1. Calculate the degree of unsaturation in each formula below.
   a) \( \text{C}_4\text{H}_7\text{OH} \)
   b) \( \text{C}_6\text{H}_3\text{NH}_2 \)
   c) [Chemical structure image]

2. Draw structures corresponding to each IUPAC name below. Either condensed or line structures may be used.
   a) 3-chloro-1,2-dimethylcyclohexene
   b) (E)-3-methylhex-3-ene
   c) Trans-2-methylhex-3-ene

3. Assign E or Z configurations to each alkene below.
   [Chemical structure images]
4. Rank the carbocations below in order of increasing stability (most stable = 1; least stable = 4).

5. On treatment with HBr, the following alkene undergoes addition and rearrangement to yield 1-bromo-1-propylcyclohexane. Using curved arrows, propose a mechanism to account for this result.
6. Draw a detailed mechanism for the reaction of 2-butanol with sulfuric acid. Show all possible products. Rank the products by which you predict would be formed in the highest yield (Highest Yield 1st - Lowest Yield 3rd)

\[
\text{OH} \quad \text{H}_2\text{SO}_4
\]

7. Which energy difference corresponds to the activation energy of the rate-limiting step for A to E transformation?

8. Classify each reaction as a(n):
   a. addition
   b. elimination
   c. substitution

\[
\text{CH}_2\text{Cl} + \text{CH}_3\text{CH(NH}_2\text{)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \rightarrow \text{CH}_2\text{CH}\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} + \text{CH}_3\text{CH(NH}_2\text{)}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}
\]

\[
\text{OH} \quad \text{Sulfuric Acid} \quad \text{H}_2\text{C} = \text{CH}_2
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{CN}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{Br}^-
\]
9. An alternative step in chlorination of methane might be as follows:

\[ \text{Cl}^- + \text{CH}_4 \rightarrow \text{CH}_3\text{Cl} + \text{H}^- \]

Use the Bond Dissociation Energies from the table below to calculate the enthalpy of this step.

<table>
<thead>
<tr>
<th>bond</th>
<th>CH$_3$–H</th>
<th>CH$_3$–Cl</th>
<th>H–Cl</th>
<th>H–H</th>
<th>Cl–Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE (kJ/mol)</td>
<td>438</td>
<td>351</td>
<td>432</td>
<td>436</td>
<td>243</td>
</tr>
</tbody>
</table>

Enthalpy ________

Is this step exothermic or endothermic?

The following reaction has the thermodynamic parameters listed below.

\[ \text{HO}^- + \text{CH}_3\text{Cl} \rightleftharpoons \text{CH}_3\text{OH} + \text{Cl}^- \]

\[ \Delta H^\circ = -75 \text{ kJ/mol} \]
\[ \Delta S^\circ = 54 \text{ J/K·mol} \]
\[ T = 25^\circ \text{C} \]

10. Is the reaction exothermic or endothermic?

11. What is the value of $\Delta G^\circ$ at this temperature?

12. Is the reaction favorable (spontaneous) or unfavorable (nonsenspontaneous) at 25°C?
13. Draw an example of an energy diagram for a three-step reaction with $K_{eq} > 1$. Identify $\Delta G^\circ$, transition states, and intermediates.

14. Below are all the chemical structures and intermediates involved in this reaction which results in two different products. On the structures provided, show all electron flow using the arrow formation for the complete stepwise mechanism for this reaction which leads to each of the two products.
15. Complete the following reactions filling in the missing product.

a) \[
\text{BH}_3\text{THF} \\
\text{OH}^+, \text{H}_2\text{O}_2
\]

b) \[
\text{Br}_2
\]

c) \[
\text{Br}_2 \\
\text{H}_2\text{O}
\]

d) \[
\text{KMnO}_4
\]

e) \[
\text{HBr}
\]

f) \[
\text{H}_2 \\
Pd
\]

g) \[
\text{CHCl}_3 \\
\text{KOH}
\]
16. Complete the following reactions filling in the missing reactant or product.

a) \[
\begin{align*}
\text{OsO}_4 & \quad \rightarrow \\
\text{NaHSO}_3, \text{H}_2\text{O} & 
\end{align*}
\]

b) \[
\begin{align*}
\text{Hg(OAc)}_2 & \quad \rightarrow \\
\text{OH}^-, \text{NaBH}_4 & 
\end{align*}
\]

c) \[
\begin{align*}
\text{KMnO}_4 & \quad \rightarrow \\
\text{H}_3\text{O}^+ & 
\end{align*}
\]
1. Calculate the degree of unsaturation in each formula below.
   a) \( \text{C}_4\text{H}_9\text{OH} \)
   \[
   \frac{2(4) - 8 + 2}{2} = 1
   \]
   b) \( \text{C}_6\text{H}_7\text{NH}_2 \)
   \[
   \frac{2(6) + 1 - 7 + 2}{2} = 1
   \]
   c) [Structure image]

