46th International Chemistry Olympiad
July 25, 2014
Hanoi, Vietnam

THEORETICAL EXAMINATION
WITH ANSWER SHEETS GRADING

Country:
Name as in passport:
Student Code:
Language:

Chemistry: The flavor of life
GENERAL INTRODUCTION

- You have **additional 15 minutes** to read the whole set.
- This booklet is composed of 9 problems. You have **5 hours to fulfill the problems**. Failure to stop after the STOP command may result in zero points for the current task.
- Write down answers and calculations within the designated boxes. Give your work where required.
- Use only the pen and calculator provided.
- The draft papers are provided. If you need more draft paper, use the back side of the paper. Answers on the back side and the draft papers will NOT be marked.
- There are **52 pages** in the booklet including the answer boxes, Cover Sheet and Periodic Table.
- The official English version is available on demand for clarification only.
- Need to go to the restroom – raise your hand. You will be guided there.
- **After the STOP signal** put your booklet in the envelope (do not seal), leave at your table. Do not leave the room without permission.

*Good luck!*

*Chemistry: The flavor of life*
### Physical Constants, Units, Formulas and Equations

<table>
<thead>
<tr>
<th>Physical Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avogadro's constant</td>
<td>$N_A = 6.0221 \times 10^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Universal gas constant</td>
<td>$R = 8.3145$ J·K$^{-1}$·mol$^{-1}$</td>
</tr>
<tr>
<td>Speed of light</td>
<td>$c = 2.9979 \times 10^8$ m·s$^{-1}$</td>
</tr>
<tr>
<td>Planck's constant</td>
<td>$h = 6.6261 \times 10^{-34}$ J·s</td>
</tr>
<tr>
<td>Standard pressure</td>
<td>$p^\circ = 1$ bar = $10^5$ Pa</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>1 atm = $1.01325 \times 10^5$ Pa = 760 mmHg</td>
</tr>
<tr>
<td>Zero of the Celsius scale</td>
<td>273.15 K</td>
</tr>
<tr>
<td>Mass of electron</td>
<td>$m_e = 9.1094 \times 10^{-31}$ kg</td>
</tr>
</tbody>
</table>

1 nanometer (nm) = $10^{-9}$ m; 1 angstrom (Å) = $10^{-10}$ m
1 electron volt (eV) = $1.6022 \times 10^{-19}$ J = 96485 J·mol$^{-1}$

<table>
<thead>
<tr>
<th>Formula Description</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy of a light quantum with wavelength $\lambda$</td>
<td>$E = \frac{hc}{\lambda}$</td>
</tr>
<tr>
<td>Energy of one mole of photons</td>
<td>$E_m = \frac{hcN_A}{\lambda}$</td>
</tr>
<tr>
<td>Gibbs energy</td>
<td>$G = H - TS$</td>
</tr>
<tr>
<td>Relation between equilibrium constant and standard Gibbs energy</td>
<td>$K = \exp\left(-\frac{\Delta G^o}{RT}\right)$</td>
</tr>
<tr>
<td>van’t Hoff equation in integral form</td>
<td>$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$</td>
</tr>
<tr>
<td>Relationship between internal energy, heat and work</td>
<td>$\Delta U = q + w$</td>
</tr>
<tr>
<td>Molar heat capacity at constant volume</td>
<td>$C_{v,m} = \left(\frac{dU}{dT}\right)_v$</td>
</tr>
<tr>
<td>Change in internal energy from $T_1$ to $T_2$ assuming constant $C_{v,m}$</td>
<td>$U(T_2) = U(T_1) + nC_{v,m}(T_2 - T_1)$,</td>
</tr>
<tr>
<td>Spin only formula relating number of unpaired electrons to effective magnetic moment</td>
<td>$\mu_{eff} = \sqrt{n(n+2)}$ B.M.</td>
</tr>
</tbody>
</table>
Problem 1. Particles in a box: polyenes

In quantum mechanics, the movement of $\pi$ electrons along a neutral chain of conjugated carbon atoms may be modeled using the ‘particle in a box’ method. The energy of the $\pi$ electrons is given by the following equation:

$$E_n = \frac{n^2 \hbar^2}{8mL^2}$$

where $n$ is the quantum number ($n = 1, 2, 3, \ldots$), $\hbar$ is Planck’s constant, $m$ is the mass of electron, and $L$ is the length of the box which may be approximated by $L = (k + 2) \times 1.40$ Å ($k$ being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength $\lambda$ may promote a $\pi$ electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength $\lambda$, to the number of double bonds $k$ and constant $B$ is as follows:

$$\lambda \text{ (nm)} = B \times \frac{(k + 2)^2}{(2k + 1)}$$

Equation 1

1. Using this semi-empirical formula with $B = 65.01$ nm calculate the value of the wavelength $\lambda$ (nm) for octatetraene (CH$_2$ = CH – CH = CH – CH = CH = CH = CH$_2$).

1. From the given semi-empirical formula, the wavelength $\lambda$ (nm) is calculated as follows:

$$\lambda \text{ (nm)} = 65.01 \times \frac{(k + 2)^2}{(2k + 1)}$$

For octatetraene molecule, with $k = 4$; $\lambda = 260.0$ nm
2. **Derive** Equation 1 (an expression for the wavelength \( \lambda \) (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of \( k \) and the fundamental constants, and hence **calculate** theoretical value of the constant \( B_{\text{calc.}} \).

2. The formula: 
\[
E = \frac{n^2 \hbar^2}{8mL^2} 
\]

\( \Delta E \) is calculated as: 
\[
\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = h \nu = \frac{hc}{\lambda} 
\]

In which, \( \lambda \) and \( \nu \) are wavelength and frequency for the corresponding photon respectively, \( k \) is the quantum number for the HOMO, which is equal to the number of double bonds. So, we have:

\[
\Delta E = \frac{h^2}{8mL^2}[(k+1)^2 - k^2] = \frac{hc}{\lambda} = \frac{h^2}{8mL^2}[2k+1] \quad (3)
\]

Replace \( L = (k + 2) \times 1.40 \text{ Å} \) into (3):

\[
\begin{align*}
\frac{hc}{\lambda} &= \frac{h^2(2k+1)}{8m[(k+2)\times1.40 \times 10^{-10}]^2} \\
\Rightarrow \lambda &= \frac{8m[(k+2)\times1.40 \times 10^{-10}]^2}{h(2k+1)} \\
\Rightarrow \lambda &= \frac{8 \times 9.1094 \times 10^{-31} \times 2.9979 \times 10^8 \times (1.40 \times 10^{-10})^2}{6.6261 \times 10^{-34}} \times \frac{(k+2)^2}{(2k+1)} \\
\Rightarrow \lambda (m) &= 6.462 \times 10^{-8} \times \frac{(k+2)^2}{(2k+1)}; \quad \Rightarrow \lambda (nm) = 64.62 \times \frac{(k+2)^2}{(2k+1)} \quad (4)
\end{align*}
\]

\( B_{\text{calc.}} = 64.6 \text{ nm} \)

3. We wish to synthesize a linear polyene for which the excitation of a \( \pi \) electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, **determine** the number of conjugated double bonds \( k \) in this polyene and **give** its structure. [If you did not solve Part 2, use the semi-empirical Equation 1 with \( B = 65.01 \text{ nm} \) to complete Part 3.]

3. With \( \lambda = 600 \text{ nm} \), we have

\[
\frac{600}{64.62} = \frac{(k+2)^2}{(2k+1)} = 9.285 \Rightarrow k^2 - 14.57k - 5.285 = 0
\]

Solve the equation to obtain: \( k_1 = 14.92 \), \( k_2 = -0.355 \) (Eliminated).
Thus, \( k = 15 \).
So, the formula of polyene is:
\[
\text{CH}_2 = \text{CH} - (\text{CH} = \text{CH})_{13} - \text{CH} = \text{CH}_2
\]

2 points

4. For the polyene molecule found in Part 3, **calculate** the difference in energy between the HOMO and the LUMO, \( \Delta E \), \( \text{(kJ·mol}^{-1}) \).

*In case Part 3 was not solved, take \( k = 5 \) to solve this problem.*

\[
\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = \frac{\hbar^2}{8mL^2} \left[ (k+1)^2 - k^2 \right]
\]

\[
\Delta E = \left( \frac{6.6261 \times 10^{-34}}{8 \times 9.1094 \times 10^{-31} \times (1.40 \times 10^{-10})^2} \right) \times \left( \frac{2k+1}{(k+2)^2} \right) \text{ (kJ·mol}^{-1})
\]

\[
\Delta E = 1851 \times \left( \frac{2k+1}{(k+2)^2} \right) \text{ (kJ/mol)}
\]

For polyene with \( k = 15 \):

\( \Delta E = 199 \text{ kJ·mol}^{-1} \).

Taking the value of \( k = 5 \):

\( \Delta E = 415 \text{ kJ·mol}^{-1} \)

4 points

5. The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions \( L_x, L_y \), and \( L_z \), yielding the following expression for the allowed energy levels:

\[
E_{n_x,n_y,n_z} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)
\]

The three quantum numbers \( n_x, n_y, \) and \( n_z \) must be integer values and are independent of each other.

**5.1 Give** the expressions for the three **different** lowest energies, assuming that the box is cubic with a length of \( L \).

\[
E_{111} = \frac{\hbar^2(1^2 + 1^2 + 1^2)}{8mL^2} = \frac{3\hbar^2}{8mL^2}
\]

1 point
\[ E_{112} = \frac{\hbar^2(1^2 + 1^2 + 2^2)}{8mL^2} = \frac{6\hbar^2}{8mL^2} = E_{121} = E_{211} \]
\[ E_{122} = \frac{\hbar^2(1^2 + 2^2 + 2^2)}{8mL^2} = \frac{9\hbar^2}{8mL^2} = E_{212} = E_{221} \]

5.2 Levels with the same energy are said to be degenerate. **Draw** a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.

- **E\(_{111}\)**: only a single state.
- **E\(_{112}\)**: triple degenerate, either \(n_x\), \(n_y\) or \(n_z\) can equal to 2.
- **E\(_{122}\)**: triple degenerate, either \(n_x\), \(n_y\) or \(n_z\) can equal to 1.
- **E\(_{222}\)**: single state.

**Energy diagram:**

- **E\(_{222}\)**: single state.
- **E\(_{122}\)**: triple degenerate, either \(n_x\), \(n_y\) or \(n_z\) can equal to 1.
- **E\(_{112}\)**: triple degenerate, either \(n_x\), \(n_y\) or \(n_z\) can equal to 2.
- **E\(_{111}\)**: only a single state.

