1. Identify the acid, base, conjugate acid and conjugate base in each acid-base reaction.

   a. \( \text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{OH} \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_5\text{O}^- \)  
      base                           acid                           conj. acid                           conj. base

   b. \( \text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{O}^- + \text{Cl}^+ \)  
      base                           acid                           conj. acid                           conj. base

   c. \( \text{C}=\text{O} + \text{KNH}_2 \rightarrow \text{C}=\text{O}^- + \text{NH}_3 + \text{K}^+ \)  
      acid                           base                           conj. base                           conj. acid                           (spectator ion)

2. Fill in the blanks to complete each sentence.

   a. The base in an acid-base reaction is often **negatively** charged.  
      positively or negatively

   b. The base in a Brønsted-Lowry acid-base reaction **accepts** a hydrogen atom.  
      accepts or donates

3. Give the products of each reaction, as indicated by the curved arrow mechanism. Identify the acid and base in each reaction. Include all lone pairs and formal charge in the products.

   a. \( \text{H} \rightarrow \text{O}^- \text{O}=\text{H} \text{N}^{-} \text{O}=\text{H} \rightarrow \text{H} \text{O}^=\text{H} + \text{N}^{-} \text{O}=\text{H} \)  
      base                           acid

   b. \( \text{H} \text{O}^=\text{H} \rightarrow \text{H} \text{O}^- \text{C}=\text{N}^- \rightarrow \text{H} \text{O}^- \text{C}=\text{N}^- + \text{H}_2\text{C}^=\text{N}^- \)  
      acid                           base
4. Use curved arrows to show the mechanism for each acid-base reaction.

a. \[
\text{H} - \text{N}^\oplus \text{H} + \text{C} = \text{C} \cdot \text{CH}_3 \quad \xrightarrow{\text{curved arrows}} \quad \text{H} - \text{N}^\cdot \text{H} + \text{H} \cdot \text{C} = \text{C} \cdot \text{CH}_3
\]

b. \[
\text{H} \cdot \text{C} = \text{C} \cdot \text{H} + \text{C}_6\text{H}_4\text{O} \quad \xrightarrow[\text{curved arrows}]{\text{O}} \quad \text{H} \cdot \text{C} = \text{C} \cdot \text{H} + \text{C}_6\text{H}_4\text{O}^\cdot
\]

5. In all equilibrium processes, there must be a mechanism for the reaction in both directions. Give the curved arrow mechanism for both the forward and backward reactions of this acid-base reaction.

\[
\text{O} \quad \text{H} - \text{C} - \text{H} + \text{H} - \text{O}^\oplus \text{H} \quad \xrightleftharpoons[\text{curved arrows}]{\text{O} \quad \text{H}} \quad \text{H} - \text{C} - \text{H} + \text{H}_2\text{O}
\]

6. Methanol (CH\text{3OH}) is “amphoteric”, meaning it can act as both a Brønsted acid and a Brønsted base. Give the likely products of these reactions, and indicate whether methanol is acting in each as an acid or base.

**(Base)** \[
\text{CH}_3\text{OH} + \text{HCl} \rightarrow \text{CH}_3\text{OH}^+ + \text{Cl}^-
\]

**(Acid)** \[
\text{CH}_3\text{OH} + \text{NaNH}_2 \rightarrow \text{CH}_3\text{ONa} + \text{NH}_3 \quad \text{(Recall \text{CH}_3\text{ONa} means \text{CH}_3\text{O}^- \text{Na}^+)}
\]
7. Use a \( pK_a \) table to determine the direction of the equilibrium for these acid-base reactions.

a. \( HF + NH_3 \leftrightarrow F^- + NH_4^+ \)
   - HF acid: \( pK_a = 3.2 \)
   - \( NH_4^+ \) conj. acid: \( pK_a = 9.2 \)
   - Eq forward \( \rightarrow \) (favors weaker acid)

b. \( CH_3NH_2^- + CH_3CH_2OH \leftrightarrow CH_3NH_2 + CH_3CH_2O^- \)
   - \( CH_3CH_2OH \) acid: \( pK_a = 16 \)
   - \( CH_3NH_2 \) conj. acid: \( pK_a = 38 \)
   - Eq forward \( \rightarrow \)

c. \( HCO_3^- + HCH_3 \leftrightarrow H_2CO_3 + HCH_2^- \)
   - Aldehyde acid: \( pK_a = 17 \)
   - \( H_2CO_3 \) conj. acid: \( pK_a = 6.35 \)
   - Eq backward \( \leftarrow \)

