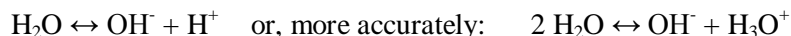


# Acids and Bases in Dilute Aqueous Solution

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## The Basics

Water is not actually just H<sub>2</sub>O, it exists in equilibrium with hydrogen and hydroxide ions:



This second equation more closely represents reality, but for the sake of simplicity we will often use H<sup>+</sup> in place of H<sub>3</sub>O<sup>+</sup>. The dissociation of water is small enough that the concentration of H<sub>2</sub>O remains approximately constant. Therefore, to keep this system in equilibrium, the concentrations of H<sup>+</sup> and OH<sup>-</sup> must be inversely related. That is to say any increase in hydrogen ion concentration, [H<sup>+</sup>], is accompanied by a decrease in hydroxide ion concentration, [OH<sup>-</sup>]. The pH value attributed to a solution comes from these concentrations:

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

A higher H<sup>+</sup> concentration corresponds to a lower pH and vice-versa.

Acids, then, are compounds that lower the pH of a solution by dissociating to release H<sup>+</sup> ions. They are hydrogen-containing compounds with the potential to give up a proton in solution (technically we are referring to Bronsted-Lowry acids here). Two common examples include the strong acid hydrochloric acid (HCl) and the weak acid acetic acid (H<sub>3</sub>CCOOH). An acid that has lost its proton is referred to as the conjugate base of the acid.

A base may or may not include hydrogen atoms and may or may not be charged. All bases, however, can accept a proton to form a neutral or positively-charged conjugate acid. Dissolved bases raise the pH of a solution by reacting with H<sup>+</sup> which lowers the overall H<sup>+</sup> concentration. Ammonia (NH<sub>3</sub>) is an example of a neutral base, and ammonium (NH<sub>4</sub><sup>+</sup>) is the corresponding conjugate acid. Hydroxide (OH<sup>-</sup>) is a strong, negatively-charged base whose conjugate acid is water (H<sub>2</sub>O).

Note that many compounds can act as either an acid or a base, depending on conditions. Some abbreviations that are used in the following discussion are:

H<sub>x</sub>A = generalized acid, bound to x number of protons

A = generalized conjugate base, also A<sup>-</sup>, A<sup>2-</sup>, etc.

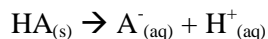
B = generalized base

H<sub>x</sub>B = protonated form of the base, bound to x number of protons

## Solutions of Acids and Bases

### *Acids*

When an acid (HA) is dissolved in water, it dissociates and releases a proton, lowering the pH.

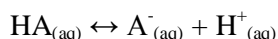


For example, hydrochloric acid dissociates completely into hydrogen and chloride ions:

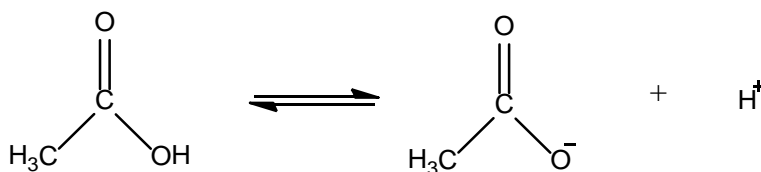


Acids that dissociate completely are called strong acids. The  $[\text{H}^{+}]$  can be derived directly from the amount of acid dissolved. For instance if 0.1 mol of HCl is dissolved in 1 L of water, the resultant  $[\text{H}^{+}]$  is 0.1 M and the pH is 1. Other common strong acids include HBr, HI,  $\text{HClO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (only the first proton; bisulfate is a weak acid). The conjugate bases of each of these strong acids ( $\text{Cl}^{-}$ ,  $\text{I}^{-}$ , etc.) are very stable anions in solution.

Many acids do not completely dissociate in neutral water. We refer to these as weak acids, and they exist in equilibrium with a substantial concentration of the conjugate base and water:



For acetic acid this equilibrium is represented by:



All three species can exist simultaneously in solution, the relative amounts depend on the pH, the formal concentration of the acid, and the  $\text{pK}_a$  of the weak acid, among other factors.