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(_{222})</td>
<td>Single state</td>
</tr>
<tr>
<td>E(_{122})</td>
<td>Triple degenerate</td>
</tr>
<tr>
<td>E(_{112})</td>
<td>Triple degenerate</td>
</tr>
<tr>
<td>E(_{111})</td>
<td>Single state</td>
</tr>
</tbody>
</table>

4 pts
Problem 2. Dissociating Gas Cycle

Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:

\[
\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)
\]

1.00 mole of N\textsubscript{2}O\textsubscript{4} was put into an empty vessel with a fixed volume of 24.44 dm\textsuperscript{3}. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

1a. **Calculate** \(\Delta G^0\) of the reaction at 298K, assuming the gases are ideal.

1b. **Calculate** \(\Delta H^0\) and \(\Delta S^0\) of the reaction, assuming that they do not change significantly with temperature.

**1a.**

\[
\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2
\]

Initial molar number

\[
\begin{array}{c|c}
\text{N}_2\text{O}_4 & \text{2 NO}_2 \\
\hline
1 & 0
\end{array}
\]

At equilibrium

\[
\begin{array}{c|c}
\text{N}_2\text{O}_4 & \text{2 NO}_2 \\
\hline
1 - x & 2x
\end{array}
\]

\(n_{\text{total,equi.}} = 1 - x + 2x = 1 + x\) (mol)

\(P_{\text{total,equi}} = P_{\text{ini}}(1 + x)\)

\((P_{\text{ini}} \text{ - initial pressure; } n_{\text{total,equi.}} \text{ - total molar number of gases at equilibrium; } P_{\text{total,equi}} \text{ - total pressure of gases at equilibrium; } x \text{ - number of moles N}_2\text{O}_4 \text{ dissociated).}\)

\[
n_{\text{total,equi.}} = \frac{PV}{RT} = \frac{(1.190 \text{ bar})(\frac{10^5 \text{ Pa}}{1 \text{ bar}})(24.44 \text{ dm}^3)}{(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = 1.174 \text{ (mol)}
\]

\(1.174 = 1 + x\)

\(4\) pts
\( x = 0.174 \) (mol)

**\( \Delta G^0 \) at 298 K**

At equilibrium:

\[
P_{\text{\(N_2O_4\)}} = \frac{1-x}{1+x} \times P_{\text{total}} = \frac{1-0.174}{1+0.174} \times (1.190 \text{ bar}) = 0.837 \text{ bar}
\]

\[
P_{\text{\(NO_2\)}} = \frac{2x}{1+x} \times P_{\text{total}} = \frac{2 \times 0.174}{1+0.174} \times (1.190 \text{ bar}) = 0.353 \text{ bar}
\]

\[
K_{298} = \left( \frac{P_{\text{\(NO_2\)}}}{P^0} \right)^2 = \left( \frac{0.353}{1} \right)^2 = 0.1489
\]

At 298 K,

\[
\Delta G^0 = -RT \ln K_{298} = -8.3145 \times 298 \times \ln(0.1489) = 4719 \text{ (J \cdot mol}^{-1}) = 4.72 \text{ (kJ \cdot mol}^{-1})
\]

1b. **\( \Delta G^0 \) at 348 K**

\[
n_{\text{total, equi}} = \frac{PV}{RT} = \frac{(1.886 \text{ bar})(10^5 \text{ Pa})}{(8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(348 \text{ K})} = 1.593 \text{ (mol)}
\]

1.593 = 1 + x

x = 0.593 (mol)

At equilibrium:

\[
P_{\text{\(N_2O_4\)}} = \frac{1-x}{1+x} \times P_{\text{total}} = \frac{1-0.593}{1+0.593} \times (1.886 \text{ bar}) = 0.482 \text{ bar}
\]

\[
P_{\text{\(NO_2\)}} = \frac{2x}{1+x} \times P_{\text{total}} = \frac{2 \times 0.593}{1+0.593} \times (1.886 \text{ bar}) = 1.404 \text{ bar}
\]

\[
\Rightarrow K_{348} = \left( \frac{P_{\text{\(NO_2\)}}}{P^0} \right)^2 = \left( \frac{1.404}{1} \right)^2 = 4.0897
\]

At 348 K,

\[
\Delta G^0 = -RT \ln K_{348} = -8.3145 \times 348 \times \ln(4.0897) = -4075 \text{ (J \cdot mol}^{-1}) = -4.07 \text{ (kJ \cdot mol}^{-1})
\]
\[ \Delta S^0 \]
\[ \Delta G^0_{348} = -4.07 \text{ kJ} = \Delta H - 348 \Delta S \] (1)
\[ \Delta G^0_{298} = 4.72 \text{ kJ} = \Delta H - 298 \Delta S \] (2)
(2) - (1) $\rightarrow$ \[ \Delta S = 0.176 \text{ kJ/mol}^{-1}\cdot\text{K}^{-1} \]
\[ \Delta H^0 \]
\[ \Delta H^0 = 4.720 + 298 \times 0.176 = 57.2 \text{ (kJ/mol)} \] 4pts

*If you cannot calculate $\Delta H^0$, use $\Delta H^0 = 30.0 \text{ kJ/mol}^{-1}$ for further calculations.*

The tendency of N\(_2\)O\(_4\) to dissociate reversibly into NO\(_2\) enables its potential use in advanced power generation systems. A simplified scheme for one such system is shown below in Figure (a). Initially, "cool" N\(_2\)O\(_4\) is compressed (1 $\rightarrow$ 2) in a compressor (X), and heated (2 $\rightarrow$ 3). Some N\(_2\)O\(_4\) dissociates into NO\(_2\). The hot mixture is expanded (3 $\rightarrow$ 4) through a turbine (Y), resulting in a decrease in both temperature and pressure. The mixture is then cooled further (4 $\rightarrow$ 1) in a heat sink (Z), to promote the reformation of N\(_2\)O\(_4\). This recombination reduces the pressure, thus facilitates the compression of N\(_2\)O\(_4\) to start a new cycle. All these processes are assumed to take place reversibly.

![Diagram](image)

To understand the benefits of using reversible dissociating gases such as N\(_2\)O\(_4\), we will focus on step 3 $\rightarrow$ 4 and consider an ideal gas turbine working with 1 mol of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, no heat is exchanged.
2. **Give the equation** to calculate the work done by the system \( w(\text{air}) \) during the reversible adiabatic expansion for 1 mol of air during stage 3 \( \rightarrow \) 4. Assume that \( C\text{v,m}(\text{air}) \) (the isochoric molar heat capacity of air) is constant, and the temperature changes from \( T_3 \) to \( T_4 \).

\[
\Delta U = q + w; \quad \text{work done by turbine } w(\text{air}) = -w \\
q = 0, \text{ thus } w(\text{air}) = \Delta U = C_{\text{v,m}}(\text{air})[T_3 - T_4]
\]

3. **Estimate** the ratio \( w_{\text{N}_2\text{O}_4}/w(\text{air}) \), in which \( w_{\text{N}_2\text{O}_4} \) is the work done by the gas during the reversible adiabatic expansion process 3 \( \rightarrow \) 4 with the cycle working with 1 mol of \( \text{N}_2\text{O}_4 \), \( T_3 \) and \( T_4 \) are the same as in Part 2. Take the conditions at stage 3 to be \( T_3 = 440 \) K and \( P_3 = 12.156 \) bar and assume that:

(i) the gas is at its equilibrium composition at stage 3;

(ii) \( C_{\text{v,m}} \) for the gas is the same as for air;

(iii) the adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture (\( \text{N}_2\text{O}_4 + \text{NO}_2 \)) is unchanged until the expansion is completed.

\[
\ln \frac{K_{440}}{K_{348}} = \frac{\Delta H^0}{R} \left( \frac{1}{348} - \frac{1}{440} \right) = \frac{57200}{8.3145} \left( \frac{1}{348} - \frac{1}{440} \right)
\]

\[
\ln K_{440} = \ln K_{348} + \frac{57200}{8.3145} \times \left( \frac{1}{348} - \frac{1}{440} \right) = \ln 4.0897 + \frac{57200}{8.3145} \times \left( \frac{1}{348} - \frac{1}{440} \right) = 5.542
\]

\[\rightarrow K_{440} = 255.2\]

\[\text{N}_2\text{O}_4 \quad \rightarrow \quad 2 \text{ NO}_2 \quad (1)\]

Initial molar number

\[
\begin{align*}
\text{At equilibrium} & & \\
1 & \quad 0 \\
1 - x & \quad 2x
\end{align*}
\]

\( n_{\text{total}} = 1 - x + 2x = 1 + x \) (mol); \( P_{\text{total}} = 12.156 \) bar

At equilibrium:

\[
\begin{align*}
P_{\text{N}_2\text{O}_4} &= \frac{1-x}{1+x} \times 12.156 \text{ (bar)} \\
P_{\text{NO}_2} &= \frac{2x}{1+x} \times 12.156 \text{ (bar)}
\end{align*}
\]
\[
\Rightarrow K_{440} = \left( \frac{P_{NO}}{P^0} \right)^2 = \left( \frac{2x \times 12.156}{1+x} \right)^2 = 255.2
\]

\[
\left( \frac{P_{N_2O_4}}{P^0} \right) = \left( \frac{1-x \times 12.156}{1+x} \right)
\]

\[
(P^0 = 1 \text{ bar}) \quad \Rightarrow \quad \frac{2x}{1+x} = 20.99 \Rightarrow \quad \frac{4x^2}{1-x^2} = 20.99 \Rightarrow \quad 4x^2 = 20.99 - 20.99x^2
\]

\[
\Rightarrow 24.99x^2 = 20.99 \quad \Rightarrow \quad x = 0.92; \quad n_{\text{total}} = 1 + x = 1.92
\]

\[
\Rightarrow w_{N_2O_4} = 1.92 \times C_{v, \text{air}} \times (T_3 - T_4); \quad \Rightarrow \quad \frac{w_{N_2O_4}}{w_{\text{air}}} = 1.92
\]
**Problem 3. High-valent Silver Compounds**

Silver chemistry is dominated by Ag(I) compounds. Compounds of silver in higher oxidation state (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electro-chemical oxidations or in chemical oxidations using powerful oxidizing agents.

