

pH and pKa

What does pKa tell you?

- pKa tells you if a given molecule is going to either give a proton to water at a certain pH, or remove a proton
- A pKa of 2 for substance “X” means that at a pH of 2, X is at its equilibrium point.
- If the pH falls to 1, then X will accept a proton because there are so darn many available (pH 1 means very acidic—lots of protons) and form XH
- If the pH rises to 3, then X will give up a proton and exist as X⁻
- *At any pH above 2, X is a stable negative ion*
- *So X is a fairly strong acid*

pKa of bases

- Now consider substance “Y”
- Y has a pKa of 13, so at any pH less than 13, Y will accept protons and form YH
- If the pH rises above 13, then Y will be deprotonated and exist in a stable form as Y^-
- *Y will remove protons at a pH greater than that of neutral water, so Y is a base*

Kinda complicated, but...

Monoprotic acids

Acetic acid

($K_a = 1.74 \times 10^{-5} \text{ M}$)

Ammonium ion

($K_a = 5.62 \times 10^{-10} \text{ M}$)

Diprotic acids

Carbonic acid

($K_a = 1.70 \times 10^{-4} \text{ M}$);

Bicarbonate

($K_a = 6.31 \times 10^{-11} \text{ M}$)

Glycine, carboxyl

($K_a = 4.57 \times 10^{-3} \text{ M}$);

Glycine, amino

($K_a = 2.51 \times 10^{-10} \text{ M}$)

Triprotic acids

Phosphoric acid

($K_a = 7.25 \times 10^{-3} \text{ M}$);

Dihydrogen phosphate

($K_a = 1.38 \times 10^{-7} \text{ M}$);

Monohydrogen phosphate

($K_a = 3.98 \times 10^{-13} \text{ M}$)

