaction*:

- 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 H₃O⁺.

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



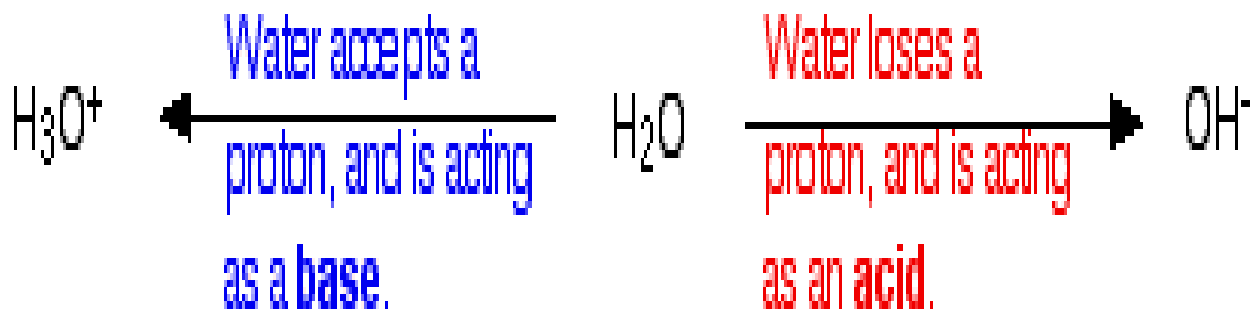
When the acid, HA, loses a proton it forms a base, A^- . When the base, A^- , accepts a proton back again, it obviously reforms the acid, HA. These two are a conjugate pair.

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

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***.



The Lewis Theory of acids and bases

This theory extends well beyond the things you normally think of as acids and bases.

The theory

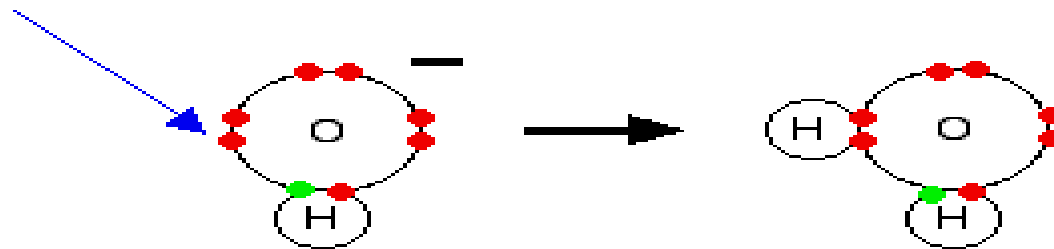
- An acid is an electron pair acceptor.
- A base is an electron pair donor.

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

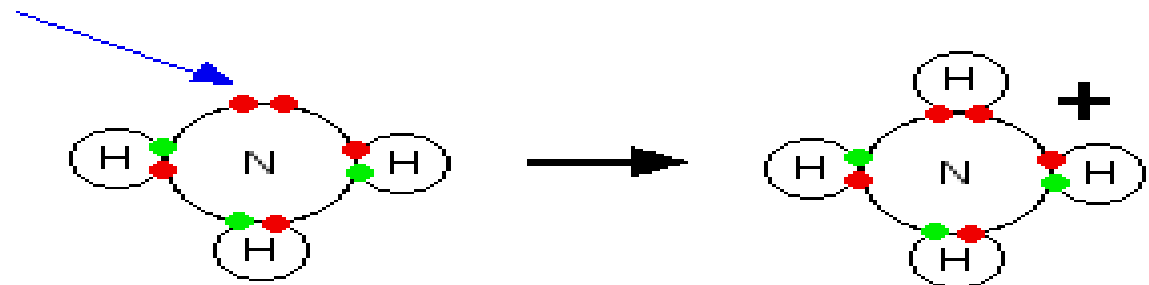
Lewis bases

It is easiest to see the relationship by looking at exactly what Bronsted-Lowry bases do when they accept hydrogen ions. Three Bronsted-Lowry bases we've looked at are hydroxide ions, ammonia and water, and they are typical of all the rest.