### **Bases**

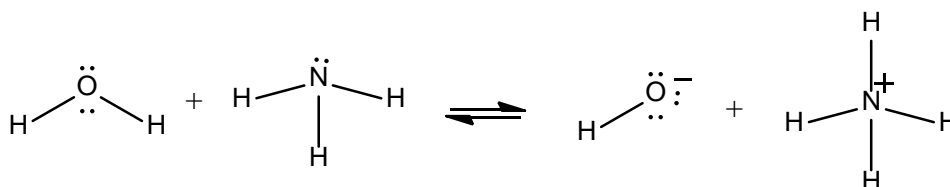
In water, bases either release or form hydroxide ( $\text{OH}^{-}$ ) ions to raise the pH. Recall from our original discussion of the equilibrium of water that an increase in  $[\text{OH}^{-}]$  corresponds to a decrease in  $[\text{H}^{+}]$  and a rise in pH. Many strong bases consist of the hydroxide ion and a metal (M) that dissociate in water.



Examples include NaOH and  $\text{Ba}(\text{OH})_2$



Other bases, such as ammonia, react with water to form  $\text{OH}^{-}$  ions, also raising the pH.



Ammonia, like many neutral nitrogen-containing compounds, is a weak base. Like weak acids, weak bases exist in equilibrium with water. The relative amounts of different species depend on the pH, the concentration of base, and the  $\text{pK}_a$  of the weak base, among other factors.

## ***pK<sub>a</sub>***

As mentioned above, weak acids exist in equilibrium with water. Like all equilibria, these systems can be described using an equilibrium expression.

For the reaction of a weak acid,  $\text{HA}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \leftrightarrow \text{A}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})}$ ,

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

Every acid has a characteristic  $\text{pK}_a$  where

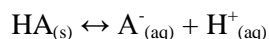
$$\text{pK}_a = -\log K_a$$

Note the similarity to

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

When a weak acid is dissolved in a solution that is maintained at precisely the  $\text{pK}_a$  of said acid, half of the acid exists in the protonated form (HA) and half as the deprotonated conjugate base ( $\text{A}^{-}$ ). For example, if one mole of acetic acid was dissolved in a solution at its  $\text{pK}_a$  (4.76), 0.5 moles would remain as acetic acid while 0.5 moles would dissociate into acetate and  $\text{H}^{+}$  (recall that this is the same as  $\text{H}_3\text{O}^{+}$  for the purposes of this discussion.)

Now imagine lowering the pH of this solution. This is the same as adding  $\text{H}^{+}$  to the system in our original weak acid equilibrium equation.



By LeChatelier's principle, you may remember that adding "product" forces the equilibrium to the left, raising the concentration of the *neutral* protonated acid (HA). It may help to picture this: a lower pH means that there are more protons floating around, making it more likely that they will attach to the conjugate base. At a pH more than two units below the  $\text{pK}_a$ , essentially all of the weak acid is protonated.

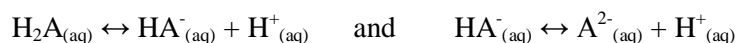
The same logic can be applied to a solution whose pH is above the  $\text{pK}_a$  of a given weak acid. In this case, the acid is more likely to be deprotonated, in its *ionized* conjugate base form ( $\text{A}^{-}$ ). If the pH is more than about 1 unit above the  $\text{pK}_a$ , essentially all of the weak acid has dissociated into  $\text{H}^{+}$  and  $\text{A}^{-}$ .

Note that a lower  $\text{pK}_a$  indicates a stronger acid and a more stable conjugate base. For a strong acid, the  $\text{pK}_a$  is lower than that of the hydronium ion ( $\text{H}_3\text{O}^{+}$ ,  $\text{pK}_a = -1.74$ ). The dissociation of the acid and formation of the hydronium ion is favored, leading to complete dissociation in typical aqueous solutions.

## ***Polyprotic acids***

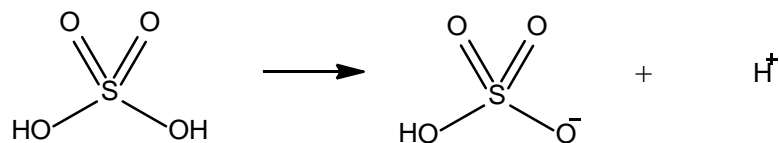
Polyprotic acids contain more than one hydrogen atom with the potential to dissociate. Each hydrogen atom is associated with a different  $\text{pK}_a$  and a different equilibrium equation.