1. In some peroxydisulfate (S\(_2\)O\(_8\)) oxidations catalyzed by Ag\(^+\), black solid (A) with the composition AgO can be isolated.

   1a. **Choose** the appropriate magnetic behaviour of A if it exists as Ag\(^{II}\)O.

   - Diamagnetic
   - Paramagnetic

   Single crystal X-ray studies reveal that the lattice of A contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, A should be assigned as Ag\(^+\)Ag\(^{III}\)O\(_2\) rather than Ag\(^{II}\)O.

   1b. **Assign** the oxidation number of Ag1 and Ag2.

   - Oxidation number of Ag1: ...........+1
   - Oxidation number of Ag2: ...........+3

   2 points
1c. **What** is the coordination number of O atoms in the lattice of A?

The coordination number of O atoms = ... 3 ... 1 point

1d. **How many** Ag\(^{I}\) and Ag\(^{III}\) bond to one O atom in the lattice of A?

Number of Ag\(^{I}\) = ....... 1
Number of Ag\(^{III}\) = ....... 2 ... 2 points

1e. **Predict** the magnetic behaviour of A. **Check** the appropriate box below.

- [ ] Diamagnetic
- [x] Paramagnetic

The Ag\(^{I}\) is d\(^{10}\) hence diamagnetic; the Ag\(^{III}\) is square planar d\(^{8}\) also diamagnetic

1f. The compound A can also be formed on warming a solution of Ag\(^{+}\) with peroxydisulfate. **Write down** the equation for the formation of A.

\[ \text{S}_2\text{O}_8^{2-} (aq) + 2\text{Ag}^{+} (aq) + 2\text{H}_2\text{O} (l) \rightarrow 2\text{SO}_4^{2-} (aq) + \text{Ag}^{I}\text{Ag}^{III}_{2} (s) + 4\text{H}^{+} (aq) \] ... 1 point

2. Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound A is not a Ag\(^{II}\)O. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Standard enthalpy of formation (kJ·mol(^{-1}))</th>
<th>1st ionization (kJ·mol(^{-1}))</th>
<th>2nd ionization (kJ·mol(^{-1}))</th>
<th>3rd ionization (kJ·mol(^{-1}))</th>
<th>1st electron affinity (kJ·mol(^{-1}))</th>
<th>2nd electron affinity (kJ·mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(g)</td>
<td>337.4</td>
<td>751.7</td>
<td>1964.1</td>
<td>3560.2</td>
<td>-141.0</td>
<td>844.0</td>
</tr>
<tr>
<td>Ag(g)</td>
<td>284.9</td>
<td>737.2</td>
<td>2080.2</td>
<td>3367.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(g)</td>
<td>249.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The relationship between the lattice dissociation energy \((U_{lat})\) and the lattice dissociation enthalpy \((\Delta H_{lat})\) for monoatomic ion lattices is:

\[
\Delta H_{lat} = U_{lat} + nRT
\]

where \(n\) is the number of ions in the formula unit.

2a. Calculate \(U_{lat}\) at 298 K of \(\text{Ag}^{I}\text{Ag}^{III}\text{O}_2\) and \(\text{Cu}^{II}\text{O}\). Assume that they are ionic compounds.

### \(U_{lat}\) of \(\text{Ag}^{I}\text{Ag}^{III}\text{O}_2\)

Calculations:

\[
\Delta H_{lat} (\text{Ag}^{I}\text{Ag}^{III}\text{O}_2) = 2 \Delta H^\circ_f (\text{O}^2-) + \Delta H^\circ_f (\text{Ag}^+) + \Delta H^\circ_f (\text{Ag}^{3+}) - \Delta H^\circ_f (\text{Ag}^{I}\text{Ag}^{III}\text{O}_2)
\]

\[
= (2 \times 249 - 2 \times 141 + 2 \times 844) + (284.9 + 737.2 + 284.9 + 737.2 + 2080.2 + 3367.2) - (-24.3)
\]

\[
= +9419.9 \text{ (kJ·mol}^{-1})
\]

\[
U_{lat} (\text{Ag}^{I}\text{Ag}^{III}\text{O}_2) = \Delta H_{lat} (\text{Ag}^{I}\text{Ag}^{III}\text{O}_2) - 4RT
\]

\[
= +9419.9 - 10.0 = +9409.9 \text{ (kJ·mol}^{-1})\]  

(3 points)  

(no penalty if negative sign)

### \(U_{lat}\) of \(\text{Cu}^{II}\text{O}\)

Calculations for: \(U_{lat}\) of \(\text{Cu}^{II}\text{O}\)

\[
\Delta H_{lat} (\text{Cu}^{II}\text{O}) = \Delta H^\circ_f (\text{O}^2-) + \Delta H^\circ_f (\text{Cu}^{2+}) - \Delta H^\circ_f (\text{Cu}^{II}\text{O})
\]

\[
= (249 - 141 + 844) + (337.4 + 751.7 + 1964.1) - (-157.3)
\]

\[
= 4162.5 \text{ (kJ·mol}^{-1})
\]

\[
U_{lat} (\text{Cu}^{II}\text{O}) = \Delta H_{lat} (\text{Cu}^{II}\text{O}) - 2RT = 4162.5 - 5.0 = 4157.5 \text{ (kJ·mol}^{-1})\]  

(3 points)  

(no penalty if negative sign)

If you cannot calculate the \(U_{lat}\) of \(\text{Ag}^{I}\text{Ag}^{III}\text{O}_2\) and \(\text{Cu}^{II}\text{O}\), use following values for further calculations: \(U_{lat}\) of \(\text{Ag}^{I}\text{Ag}^{III}\text{O}_2 = 8310.0 \text{ kJ·mol}^{-1}\); \(U_{lat}\) of \(\text{Cu}^{II}\text{O} = 3600.0 \text{ kJ·mol}^{-1}\).
The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

\[ U_{\text{lat}} = C \times \left( \frac{1}{V_m} \right)^{\frac{1}{3}} \]

Where: \( V_m \) (nm\(^3\)) is the volume of the formula unit and \( C \) (kJ·nm·mol\(^{-1}\)) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

<table>
<thead>
<tr>
<th>Oxides</th>
<th>( V_m ) (nm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{II})O</td>
<td>0.02030</td>
</tr>
<tr>
<td>Ag(^{II/III})_2O(_3)</td>
<td>0.06182</td>
</tr>
<tr>
<td>Ag(^{II})Ag(^{III})_2O(_4)</td>
<td>0.08985</td>
</tr>
</tbody>
</table>

2b. **Calculate** \( U_{\text{lat}} \) for the hypothetical compound Ag\(^{II}\)O. Assume that Ag\(^{II}\)O and Cu\(^{II}\)O have the same type of lattice, and that \( V_m \) (Ag\(^{II}\)O) = \( V_m \) (Ag\(^{II/III}\)_2O\(_4\)) - \( V_m \) (Ag\(^{III}\)_2O\(_3\)).

Calculations:

\[
V_m (\text{Ag}^{II}O) = V_m (\text{Ag}^{II} \text{Ag}^{III} \text{O}_4) - V_m (\text{Ag}^{III} \text{O}_3) = 0.08985 - 0.06182 = 0.02803 \text{ nm}^3 
\]

From the relationship \( U_{\text{lat}} = C \times (V_m)^{-\frac{1}{3}} \) we have

\[
\frac{U_{\text{lat}} \text{ (Ag oxide)}}{U_{\text{lat}} \text{ (Cu oxide)}} = \left[ \frac{V_m \text{ (Cu oxide)}}{V_m \text{ (Ag oxide)}} \right]^{\frac{1}{3}}
\]

\[
U_{\text{lat}} \text{ (Ag}^{II}\text{O)} = 4157.5 \times \sqrt[3]{\frac{0.02030}{0.02803}} = 3733.6 \text{ (kJ·mol}^{-1}\text{)} \quad \text{3 points}
\]

Answer: 3733.6 (kJ·mol\(^{-1}\)) [or 3232.9 kJ·mol\(^{-1}\) if using \( U_{\text{lat}} \) Cu\(^{II}\)O = 3600 kJ·mol\(^{-1}\)].

2c. By constructing an appropriate thermodynamic cycle or otherwise, **estimate** the enthalpy change for the solid-state transformation from Ag\(^{II}\)O to 1 mole of Ag\(^{II}\)Ag\(^{III}\)_2O\(_2\).

(Use \( U_{\text{lat}} \) Ag\(^{II}\)O = 3180.0 kJ·mol\(^{-1}\) and \( U_{\text{lat}} \) Ag\(^{II}\)Ag\(^{III}\)_2O\(_2\) = 8310.0 kJ·mol\(^{-1}\) if you cannot calculate \( U_{\text{lat}} \) Ag\(^{II}\)O in Part 2b).
2Ag\textsuperscript{II}O\textsubscript{(s)} $\xleftarrow{}$ $\Delta H_{\text{rxn}}$ $\rightarrow$ 2Ag\textsuperscript{I}Ag\textsuperscript{III}O\textsubscript{2} \textsubscript{(s)}

\[2U_{\text{lat}}(\text{AgO}) + 4RT - U_{\text{lat}}(\text{AgIAGIII}O) - 4RT\]

\[2\text{Ag}^{2+}\textsubscript{(g)} + 2\text{O}^{2-}\textsubscript{(g)} \xrightarrow{IE_3(\text{Ag}) - IE_2(\text{Ag})} \text{Ag}^{+}\textsubscript{(g)} + \text{Ag}^{3+}\textsubscript{(g)} + 2\text{O}^{2-}\textsubscript{(g)}\]

Calculations:

\[\Delta H_{\text{rxn}} = 2U_{\text{lat}}(\text{Ag}^{\text{II}}\text{O}) + 4RT + IE_3 - IE_2 - U_{\text{lat}}(\text{AgIAGIII}O) - 4RT\]

\[= 2 \times 3733.6 + 3367.2 - 2080.2 - 9409.9\]

\[= -655.7 \text{ (kJ/mol)} \text{ or -663.0 kJ/mol} \text{ using given } U_{\text{lat}} \text{ values} \quad 4 \text{ pts}\]

2d. Indicate which compound is thermodynamically more stable by checking the appropriate box below.

\[
\begin{array}{c|c}
\text{Ag}^{\text{II}}\text{O} & \text{AgIAGIII}O_2 \\
\hline
\square & \square \\
\end{array}
\]

\[x \quad 1 \text{ point}\]

3. When Ag\textsuperscript{I}Ag\textsuperscript{III}O\textsubscript{2} is dissolved in aqueous HClO\textsubscript{4} solution, a paramagnetic compound (B) is first formed then slowly decomposes to form a diamagnetic compound (C). Given that B and C are the only compounds containing silver formed in these reactions, write down the equations for the formation of B and C.