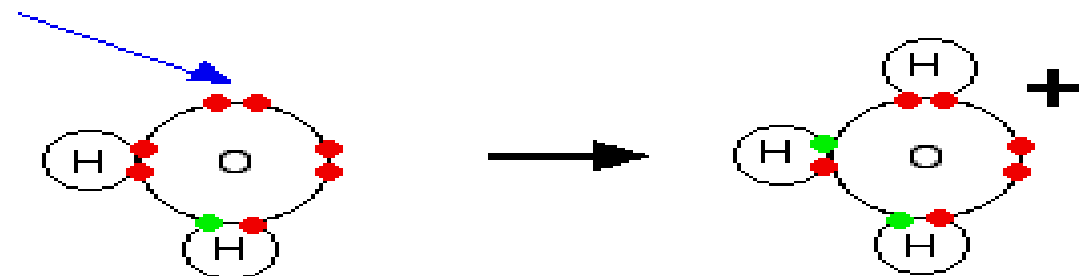
A hydroxide ion picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



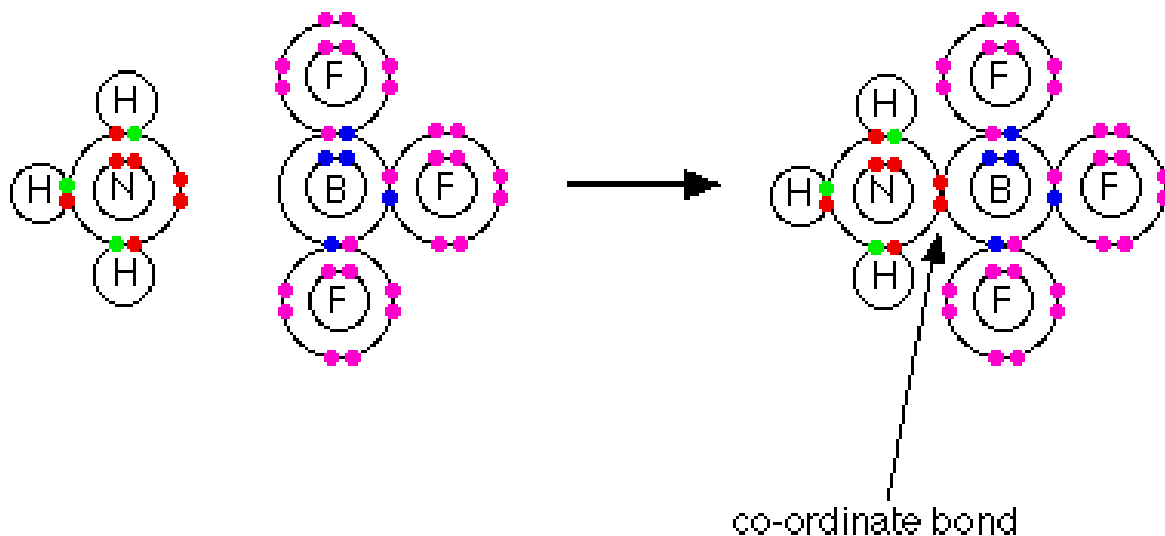
Ammonia picks up a hydrogen ion by attaching it to the lone pair on the nitrogen.



Water picks up a hydrogen ion by attaching it to one of the lone pairs on the oxygen.



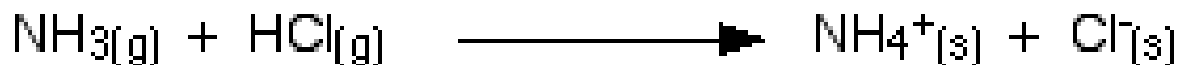
Ammonia reacts with BF_3 by using its lone pair to form a co-ordinate bond with the empty orbital on the boron.



