Chemistry 231 – Elementary Organic Chemistry
Problem Set – Acidity & Basicity

1. Consider the following organic/inorganic acids. For each, indicate the most acidic proton. Explain your reasoning.

   a. $\text{HO}_2\text{CCH}_2\text{OH}$

   b. $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

   c. Hydroxylamine, $\text{NH}_2\text{OH}$

   d. $\text{HC≡C(CH}_3)_3$

2. The conversion of alcohols into alkenes, a process referred to as dehydration, occurs in multiple steps, two of which are reproduced below.

   a. Classify each reaction step as a Lewis acid-base reaction or a Brønsted acid-base reaction.
   b. Using the curved-arrow formalism/notation, indicate the movement of electrons for each of the steps indicated.
   c. One of the reaction species generated in this two step sequence contains a positively charged carbon atom (called a carbocation). What are both the orbital hybridization and bonding geometry at this carbocation?

   \[
   \begin{align*}
   \text{(1)} & \quad \text{OH} + \text{H}^+ \text{O}^- \rightarrow \text{O}_2\text{H}^+ \text{OH} \\
   \text{(2)} & \quad \text{O}_2\text{H}^+ \text{OH} \rightarrow \text{O}_2\text{H}^+ + \text{O}^- \text{H} \\
   \end{align*}
   \]

3. a. What is a Lewis acid and how does it differ from a Brønsted acid?
   b. What is a Lewis base and how does it differ from a nucleophile?

4. Using the curved-arrow formalism/notation, indicate the movement of electrons in the reaction of hydrochloric acid with hydroxide ion ($\text{OH}^-$).

5. The acid HI ($\text{pK}_a = -10$) is considerably stronger than HCl ($\text{pK}_a = -8$). Why does a 0.001 $M$ aqueous solution of either acid in water result in the same pH?
6. Pictured here is a portion of a two deoxyribonucleic acid (DNA) strands containing both G-C and A-T base pairings. Identify by name each of the functional groups present below (indicated by circles).

7. Hydride ion (H\textsuperscript{-}) is known in the form of salts such as sodium hydride, NaH. When sodium hydride is added to water, it is converted completely into hydrogen gas (H\textsubscript{2}). What does this say about H\textsubscript{2} as an acid relative to water?

8. Consider the following pairs of organic/inorganic acids and bases. For each, denote which is the stronger acid/base. Explain your reasoning.
   
   a. Stronger Acid:  Cyclopropane  Cyclohexane
   b. Stronger Acid:  CH\textsubscript{3}CO\textsubscript{2}H  CF\textsubscript{3}CO\textsubscript{2}H
   c. Stronger Base:  H\textsubscript{2}O  OH\textsuperscript{-}
   d. Stronger Base:  NH\textsubscript{3}  PH\textsubscript{3}
9. Succinic acid has two carboxylic acid groups and consequently undergoes two ionization reactions. The $pK_a$ for the first ionization of succinic acid is 4.19; the $pK_a$ for the second is 5.57. For comparison, the $pK_a$ of acetic acid is 4.76.

\[\text{O} \quad \text{O} \quad \text{HO} \quad \text{C} \quad \text{O} \quad \text{OH} \quad \text{Succinic Acid} \quad \text{H}_3\text{C} \quad \text{O} \quad \text{OH} \quad \text{Acetic Acid}\]

- Write out equations for the first and second ionizations of succinic acid. Label each with the appropriate $pK_a$ value.
- Explain why the first $pK_a$ of succinic acid is lower than the $pK_a$ of acetic acid.
- Explain why the second $pK_a$ of succinic acid is higher than the $pK_a$ of acetic acid.
- Malonic acid $[\text{CH}_2(\text{CO}_2\text{H})_2]$ is a member of the same series of dicarboxylic acids as succinic acid. How do you expect the difference between the first and second $pK_a$ values to change in malonic v. succinic acid? Explain.