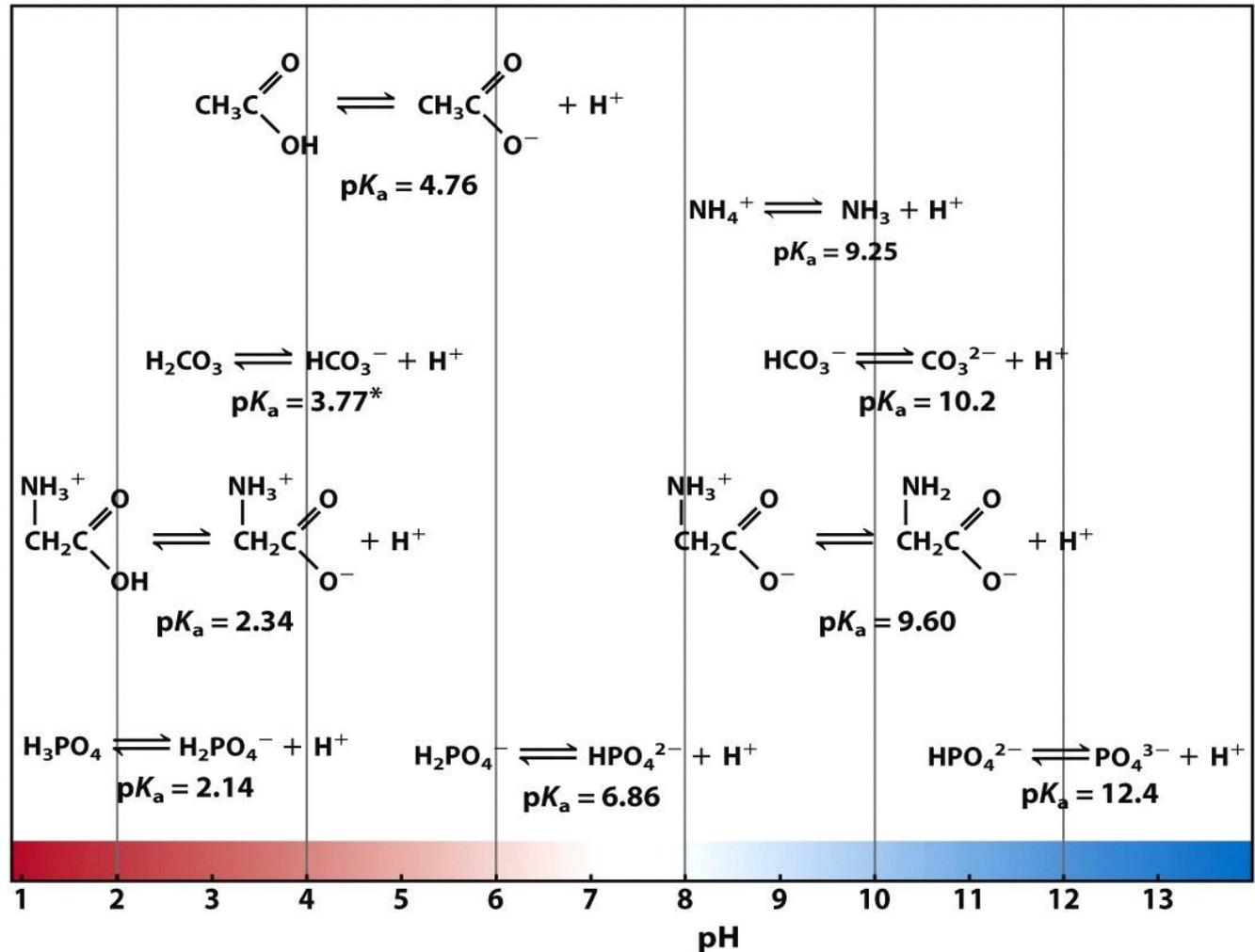


Figure 2-15

Lehninger Principles of Biochemistry, Fifth Edition

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pH versus pKa

- pH tells you about the solution, it says how many free Hydrogen ions are available in a solution, and that's it
- pKa is more specific, it tells you how a certain molecule will react when in a solution that is at a specific pH
- ****important misconception**** pH depends on how much H⁺ you have, not what gave you those H⁺ ions, you can have a stronger acid from vinegar than HCl by using different concentrations of each

pH versus pKa

- So 100 molecules of HCl dissolved in water will give you the *same* pH as 1000 molecules of acetic acid!
- pH changes with concentrations, but pKa is a constant value for every molecule
- You can determine the pH if you know what you've got, how much of it you've got, and what its pKa is
- pH and pKa are related by the following equation:

$$\text{pH} = \text{pKa} + \log \left(\frac{\text{concentration of conjugate base}}{\text{conc. of acid}} \right)$$

Example of pH/pKa

- For acetic acid, the pKa is 4.76
- Say you have equal concentrations of acetate (the conjugate base of acetic acid) and acetic acid, what would the pH be?
- $\text{pH} = \text{pKa} (4.76) + \log (\text{acetate}^-)/(\text{acetic acid})$
- The log of 1 = 0
- So the pH is 4.76 when acetate and acetic acid are at *equilibrium (this is a weak acid)*
- What about when they are not? Say you have 10 times more acetate than acetic acid, what is the pH? What about 10 times as much acetic acid than you have acetate?

A different example

- Ammonium has a pKa of 9.24
- What is the pH when ammonium and ammonia are equal in concentration?
- $\text{pH} = 9.24 + \log (\text{ammonia})/(\text{ammonium})$
- $\text{pH} = 9.24 + 0$, so $\text{pH} = 9.24$
- What if there is more ammonium? Say, by a factor of 10?
- $\text{pH} = 9.24 + \log (1)/(10)$
- $\text{pH} = 9.24 + (-1)$, or 8.24, so adding more ammonium makes the solution *more acidic*

A word on naming...

- Because traditional terms can be confusing, a system exists to tell us what (chemical species) we are dealing with
- If we refer to something as an “acid”, we are saying it, at that moment, has an available proton to donate to a solution
- If we refer to something as a “base”, we are referring to the deprotonated form, which is negatively charged (and could possibly take a proton)

Name games...