As far as the ammonia is concerned, it is behaving exactly the same as when it reacts with a hydrogen ion - it is using its lone pair to form a co-ordinate bond. If you are going to describe it as a base in one case, it makes sense to describe it as one in the other case as well.

Lewis acids

Lewis acids are electron pair acceptors. In the above example, the BF_3 is acting as the Lewis acid by accepting the nitrogen's lone pair. On the Bronsted-Lowry theory, the BF_3 has nothing remotely acidic about it. This is an extension of the term *acid* well beyond any common use. What about more obviously acid-base reactions - like, for example, the reaction between ammonia and hydrogen chloride gas?

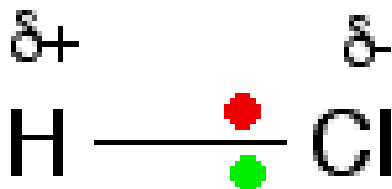


What *exactly* is accepting the lone pair of electrons on the nitrogen. Textbooks often write this as if the ammonia is donating its lone pair to a hydrogen ion - a simple proton with no electrons around it.

There isn't an empty orbital anywhere on the HCl which can accept a pair of electrons.

Why, then, is the HCl a Lewis acid?

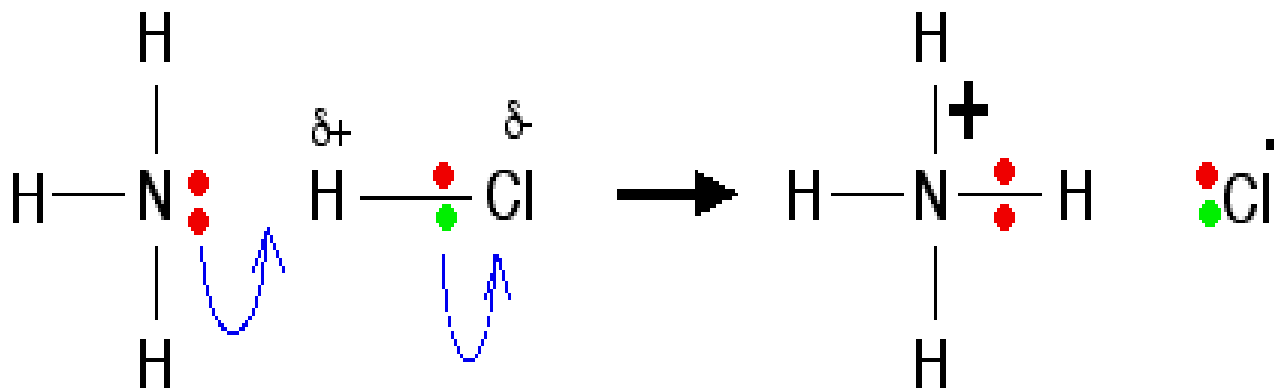
Chlorine is more electronegative than hydrogen, and that means that the hydrogen chloride will be a polar molecule. The electrons in the hydrogen-chlorine bond will be attracted towards the chlorine end, leaving the hydrogen slightly positive and the chlorine slightly negative.



The lone pair on the nitrogen of an ammonia molecule is attracted to the slightly positive hydrogen atom in the HCl. As it approaches it, the electrons in the hydrogen-chlorine bond are repelled still further towards the chlorine.

Eventually, **a co-ordinate bond is formed between the nitrogen and the hydrogen, and the chlorine breaks away as a chloride ion.**

This is best shown using the "curly arrow" notation commonly used in organic reaction mechanisms.



HSAB theory

The **HSAB concept** is an [initialism](#) for "hard and soft [\(Lewis\) acids and bases](#)". Also known as the **Pearson acid base concept**, HSAB is widely used in [chemistry](#) for explaining stability of [compounds](#), [reaction](#) mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to [chemical species](#). 'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable. The concept is a way of applying the notion of [orbital overlap](#) to specific chemical cases.

