1. (15 points)
   a. Arrange the following compounds in order of increasing boiling point: nonane, decane, heptane.
      \[ \text{_____________<_____________<_____________} \]

   b. Arrange the following compounds in order of increasing basicity: Cl\(^-\), (CH\(_3\))\(_2\)P\(^-\), CH\(_3\)S\(^-\).
      \[ \text{_____________<_____________<_____________} \]

   c. Arrange the following compounds in order of increasing acidity: CH\(_3\)CH\(_2\)SeH, CH\(_3\)CH\(_2\)SH, CH\(_3\)CH\(_2\)OH.
      \[ \text{_____________<_____________<_____________} \]

   d. Arrange the following compounds in order of increasing dipole moment: CH\(_2\)I\(_2\), CH\(_2\)Br\(_2\), CH\(_2\)Cl\(_2\).
      \[ \text{_____________<_____________<_____________} \]

   e. Arrange the following equilibrium constants \(K_1\), \(K_2\), and \(K_3\) in order of increasing value:
      \[
      \begin{align*}
      \text{CCl}_3\text{C}-\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CCl}_3\text{O}^- + \text{H}_3\text{O}^+ & K_1 \\
      \text{CCl}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CCl}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+ & K_2 \\
      \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} & \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+ & K_3 \\
      \end{align*}
      \]
      \[ \text{_____________<_____________<_____________} \]
2. Provide brief explanations for each of the following. (21 points)

a. The relative energies of anti-anti pentane, gauche(+)-gauche(+) pentane, and gauche(+)-gauche(-) pentane are 0, 1.62, and 3.32 kcal/mol respectively. (Hint: Why is the energy of gauche(+)-gauche(-) pentane so high?)

b. Rotation about the C–N bond of \(N,N\)-dimethylacetamide occurs much more slowly than rotation about the C–N bond of dimethylethylamine. (Hint: Why is the nitrogen atom of \(N,N\)-dimethylacetamide planar, while the nitrogen atom of dimethylethylamine is pyramidal?)

c. The heat of combustion (amount of heat released upon burning one mole) of methylcyclobutane is greater than the heat of combustion of cyclopentane. (Hint: What is the relationship between the two molecules and how do they differ in geometry?)
3. 1,2-Dibromoethane (CH$_2$Br–CH$_2$Br) exists as mixture of 82% of the anti conformer and 9% of each of the two gauche conformers at 298 K. (10 points)

a. Calculate the equilibrium constant for the equilibrium between the anti conformer and either one of the gauche conformers.

b. Calculate the difference in free energy between the anti conformer and either one of the gauche conformers.
4. The following reactions are called cycloaddition reactions, because they involve the addition of two components together to form a ring. (20 points)

a. Use the curved-arrow formalism to show the mechanism (flow of electrons) in the following reaction. (This cycloaddition reaction is named the Diels-Alder reaction after its discoverers.)

\[ \text{first reactant} + \text{second reactant} \rightarrow \text{product} \]

b. Use the curved arrow formalism to shown the flow of electrons in the following reaction. (This one is called a dipolar cycloaddition reaction, because the first reactant has two formal charges, which comprise a dipole.)

\[ \text{first reactant} + \text{second reactant} \rightarrow \text{product} \]

c. In part a, skeletal structures are used to represent the reactants and product. Write the molecular formulas of these compounds:

first reactant _____________  second reactant _____________  product _____________
5. (19 points)
   a. Draw Newman projections for each of the three conformers (staggered conformations) about the C2-C3 bond of 2,3-dimethylbutane. Label each conformation with the dihedral angle \( \theta \) about the C2-C3 bond. (We will define \( \theta \) such that the methyl groups eclipse with methyl groups and the hydrogen atoms eclipse with hydrogen atoms when \( \theta = 0 \).)

   b. Which of these three conformers do you think is (are) highest in energy? Why?

   c. Draw Newman projections for each of the three eclipsed conformations about the C2-C3 bond of 2,3-dimethylbutane. Label each conformation with the dihedral angle \( \theta \) about the C2-C3 bond. (We will define \( \theta \) such that the methyl groups eclipse with methyl groups and the hydrogen atoms eclipse with hydrogen atoms when \( \theta = 0 \).)

   d. Sketch a curve of potential energy vs. dihedral angle \( \theta \) about the C2-C3 bond for 2,3-dimethylbutane. Your curve should show the relative stabilities of the different conformations but should not attempt to provide numerical values for relative energies.
6. (15 points)  
Formaldehyde undergoes acid-catalyzed hydration, as shown below.

\[
\begin{align*}
\text{HCHO} + \text{H}_2\text{O}^+ &\rightarrow \text{HCOO}^- + \text{H}_3\text{O}^+ \\
\text{formaldehyde} &\quad \text{hydrate}
\end{align*}
\]

The mechanism of this reaction involves three steps and is shown below using the curved arrow formalism.

1. \[
\begin{align*}
\text{HCHO} + \text{H}_2\text{O}^+ &\rightarrow \text{HCOO}^- + \text{H}_3\text{O}^+ \\
\end{align*}
\]

2. \[
\begin{align*}
\text{HCOO}^- + \text{H}_2\text{O}^+ &\rightarrow \text{H}_2\text{O} + \text{HCOO}^- \\
\end{align*}
\]

3. \[
\begin{align*}
\text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} \\
\end{align*}
\]

The reverse reaction consists of the acid-catalyzed loss of water from the hydrate, as shown below.

\[
\begin{align*}
\text{HCOO}^- + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} + \text{HCOO}^- \\
\end{align*}
\]

Write the three-step mechanism of the reverse reaction, using the curved arrow formalism. Make sure to show all lone pairs of electrons and charges.

1. \[
\begin{align*}
\text{HCOO}^- + \text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} + \text{HCOO}^- \\
\end{align*}
\]

2. \[
\begin{align*}
\text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} \\
\end{align*}
\]

3. \[
\begin{align*}
\text{H}_2\text{O} &\rightarrow \text{H}_2\text{O} \\
\end{align*}
\]