2. Draw structures corresponding to each IUPAC name below. Either condensed or line structures may be used.
   a) 3-chloro-1,2-dimethylcyclohexene
   [Structure image]
   b) (E) 3-methylhex-3-ene
   [Structure image]
   c) Trans-2-methylhex-3-ene
   [Structure image]

3. Assign E or Z configurations to each alkene below.
   a) [Structure image]
   (Z)
   b) [Structure image]
   (E)
4. Rank the carbocations below in order of increasing stability (most stable = 1; least stable = 4).

\[ \begin{array}{cccc}
    & + & + & + \\
\text{3°} & 1° & 2° & 2° \\
\hline
1 & 4 & 2 & 3
\end{array} \]

5. On treatment with HBr, the following alkene undergoes addition and rearrangement to yield 1-bromo-1-propylcyclohexane. Using curved arrows, propose a mechanism to account for this result.
6. Draw a detailed mechanism for the reaction of 2-butanol with sulfuric acid. Show all possible products. Rank the products by which you predict would be formed in the highest yield (Highest Yield 1st - Lowest Yield 3rd).

7. Which energy difference corresponds to the activation energy of the rate-limiting step for A to E transformation?

8. Classify each reaction as a(n):
   a. addition
   b. elimination
   c. substitution

---

3 B E

3 B E

Sulfuric Acid

3 B E

---

C S
9. An alternative step in chlorination of methane might be as follows:

\[
\text{Cl}^- + \text{CH}_4 \rightarrow \text{CH}_3\text{Cl} + \cdot \text{H}
\]

Use the Bond Dissociation Energies from the table below to calculate the enthalpy of this step.

<table>
<thead>
<tr>
<th>bond</th>
<th>CH$_3$–H</th>
<th>CH$_3$–Cl</th>
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<td>BDE (kJ/mol)</td>
<td>438</td>
<td>351</td>
<td>432</td>
<td>436</td>
<td>243</td>
</tr>
</tbody>
</table>

\[
\text{Enthalpy} = \frac{438}{-351} = 87
\]

Is this step exothermic or endothermic?

3. **Endothermic**

The following reaction has the thermodynamic parameters listed below.

\[
\text{HO}^- + \text{CH}_3\text{Cl} \rightleftharpoons \text{CH}_3\text{OH} + \text{Cl}^-
\]

\[
\Delta H^o = -75 \text{ kJ/mol}
\]

\[
\Delta S^o = 54 \text{ J/K/mol}
\]

\[
T = 25^\circ C
\]

10. Is the reaction exothermic or endothermic?

2. **Exothermic**

11. What is the value of \(\Delta G^o\) at this temperature?

\[
\Delta G = \Delta H - T \Delta S
\]

\[
= -75 \text{ kJ} - 298 \left( \frac{54}{1000} \right) = -75 - 16 = -91 \text{ kJ/mol}
\]

12. Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at 25°C?

2. **Spontaneous**
13. Draw an example of an energy diagram for a three-step reaction with $K_{eq} > 1$. Identify $\Delta G^0$, transition states, and intermediates.

14. Below are all the chemical structures and intermediates involved in this reaction which results in two different products. On the structures provided, show all electron flow using the arrow formation for the complete stepwise mechanism for this reaction which leads to each of the two products.
15. Complete the following reactions filling in the missing product. (3 each)

a) $\text{BH}_3\text{THF}$

b) $\text{Br}_2$

c) $\text{Br}_2$

b) $\text{KMnO}_4$

d) $\text{HBr}$

e) $\text{H}_2$ (Pd)

e) $\text{CHCl}_3$ (KOH)
16. Complete the following reactions filling in the missing reactant or product.

a) \[
\text{CH}_3\text{C} = \text{CH} \overset{\text{OsO}_4}{\text{NaHSO}_3, \text{H}_2\text{O}} \rightarrow \text{CH}_3\text{C} = \text{CHOH} \]

b) \[
\text{C}_6\text{H}_{12} \overset{\text{Hg(OAc)}_2}{\text{OH}^+, \text{NaBH}_4} \rightarrow \text{C}_6\text{H}_{12}\text{OH} \]

c) \[
\text{CH}_3\text{C} = \text{CH} \overset{\text{KMnO}_4}{\text{H}_2\text{O}^+} \rightarrow \text{C}_6\text{H}_{12}\text{CO} \]
1. Draw curved arrows to show electron reorganization for the reaction step below. Make the ends of your curved arrows specify the destination of the reorganizing electron pair as precisely as possible.

2. Draw the products of the reaction shown. Electron flow is indicated with curved arrows. Include all valence electrons in your answer.

3. Estimate the gas phase enthalpy change using bond dissociation enthalpies from the Reference Table.

\[ \text{C}_6\text{H}_5\text{H} + \text{Cl} \rightarrow \text{C}_6\text{H}_5\text{H}^+ + \text{H}-\text{Cl} \]

\[ \Delta H = 42 \text{ kJ/mol} \]

2a) Is the reaction exothermic or endothermic? **Endothermic**

2b) Is the reaction likely to proceed spontaneously in the direction written? **No**
4. Use the reaction energy diagram below to answer the following questions.

