

Do pH in Your Head

Every aqueous solution has a degree of acidity or of basicity; that is, every aqueous solution has a pH. There are two factors that will determine the pH of a solution. These are the acidic or basic strengths of the solute (the material that is added to water), and the concentration of the solute. If you express acidities and basicities as pK_a values, you can easily estimate the approximate pH of the aqueous solutions of many acids, bases and their salts and their buffers. This handout shows you how to do this.

All Solutions: the pH will lie between 0 and 14

First, the pH of any dilute aqueous solution (1 molar or less in concentration) will be between 0 and 14. A 1 molar solution of the strongest acid known will have a pH of about 0 (a hydronium ion concentration of about 1 mole per liter), and a 1 molar solution of the strongest base known will have a pH of about 14 (a hydroxide concentration of about 1 mole per liter).

Second, pure water will have a pH of 7 (both the hydronium ion concentration and the hydroxide ion concentration will be 1×10^{-7} molar).

Solutions of Acids: the pH will lie between 0 and 7

If you add an acid, a substance that can transfer protons to water molecules, you will produce an acidic solution, a solution whose pH lies between 0 and 7.

Strong acids; pK_a of the acid is zero or negative

If you make a 1 molar solution of a "strong" acid like hydrogen chloride, "all" the molecules will donate their acidic proton to water; the solution will be 1 molar in hydronium ion; the pH of the solution will be 0. Other strong acids, (characterized by zero or negative pK_a) values, will behave similarly; such acids include hydrobromic acid, hydroiodic acid, nitric acid, perchloric acid, and sulfuric acid.

Less concentrated solutions of strong acids will be less acidic. Thus 0.1 molar hydrochloric acid will be 0.1 molar in hydronium ion and will have a pH of

only 1; 0.01 molar hydrochloric acid will have a pH of 2, and an infinitely dilute solution of hydrochloric acid (or any acid or base, strong or weak) will have a pH of 7. Thus first aid for spills of acids or bases is *dilution*, not neutralization

Weak Acids; pK_a of the acid is between 2 and 12

If you make a 1 molar solution of a “weak” acid like acetic acid, only a fraction of the acetic acid molecules will donate their most acidic proton to water. The resulting solution will be less acidic than a solution of a strong acid of the same concentration. More precisely, 1 molar acetic acid, whose pK_a is about 4.8, will have a pH of only 2.4, which is less acidic than 1 molar hydrochloric acid, whose pH will be 0.

A shortcut to the pH of 2.4 for 1 molar acetic acid is to see that 2.4 equals $1/2$ of 4.8, the pK_a of acetic acid. This is because the essential mathematical operation for the calculation of the pH of a 1 molar solution of a weak acid is taking the square root of the acid ionization constant; dividing the log of a number by 2 is equivalent to taking the square root of the number.

If you are willing to round the acid ionization constants for weak acids to the nearest power of ten, the math gets even easier. Thus if you take 5 as the pK_a for acetic acid you can estimate the pH of 1 molar acetic acid to be 2.5, a value that is for most purposes just as useful as 2.4. You can thus estimate that a 1 molar solution of a slightly stronger acid such as formic acid, $pK_a = 4$, will have a pH of 2, and that a 1 molar solution of a somewhat weaker acid such as phenol, $pK_a = 10$, will have a pH of about 5. One molar solutions of still weaker acids will be still less acidic, and you can be confident that solutions of ethanol or sugar, pK_a about 14, will be no more acidic than pure water. In general, an aqueous solution of a substance whose most acidic proton has a pK_a greater than 14 will be neutral.

Just as you know that a 0.01 molar solution of HCl is less acidic than a 1 molar solution of HCl you would expect a 0.01 molar solution of acetic acid to be less acidic than a 1 molar solution of this acid. When you do the math you find that 0.01 molar acetic acid will have a pH of 3.4, which is 1 pH unit to the basic side of 2.4, the pH of 1 molar acetic acid. The shortcut, apparently, is that for each factor of 100 by which the solution is diluted the pH is 1 unit closer to 7. This is consistent with the idea that the more dilute the solution the more nearly its pH will be 7. This also reflects the fact that $1/2[\log 100] = 1/2[2] = 1$. You might now anticipate that the pH of 0.1 molar acetic acid should be half way between 2.4 and 3.4, or $2.4 + 1/2[1] = 2.9$; you would be right.

