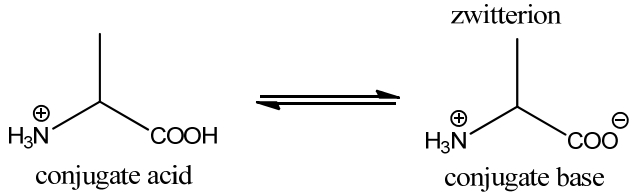
Discussion Exercise 2: Polyprotic Acids

Skill 1: Drawing conjugate acids and conjugate bases of polyprotic acids

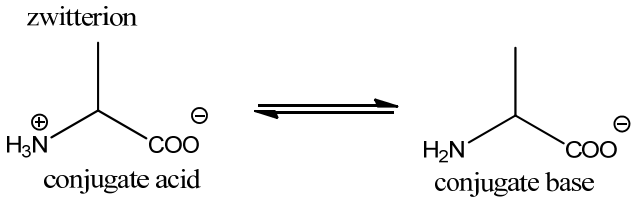
- With polyprotic acids, it is important to remember which proton you are dealing with when drawing conjugate acids and conjugate bases
- Conjugate acids can be either neutral or positively formally charged; conjugate bases can be either

To write out the reactions of a compound that has more than one acidic proton, you need to know which proton is more acidic, because it will be the first one donated. You should often be able to determine this using principles of organic chemistry structure, but you should always be able to determine them based on pKa values, if known. For example, consider alanine. From chemical principles, you know that carboxylic acids are more acidic than protonated amines. The pKa values are 2.4 and 9.9 respectively. That means that we can draw two equilibrium acid/base reactions for alanine, and we can determine that loss of the carboxylic acid proton occurs first.

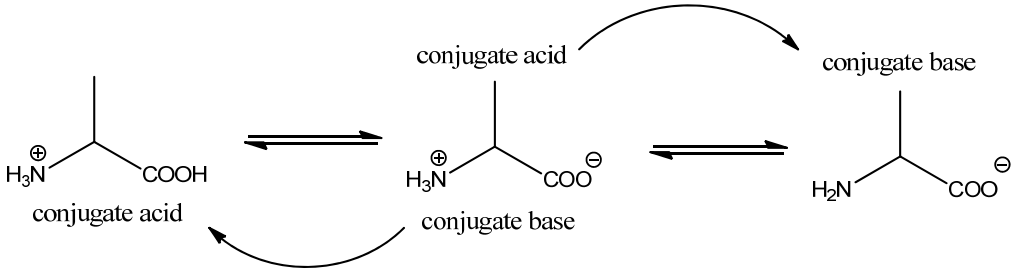
Reaction 1: pKa = 2.4



Reaction 2: pKa = 9.9

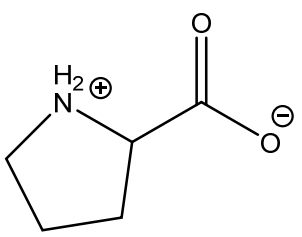


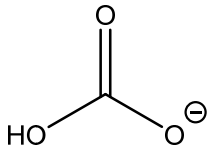
Confusion comes in when we ask the question, "Is the zwitterionic structure a conjugate acid or a conjugate base?" The answer is yes to both—the key is that, when discussing conjugate acids and bases, you need to define to which structure they are conjugate. Notice that the product of reaction 1 is the reactant of reaction 2. We can put both reactions together since they are all in equilibrium.

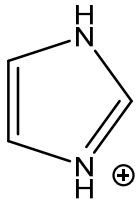


KEY POINT: Be sure you know what reaction you are talking about before deciding if a structure is a conjugate acid or a conjugate base!

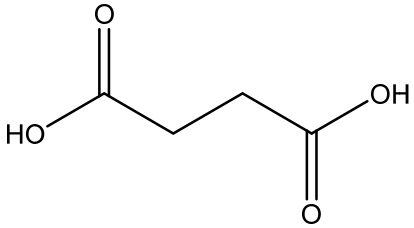
Problem 1: Draw the conjugate acid and the conjugate base of each of these compounds. (Consider the pKa values of the functional groups!)







Problem 2: The first pKa of succinic acid is 4.2 and the second pKa of succinic acid is 5.6. How can the same functional group have different pKa values?