![Reaction Energy Diagram]

- a) Calculate the activation energy, $\Delta G^\dagger$, for the step B to C.
  
  \[11 \rightarrow 24 \sim 13 \text{ kcal/mol}\]

- b) Calculate the overall energy change, $\Delta G^\circ$, for the process A to B.
  
  \[5 \rightarrow 11 \sim 6 \text{ kcal/mol}\]

- c) Which step is faster: B to C or A to B? $\text{Prod}_2 \rightarrow \text{Prod}_3$ ?
  
  2

- d) Label the reactant, product, intermediate(s) and transition state(s) on the diagram.
  
  5

5. Calculate the degree of unsaturation in each formula below.

- a) $\text{C}_5\text{H}_4\text{Br}_2$ \[\frac{10 - 4 - 2 + 2}{2} = 3\]

- b) $\text{C}_7\text{H}_7\text{NO}_4$ \[\frac{14 + 1 - 7 + 2}{2} = 5\]

- c) \[
  \begin{array}{c}
  \text{Ph} \\
  \text{C} \\
  \text{O} \\
  \text{C} \\
  \text{Cl}
  \end{array}
  \] \[6\]
6. Label the hybridization for each carbon on the molecule below.

7. Draw structures corresponding to each IUPAC name below. Either condensed or line structures may be used.

   a) (cis)-4-methyl-2-pentene

   b) (E)-2,3,4-trimethyl-3-hexene

8. Assign E or Z configurations to each alkene below.
9. Which of the alkenes below is the least stable (highest in energy)?

\[ \text{A} \]

10. Rank the carbocations below in order of increasing stability (most stable = 1; least stable = 4).

\[ \text{2} \quad \text{4} \quad \text{4} \quad \text{3} \]

11. Classify each reaction as a(n):

a. addition  
b. elimination  
c. substitution

\[ \text{B} \]

1. Addition
2. Elimination

\[ \text{C} \]

1. Substitution

\[ \text{A} \]

1. Addition
12. Show the mechanism, using curved arrows, for the free radical reaction shown below. Show the initiation and propagation steps.

Initiation Step 1

Initiation Step 2

Propagation Step 1

Propagation Step 2
13. On treatment with HBr, the following alkene undergoes addition and rearrangement to yield 1-bromo-1-propylcyclohexane. Using curved arrows, propose a mechanism to account for this result.

14. Complete the following reaction, showing all possible products. Rank the products by which you predict would be formed in the highest yield (Highest Yield 1st - Lowest Yield 3rd.)
The following reaction has the thermodynamic parameters listed below.

\[ 
\text{CH}_3\text{CH}_2\text{OH} \quad \text{H}_2\text{O} \quad \text{C} = \text{C} \quad \text{C} = \text{C} 
\]

\[ \Delta H^\circ = -44 \text{ kJ/mol} \]
\[ \Delta S^\circ = -0.12 \text{ kJ/K mol} \]
\[ T = 25^\circ \text{C} \]

15. Is the reaction exothermic or endothermic?
- **Exothermic**

16. What is the value of \( \Delta G^\circ \) at this temperature?

\[ \Delta G = \Delta H - T\Delta S \]
\[ \Delta G = -44 - 298(-0.12) \]
\[ = -44 + 35.76 \]

17. Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at 25°C?
- **Spontaneous**

18. Complete the following reactions.

a) 
\[
\text{OsO}_4 \quad \text{NaHSO}_3, \text{H}_2\text{O} \quad \text{CH}_3\text{CH}_2\text{OH} \quad \text{H}_3\text{O}^+ \quad \text{NaBH}_4
\]

b) 
\[
\text{Hg(OAc)}_2 \quad \text{OH}, \text{NaBH}_4
\]

c) 
\[
\text{KMnO}_4 \quad \text{H}_3\text{O}^+
\]
19. Complete the following reactions.

a) \[
\begin{align*}
\text{CH}_3\text{OH} & \xrightarrow{\text{BH}_3\text{THF}} \text{HOH} \\
\text{OH}^{-}, \text{H}_2\text{O}_2 & \xrightarrow{} & \text{HOH}
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{\text{KMnO}_4} \text{H}_2\text{O}^{+}, \text{heat} \\
& \xrightarrow{}
\end{align*}
\]

c) \[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{\text{HBr}} \text{Br} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{Br} \\
& \xrightarrow{} \text{Br} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{Br}
\end{align*}
\]

d) \[
\begin{align*}
\text{CH}_2=\text{CH} & \xrightarrow{\text{Br}_2} \\
& \xrightarrow{}
\end{align*}
\]

e) \[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{\text{Br}_2} \text{H}_2\text{O} \\
& \xrightarrow{}
\end{align*}
\]

f) \[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{\text{H}_2} \text{Pd} \\
& \xrightarrow{}
\end{align*}
\]

g) \[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{\text{CHCl}_3} \text{KOH} \\
& \xrightarrow{}
\end{align*}
\]