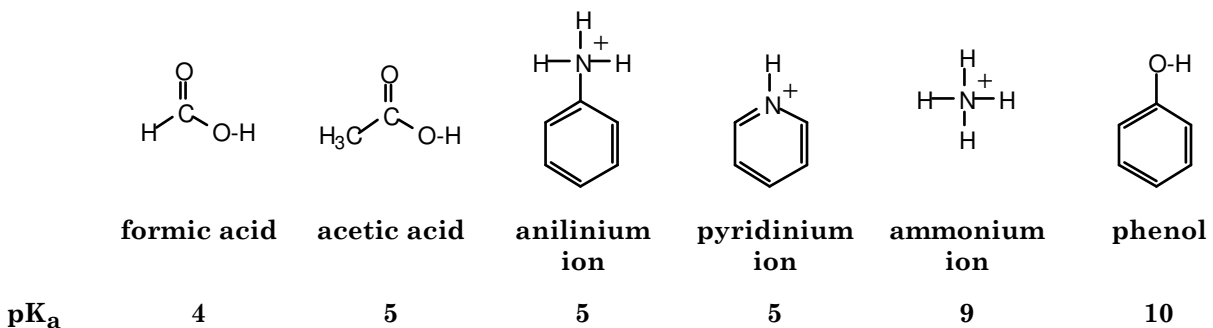
Summary of solutions of acids.

Strong acids are completely ionized; 1 molar solutions will have a pH of 0, and less concentrated solutions will be less acidic. Weak acids are not completely ionized and 1 molar solutions will have a pH equal to $1/2[\text{pK}_a]$. Less concentrated solutions of weak acids will be still less acidic, and if the acid is very weak the solution will be no more acidic than pure water.

Table 1 presents a summary of several examples and reveals the pattern.

Table 1

Acid	Approximate pK_a	Approximate pH of 1.0 molar solution	Approximate pH of 0.01 molar solution
hydrogen chloride	-5	0	2
formic acid	4	2	3
acetic acid	5	2.5	3.5
anilinium ion	5	2.5	3.5
pyridinium ion	5	2.5	3.5
ammonium ion	9	4.5	5.5
phenol	10	5	6
ethanol	16	7	7



Solutions of Bases: the pH will lie between 7 and 14

If you add a base, a source of hydroxide ion, to pure water you will have a basic solution. You can also produce basic solutions by adding substances that consume hydronium ion; salts of weak acids are such substances.

Strong bases

Strong bases are hydroxide ion donors that are completely ionized in water. The most common example of such a base is sodium hydroxide, and a 1 molar solution of sodium hydroxide will be 1 molar in hydroxide ion. The solution will therefore be 1×10^{-14} molar in hydronium ion, and will thus have a pH of 14. Potassium hydroxide behaves in the same way.

You can see that less concentrated solutions of strong bases will be less basic. For example, 0.1 molar sodium hydroxide will have a pH of 13, and 0.01 molar NaOH will have a pH of 12. Finally, just as is true of an infinitely dilute solution of an acid, an infinitely dilute solution of a base will have a pH of 7.

Salts of weak acids and strong bases

You have been told that the solutions of the salt of a weak acid and a strong base will be basic. An example of such a salt is sodium acetate, the salt of acetic acid, a weak acid, and sodium hydroxide, a strong base. The acetate ions will react to a small extent with water to form a small number of acetic acid molecules and an equally small number of hydroxide ions. The sodium ions will not react at all with water, and so the solution of 1 mole of sodium acetate in 1 liter of water will be slightly more basic than pure water due to the production of hydroxide ions; you have probably done a problem that shows that 1 molar sodium acetate should have a pH of about 9.4.

A shortcut to the value of 9.4 for the pH of 1 molar sodium acetate is to see that just as the pH of 1 molar acetic acid is 2.4 pH units “on the basic side” of 0, the pH of 1 molar sodium acetate is 2.4 pH units “on the basic side” of 7. This result is, again, based on the essential mathematical operation for the calculation of the pH of a 1 molar solution of the salt of a weak acid and a strong base. This operation is to take the square root of [(ionization constant of the acid) \times (ion product of water)]. Taking the shortcut, then, the pH is $1/2[\text{p}K_a + \text{p}K_w]$. For sodium acetate this is $1/2[4.8 + 14] = 2.4 + 7 = 9.4$. If we were to round the $\text{p}K_a$ value for acetic acid to 5, we would then estimate the pH of 1 molar sodium acetate to be 9.5.

If the weak acid is a little stronger, having a $\text{p}K_a$ of, say, 4, you can estimate that a 1 molar solution of its sodium salt should have a pH of $4/2 + 7 = 9$. The salt of the stronger weak acid undergoes hydrolysis to a lesser extent, and solutions of its salt are less basic. A 1 molar solution of this acid would have a pH of $4/2 = 2$. In general, the more acidic the weak acid the less basic will be its salts.

Picking a weak acid more or less at random, you could predict that a 1 molar solution of fluoroacetic acid, $pK_a = 2.6$, should have a pH of about 1.3, and a 1 molar solution of sodium fluoroacetate should have a pH of about 8.3.

You can see that taking this trend to the extreme gives us something you know to be true: a 1 molar solution of hydrogen chloride should have a pH of 0, and a 1 molar solution of sodium chloride should have a pH of 7.