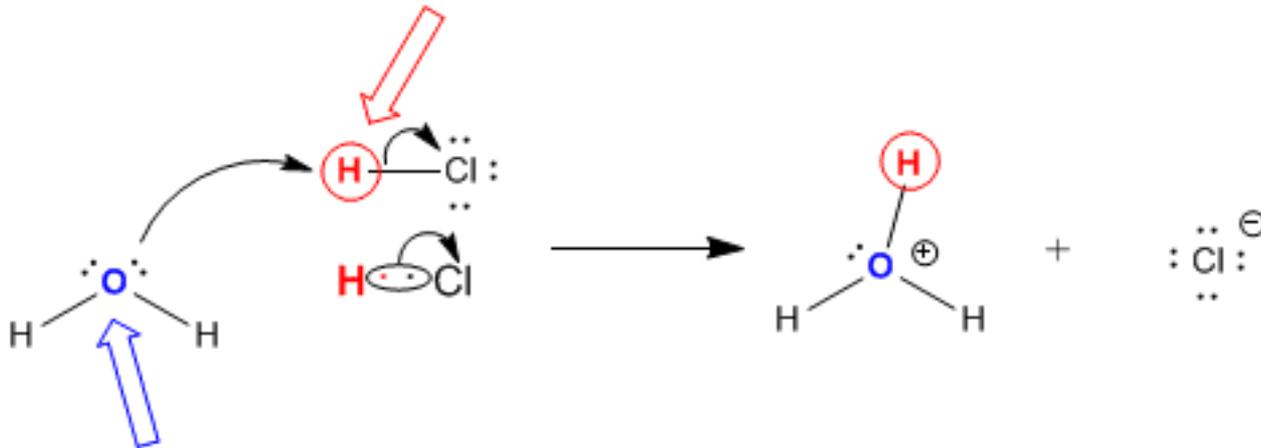
- So, for example, when we say “acetic acid”, we are referring specifically to the protonated form, which only exists when the pH is *below* 4.76
- This is lower than the conditions inside most cells
- If the pH is above 4.76, we are no longer dealing with the protonated form, so we instead refer to it as “acetate”
- We make a *lot of acetate*, by the way...

What does all this mean?

- An acid gives up protons in solution
- A base removes protons from solution
- The pKa tells you what the pH has to be in order for something to give/take a proton
- Some things we call acids (like ammonium) do donate protons, but the solution must be a base for them to do so-they only give us an acidic pH when we have them in high concentrations (relative to their conjugates)

Another look

- Consider the illustration below:
- The Chlorine in the HCl gives up its Hydrogen to water, forming Hydronium and a *Chloride* ion
- The Chlorine is negative, so why doesn't it take the Hydrogen back?
- Chlorine is stable as an ion (very low pKa) and water has a **high dielectric**, so charges are easily stabilized. This results in a very strongly acidic solution



A more important application

- Part of biochemistry involves determining the charges and locations of those charges on molecules in cells, because that tells us how they will react with other molecules
- So if the pH of a cell is near neutral, we can tell if a given molecule would be protonated or not, and this will tell us how that molecule will react with other molecules
- It is important to understand that although “positives and negatives attract”, in solution, some molecules are more stable as charged molecules and are only “neutral” *if the pH is greater than the pKa of a molecule!*

Reactivity in biological molecules

- “Neutral” molecules are stable, and stable means non-reactive
- For biological reactions to be possible, the molecules involved *must* be able to react and form bonds and make new molecules
- Because biological systems are near neutral in pH, many molecules exist as charged molecules, which makes them reactive—and **this** is what makes the reactions in biology possible!!!
- Because...

Water has a ...

- High dielectric constant
- This means, water preserves the charges on molecules
- So even though acetate/acetic acid is “an acid”, it has a pKa of 4.76. At a *physiological* pH, it is *deprotonated*, which means it is no longer, strictly speaking, an “acid”, because it no longer has a proton to donate
- The traditional way of thinking about acids and bases only works in a beakers of distilled water in someone’s lab. Biological systems are much more complicated...

End of section