For a diprotic acid,  $\text{H}_2\text{A}$ , the two equations are:

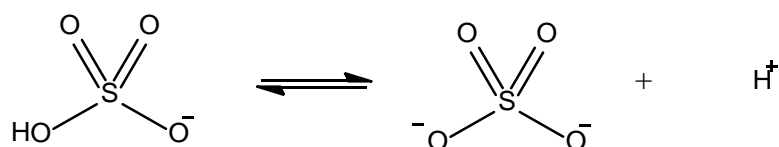


The higher  $pK_a$  corresponds to the pH at which equal concentrations of  $HA^-$  and  $A^{2-}$  are present. The second  $pK_a$  corresponds to the second equilibrium, between  $H_2A$  and  $HA^-$ .

In the case of sulfuric acid,  $H_2SO_4$ , the  $pK_a$  values associated with the loss of the first and second proton are -3 and 2, respectively. Thus, sulfuric acid dissociates completely to form the conjugate base, hydrogen sulfate ( $HSO_4^-$ , also known as bisulfate).

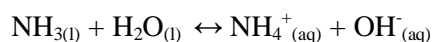


Hydrogen sulfate then acts as a weak acid, existing in equilibrium with sulfate ( $SO_4^{2-}$ ).

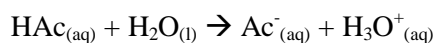


Remember that at pH levels below the  $pK_a$ , the acid form is prevalent while the pictured conjugate base predominates above the  $pK_a$ . Many commonly-used acids (acetic, benzoic, etc.) are neutral below their  $pK_a$  and negatively-charged above. The amine compounds (ammonium, etc.), by contrast, are neutral above their  $pK_a$  and positively charged below.

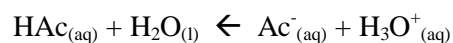
In Table 1 below, compounds with  $pK_a$  values above 7 are in the “Weak Acid” form in neutral water while those with  $pK_a$  values below 7 dissociate into the “Conjugate Base” and a proton in neutral water. Note that the conjugate base of ammonium is the common weak base ammonia. Recall the equilibrium reaction of ammonia and water:



At a pH around 7,  $\text{NH}_4^+$  is favored over  $\text{NH}_3$  ( $9.74 > 7$ ); so the right side of this equation is favored and  $\text{OH}^-$  is produced. The pH is raised, just as we expect for the base ammonia. Note that any conjugate base of a weak acid is also a weak base. It can have the same effect when it is dissolved in a solution with a pH lower than the  $pK_a$ .



above pH 4.76

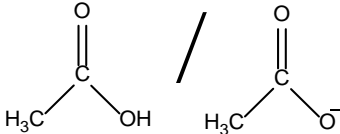
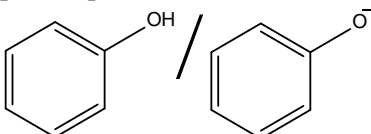
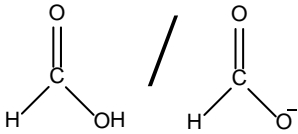
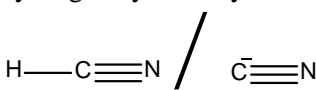
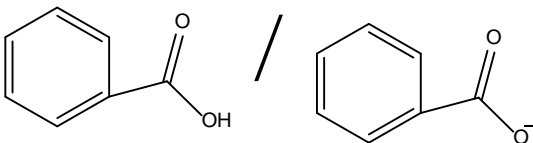
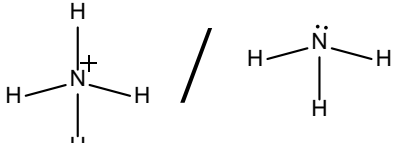
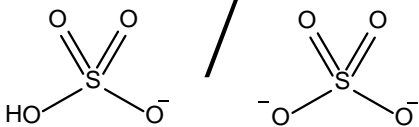
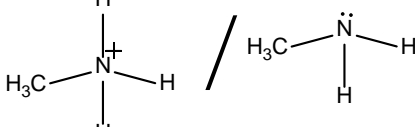
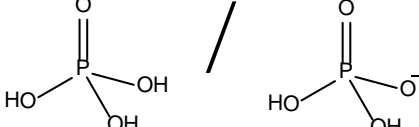
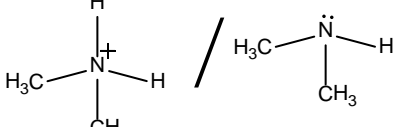
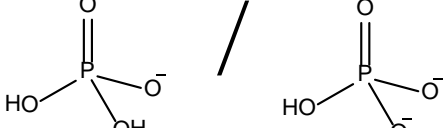
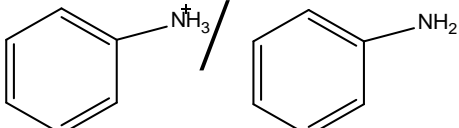
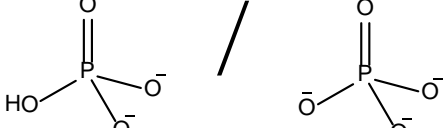
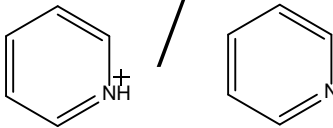