Hard acids and hard bases tend to have the following characteristics:

small atomic/ionic radius

high [oxidation state](#)

low [polarizability](#)

high [electronegativity](#) (bases)

hard bases have highest-occupied molecular orbitals ([HOMO](#)) of low energy, and hard acids have lowest-unoccupied molecular orbitals ([LUMO](#)) of high energy.[\[7\]\[8\]](#)

Examples of hard acids are: H^+ , light [alkali](#) ions (Li through K all have small ionic radius), Ti^{4+} , Cr^{3+} , Cr^{6+} , BF_3 . Examples of hard bases are: OH^- , F^- , Cl^- , NH_3 , CH_3COO^- , CO_3^{2-} . The affinity of hard acids and hard bases for each other is mainly [ionic](#) in nature.

Soft acids and soft bases tend to have the following characteristics:

large atomic/ionic radius
low or zero oxidation state bonding
high polarizability
low electronegativity

soft bases have HOMO of higher energy than hard bases, and soft acids have LUMO of lower energy than hard acids. (However the soft-base HOMO energies are still lower than the soft-acid LUMO energies.)[\[7\]\[8\]](#)

Examples of soft acids are: CH_3Hg^+ , Pt^{2+} , Pd^{2+} , Ag^+ , Au^+ , Hg^{2+} , Hg_2^{2+} , Cd^{2+} , BH_3 . Examples of soft bases are: H^- , R_3P , SCN^- , I^- . The affinity of soft acids and bases for each other is mainly covalent in nature.

Acids				Bases			
hard		soft		hard		soft	
<u>Hydronium</u>	H_3O^+	<u>Mercury</u>	CH_3Hg^+ , Hg^{2+} , Hg_2^{2+}	<u>Hydroxide</u>	OH^-	<u>Hydride</u>	H^-
<u>Alkali metals</u>	Li^+, Na^+, K^+	<u>Platinum</u>	Pt^{2+}	<u>Alkoxide</u>	RO^-	<u>Thiolate</u>	RS^-
<u>Titanium</u>	Ti^{4+}	<u>Palladium</u>	Pd^{2+}	<u>Halogens</u>	F^-, Cl^-	<u>Halogens</u>	I^-
<u>Chromium</u>	Cr^{3+}, Cr^{6+}	<u>Silver</u>	Ag^+	<u>Ammonia</u>	NH_3	<u>Phosphine</u>	PR_3
<u>Boron trifluoride</u>	BF_3	<u>borane</u>	BH_3	<u>Carboxylate</u>	CH_3COO^-	<u>Thiocyanate</u>	SCN^-
<u>Carbocation</u>	R_3C^+	<u>P-chloranil</u>		<u>Carbonate</u>	CO_3^{2-}	<u>carbon monoxide</u>	CO
<u>Lanthanides</u>	Ln^{3+}	<u>bulk Metals</u>	M^0	<u>Hydrazine</u>	N_2H_4	<u>Benzene</u>	C_6H_6
		<u>Gold</u>	Au^+				

Table 1. Hard and soft acids and bases

Borderline cases are also identified:

borderline acids are [trimethylborane](#), [sulfur dioxide](#) and [ferrous](#) Fe^{2+} , [cobalt](#) Co^{2+} [caesium](#) Cs^+ and [lead](#) Pb^{2+} cations. **Borderline bases** are: [aniline](#), [pyridine](#), [nitrogen](#) N_2 and the [azide](#), [bromide](#), [nitrate](#) and [sulfate](#) anions.

Generally speaking, acids and bases interact and the most stable interactions are hard-hard ([ionogenic](#) character) and soft-soft ([covalent](#) character).

An attempt to quantify the 'softness' of a base consists in determining the [equilibrium constant](#) for the following equilibrium:



Where CH_3Hg^+ ([methylmercury](#) ion) is a very soft acid and H^+ (proton) is a hard acid, which compete for B (the base to be classified).

pH and Buffers Defined

pH is a measure of the concentration of H^+ [H_3O^+] ions in a solution. Only the concentration of H^+ and OH^- molecules determine the pH. When the concentration of H^+ and OH^- ions are equal, the solution is said to be neutral. If there are more H^+ than OH^- molecules the solution is acidic, and if there are more OH^- than H^+ molecules, the solution is basic.