For B:

\[\text{AgIAGIII}O_2 \text{ (s)} + 4 \text{ HClO}_4 \text{ (aq)} \rightarrow 2\text{Ag(ClO}_4)_2 \text{ (aq)} + 2 \text{H}_2\text{O} \text{ (l)} \quad 1 \text{ point}\]

For C:

\[4\text{Ag(ClO}_4)_2 \text{ (aq)} + 2 \text{H}_2\text{O} \text{ (l)} \rightarrow 4 \text{ AgClO}_4 \text{ (aq)} + 4 \text{HClO}_4 \text{ (aq)} + \text{O}_2 \text{ (g)} \quad 1 \text{ point}\]
4. Oxidation of Ag\(^{+}\) with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex Z is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of AgNO\(_3\) and 2 mL of pyridine (d = 0.982 g/mL) is added to a stirred, ice-cold aqueous solution of 5.000 g of K\(_2\)S\(_2\)O\(_8\). The reaction mixture becomes yellow, then an orange solid (Z) is formed which has a mass of 1.719 g when dried.

Elemental analysis of Z shows the mass percentages of C, H, N elements are 38.96\%, 3.28\%, 9.09\%, respectively.

A 0.6164 g Z is added to aqueous NH\(_3\). The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (D). The filtrate is collected and treated with excess BaCl\(_2\) solution to obtain 0.4668 g (when dry) of white precipitate (E).

4a. **Determine** the empirical formula of Z and calculate the percentage yield in the preparation.

### Calculations:

- Mole Ag in 0.6164 g of Z = mole of AgCl = 0.001 mole
- Mole SO\(_4^{2-}\) from 0.6160 g of Z = mole BaSO\(_4\) = 0.002 mol
- Mass percentage of Ag = 0.001×107.87/0.6164 = 17.50 %
- Mass percentage of SO\(_4^{2-}\) = 0.002×96.06/0.6164 = 31.17 %
- From EA:

\[
\text{Ratio Ag}^{2+} : \text{SO}_4^{2-} : C : H : N = \frac{17.50}{107.87} : \frac{31.17}{192.12} : \frac{38.96}{12.01} : \frac{3.28}{1.01} : \frac{9.09}{14.01} = 1 : 2 : 20 : 20 : 4
\]

The empirical formula of Z is: C\(_{20}\)H\(_{20}\)AgN\(_4\)O\(_8\)S\(_2\)  

\[
\text{Yield} = \frac{1.719}{0.500} \times 100\% = 94.7\% \quad 2 \text{ points}
\]

1 point
4b. Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in Z, the effective magnetic moment ($\mu_{\text{eff}}$) of Z was determined and found to be 1.78 BM. Use the spin only formula to determine the number of unpaired electrons in Z and the molecular formula of Z. (Z contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)

\[-\frac{\sqrt{n(n+2)}}{78.1} = 1.78 \quad (n \text{ is number of unpaired electron of Ag})
\]
\[-n = 1, \text{ corresponds to } \text{Ag}^{II} \quad (d^9)
\]

Most rational molecular formula of Z is $[\text{Ag}^{II}(\text{Py})_4](\text{S}_2\text{O}_8)$

4c. Write down all chemical equations for the preparation of Z, and its analysis.

**Formation of Z:**

$2\text{Ag}^{+} (aq) + 8\text{Py} \quad (l) + 3\text{S}_2\text{O}_8^{2-} (aq) \rightarrow 2[\text{Ag}^{II}(\text{Py})_4](\text{S}_2\text{O}_8) \quad (s) + 2\text{SO}_4^{2-} (aq)$

2 pts

**Destruction of Z with NH$_3$:**

$[\text{Ag}^{II}(\text{Py})_4](\text{S}_2\text{O}_8) \quad (s) + 6\text{NH}_3 \quad (l) \rightarrow [\text{Ag}^{II}(\text{NH}_3)_2]^+ \quad (aq) + \frac{1}{2} \text{N}_2 \quad (g) + 2\text{SO}_4^{2-} \quad (aq) + 3\text{NH}_4^+ \quad (aq) + 4\text{Py} \quad (l)$

(All reasonable N-containing products and O$_2$ are acceptable)

2 pts

**Formation of D:**

$[\text{Ag}^{II}(\text{NH}_3)_2]^+ \quad (aq) + 2\text{H}^+ \quad (aq) + \text{Cl}^- \quad (aq) \rightarrow \text{AgCl} \quad (s) + 2\text{NH}_4^+ \quad (aq)$

1 pt

**Formation of E:**

$\text{Ba}^{2+} \quad (aq) + \text{SO}_4^{2-} \quad (aq) \rightarrow \text{BaSO}_4 \quad (s)$

1 pt
Problem 4. Zeise’s Salt

1. Zeise's salt, K[PtCl₃C₂H₄], was one of the first organometallic compounds to be reported. W. C. Zeise, a professor at the University of Copenhagen, prepared this compound in 1827 by reacting PtCl₄ with boiling ethanol and then adding potassium chloride (Method 1). This compound may also be prepared by refluxing a mixture of K₂[PtCl₆] and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from K₂[PtCl₄] and ethylene (Method 3).

1a. Write balanced equations for each of the above mentioned preparations of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise’s salt consumes 2 moles of ethanol.

\[
\begin{align*}
\text{PtCl}_4 + 2 \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{H[PtCl}_3\text{C}_2\text{H}_4] + \text{CH}_3\text{CH=O} + \text{HCl} + \text{H}_2\text{O} \\
\text{H[PtCl}_3\text{C}_2\text{H}_4] + \text{KCl} & \rightarrow \text{K[PtCl}_3\text{C}_2\text{H}_4] + \text{HCl} \\
\text{K}_2\text{[PtCl}_6] + 2 \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{K[PtCl}_3\text{C}_2\text{H}_4] + \text{CH}_3\text{CH=O} + \text{KCl} + 2 \text{HCl} + \text{H}_2\text{O} \\
\text{K}_2\text{[PtCl}_4] + \text{C}_2\text{H}_4 & \rightarrow \text{K[PtCl}_3\text{C}_2\text{H}_4] + \text{KCl}
\end{align*}
\]

1 pt for each (2 pts if the first two reactions combined), total of 4 pts

1b. Mass spectrometry of the anion [PtCl₃C₂H₄]⁻ shows one set of peaks with mass numbers 325-337 au and various intensities.

Calculate the mass number of the anion which consists of the largest natural abundance isotopes (using given below data).
Isotope  
\[ ^{192}_{78}\text{Pt} \quad ^{194}_{78}\text{Pt} \quad ^{195}_{78}\text{Pt} \quad ^{196}_{78}\text{Pt} \quad ^{198}_{78}\text{Pt} \quad ^{35}_{17}\text{Cl} \quad ^{37}_{17}\text{Cl} \quad ^{12}_{6}\text{C} \quad ^{13}_{6}\text{C} \quad ^{1}_{1}\text{H} \]

Natural abundance, \%
0.8 32.9 33.8 25.3 7.2 75.8 24.2 98.9 1.1 99.99

Calculations:
\[
195 + 3 \times 35 + 2 \times 12 + 4 \times 1 = 328 \quad \text{1 pt}
\]

2. Some early structures proposed for Zeise’s salt anion were:

\[
\text{Structure} \quad \text{Number of different environments of hydrogen} \quad \text{Number of different environments of carbon}
\]

<table>
<thead>
<tr>
<th>Structure</th>
<th>2</th>
<th>lpt</th>
<th>2</th>
<th>lpt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In structure Z1, Z2, and Z5 both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

2a. NMR spectroscopy allowed the structure for Zeise’s salt to be determined as structure Z4. For each structure Z1-Z5, indicate in the table below how many hydrogen atoms are in different environments, and how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are?
3. For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position trans to themselves (the trans effect). The ordering of ligands is:

\[ \text{CO, CN}^-, \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^+ > \text{CH}_3^- > \text{C}_6\text{H}_5^- > \Gamma > \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{Py} > \text{NH}_3 > \text{OH}^- > \text{H}_2\text{O} \]

In above series a left ligand has stronger trans effect than a right ligand.

Some reactions of Zeise’s salt and the complex \([\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2]\) are given below.

3a. Draw the structure of A, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.
3b. **Draw** the structures of B, C, D, E, F and G.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl(\text{Pt})NH(_2)Me Cl (\text{Cl})</td>
<td>Cl(\text{Pt})NH(_2\text{C}_6\text{H}_5) Cl (\text{Cl})</td>
<td>K[\text{C}_6\text{H}_5]Cl(\text{Pt})Cl (\text{Cl})</td>
</tr>
<tr>
<td></td>
<td>1 pt</td>
<td>1 pt</td>
<td>1 pt</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K[\text{C}_6\text{H}_5]Cl(\text{Pt})Py (\text{Cl})</td>
<td>Cl(\text{Pt})(\text{H}_2) (\text{N}) (\text{Cl})</td>
<td>Cl(\text{Pt})(\text{Cl}) C</td>
</tr>
<tr>
<td></td>
<td>1 pt</td>
<td>1 pt</td>
<td>1 pt</td>
</tr>
</tbody>
</table>

3c. **Suggest** the driving force(s) for the formation of D and F by choosing one or more of the following statements (for example, i and ii):

i) Formation of gas

ii) Formation of liquid

iii) Trans effect

iv) Chelate effect

<table>
<thead>
<tr>
<th>Structure</th>
<th>D</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driving force(s)</td>
<td>i</td>
<td>iii and iv</td>
</tr>
<tr>
<td></td>
<td>2 pts</td>
<td>2 pts</td>
</tr>
</tbody>
</table>
Problem 5. Acid-base Equilibria in Water

A solution (X) contains two weak monoprotic acids (those having one acidic proton); HA with the acid dissociation constant of $K_{HA} = 1.74 \times 10^{-7}$, and HB with the acid dissociation constant of $K_{HB} = 1.34 \times 10^{-7}$. The solution X has a pH of 3.75.

1. Titration of 100 mL solution X requires 100 mL of 0.220 M NaOH solution for completion. Calculate the initial (total) concentration (mol·L⁻¹) of each acid in the solution X. Use reasonable approximations where appropriate. [$K_w = 1.00 \times 10^{-14}$ at 298 K.]