below pH 4.76

While the aliphatic amines (ammonia, methylammonia, dimethylammonia, etc.) are all weak bases, with conjugate acid  $pK_a$  values above 7, you may notice that the aromatic amines (aniline, pyridine) are much weaker bases with conjugate acid  $pK_a$  values below 7. In neutral water, aromatic amines remain uncharged and do not produce  $\text{OH}^-$  ions or raise the pH. The lone pair electrons on the nitrogen- which are highly nucleophilic on aliphatic amines- participate in the aromatic pi bonds. This resonance stabilization of the free base is disrupted when it is protonated. A more stable base corresponds to a stronger conjugate acid; as a result, anilinium is more likely to dissociate in water than ammonium.

This is an important concept. First, a weak acid/conjugate base pair is the same two compounds as a weak base/conjugate acid pair. Then, the strength of an acid is directly related to the stability of the conjugate base and inversely proportional to the strength of the base. So for any hydrogen-containing compound, you can estimate its acidity by looking at the theoretical conjugate base and vice versa for bases.

Table 1. Some common weak acids and their corresponding  $pK_a$ 's<sup>1</sup>:

Weak Acid/Conjugate base	$pK_a$	Weak Acid/Conjugate base	$pK_a$
acetic acid/acetate 	4.76	phenol/phenolate 	9.9
formic acid/formate 	3.77	hydrogen cyanide/cyanide 	9.3
benzoic acid/benzoate 	4.2	Ammonium/ammonia 	9.4
hydrogen sulfate/sulfate 	2	Methylammonium/methylammonia 	10.64
phosphoric acid/dihydrogen phosphate 	1.97	Dimethylammonium/dimethylammonia 	10.73
dihydrogen phosphate/hydrogen phosphate 	7.21	Anilinium/aniline 	4.6
Hydrogen phosphate/phosphate 	12.5	Pyridinium/pyridine 	5.2
1. <a href="http://www.chem.wisc.edu/areas/reich/pkatable/">http://www.chem.wisc.edu/areas/reich/pkatable/</a>			

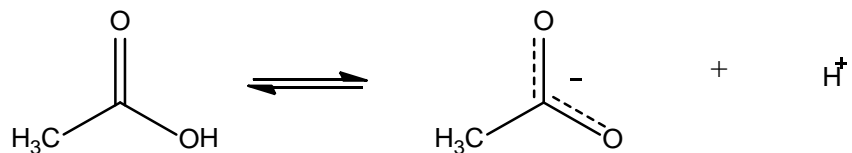
These can also be considered “conjugate acid/weak base” pairs. In this mindset, a higher  $pK_a$  indicates a *stronger* base.

***How to know if a compound is an acid or a base- some general pointers***

The easiest way is often to look at the name. The word acid in a name probably indicates that it will at least partially dissociate into a proton and the conjugate base in water.

Few compounds have the word base in the name, but many ionic metal-hydroxide molecules are strong bases.

Many weak acids contain a proton bound to an oxygen atom. More than one oxygen is usually present bound to a non-metal, with one oxygen doubly-bound. Carboxylic acids are a good example, though the name also gives away their identity. Chemically, this is because the oxygen-carbon-oxygen conjugation stabilizes the negative charge on the conjugate base.



Sulfur and phosphorous can play similar roles to carbon in the above example. The negative charge is distributed throughout the molecule's pi bonds.

Weak bases, as mentioned above, often include an aliphatic amine group. The free lone pair on the nitrogen attracts the positively-charged proton from a water molecule. The resultant quaternary nitrogen still has eight valence electrons and is therefore stable in solution.

Other weak bases, such as cyanide and phenolate, are negatively-charged conjugate bases of very weak bases.