Buffers

To be able to add a strong acid or base to a solution without causing a large change in the pH, we need to create a buffer solution. A buffer solution contains both a weak acid (HA) and its conjugate base (A^-).

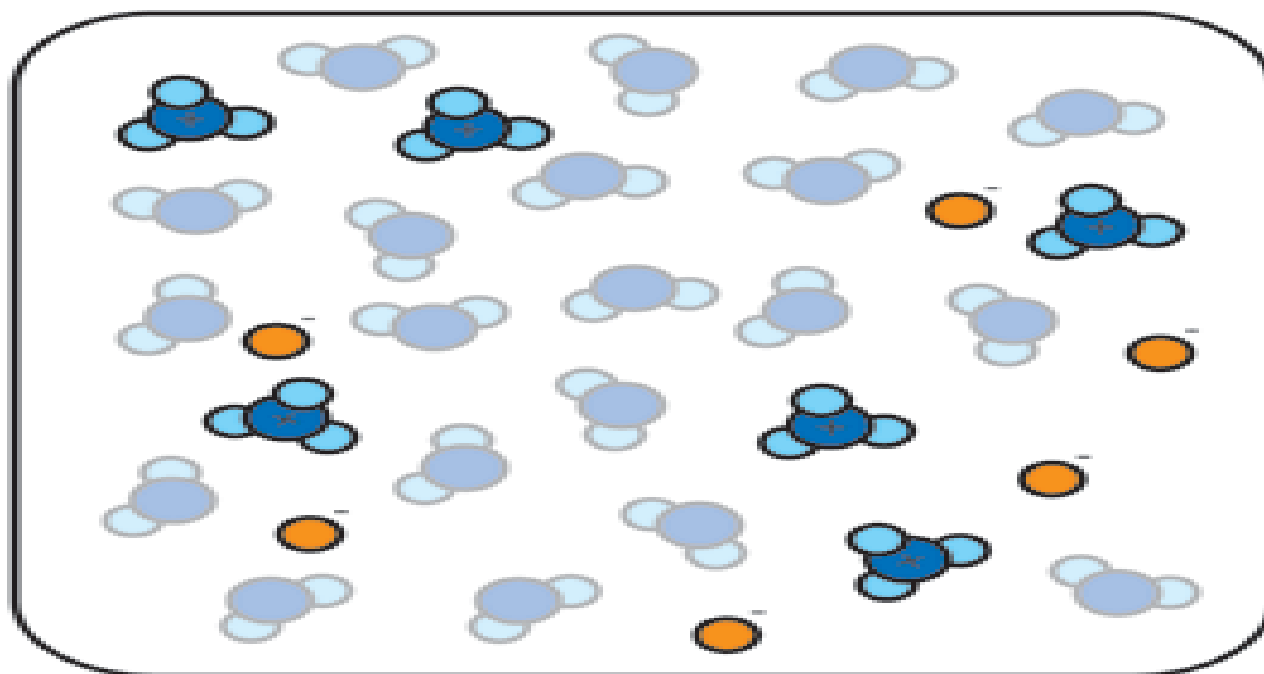
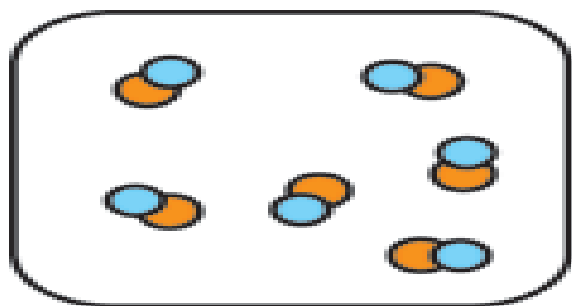
pH in the Absence of a Buffer