Solution: In solution X, $H^+$ was produced from the reactions:

\[
HA \iff H^+ + A^- \quad \text{and} \quad HB \iff H^+ + B^- \quad \text{and} \quad H_2O \iff H^+ + OH^-
\]

The positive and negative charges in an aqueous solution must balance. Thus the charge balance expression is:

\[
[OH^-] + [A^-] + [B^-] = [H^+]
\] (Eq.1)

In the acidic solution (pH = 3.75), $[OH^-]$ can be neglected, so:

\[
[A^-] + [B^-] = [H^+] \quad \text{(Eq. 2)}
\]

From equilibrium expression:

\[
\frac{[H^+] \times [A^-]}{[HA]} = K_{HA}
\]

and $[HA] = [HA]_i - [A^-]$ (where $[HA]_i$ is the initial concentration)

So:

\[
[H^+] \times [A^-] = K_{HA} \times [HA] = K_{HA} \left([HA]_i - [A^-]\right)
\]

Thus, the equilibrium concentration of $[A^-]$ can be presented as:

\[
[A^-] = \frac{K_{HA} \times [HA]_i}{K_{HA} + [H^+]} = \frac{K_{HA} \times [HA]_i}{[HA]_i + [H^+]}
\]

Similarly, the equilibrium concentration of $[B^-]$ can be presented as:
\[
[B^-] = \frac{K_{HB} \times [HB]_i}{K_{HB} + [H^+]}
\]

Substitute equilibrium concentrations of \([A^-]\) and \([B^-]\) into Eq.2:
\[
\frac{K_{HA} \times [HA]_i}{K_{HA} + [H^+]} + \frac{K_{HB} \times [HB]_i}{K_{HB} + [H^+]} = [H^+]
\]

Since \(K_{HA}\), \(K_{HB}\) are much smaller than \([H^+]\), thus:
\[
\frac{K_{HA} \times [HA]_i}{[H^+]} + \frac{K_{HB} \times [HB]_i}{[H^+]} = [H^+]
\]
or \(1.74 \times 10^{-7} \times [HA]_i + 1.34 \times 10^{-7} \times [HB]_i = [H^+]^2 = (10^{-3.75})^2\)
\(1.74 \times [HA]_i + 1.34 \times [HB]_i = 0.316\) \(\text{ (Eq. 3)}\)

Neutralization reactions show:
\[
\begin{align*}
\text{HA} + \text{NaOH} & \rightarrow \text{NaA} + \text{H}_2\text{O} \\
\text{HB} + \text{NaOH} & \rightarrow \text{NaB} + \text{H}_2\text{O}
\end{align*}
\]

\(n_{HA} + n_{HB} = n_{NaOH}\)
or \(([HA]_i + [HB]_i) \times 0.1 \text{ L} = 0.220 \text{ M} \times 0.1 \text{ L}\)

\([HA]_i + [HB]_i = 0.220 \text{ M} \quad \text{(Eq. 4)}\)

Solving Eq.3 and Eq.4 gives: \( [HA]_i = 0.053 \text{ M} \) and \( [HB]_i = 0.167 \text{ M} \)

Concentration of HA = 0.053 M
Concentration of HB = 0.167 M

2. **Calculate** the pH of the solution \(Y\) which initially contains \(6.00 \times 10^{-2}\) M of NaA and \(4.00 \times 10^{-2}\) M of NaB.

Solution:
Solution \(Y\) contains NaA 0.06 M and NaB 0.04 M. The solution is basic, \(\text{OH}^-\) was produced from the reactions:
\[
\begin{align*}
\text{NaA} + \text{H}_2\text{O} & \rightleftharpoons \text{HA} + \text{OH}^- & K_{b,A} = K_w/K_{HA} = 5.75 \times 10^{-8} \\
\text{NaB} + \text{H}_2\text{O} & \rightleftharpoons \text{HB} + \text{OH}^- & K_{b,B} = K_w/K_{HB} = 7.46 \times 10^{-8} \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- & K_w = 1.00 \times 10^{-14}
\end{align*}
\]
and we have:
\[ [H^+] + [HA] + [HB] = [OH^-] \quad \text{(Eq. 5)} \]

In the basic solution, \([H^+]\) can be neglected, so:
\[ [HA] + [HB] = [OH^-] \quad \text{(Eq. 6)} \]

From equilibrium expression:
\[ \frac{[OH^-][HA]}{[A^-]} = K_{b,A} \]

and \[ [A^-] = 0.06 - [HA] \]

Thus, the equilibrium concentration of HA can be presented as:
\[ [HA] = \frac{K_{b,A} \times 0.06}{K_{b,A} + [OH^-]} \]

Similarly, the equilibrium concentration of HB can be presented as:
\[ [HB] = \frac{K_{b,B} \times 0.04}{K_{b,B} + [OH^-]} \]

Substitute equilibrium concentrations of HA and HB into Eq. 6:
\[ \frac{K_{b,A} \times 0.06}{K_{b,A} + [OH^-]} + \frac{K_{b,B} \times 0.04}{K_{b,B} + [OH^-]} = [OH^-] \]

Assume that \(K_{b,A}\) and \(K_{b,B}\) are much smaller than \([OH^-]\) (*), thus:
\[ [OH^-]^2 = 5.75 \times 10^{-8} \times 0.06 + 7.46 \times 10^{-8} \times 0.04 \]
\[ [OH^-] = 8.02 \times 10^{-5} \quad \text{(the assumption (*) is justified)} \]

So \( \text{pOH} = 4.10 \) and \( \text{pH} = 9.90 \)

3. Adding large amounts of distilled water to solution X gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero. Calculate the percentage of dissociation of each acid in this dilute solution.

Solution: HA in the dilute solution:
\[ [A^-] = \alpha \times [HA]_i \]
\[ [HA] = (1 - \alpha) \times [HA]_i \]
\[ [H^+] = 10^{-7} \]

Substitute these equilibrium concentrations into \(K_{HA}\) expression:
\[ \frac{10^{-7} \times \alpha \times [HA]_i}{(1 - \alpha) \times [HA]_i} = K_{HA} \quad \text{or} \quad \frac{10^{-7} \times \alpha}{(1 - \alpha)} = 1.74 \times 10^{-7} \]

Solving the equation gives: \(\alpha = 0.635\)

Similarly, for HB:
\[ \frac{10^{-7} \times \alpha}{(1 - \alpha)} = 1.34 \times 10^{-7} \]
Solving the equation gives: $\alpha = 0.573$
- The percentage of dissociation of HA = $65.5\%$
- The percentage of dissociation of HB = $57.3\%$  

4. A buffer solution is added to solution Y to maintain a pH of 10.0. Assume no change in volume of the resulting solution Z.

**Calculate** the solubility (in mol·L$^{-1}$) of a substance M(OH)$_2$ in Z, given that the anions A$^-$ and B$^-$ can form complexes with M$^{2+}$:

$$\text{M(OH)}_2 \rightleftharpoons \text{M}^{2+} + 2\text{OH}^- \quad K_{sp} = 3.10 \times 10^{-12}$$
$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = 1.00 \times 10^{-14}$$
$$\text{M}^{2+} + \text{A}^- \rightleftharpoons [\text{MA}]^+ \quad K_1 = 2.1 \times 10^3$$
$$[\text{MA}]^+ + \text{A}^- \rightleftharpoons [\text{MA}_2] \quad K_2 = 5.0 \times 10^2$$
$$\text{M}^{2+} + \text{B}^- \rightleftharpoons [\text{MB}]^+ \quad K'_1 = 6.2 \times 10^3$$
$$[\text{MB}]^+ + \text{B}^- \rightleftharpoons [\text{MB}_2] \quad K'_2 = 3.3 \times 10^2$$

**Solution:**

M(OH)$_2 \rightleftharpoons \text{M}^{2+} + 2\text{OH}^-$ \quad $K_{sp} = 3.10 \times 10^{-12}$
H$_2$O $\rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = 1.00 \times 10^{-14}$
M$^{2+} + \text{A}^- \rightleftharpoons [\text{MA}]^+ \quad K_1 = 2.1 \times 10^3$
[MA]$^+ + \text{A}^- \rightleftharpoons [\text{MA}_2] \quad K_2 = 5.0 \times 10^2$
M$^{2+} + \text{B}^- \rightleftharpoons [\text{MB}]^+ \quad K'_1 = 6.2 \times 10^3$
[MB]$^+ + \text{B}^- \rightleftharpoons [\text{MB}_2] \quad K'_2 = 3.3 \times 10^2$

Solubility of M(OH)$_2 = s = [\text{M}^{2+}] + [\text{MA}^+] + [\text{MA}_2] + [\text{MB}^+] + [\text{MB}_2]$

pH of Z = 10.0

$$[\text{M}^{2+}] = \frac{K_{sp}}{[\text{OH}^-]^2} = \frac{3.10 \times 10^{-12}}{(10^{-4})^2} = 3.10 \times 10^{-4} \text{ M} \quad \text{Eq.1}$$

At pH = 10.0

$$[\text{A}^-]_{total} = \frac{K_{HA} \times 0.06}{(K_{HA} + 10^{-10})} = 0.06$$

$$[\text{MA}^+] = K_1[M^{2+}][\text{A}^-] = 2.1 \times 10^3 \times 3.10 \times 10^{-4} \times [\text{A}^-] = 0.651 \times [\text{A}^-] \quad \text{Eq. 3}$$
$$[\text{MA}_2] = K_1K_2[M^{2+}][\text{A}^-]^2 = 325.5 \times [\text{A}^-]^2 \quad \text{Eq. 4}$$
$$[\text{A}^-]_{total} = [\text{A}^-] + [\text{MA}^+] + 2 \times [\text{MA}_2] = 0.06 \text{ M} \quad \text{Eq. 5}$$

Substitute Eq. 3 and Eq. 4 into Eq. 5:

$$[\text{A}^-] + 0.651 \times [\text{A}^-] + 2 \times 325.5 \times [\text{A}^-]^2 = 0.06$$

2 pts
Solve this equation: \([A^-] = 8.42 \times 10^{-3} \text{ M}\)

Substitute this value into Eq. 3 and Eq. 4:

\([MA^-] = 0.651 \times [A^-] = 5.48 \times 10^{-3} \text{ M}\)
\([MA_2] = 325.5 \times [A^-]^2 = 2.31 \times 10^{-2} \text{ M}\)