Finally, just as less concentrated solutions of acids are less acidic so less concentrated solutions of bases are less basic, both types of solutions approaching a pH of 7 at infinite dilution.

Weak Bronsted bases

A substance that can act as a proton acceptor toward water will produce an aqueous solution whose pH is between 7 and 14.

Because the pyridinium ion is about as acidic as acetic acid, pyridine will be as basic as acetate ion. Since the behavior of pyridine will be the same as that of acetate ion the math will be the same, and the pH of 1 molar pyridine should be about $5/2 + 7 = 9.5$.

Summary of solutions of bases.

An aqueous solution of a weak base will have a pH between 7 and 14. A stronger base will give a more basic solution. Less concentrated solutions will be less basic. **Table 2** presents a summary of several examples and reveals the pattern.

Table 2

Base	Approximate pK_a of the conjugate acid	Approximate pH of 1.0 molar solution	Approximate pH of 0.01 molar solution
sodium acetate	5	9.5	8.5
pyridine	5	9.5	8.5
aniline	5	9.5	8.5
ammonia	9	11.5	10.5
sodium phenoxide	10	12	11
sodium hydroxide	15.7	14	12
sodium ethoxide	16	14	12
sodium amide	35	14	12

Ethoxide ion and amide ion are so basic that they react “completely” with water to produce hydroxide ion. Thus 1 mole of either ethoxide ion or amide ion in 1 liter of water will give 1 mole of hydroxide ion, and a solution whose pH will be 14.

Solutions of Salts: The pH will tend toward 7

Salts are ionic substances in which the ions are neither the proton or the hydroxide ion. Depending upon the relative tendencies of the two ions to react with water in such a way that protons or hydroxide ions are formed, solutions of salts may be either somewhat acidic, somewhat basic, or nearly neutral. There are four possibilities, and when you see which possibility is represented, you can quickly decide whether the solution will be slightly acidic, slightly basic, or just about neutral. If you know the approximate pK_a values of the relevant ions you can estimate quite well the pH of the solution.

Salts of a strong acid and a strong base: the solution will be neutral

Salts of a strong acid and a strong base, substances such as sodium chloride, potassium bromide, sodium nitrate, and potassium iodide will all give solutions with a pH of practically 7. Neither ion shows any tendency to react with water to produce either hydronium ion or hydroxide ion.

Salts of a strong acid and a weak base: the solution will be acidic

Salts of strong acids and weak bases, substances such as pyridinium chloride and ammonium bromide, will give acidic solutions, as we have seen. In these salts the anion does not react with water to give hydroxide ion, but the cation does react with water to produce hydronium ion. The solution will therefore be acidic. **Table 1** illustrates this possibility.

Salts of a weak acid and a strong base: the solution will be basic

Salts of weak acids and strong bases, substances such as sodium acetate and sodium phenoxide, will give basic solutions, as we have also seen. In these salts the cation does not react with water to give hydronium ion, but the anion does react with water to produce hydroxide ion. The solution will therefore be basic. **Table 2** illustrates this possibility.

Salts of weak acids and weak bases: the solution can be either slightly acidic or slightly basic

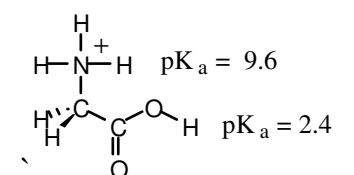
Salts of weak acids and weak bases can give solutions that are either slightly acidic or slightly basic, depending upon the relative strengths of the acids and bases that have combined to give the salt. If the weak acid is stronger than the weak base, the solution will be slightly acidic; if the weak base is stronger than the weak acid, the solution will be slightly basic. The numerical value of the pH is half way between the pK_a values of the weak acid and the conjugate acid of the weak base. The case of ammonium phenoxide provides an example.

You can see from **Table 1** that 1 molar ammonium chloride will give a solution of $pH = 4.5$, and from **Table 2** that 1 molar sodium phenoxide will give a solution of $pH = 12$. Thus you see that the phenoxide ion as a base is stronger than the ammonium ion as an acid. When they are put into competition in the same solution the phenoxide ion will “win” and the solution will be **slightly basic**; the pH of the solution will be about 9.5, a pH half way between the pK_a of 9 for the ammonium ion and 10 for phenol.

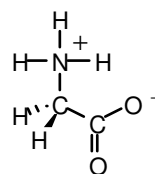
Other examples could include anilinium acetate, where the anilinium ion is a stronger acid than acetate ion is a base (solutions of this salt will have a pH of 5), and ammonium acetate, where the ammonium ion as an acid and the acetate ion as a base are equal in strength, with the result that solutions of ammonium acetate will have a pH of about 7.

These examples and several others are presented in **Table 3**.