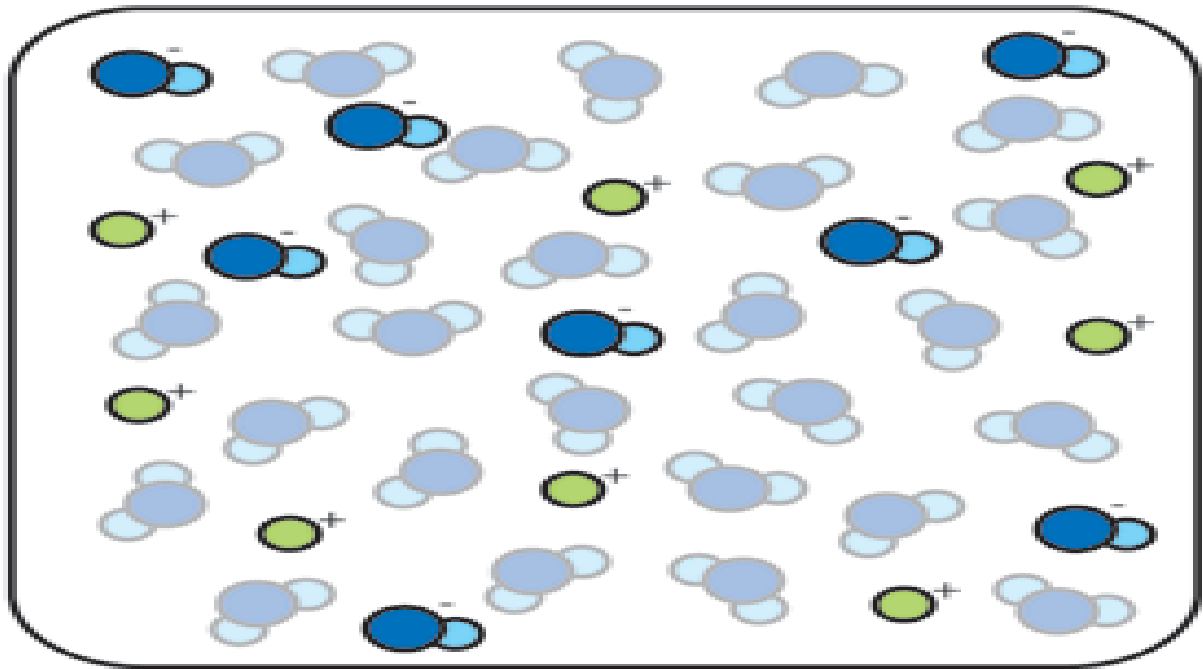
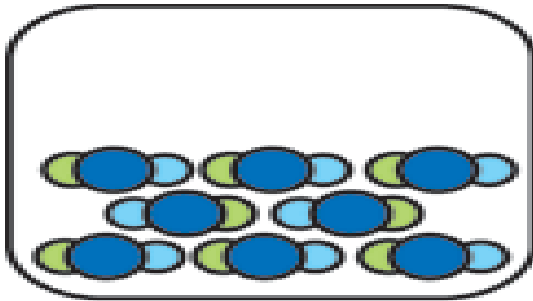
If we add a strong acid or strong base to water, the pH will change dramatically. For instance, adding a strong acid such as HCl to water results in the reaction



In other words, the proton (H^+) from the acid binds to neutral water molecules to form H_3O^+ raising the concentration of H^+ . The resulting large concentration of (H^+) makes the solution more acidic and leads to a **dramatic drop in the pH.**

Solid NaOH consists of Na^+ and OH^- ions packed into a crystalline lattice. When this solid is added to water, the ions float apart leading to extra OH^- ions in the water: $\text{NaOH} \rightarrow \text{OH}^- + \text{Na}^+$. The resulting large concentration of OH^- makes the solution more basic and leads to a dramatic increase in the pH. (Remember that since the product of concentrations, $[\text{OH}^-][\text{H}^+]$, remains fixed at $K_w=10^{-14}$, as the concentration of OH^- ions goes up, the concentration of H^+ ions goes down.)