Similarly,

\([B^-]_{\text{total}} = 0.04 \text{ M}\)

\([MB^+] = K_c[M^{2+}][B^-] = 6.2 \times 10^{3} \times 3.10 \times 10^{-4} \times [B^-] = 1.92 \times [B^-]\) \hspace{1cm} \text{Eq. 6}

\([MB_2] = K_c^2[M^{2+}][B^-]^2 = 634.3 \times [B^-]^2\) \hspace{1cm} \text{Eq. 7}

\([B^-]_{\text{total}} = [B^-] + [MB^+] + 2 \times [MB_2] = 0.04 \text{ M}\) \hspace{1cm} \text{Eq. 8} \hspace{1cm} 2 \text{pts}

Substitute Eq. 6 and Eq. 7 into Eq. 8:

\([B^-] + 1.92 \times [B^-] + 2 \times 634.3 \times [B^-]^2 = 0.04\)

Solve this equation: \([B^-] = 4.58 \times 10^{-3} \text{ M}\)

Substitute this value into Eq. 6 and Eq. 7:

\([MB^+] = 1.92 \times [B^-] = 8.79 \times 10^{-3} \text{ M}\)
\([MB_2] = 634.3 \times [B^-]^2 = 1.33 \times 10^{-2} \text{ M}\)

Thus, solubility of M(OH)$_2$ in Z is $s'$

$s' = 3.10 \times 10^{-4} + 5.48 \times 10^{-3} + 2.31 \times 10^{-2} + 8.79 \times 10^{-3} + 1.33 \times 10^{-2} = 5.10 \times 10^{-2} \text{ M}$

Answer: Solubility of M(OH)$_2$ in Z = $5.10 \times 10^{-2} \text{ M}$. \hspace{1cm} 2 points
Problem 6. Chemical Kinetics

The transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to synthesize arylamines. The overall reaction for the nickel-catalyzed amination of aryl chloride in basic conditions is:

\[
\text{ArCl} \quad + \quad \text{RNH}_2 \quad \xrightarrow{\text{NiLL}', \text{NaO}^+\text{Bu}, \text{Solvent}} \quad \text{Ar-NHR} \quad + \quad \text{HCl}
\]

in which NiLL’ is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

6a. To determine the reaction order with respect to each reactant, the dependence of the initial rate of the reaction on the concentrations of each reagent was carried out with all other reagents present in large excess. Some kinetic data at 298 K are shown in the tables below. (Use the grids if you like)

<table>
<thead>
<tr>
<th>[ArCl] (M)</th>
<th>Initial rate (M s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>(1.88 \times 10^{-5})</td>
</tr>
<tr>
<td>0.2</td>
<td>(4.13 \times 10^{-5})</td>
</tr>
<tr>
<td>0.4</td>
<td>(9.42 \times 10^{-5})</td>
</tr>
<tr>
<td>0.6</td>
<td>(1.50 \times 10^{-4})</td>
</tr>
<tr>
<td>[NiLL$^*$] (M)</td>
<td>Initial rate (M s$^{-1}$)</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>$6 \times 10^{-3}$</td>
<td>$4.12 \times 10^{-5}$</td>
</tr>
<tr>
<td>$9 \times 10^{-3}$</td>
<td>$6.01 \times 10^{-5}$</td>
</tr>
<tr>
<td>$1.2 \times 10^{-2}$</td>
<td>$7.80 \times 10^{-5}$</td>
</tr>
<tr>
<td>$1.5 \times 10^{-2}$</td>
<td>$1.10 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[L$^*$] (M)</th>
<th>Initial rate (M s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>$5.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.09</td>
<td>$4.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.12</td>
<td>$3.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>0.15</td>
<td>$2.8 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

**Determine** the order with respect to the reagents assuming they are integers.

- Order with respect to [ArCl] = 1
- Order with respect to [NiLL$^*$] = 1
- Order with respect to [L$^*$] = -1  
  
  6 pts
6b. To study the mechanism for this reaction, $^1$H, $^{31}$P, $^{19}$F, and $^{13}$C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, NiL(Ar)Cl, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL’ (step 1) at 50 °C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

\[
\text{NiLL’} \xrightarrow{k_1} \text{NiL} + L’ \quad (1)
\]

\[
\text{NiL} + \text{ArCl} \xrightarrow{k_2} \text{NiL(Ar)Cl} \quad (2)
\]

Using the steady state approximation, derive an expression for the rate equation for the formation of [NiL(Ar)Cl].

The rate law expression for the formation of NiLAr(Cl)

\[
\text{rate} = \frac{k_1 k_2 [\text{NiLL’}] [\text{ArCl}]}{k_{-1} [L’] + k_2 [\text{ArCl}]} = \frac{k_1 (k_2 / k_{-1}) [\text{NiLL’}] [\text{ArCl}]}{[L’] + (k_2 / k_{-1}) [\text{ArCl}]} \quad 8 \text{ pts}
\]

(4pts for [NiL] calculation)

(4 pts for rate calculation)
The next steps in the overall reaction involve the amine (RNH₂) and tBuONa. To determine the order with respect to RNH₂ and tBuONa, the dependence of the initial rates of the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

<table>
<thead>
<tr>
<th>[NaOtBu], (M)</th>
<th>Initial rate (M·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>4.16 × 10⁻⁵</td>
</tr>
<tr>
<td>0.6</td>
<td>4.12 × 10⁻⁵</td>
</tr>
<tr>
<td>0.9</td>
<td>4.24 × 10⁻⁵</td>
</tr>
<tr>
<td>1.2</td>
<td>4.20 × 10⁻⁵</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[RNH₂] (M)</th>
<th>Initial rate (M·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>4.12 × 10⁻⁵</td>
</tr>
<tr>
<td>0.6</td>
<td>4.26 × 10⁻⁵</td>
</tr>
<tr>
<td>0.9</td>
<td>4.21 × 10⁻⁵</td>
</tr>
<tr>
<td>1.2</td>
<td>4.23 × 10⁻⁵</td>
</tr>
</tbody>
</table>
6c. **Determine** the order with each of these reagents, assuming each is an integer.
*(Use the grids if you like)*

- Order with respect to [NaO\(^t\)Bu] = 0  
  2 pts
- Order with respect to [RNH\(_2\)] = 0  
  2 pts

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining.

A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:

\[
\begin{align*}
\text{NiLL'} & \xrightleftharpoons[k_1]{k_2} \text{NiL} + L' \\
\text{NiL} + \text{ArCl} & \xrightarrow[k_3]{k_4} \text{NiL}\text{Ar}{\text{Cl}} \\
\text{NiL}\text{Ar}{\text{Cl}} + \text{NH}_2\text{R} + \text{NaO}^t\text{Bu} & \xrightarrow{[\text{NiL}]} \text{NiL}\text{(Ar)NHR} + ^t\text{BuOH} + \text{NaCl}
\end{align*}
\]

6d. **Use** the steady-state approximation and material balance equation to **derive** the rate law for \(d[\text{ArNHR}] / dt\) for the above mechanism in terms of the initial concentration of the catalyst \([\text{NiLL'}]_0\) and concentrations of \([\text{ArCl}], [\text{NH}_2\text{R}], [\text{NaO}^t\text{Bu}], \) and \([L']\).

Using the mechanism depicted by Reaction (1) through (4), the rate equation:

\[
\begin{align*}
\frac{d[\text{NiLL'}]}{dt} & = -k_1[\text{NiLL'}] + k_2[\text{NiL}][L'] \\
\frac{d[\text{NiL}]}{dt} & = k_1[\text{NiLL'}] - k_2[\text{NiL}][L'] - k_3[\text{NiL}][\text{ArCl}] + k_4[\text{NiL}][\text{ArNHR}]
\end{align*}
\]

Apply the steady-state approximation to the concentrations for the intermediates:

\[
\begin{align*}
\frac{d[\text{NiL}]}{dt} & = 0 \\
k_1[\text{NiLL'}] & = k_3[\text{NiL}][\text{ArCl}] + k_2[\text{NiL}][\text{ArCl}] - k_4[\text{NiL}][\text{ArNHR}]  \\
\frac{d[\text{NiL}][\text{ArCl}]}{dt} & = k_3[\text{NiL}][\text{ArCl}] - k_5[\text{NH}_2\text{R}][\text{NaO}^t\text{Bu}][\text{NiL}][\text{ArCl}] = 0 \\
[\text{NiL}][\text{ArCl}] & = \frac{k_2[\text{ArCl}][\text{NiL}]}{k_3[\text{NH}_2\text{R}][\text{NaO}^t\text{Bu}]}  \\
\end{align*}
\]
\[
\frac{d[NiL(Ar)NHR]}{dt} = k_3[NiL(Ar)Cl][NH_2R][NaOBu] - k_4[NiL(Ar)NHR] = 0
\]

\[
[NiL(Ar)NHR] = \frac{k_3}{k_4} \frac{[NiL(Ar)Cl][NH_2R][NaOBu]}{[NiL(Ar)NHR]} \quad \text{(Equation 3)}
\]

Substitute Equation 2 into Equation 3:
\[
[NiL(Ar)NHR] = \frac{k_3}{k_4} \frac{[NH_2R][NaOBu]}{k_3} \frac{[ArCl][NiL]}{[NH_2R][NaOBu]} = \frac{k_3}{k_4} [ArCl][NiL] \quad \text{(Eq. 4)} \quad 1 \text{pt}
\]

Substitute Equation 4 into Equation 1:
\[
k_1[NiLL'] = k_1[NiL][L'] + k_2[NiL][ArCl] - k_4[NiL(Ar)NHR]
\]
\[
k_1[NiLL'] = k_1[NiL][L'] + k_2[NiL][ArCl] - k_4 \times \frac{k_2}{k_4} [ArCl][NiL] = k_1[NiL][L'] \quad \text{(Eq. 5)}
\]

The material balance equation with respect to the catalyst is
\[
[NiLL']_0 = [NiLL'] + [NiL] + [NiLAr(Cl)] + [NiLAr(Cl)NH_2R] \quad 2 \text{ pts}
\]

\[
[NiLL']_0 = \frac{k_1}{k_1} [NiL][L'] + [NiL] + \frac{k_2}{k_3} \frac{[NiL][ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4} [NiL][ArCl]
\]

\[
[NiLL']_0 = [NiL] \left[ \frac{k_1}{k_1} [L'] + 1 + \frac{k_2}{k_3} \frac{[ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4} [ArCl] \right] \quad 3 \text{ pts}
\]

\[
[NiL] = \frac{[NiLL']_0 \times k_1 k_2 k_3 k_4 [NH_2R][NaOBu]}{k_1 k_2 k_3 k_4 [L'][NH_2R][NaOBu] + k_1 k_2 k_3 [NH_2R][NaOBu] + k_1 k_2 k_3 k_4 [ArCl] + k_1 k_2 k_3 [ArCl][NH_2R][NaOBu]}
\]