An example of relevance in biochemistry is provided by the amino acid **glycine**. Glycine, or aminoacetic acid, exists as an inner salt, and so in analogy with ammonium acetate the pH of 1 molar glycine will be half way between the pK_a of the carboxyl group of glycine (2.4) and the pK_a of the ammonium group of glycine (9.6). The half way pH is $[2.4 + 9.6]/2 = 12/2 = 6$. This half way pH is also called the **isoelectric pH**, or the isoelectric “point” on the pH scale. It is the pH at which, over a period of time each glycine molecule is, on the average, neutral.



conjugate acid of glycine



glycine
pH in pure water = 6.2

It is generally true that solutions of amino acids without acidic or basic side chains will give aqueous solutions with a pH of 6, a pH half way between the pK_a of the carboxyl group (close to 2.5) and the pK_a of the ammonium group (close to 9.5).

Summary of solutions of salts of weak acids and weak bases

Solutions of salts will be weakly acidic, neutral, or weakly basic, depending upon which ion is the stronger acid or the stronger base. The exact pH will be the average of the two relevant pK_a values.

The pH of solutions of several salts are presented in **Table 3**.

Table 3

Salt	Approximate pK_a of acid	Approximate pK_a of conj acid of base	Approximate pH of 1 molar solution
sodium chloride			7
ammonium phenoxide	9	10	9.5
anilinium acetate	5	5	5
ammonium acetate	9	5	7
pyridinium acetate	5	5	5
glycine	9.6	2.4	6
alanine	9.7	2.3	6

Solutions of Conjugate Pairs

Sometimes you will prepare an aqueous solution that contains both an acid, such as acetic acid, and its conjugate base, in this case an acetate salt, perhaps sodium acetate. When you do this, the pH of the resulting solution will be close to the pK_a of acetic acid, the exact value of the pH depending upon the **ratio** of the concentrations of the members of the conjugate pair.

The isoconjugate pH

If you should dissolve equimolar amounts of acetic acid and sodium acetate in water, the ratio of acetic acid molecules to acetate ions, the members of this conjugate pair, will be 1 to 1, and the pH of the solution will equal the 4.8, the pK_a of acetic acid, the acidic member of this conjugate pair. For the

conjugate pair acetic acid and acetate ion, the pH of 4.8 is the **isoconjugate pH** or isoconjugate “point” on the pH scale.

Deviations from the isoconjugate pH

If you prepare a solution in which the acidic member of the conjugate pair predominates, the pH of the solution will be “on the acidic side” of the isoconjugate pH. Conversely, if you prepare a solution in which the basic member of the conjugate pair predominates the pH of the solution will be “on the basic side” of the isoconjugate pH.

The degree to which the pH of the solution deviates from the isoconjugate pH equals the log of the ratio of the members of the conjugate pair. If the ratio is 10 to 1, the deviation is 1 pH unit, and smaller ratios will give smaller deviations. And, of course, as the ratio approaches 1 to 1, the deviation will approach 0; the log of 1 is 0, and the pH will equal the pK_a . The math here follows the Henderson-Hasselbalch equation, but if you round the pK_a values to integers and ratios to powers of 10 you can do the math in your head to get approximate values that are quite adequate.

Table 4 illustrates the pattern for deviations from the isoconjugate pH.

Table 4

ratio of members of conjugate pair	log of ratio of members of conjugate pair	deviation from isoconjugate pH
1000 to 1	3.0	3.0
100 to 1	2.0	2.0
10 to 1	1.0	1.0
5 to 1	0.7	0.7
2 to 1	0.3	0.3
1 to 1	0.0	0.0

Buffers

You may have recognized the solutions that we have just described as buffered solutions, solutions that resist a change in pH either by dilution or by the addition of small amounts of acids and bases.

These solutions resist a change in pH by dilution because the pH is determined by the *ratio* of the concentrations of the members of the conjugate pair. Although dilution will change the concentrations of both members of the conjugate pair, dilution will not change their ratio.

These solutions will also resist a change in pH upon the addition of small amounts of either acid or base. Continuing with the acetic acid/acetate ion solution, so long as added acid or base does not reduce either acetate ion or acetic acid below 1/10 of the total of acetate ion plus acetic acid, the ratio of the members of this conjugate pair will stay within the range of 10:1 to 1:10 and the pH of the solution will stay within 1 pH unit of the isoconjugate pH. We call solutions such as this, which resist these efforts to change the pH, **buffered solutions**.

Table 5 presents examples of acetic acid/acetate ion buffers. The isoconjugate pH of this pair is about 4.8.

Table 5

acetic acid to acetate ion ratio	pH of the solution
10 to 1	3.8
5 to 1	4.1
2 to 1	4.5
1 to 1	4.8
1 to 2	5.1
1 to 5	5.5
1 to 10	5.8