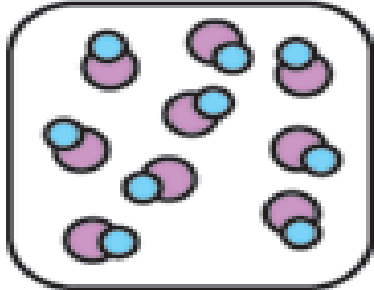
How Buffers Work

How does a mixture of a weak acid and its conjugate base help buffer a solution against pH changes?

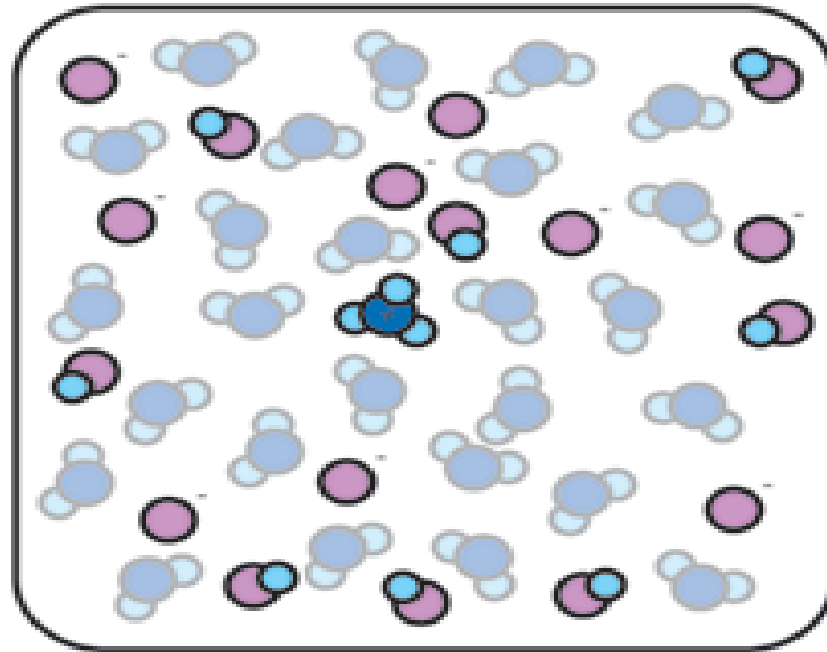
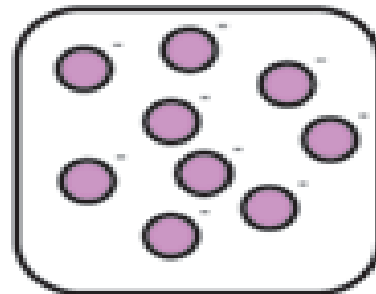
If we mix a weak acid (HA) with its conjugate base (A^-), both the acid and base components remain present in the solution. This is because they do not undergo any reactions that significantly alter their concentrations. The acid and conjugate base may react with one another, $HA + A^- \rightarrow A^- + HA$, but when they do so, they simply trade places and the concentrations $[HA]$ and $[A^-]$ do not change. In addition, HA and A^- only rarely react with water. By definition, a weak acid is one that only rarely dissociates in water (that is, only rarely will the acid lose its proton H^+ to water). Likewise, since the conjugate base A^- is a weak base, it rarely steals a proton H^+ from water.

So, the weak acid and weak base remain in the solution with high concentrations since they only rarely react with the water. However, they are very likely to react with any added strong base or strong acid.