\text{Equation 6}

Substituting Equation 6 into the differential rate for [ArCl]:
\[
- \frac{d[ArCl]}{dt} = k_2 [ArCl][NiL], \text{ results in the following predicted rate law expression for the reaction mechanism:}
\]
\[
d[ArNHR]/dt = - \frac{d[ArCl]}{dt} = \]
\[
k_2[ArCl][NiL] = k_1 k_2 k_3 k_4 [ArCl][NiLL']_0[NaO'Bu][NH_2R] + k_1 k_2 k_3 [ArCl][NH_2R][NaOBu][L'] + k_1 k_2 k_4 [NaOBu][NH_2R] + k_1 k_2 k_3 [ArCl][NH_2R][NaOBu]
\]

4 pts
6e. **Give** the simplified form of the rate equation in 6d assuming that \( k_1 \) is very small.

\[
d[\text{ArNHR}] / dt = -d[\text{ArCl}] / dt = k_2 [\text{ArCl}] [\text{NiL}] = k_1 k_2 [\text{ArCl}][\text{NiLL'}]_0 / k_{-1}[\text{L'}]
\]

(i.e. consistent with all the orders of reaction as found in the beginning) 2 pts
Problem 7. Synthesis of Artemisinin

(+)-Artemisinin, isolated from *Artemisia annua* L. (Qinghao, *Compositae*) is a potent antimalarial effective against resistant strains of *Plasmodium*. A simple route for the synthesis of Artemisinin is outlined below.

First, pyrolysis of (+)-2-Carene broke the cyclopropane ring forming, among other products, (1R)-(+)-*trans*-isolimonene *A* (C_{10}H_{16}), which then was subjected to regioselective hydroboration using dicyclohexylborane to give the required alcohol *B* in 82% yield as a mixture of diastereoisomers. In the next step, *B* was converted to the corresponding γ,δ-unsaturated acid *C* in 80% yield by Jones’ oxidation.

7a. **Draw** the structures (with stereochemistry) of the compounds A-C.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure A" /></td>
<td><img src="image" alt="Structure B" /></td>
<td><img src="image" alt="Structure C" /></td>
</tr>
</tbody>
</table>

4 pts (2 pts if wrong stereochemistry)  4 pts  4 pts
The acid C was subjected to iodolactonization using KI, I₂ in aqueous. NaHCO₃ solution to afford diastereomeric iodolactones D and E (which differ in stereochemistry only at C₃) in 70% yield.

![Chemical Reaction](image)

**7b. Draw** the structures (with stereochemistry) of the compounds D and E.

<table>
<thead>
<tr>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure D" /></td>
<td><img src="image" alt="Structure E" /></td>
</tr>
</tbody>
</table>

4 pts 4pts

The acid C was converted to diastereomeric iodolactones D and E (epimeric at the chiral center C₃). Look at the number-indicated in the structure F in the next step.

The iodolactone D was subjected to an intermolecular radical reaction with ketone X using tris(trimethylsilyl)silane (TTMSS) and AIBN (azobisisobutyronitrile) in a catalytic amount, refluxing in toluene to yield the corresponding alkylated lactone F in 72% yield as a mixture of diastereoisomers which differ only in stereochemistry at C₇ along with compound G (~10%) and the reduced product H, C₁₀H₁₆O₂ (<5%).
7c. Draw the structures (with stereochemistry) of compound H and the reagent X.

Because alkylated lactone F is known, we can deduce the reagent X as methyl vinyl ketone. H is the reduced product of D.

<table>
<thead>
<tr>
<th>X</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Methyl Vinyl Ketone" /></td>
<td><img src="image2" alt="Compund H" /></td>
</tr>
</tbody>
</table>

The keto group of F reacted with ethanethiol and BF₃•Et₂O in dichloromethane (DCM) at 0 ºC to afford two diastereomers: thioketal lactones I and J in nearly quantitative yield (98%). The thioketalization facilitated the separation of the major isomer J in which the thioketal group is on the opposite face of the ring to the adjacent methyl group.

\[
\begin{align*}
\text{F} & \xrightarrow{\text{HSCH}_2\text{CH}_2\text{SH}} \text{BF}_3\cdot\text{Et}_2\text{O, DCM, 0 ºC}} \\
& \rightarrow \text{I} + \text{J}
\end{align*}
\]
7d. **Draw** the structures (with stereochemistry) of the compounds I and J.

The keto group of lactone F reacted with ethanedithiol and BF$_3$·Et$_2$O in dichloromethane to afford thioketal lactones, I and the major isomer J.

The isomer J was further subjected to alkaline hydrolysis followed by esterification with diazomethane providing hydroxy methyl ester K in 50% yield. The hydroxy methyl ester K was transformed into the keto ester L using PCC (Pyridium ChloroChromate) as the oxidizing agent in dichloromethane (DCM).

A two-dimensional NMR study of the compound L revealed that the two protons adjacent to the newly-formed carbonyl group are *cis* to each other and confirmed the structure of L.

```
J \xrightarrow{1) 10\% \text{NaOH}} \xrightarrow{2) 1\% \text{HCl}} \xrightarrow{3) \text{CH}_2\text{N}_2/\text{Et}_2\text{O}} K \xrightarrow{\text{PCC, 0}^\circ\text{C}} L
```
7e. **Draw** the structures (with stereochemistry) of the compounds K and L.

Hydrolysis followed by esterification of J provided hydroxy ester K. Oxidation of the hydroxy group in K by PCC resulted in the keto ester L in which two protons adjacent to the carbonyl group are cis-oriented.

![Structures K and L](image)

The ketone L was subjected to a Wittig reaction with methoxymethyl triphenylphosphonium chloride and KHMDS (Potassium HexaMethylDiSilazid - a strong, non-nucleophilic base) to furnish the required methyl vinyl ether M in 45% yield. Deprotection of thioketal using HgCl₂, CaCO₃ resulted in the key intermediate N (80%). Finally, the compound N was transformed into the target molecule Artemisinin by photo-oxidation followed by acid hydrolysis with 70% HClO₄.
7f. **Draw** the structures (with stereochemistry) of the compounds M and N.

The Wittig reaction of the ketone L resulted in the formation of methyl vinyl ether M. Deprotection of the thioketal group forms the intermediate N.
Problem 8. Star Anise

*Ilicium verum*, commonly called *Star anise*, is a small native evergreen tree grown in northeast Vietnam. *Star anise* fruit is used in traditional Vietnamese medicine. It is also a major ingredient in the making the flavour of ‘*phở*’, a Vietnamese favourite soup.

Acid A is isolated from the *star anise* fruit. The constitutional formula of A has been deduced from the following sequence of reactions:

\[
\begin{align*}
A \ (C_7H_{10}O_5) & \quad \xrightarrow{i) \ O_3} \quad B \ (C_7H_{10}O_7) & \quad \xrightarrow{\text{CH}_3\text{OH}, \text{H}^+} & \quad 25 \ ^\circ \text{C} \quad C \ (C_8H_{12}O_7) \\
\text{(I)} \quad & \quad \xrightarrow{\text{ii) } \text{Me}_2\text{S}} & \quad \text{(II)} \\
Y_3 + \text{OHCCHO} + \text{OHCCH(OH)CH}_2\text{COOOH} & \xrightarrow{\text{H}_2\text{O}, \text{H}^+} & \text{D} \\
Y_2 & \quad & \quad Y_1
\end{align*}
\]

(I): this overall process results in alkene cleavage at the C=C bond, with each carbon of this becoming doubly bonded to an oxygen atom.

(II): this oxidative cleavage process of 1,2-diols breaks C(OH)–C(OH) bond and produces corresponding carbonyl compounds.

8a. Draw the structures for the compounds Y_1 and Y_2 and hence deduce the structure of Y_3 and A, B, C, D, given that in A there is only one ethylenic hydrogen atom.

<table>
<thead>
<tr>
<th>Y_1</th>
<th>Y_2</th>
<th>Y_3</th>
</tr>
</thead>
</table>
| \[ \begin{align*}
\text{O} \\
\text{H} \\
\text{OH} \\
\text{O} \\
\text{O} \\
\text{H} \\
\end{align*} \] \quad 1 pt | \[ \begin{align*}
\text{O} \\
\text{H} \\
\text{C} \\
\end{align*} \] \quad 1 pt | \[ \begin{align*}
\text{CH}_3\text{OH} \\
\end{align*} \] \quad 2 pts |
Anethole, a main component of star anise oil, is an inexpensive chemical precursor for the production of many pharmaceutical drugs.

Treating anethole with sodium nitrite in acetic acid gives a crystalline solid $E$ ($C_{10}H_{10}N_2O_3$). The IR spectrum of $E$ shows there is no non-aromatic $C=\text{C}$ double bond. The $^1\text{H}$ NMR spectrum of $E$ is given below.
8b. **What differences** in the structure between E and anethole can be obtained from the \(^1\text{H} \text{ NMR data}^*?

\(i\) E contains a \textit{cis}-C=C ethylenic bond while that of anethole is \textit{trans}.

\(ii\) E cannot contain a non-aromatic C=C bond.

\(iii\) E is the adduct of anethole and N\(_2\)O\(_2\).

\(iv\) E is the adduct of anethole and N\(_2\)O\(_3\).

\(v\) E does not contain two \textit{trans} ethylenic protons as anethole.

<table>
<thead>
<tr>
<th>Pick one of the above statements</th>
</tr>
</thead>
<tbody>
<tr>
<td>From (^1\text{H} \text{ NMR data}^* )</td>
</tr>
</tbody>
</table>

On heating at 150 °C for several hours, E is partially isomerized into F. Under the same conditions, F gives the identical equilibrium mixture to that obtained from E. On heating with phosphorus trichloride, both E and F lose one oxygen atom giving compound G. Compounds E and F have the same functional groups.

\[
\begin{align*}
\text{G} & \xrightarrow{\text{PCl}_3 - \text{POCl}_3} \text{E} \xrightarrow{150 \degree \text{C}} \text{F} \xrightarrow{\text{PCl}_3 - \text{POCl}_3} \text{G}
\end{align*}
\]

The chemical shifts of methyl protons in E, F and G are given below.

