

1.13: DISTINGUISHING BETWEEN PH AND PKA

Learning Objective

- Determine relative strengths of acids and bases from their pK_a values
- Determine the form of an acid or base at a specified pH (given the pK_a)

The Henderson-Hasselbach Equation - a Quantitative View

We will use the general reaction for a weak acid to write the K_a expression.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad (1.13.2)$$

$pK_a = -\log K_a$

where each bracketed term represents the concentration of that substance in solution.

The stronger an acid, the greater the ionization, the lower the pK_a , and the lower the pH the compound will produce in solution.

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

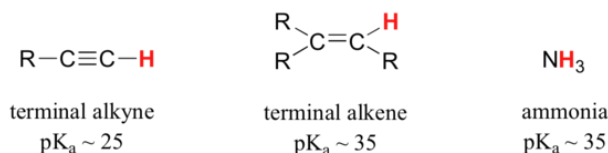
$pH = -\log [H_3O^+]$

Additional reagents can be added to a reaction solution to change the pH of the reaction conditions beyond the effects of an individual compound.

RELATIVE ACIDITY AND PKA VALUES

An application of the Henderson-Hasselbach Equation is the ability to determine the relative acidity of compounds by comparing their pK_a values. The stronger an acid, the greater the ionization, the lower the pK_a , and the lower the pH the compound will produce in solution. Some selected pK_a values for compounds in the study of organic chemistry are shown bellow. Since organic reactions can be performed in non-aqueous environments, the pH can exceed 14 and organic compounds can have pK_a values above 16. It is a variation on that line from the Wizard of Oz, "We don't live in water anymore."

sulfuric acid pK_a -10, 2.0	hydrochloric acid pK_a -7	hydronium pK_a 0.0	protonated ketone pK_a ~-7	protonated alcohol pK_a ~-3
phosphate monoester ⁽¹⁾ pK_a ~ 1, 6.5	phosphate diester ⁽¹⁾ pK_a ~ 1.5	phosphoric acid pK_a = 2.2, 7.2, 12.3	aniline pK_a = 4.6	carboxylic acid pK_a ~ 4-5
pyridinium pK_a 5.3	carbonic acid pK_a 6.4, 10.3	hydrogen cyanide pK_a 9.2	ammonium pK_a 9.2	phenol pK_a 9.9
thiol pK_a ~ 10-11	water pK_a 14.0	amide pK_a ~ 17	alcohol pK_a ~ 16-18	α -proton pK_a ~18-20

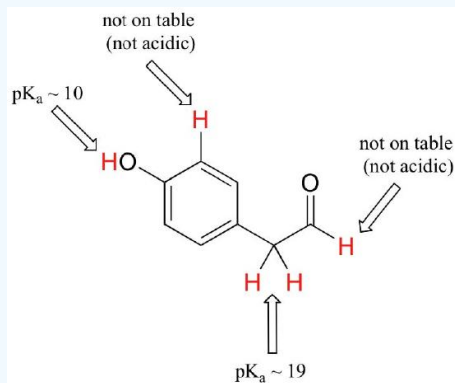


It is a very good idea to commit to memory the approximate pK_a ranges of the compounds above. A word of caution: when using the pK_a table, be absolutely sure that you are considering the correct conjugate acid/base pair. If you are asked to say something about the basicity of ammonia (NH_3) compared to that of ethoxide ion ($\text{CH}_3\text{CH}_2\text{O}^-$), 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!)

* A note on the pK_a of water: [The \$\text{pK}_a\$ of water is 14](#). Biochemistry and organic chemistry texts often list the value as 15.7. These texts have incorrectly factored the molar value for the concentration of water into the equilibrium constant. The correct derivation of the equilibrium constant involves the activity of water, which has a value of 1.

Example

While this course begins with single functional groups, we will eventually work with interesting compounds containing multiple functional groups. Recognizing which hydrogens can be ionized as acidic protons and which hydrogens can NOT, is a useful skill. Notice in this example that we need to evaluate the potential acidity at *four* different locations on the molecule.

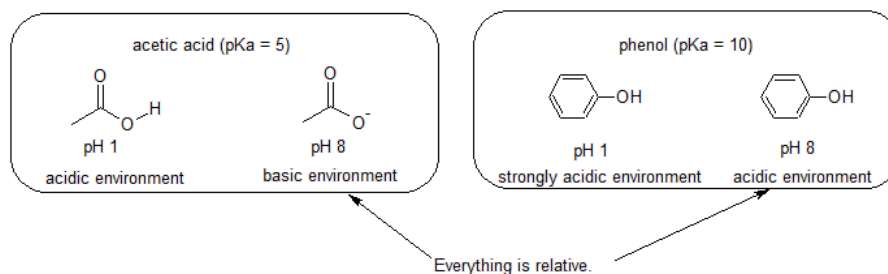


Aldehyde and aromatic protons are not at all acidic (pK_a values are above 40 – not on our table). The two protons on the carbon next to the carbonyl are slightly acidic, with pK_a values around 19-20 according to the table. The most acidic proton is on the phenol group, so if the compound were to be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

Acidic & Basic Environments - Everything is Relative in Reactivity

Because our goal is understanding dynamic chemical reactivity, we do NOT need to know the specific amount of the protonated and unprotonated forms of a compound. We simply need to know which form is predominate. When the pH of the environment is less than the pK_a of the compound, the environment is considered acidic and the compound will exist predominately in its protonated form. When the pH of the environment is greater than the pK_a of the compound, the environment is considered basic and the compound will exist predominately in its deprotonated form.

For example, the pK_a of acetic acid is about 5. At a pH of 1, the environment is considered acidic and acetic acid exists predominately in its protonated form. At pH 8, the environment is considered basic, and acetic acid becomes deprotonated to form acetate (CH_3CO_2^-). Conversely, the pK_a of phenol is 10. At pH 8, the environment is considered acidic for phenol and it remains primarily protonated.



It is also important to remember that organic chemistry does NOT have to occur in water so pKa values can be as high as 50.

Exercise

1. Complete the table below to indicate whether each compound exists predominantly in its protonated (acidic environment) or deprotonated (basic environment) form.

compound (pKa)	pH 1 environment	pH 8 environment	pH 13 environment
<chem>c1ccccc1[NH2+]</chem> pKa = 5.1			
<chem>C1CCCCC1[NH3+]</chem> pKa = 10.7			
<chem>CCO</chem> pKa = 16			
<chem>CC(=O)C</chem> pKa = 20			

Answer

1.

compound (pKa)	pH 1 environment	pH 8 environment	pH 13 environment
<chem>c1ccccc1[NH2+]</chem> pKa = 5.1	<chem>c1ccccc1[NH2+]</chem>	<chem>c1ccccc1</chem>	<chem>c1ccccc1</chem>
<chem>C1CCCCC1[NH3+]</chem> pKa = 10.7	<chem>C1CCCCC1[NH3+]</chem>	<chem>C1CCCCC1[NH3+]</chem>	<chem>C1CCCCC1N</chem>
<chem>CCO</chem> pKa = 16	<chem>CCO</chem>	<chem>CCO</chem>	<chem>CCO</chem>
<chem>CC(=O)C</chem> pKa = 20	<chem>CC(=O)C</chem>	<chem>CC(=O)C</chem>	<chem>CC(=O)C</chem>

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