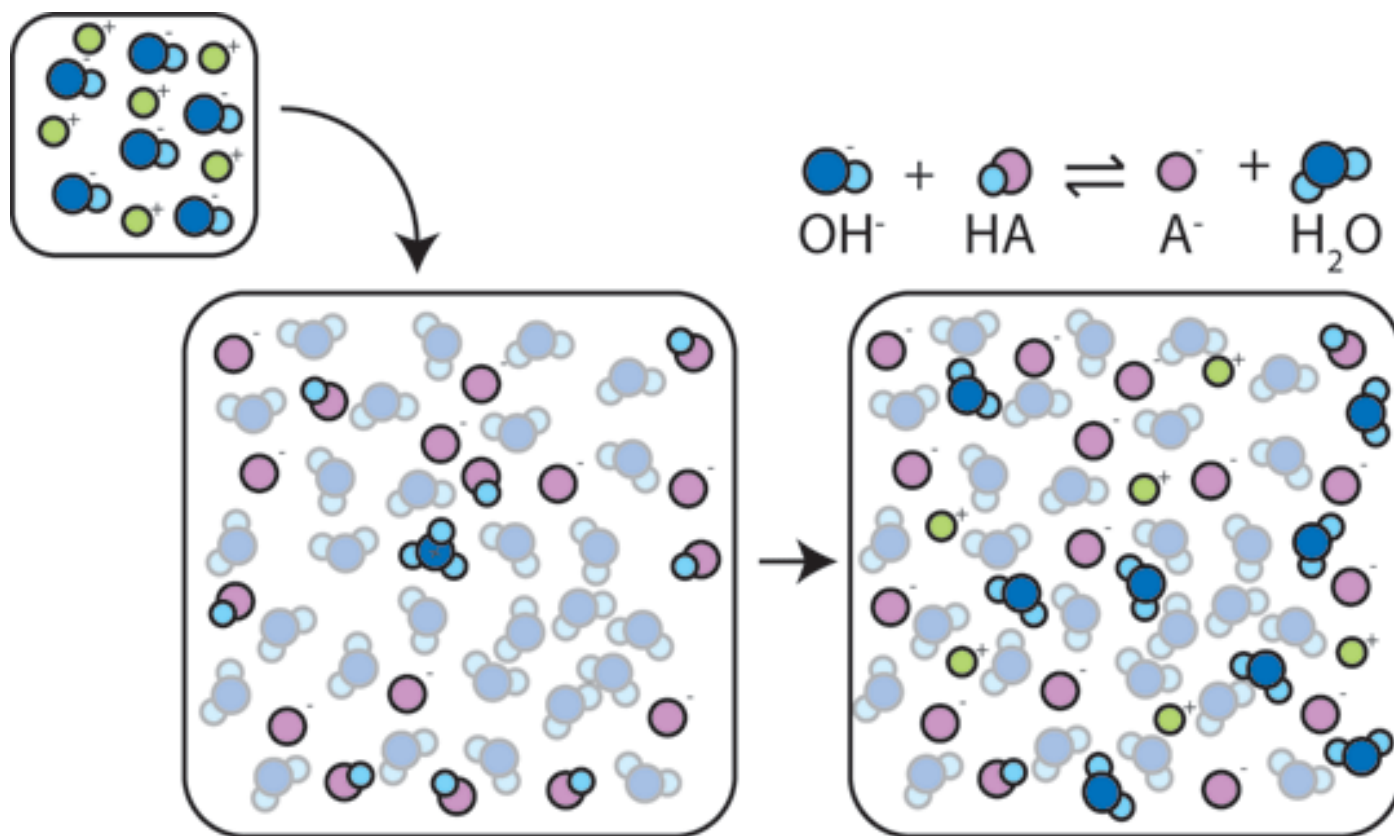
HA (weak acid)



A⁻ (weak base)



If a strong base is added to a buffer, the weak acid will give up its H^+ in order to transform the base (OH^-) into water (H_2O) and the conjugate base: $HA + OH^- \rightarrow A^- + H_2O$. Since the added OH^- is consumed by this reaction, the pH will change only slightly.



If a strong acid is added to a buffer, the weak base will react with the H^+ from the strong acid to form the weak acid HA : $H^+ + A^- \rightarrow HA$. The H^+ gets absorbed by the A^- instead of reacting with water to form H_3O^+ (H^+), so the pH changes only slightly.

