

2.7: ACID AND BASE STRENGTH

OBJECTIVES

After completing this section, you should be able to

- write the expression for the K_a of a weak acid.
- convert a given K_a value into a pK_a value, and *vice versa*.
- arrange a series of acids in order of increasing or decreasing strength, given their K_a or pK_a values.
- arrange a series of bases in order of increasing or decreasing strength, given the K_a or pK_a values of their conjugate acids.

KEY TERMS

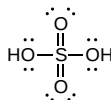
Make certain that you can define, and use in context, the key terms below.

- acidity constant, K_a
- equilibrium constant, K_{eq}

STUDY NOTES

Calculations and expressions involving K_a and pK_a were covered in detail in your first-year general chemistry course. Note that **acidity constant** is also known as the acid dissociation constant.

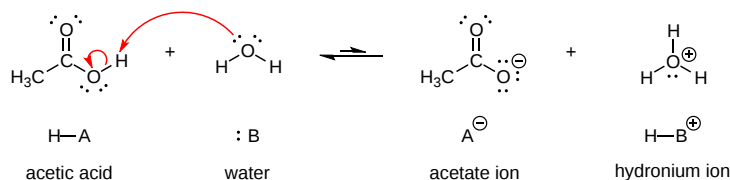
You are no doubt aware that some acids are stronger than others. Sulfuric acid is strong enough to be used as a drain cleaner, as it will rapidly dissolve clogs of hair and other organic material.



Not surprisingly, concentrated sulfuric acid will also cause painful burns if it touches your skin, and permanent damage if it gets in your eyes (there's a good reason for those safety goggles you wear in chemistry lab!). Acetic acid (vinegar), will also burn your skin and eyes, but is not nearly strong enough to make an effective drain cleaner. Water, which we know can act as a proton donor, is obviously not a very strong acid. Even hydroxide ion could *theoretically* act as an acid – it has, after all, a proton to donate – but this is not a reaction that we would normally consider to be relevant in anything but the most extreme conditions.

The relative acidity of different compounds or functional groups – in other words, their relative capacity to donate a proton to a common base under identical conditions – is quantified by a number called the **acid dissociation constant**, abbreviated K_a . The common base chosen for comparison is water.

We will consider acetic acid as our first example. When a small amount of acetic acid is added to water, a proton-transfer event (acid-base reaction) occurs to some extent.



Notice the phrase ‘to some extent’ – this reaction does *not* run to completion, with all of the acetic acid converted to acetate, its conjugate base. Rather, a *dynamic equilibrium* is reached, with proton transfer going in both directions (thus the two-way arrows) and finite concentrations of all four species in play. The nature of this equilibrium situation, as you recall from General Chemistry, is expressed by an **equilibrium constant**, K .

The equilibrium constant is actually a ratio of activities (represented by the symbol a), but activities are rarely used in courses other than analytical or physical chemistry. To simplify the discussion for general chemistry and organic chemistry courses, the activities of all of the solutes are replaced with molarities, and the activity of the solvent (usually water) is defined as having the value of 1.

In our example, we added a small amount of acetic acid to a large amount of water: water is the *solvent* for this reaction. Therefore, in the course of the reaction, the concentration of water changes very little, and the water can be treated as a pure solvent, which is always

assigned an activity of 1. The acetic acid, acetate ion and hydronium ion are all *solutes*, and so their activities are approximated with molarities. The acid dissociation constant, or K_a , for acetic acid is therefore defined as:

$$K_{eq} = \frac{a_{CH_3COO^-} \cdot a_{H_3O^+}}{a_{CH_3COOH} \cdot a_{H_2O}} \approx \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][1]}$$

Because dividing by 1 does not change the value of the constant, the "1" is usually not written, and K_a is written as:

$$K_{eq} = K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5}$$

In more general terms, the dissociation constant for a given acid is expressed as:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad (2.7.1)$$

or

$$K_a = \frac{[A][H_3O^+]}{[HA^+]} \quad (2.7.2)$$

Equation 2.7.1 applies to a neutral acid such as like HCl or acetic acid, while Equation 2.7.2 applies to a cationic acid like ammonium (NH_4^+).
