8. \( CH_3CC^- \) and \( CH_3NO_2^- \) are combined in equal concentrations and the reaction below occurs. After the system reaches equilibrium, which of the two bases would have a higher concentration? Briefly explain. You can consult a \( pK_a \) table.

\[
CH_3 \cdot C \equiv C \cdot O^- + HCH_3 \leftrightarrow CH_3 \cdot C \equiv C \cdot H^- + HCH_3 \cdot O^-\]

- \( CH_3NO_2 \) acid: \( pK_a = 10.2 \)
- Triple bond conj. acid: \( pK_a = 25 \)

Eq forward \( \rightarrow \) so that means of the two bases present (\( CH_3CC^- \) or \( CH_3NO_2^- \)), \( CH_3NO_2^- \) would have a higher concentration (products favored).

9. For the following reactions,

\[
CH_3CH_2OH + NaOH \rightarrow CH_3CH_2ONa + H_2O \quad pK_a = 16 \quad pK_a = 15.7 \quad \text{Equilibrium slightly unfavorable}
\]

\[
CH_3CH_2OH + NaH \rightarrow CH_3CH_2ONa + H_2 \quad pK_a = 16 \quad pK_a = 35 \quad \text{Equilibrium favorable (\( \rightarrow \))}
\]

a. Give the products of each reaction, and use a \( pK_a \) table to determine if each reaction is favorable or not.

b. Based on these reactions, which base is stronger, \( NaOH \) or \( NaH \)? \( NaH \), it reacts while \( NaOH \) doesn’t.
10. Give the products of each acid-base reaction. Use a $pK_a$ table to determine the direction of the equilibrium.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Products</th>
<th>$pK_a$ Values</th>
<th>Equilibrium Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. $\text{O}^- \text{O}^- + \text{C}_6\text{H}_5\text{CH}_2\text{OH} \rightarrow \text{O}^- \text{O}^- + \text{C}_6\text{H}_5\text{CH}_2\text{O}^{-} \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = 9.9$, $pK_a = 4.75$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. $\text{CH}_3\text{O}^- + H\text{C}≡\text{C}≡\text{H} \rightarrow \text{CH}_3\text{OH} + \text{C}\equiv\text{C}≡\text{H} \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = 25$, $pK_a = 15.5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c. $\text{CH}_3\text{O}^- + \text{NH}_2^- \rightarrow \text{CH}_3\text{OH} + \text{NH}_3 \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = 17$, $pK_a = 38$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d. $\text{CH}_3\text{C}≡\text{C}\text{OH} + \text{KOH} \rightarrow \text{CH}_3\text{C}≡\text{C}^-\text{O}^- + \text{K}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = 9.0$, $pK_a = 15.7$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e. $\text{H} = \text{C}\equiv\text{C} \rightleftharpoons \text{H} = \text{C}^-\text{CH}_2^- + \text{CH}_3\text{O}^- \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = 40$, $pK_a = 17$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f. $\text{O}^- \text{H}^- + \text{H}_2\text{SO}_4 \rightarrow \text{O}^- \text{H}_2\text{O}^- + \text{HSO}_4^- \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = -9$, $pK_a = -1.74$</td>
<td>(must be the base) (acid)</td>
<td></td>
</tr>
<tr>
<td>g. $\text{NH}_3 + \text{HO}^-\text{O}^-\text{O}^-\text{H} \rightarrow \text{NH}_4^+ + \text{HO}^-\text{O}^-\text{O}^-\text{H} \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = 4.75$, $pK_a = 9.2$</td>
<td>(NH$_3$ is a common base)</td>
<td></td>
</tr>
<tr>
<td>h. $\text{C}_6\text{H}_5\text{SO}_3\text{OH} + \text{CH}_3\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{SO}_3\text{O}^- + \text{CH}_3\text{NH}_3^+ \rightleftharpoons \text{Eq}$</td>
<td>$pK_a = -6.5$, $pK_a = 10.7$</td>
<td>(similar to H$_2$SO$_4$, acid) (similar to NH$_3$, base)</td>
<td></td>
</tr>
</tbody>
</table>
11. For each acid base reaction,
   - Give the products. Using a $pK_a$ table, determine the direction of equilibrium.
   - Plot the general energy diagram.
   - Draw the transition state for the reaction.