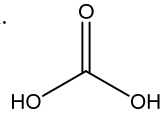
Problem 3: Phosphoric acid has three pKa values, at approximately 2, 7, and 12. Draw the conjugate acid/base pair for each of these three pKa values.

Skill 2: Determining the ionization state and net charge of a polyprotic acid at a given pH

- Use the Henderson-Hasselbalch equation conceptually to determine the ionization of the molecule
    - If the pH is higher than the pKa of a given proton, that proton "feels like" it is in base. That functional group will be deprotonated and become either neutral or negatively charged
    - If the pH is lower than the pKa of a given proton, that proton "feels like" it is in acid. That functional group will be protonated and become either netural or positively charged.
    - If the pH = pKa of a given proton, then that proton will be half conjugate acid and half conjugate base. The group of molecules will be half charged and half neutral, so the net charge will be +1/2 or -1/2.
- The net charge is a sum of all the ionizations of the polyprotic acid. The net charge does not have to be an integer. A net charge of +1.5 means that about half the molecules are in the +1 ionization state and about half are in the +2 ionization state at any given moment. (This is a simplification, but pretty accurate for our purposes.)
- For problems like these, you will use pKa values from Figure 2.11, Table 3.1, and/or the pKa values given in the problem. You should know general pKa values for functional groups, but not for particular molecules.

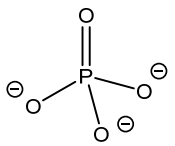
Problem 4: Draw the following molecules in the correct major ionization state at pH 7 and give their approximate net charge.

A.



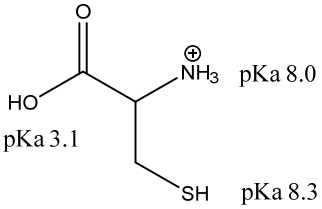
carbonic acid

B.

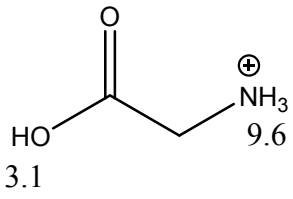


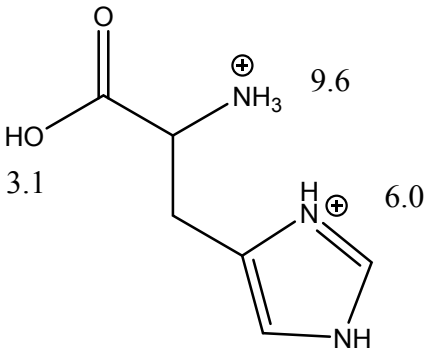
phosphate

C.



Problem 5. Draw the following molecules in their major ionization state(s) at pH 2.3, 6.0 9.6, and 12.0.

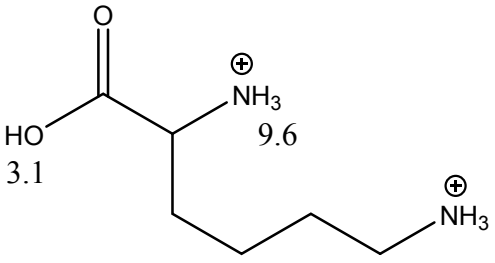




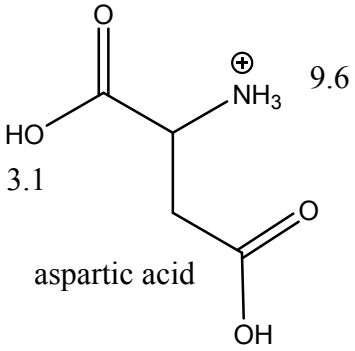
Skill 3: Estimating the isoelectric point of a polyprotic acid.

- The isoelectric point is the pH value at which a compound has a net charge of zero.
- It is often easiest to draw the acid in its fully protonated form, then remove the most acidic protons in order to reach a net charge of zero. Then average to two appropriate pKa values.

Problem 6. What is the isoelectric point for lysine and aspartic acid? (See Table 3.1)



lysine



aspartic acid

Problem 7. The titration chart below is for the amino acid alanine.

a. What is the first pKa of alanine? What is the second pKa?

b. At point A, alanine is in its completely protonated form. At point J, it is completely deprotonated. Refer to Figure 3.3 and draw these two structures.

c. What is the point at which alanine has a net zero charge?

d. What is the isoelectric point of alanine?

e. Draw the structure of alanine at its isoelectric point.