The value of $K_a = 1.75 \times 10^{-5}$ for acetic acid is very small - this means that very little dissociation actually takes place, and there is much more acetic acid in solution at equilibrium than there is acetate ion. Acetic acid is a relatively weak acid, at least when compared to sulfuric acid ($K_a = 10^9$) or hydrochloric acid ($K_a = 10^7$), both of which undergo essentially complete dissociation in water.

A number like 1.75×10^{-5} is not very easy either to say or to remember. Chemists often use **pK_a** values as a more convenient term to express relative acidity. **pK_a** is related to **K_a** by the following equation

$$pK_a = -\log K_a$$

Doing the math, we find that the pK_a of acetic acid is 4.8. The use of pK_a values allows us to express the acidity of common compounds and functional groups on a numerical scale of about -10 (very strong acid) to 50 (not acidic at all). Table 2.7.1 at the end of the text lists exact or approximate pK_a values for different types of protons that you are likely to encounter in your study of organic and biological chemistry. Looking at Table 2.7.1, you see that the pK_a of carboxylic acids are in the 4-5 range, the pK_a of sulfuric acid is -10, and the pK_a of water is 14. Alkenes and alkanes, which are not acidic at all, have pK_a values above 30. *The lower the pK_a value, the stronger the acid.*

Table 2.7.1: Representative acid constants

 sulfuric acid pK _a -10	 hydrochloric acid pK _a -7	 hydronium pK _a 0.00	 protonated ketone pK _a ~ -7	 protonated alcohol pK _a ~ -3
 phosphate monoester pK _a ~ 1	 phosphate diester pK _a ~ 1.5	 phosphoric acid pK _a 2.2	 protonated aniline pK _a ~ 4.6	 carboxylic acid pK _a ~ 4-5
 pyridinium pK _a 5.3	 carbonic acid pK _a 6.4	 hydrogen cyanide pK _a ~ 9.2	 ammonium pK _a 9.2	 phenol pK _a 9.9
 thiol pK _a ~ 10-11	 water pK _a 14.00	 amide pK _a ~ 17	 alcohol pK _a ~ 16-18	 alpha-proton pK _a ~ 18-20
	 terminal alkyne pK _a ~ 25	 terminal alkene pK _a ~ 35	 ammonia pK _a ~ 35	

It is important to realize that pK_a is *not* the same thing as pH: pK_a is an inherent property of a compound or functional group, while pH is the measure of the hydronium ion concentration in a particular aqueous solution:

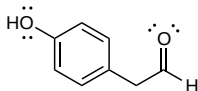
$$pH = -\log[H_3O^+]$$

Any particular acid will always have the same pK_a (assuming that we are talking about an aqueous solution at room temperature) but different aqueous solutions of the acid could have different pH values, depending on how much acid is added to how much water.

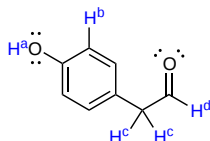
Our table of pK_a values will also allow us to compare the strengths of different bases by comparing the pK_a values of their conjugate acids. The key idea to remember is this: *the stronger the conjugate acid, the weaker the conjugate base*. Sulfuric acid is the strongest acid on our list with a pK_a value of -10 , so HSO_4^- is the weakest conjugate base. You can see that hydroxide ion is a stronger base than ammonia (NH_3), because ammonium (NH_4^+ , $pK_a = 9.2$) is a stronger acid than water ($pK_a = 14.00$).

The stronger the conjugate acid, the weaker the conjugate base.

While Table 2.7.1 provides the pK_a values of only a limited number of compounds, it can be very useful as a starting point for estimating the acidity or basicity of just about any organic molecule. Here is where your familiarity with organic functional groups will come in very handy. What, for example, is the pK_a of cyclohexanol? It is not on the table, but as it is an alcohol it is probably somewhere near that of ethanol ($pK_a = 16$). Likewise, we can use Table 2.7.1 to predict that para-hydroxyphenyl acetaldehyde, an intermediate compound in the biosynthesis of morphine, has a pK_a in the neighborhood of 10, close to that of our reference compound, phenol.