   a. $\text{CH}_3\text{N}^-\text{H} \rightarrow \text{CH}_3\text{N}\cdot\text{H} + \text{O}^-\text{H}$
      \hspace{1cm} pKa 9.9 \hspace{1cm} $\rightarrow \hspace{1cm} \text{pKa 38}$

   \[ \Delta G^0 \]

   b. $\Theta\text{Cl} \rightarrow \text{H}^-\text{N}^\Theta\text{H} \rightarrow \text{Cl}^-\text{H} + \text{H}^-\text{N}^-\text{H}$
      \hspace{1cm} pKa 9.2 \hspace{1cm} $\rightarrow \hspace{1cm} \text{pKa -7}$

   \[ \Delta G^0 \]

12. Explain the following statements:

   a. HF is a stronger acid than NH$_3$.
      
      HF is stronger because it turns into a lower energy (more stable) conjugate base. F$^-$ is more stable
      than NH$_2^-$ because F is more electronegative than N, and stabilizes the negative charge better.

   b. HCl is a weaker acid than HI.
      
      HCl is weaker because it turns into a higher energy conjugate base (or HI is stronger because it
      turns into a lower energy conjugate base). In comparing the conjugate bases, I$^-$ is more stable than
      Cl$^-$ because I$^-$ is a very large ion and the charge is dispersed around a larger region of space than in
      Cl$^-$. 
c. HNO₃ has a \( pK_a \) of -1.3 while HNO₂ has a \( pK_a \) of 3.3.

HNO₃ has a lower \( pK_a \), meaning it is more acidic. This is because its conjugate base is more stabilized (lower energy). The conjugate base of HNO₃ is stabilized by 3 equal energy resonance structures, while the conjugate base of HNO₂ has only 2 resonance structures. The charge is more spread out in nitrate (NO₃⁻) versus nitrite (NO₂⁻).

d. CH₃⁻ is a stronger base than OH⁻.

A stronger base is a less stable (higher energy) form than a weaker one. Since O is more electronegative than C, it stabilizes the negative charge better, making OH⁻ lower energy and weaker than CH₃⁻. (Note: this also implies than H₂O is a stronger acid than CH₄ since stronger acid = weaker conjugate base.)

13. Rank the species in each set from weakest to strongest acid.

a. HBr, HF, HI
   Weakest acid: HF < HBr < HI Strongest (Size of CB)

b. CH₃NH₂, HF, CH₃OH
   Weakest: CH₃NH₂ < CH₃OH < HF Strongest (e-neg trend)

c. H₂S, H₂Se, PH₃
   Weakest: PH₃ < H₂S < H₂Se Strongest

d. Oxalic acid is a diprotic acid: the first hydrogen atom has a \( pK_a \) of 1.27 and the second has a \( pK_a \) of 4.28. Explain why both hydrogen atoms do not have the same \( pK_a \) and why \( pK_{a1} \) is lower.

The first \( pK_a \) refers to removal of an H from the neutral oxalic acid to form compound Y (the CB of oxalic acid). The second \( pK_a \) refers to removal of an H from Y, to form Z (the CB of Y)- they have different \( pK_a \) values because the starting acid structures are different.

Since the conjugate base of Y is doubly charge (dianion), this increases the energy of the CB and makes Y less acidic than oxalic acid.
15. Draw the conjugate base of each structure below, including all possible resonance structures. Then explain why the second structure is more acidic than the first.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Conjugate Base</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Structure Image]</td>
<td>[Conjugate Base Image]</td>
<td>~50</td>
</tr>
<tr>
<td>[Structure Image]</td>
<td>[Conjugate Base Image]</td>
<td>~43</td>
</tr>
</tbody>
</table>

The alkane is less acidic than the second structure because its conjugate base is less stabilized, with no resonance structures. Resonance stabilizes the conjugate base of the alkene structure, as it spreads out the negative charge (and the pi bond).

16. Of the two hydrogen atoms pointed to with an arrow, which is more acidic? Explain, using structures with your answer.

The LEFT H is more acidic.

When that H is removed, the conjugate base (Q) has resonance. This stabilizes the CB as the negative charge is distributed across two oxygen atoms.

If the right H were removed, it would form the conjugate base R. Here the negative charge would be localized on only one oxygen atom. This is higher energy, and not as likely to happen.