Notice in this example that we need to evaluate the potential acidity at *four* different locations on the molecule.



$$pK_a H^a \sim 10$$

$$pK_a H^b = \text{not on table (not acidic)}$$

$$pK_a H^c \sim 19$$

$$pK_a H^d = \text{not on table (not acidic)}$$

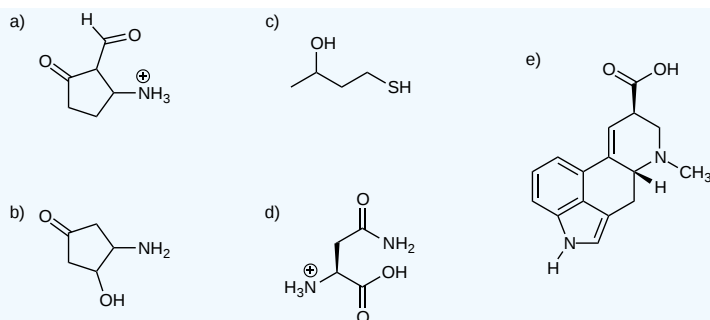
Aldehyde and aromatic protons are not at all acidic (pK_a values are above 40 – not on our table). The two protons on the carbon next to the carbonyl are slightly acidic, with pK_a values around 19-20 according to the table. The most acidic proton is on the phenol group, so if the compound were to be reacted with a single molar equivalent of strong base, this is the proton that would be donated first.

As you continue your study of organic chemistry, it will be a very good idea to commit to memory the approximate pK_a ranges of some important functional groups, including water, alcohols, phenols, ammonium, thiols, phosphates, carboxylic acids and carbons next to carbonyl groups (so-called α -carbons). These are the groups that you are most likely to see acting as acids or bases in biological organic reactions.

A word of caution: when using the [pK_a table](#), be absolutely sure that you are considering the correct conjugate acid/base pair. If you are asked to say something about the basicity of ammonia (NH_3) compared to that of ethoxide ion ($CH_3CH_2O^-$), for example, the relevant pK_a values to consider are 9.2 (the pK_a of ammonium ion) and 16 (the pK_a of ethanol). From these numbers, you know that ethoxide is the stronger base. Do not make the mistake of using the pK_a value of 38: this is the pK_a of ammonia *acting as an acid*, and tells you how basic the NH_2^- ion is (very basic!)

✓ EXAMPLE 2.7.1: ACIDIC GROUPS

Using the pK_a table, estimate pK_a values for the most acidic group on the compounds below, and draw the structure of the conjugate base that results when this group donates a proton. Use the pK_a table above and/or from the [Reference Tables](#).



Answer

- The most acidic group is the protonated amine, $pK_a \sim 5-9$
- Alpha proton by the $C=O$ group, $pK_a \sim 18-20$
- Thiol, $pK_a \sim 10$
- Carboxylic acid, $pK_a \sim 5$
- Carboxylic acid, $pK_a \sim 5$

✓ EXAMPLE 2.7.2

Acetic acid (CH_3COOH) is known to have a pK_a of 4.76. Please determine the K_a for acetic acid.

Solution

Solving for K_a algebraically you get the following:

$$pK_a = -\log(K_a)$$

$$-pK_a = \log(K_a)$$

$$10^{-pK_a} = K_a$$

Using a calculator first enter in the value for the pK_a (4.76). Then make the number negative (-4.76). Next, use the inverse log function. All calculators are slightly different so this function may appear as: ANTILOG, INV LOG, or 10^x . Often it is the second function of the LOG button.

$$K_a \text{ for acetic acid} = 10^{-pK_a} = 1.74 \times 10^{-5}$$

EXERCISES

- Write down an expression for the acidity constant of acetic acid, CH_3COOH .
- The pK_a of acetic acid is 4.72; calculate its K_a .
- The K_a of benzoic acid is 6.5×10^{-5} ; determine its pK_a .
- From your answers to the questions above, determine whether acetic acid or benzoic acid is stronger

ANSWERS

- $K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}$ or $K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$
- $pK_a = -\log_{10} K_a = 4.74$ Thus, $\log_{10} K_a = -4.72$ and $K_a = \text{anti-log}(-4.72) = 1.9 \times 10^{-5}$
- $pK_a = -\log_{10} K_a = -\log_{10} 6.5 \times 10^{-5} = -(-4.19) = 4.19$
- Benzoic acid is stronger than acetic acid. [Benzoic acid has a higher K_a and a lower pK_a .]

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