<table>
<thead>
<tr>
<th></th>
<th>\text{E}</th>
<th>\text{F}</th>
<th>\text{G}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{CH}_3-O</td>
<td>3.8 ppm</td>
<td>3.8 ppm</td>
<td>3.8 ppm</td>
</tr>
<tr>
<td>\text{CH}_3-C</td>
<td>2.3 ppm</td>
<td>2.6 ppm</td>
<td>2.6 ppm</td>
</tr>
</tbody>
</table>

8c. **Suggest** structures for E, F and G, assuming that they do NOT contain three-membered rings.

<table>
<thead>
<tr>
<th></th>
<th>\text{E}</th>
<th>\text{F}</th>
<th>\text{G}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="E structure" /></td>
<td><img src="image" alt="F structure" /></td>
<td><img src="image" alt="G structure" /></td>
</tr>
</tbody>
</table>

4 pts 4 pts 4 pts
A simplified structure for compound E is shown below; the R group does not change throughout the rest of this question. Compound E is nitrated and subsequently reduced with sodium dithionite to H. Treatment of H with sodium nitrite and hydrochloric acid at 0–5 °C and subsequently reduced with stannous chloride to provide I (R–C_7H_9N_2O). One-pot reaction (three component reaction) of H, benzaldehyde and thioglycolic acid (HSCH₂CO₂H) leads to the formation of J. Reaction of I and methyl phenyl ketone in the presence of ZnCl₂ affords K.
8d. **Give** the structures for H, I, J and K.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>I</td>
</tr>
</tbody>
</table>
| \[
\begin{array}{c}
\text{NH}_2 \\
R-\text{OCH}_3
\end{array}
\] | \[
\begin{array}{c}
\text{NHNH}_2 \\
R-\text{OCH}_3
\end{array}
\] |
| 2 pts | 2 pts |

<table>
<thead>
<tr>
<th>J</th>
<th>K</th>
</tr>
</thead>
</table>
| \[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{S} \\
R-\text{OCH}_3
\end{array}
\] | \[
\begin{array}{c}
\text{R} \\
\text{OCH}_3 \\
\text{N} \\
\text{Ph}
\end{array}
\] |
| 3 pts | 3 pts |
Problem 9. Heterocycle Preparation

Tetramethylthiurame disulfide (TMTD) is emerging as a useful reagent to prepare many sulfur-nitrogen functional groups and heterocycles in organic chemistry. The reactions of TMTD with primary amines, as well as some corresponding post-transformations of the resulting product(s) are presented in the following schemes:

(1) \[
\text{Me}_2\text{N-S-S-NMe}_2 + \text{RNH}_2 \rightarrow \text{Me}_2\text{N-SH} + \text{RHN-S-NMe}_2
\]

(2) \[
\text{Me}_2\text{N-SH} \rightarrow \text{Me}_2\text{NH} + \text{CS}_2
\]

(3) \[
\text{R-N=C=S} + \text{S} \quad \text{R-N=C=S} \rightarrow \text{Me}_2\text{N-SH} \quad \Delta
\]

(4) \[
\text{R-N=C=S} + \text{Me}_2\text{NH} \rightarrow \text{Me}_2\text{N-S-NHR}
\]

(5) \[
\text{RNH}_2 + \text{Me}_2\text{N-SH} \xrightarrow{\Delta} \text{Me}_2\text{N-S-NHR} + \text{H}_2\text{S}
\]

Similar transformations of benzohydrazides (containing nucleophilic NH\(_2\) group) and TMTD have been observed.
In the synthetic scheme below, the thiocarbamoylation reaction of an aroyl hydrazine with TMTD produces compound C containing a heterocyclic moiety from \( p \)-aminobenzoic acid.

During the formation of C from B, an intermediate B' was observed. This intermediate tautomerizes to B''. C can be formed from B' or B''.

9a. **Give** the structures of A, B, and C.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image" alt="Structure A" /></td>
<td><img src="image" alt="Structure B" /></td>
<td><img src="image" alt="Structure C" /></td>
</tr>
<tr>
<td></td>
<td>CO(_2)Me</td>
<td>CO(_2)NNHNH(_2)</td>
<td>( \text{C}<em>{11}H</em>{12}N_4O_4S_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{NH}_2 )</td>
<td>( \text{NH}_2 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 pts</td>
<td>2 pts</td>
<td>4 pts</td>
</tr>
</tbody>
</table>
9b. **Suggest** a structure for the tautomer $B''$ and **give a curly-arrow mechanism** for the formation of $C$.

![Diagram of tautomer $B''$ and its conversion to $C$](image)

4 pts

Compound $C$ was then converted to $F$ by the following pathway:

$$
\begin{align*}
\text{C} & \quad \text{HCl (gas)} \quad \text{dioxane (solvent)} \\
& \quad \text{D} \\
& \quad \text{N}_2\text{H}_4 \text{ excess} \quad \text{dioxane, 50 °C, 2 h} \\
& \quad \text{E} \quad \text{TMTD} \quad \text{DMF} \\
& \quad \text{F} \quad \text{(R-C}_8\text{H}_3\text{N}_3\text{S}_2)
\end{align*}
$$

[The group $R$ remains exactly the same throughout the rest of the question.]

9c. **Draw** the structures of $E$, and $F$. (You do not need to draw the structure for the $R$ group from this point)

<table>
<thead>
<tr>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure of E" /></td>
<td><img src="image" alt="Structure of F" /></td>
</tr>
</tbody>
</table>

2 pts | 4 pts

$E$ was only obtained when $D$ was slowly added to the solution of excess $\text{N}_2\text{H}_4$ in dioxane. If $\text{N}_2\text{H}_4$ was added to the solution of $D$ in dioxane instead, a major side product $D'$ ($\text{R}_2\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}_2$) was formed.

9d. **Give** the structure of $D'$. 

---

The 46th IChO – Theoretical Examination. Official English Version
Slightly heating D with ethanolamine (HOCH₂CH₂NH₂) in dioxane for 2 hours yielded G (R–C₉H₁₁N₂OS).

9e. **Draw** the structural formula of G.

9f. Heating G in the presence of p-toluenesulfonic acid as the catalyst could form a number of different five-membered heterocyclic products.

i) **Draw** 2 structures that have different molecular formulae.

<table>
<thead>
<tr>
<th>Eg H1</th>
<th>H3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>(3 pts)</td>
<td></td>
</tr>
</tbody>
</table>

ii) **Draw** 2 structures that are constitutional isomers. (3 pts)
### E.g. H1

(3 pts)

### E.g. H5

(3 pts)

#### iii) **Draw** 2 structures that are stereoisomers. (3 pts)

### H5

#### H7

### H7

#### H8

<table>
<thead>
<tr>
<th>H1</th>
<th>H2</th>
<th>H3</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure" /></td>
<td><img src="image2.png" alt="Structure" /></td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>2 pts</td>
<td>2 pts</td>
<td>2 pts</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H4</th>
<th>H5</th>
<th>H6</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4.png" alt="Structure" /></td>
<td><img src="image5.png" alt="Structure" /></td>
<td><img src="image6.png" alt="Structure" /></td>
</tr>
<tr>
<td>2 pts</td>
<td>2 pts</td>
<td>2 pts</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H7</th>
<th>H8</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image7.png" alt="Structure" /></td>
<td><img src="image8.png" alt="Structure" /></td>
</tr>
<tr>
<td>2 pts</td>
<td>2 pts</td>
</tr>
</tbody>
</table>
## Periodic Table of the Elements

### Transition Elements

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 H</strong></td>
<td><strong>1.008</strong></td>
<td><strong>2</strong></td>
<td><strong>2 Li</strong></td>
<td><strong>6.941</strong></td>
<td><strong>3 Be</strong></td>
<td><strong>9.012</strong></td>
<td><strong>4 B</strong></td>
<td><strong>10.81</strong></td>
<td><strong>5 C</strong></td>
<td><strong>12.01</strong></td>
<td><strong>6 N</strong></td>
</tr>
<tr>
<td><strong>7 O</strong></td>
<td><strong>16.00</strong></td>
<td><strong>8 F</strong></td>
<td><strong>19.00</strong></td>
<td><strong>9 Ne</strong></td>
<td><strong>20.18</strong></td>
<td><strong>10 Na</strong></td>
<td><strong>22.99</strong></td>
<td><strong>11 Mg</strong></td>
<td><strong>24.31</strong></td>
<td><strong>12 Al</strong></td>
<td><strong>26.98</strong></td>
</tr>
<tr>
<td><strong>13 Si</strong></td>
<td><strong>28.09</strong></td>
<td><strong>14 P</strong></td>
<td><strong>30.98</strong></td>
<td><strong>15 S</strong></td>
<td><strong>32.07</strong></td>
<td><strong>16 Cl</strong></td>
<td><strong>35.45</strong></td>
<td><strong>17 Ar</strong></td>
<td><strong>39.95</strong></td>
<td><strong>18 K</strong></td>
<td><strong>39.10</strong></td>
</tr>
<tr>
<td><strong>19 Ca</strong></td>
<td><strong>40.08</strong></td>
<td><strong>20 Sc</strong></td>
<td><strong>44.96</strong></td>
<td><strong>21 Ti</strong></td>
<td><strong>47.87</strong></td>
<td><strong>22 V</strong></td>
<td><strong>50.94</strong></td>
<td><strong>23 Cr</strong></td>
<td><strong>52.00</strong></td>
<td><strong>24 Mn</strong></td>
<td><strong>54.94</strong></td>
</tr>
<tr>
<td><strong>25 Fe</strong></td>
<td><strong>55.85</strong></td>
<td><strong>26 Co</strong></td>
<td><strong>58.93</strong></td>
<td><strong>27 Ni</strong></td>
<td><strong>58.69</strong></td>
<td><strong>28 Cu</strong></td>
<td><strong>63.55</strong></td>
<td><strong>29 Zn</strong></td>
<td><strong>65.41</strong></td>
<td><strong>30 Ga</strong></td>
<td><strong>69.72</strong></td>
</tr>
<tr>
<td><strong>31 Ge</strong></td>
<td><strong>72.61</strong></td>
<td><strong>32 As</strong></td>
<td><strong>74.92</strong></td>
<td><strong>33 Se</strong></td>
<td><strong>78.96</strong></td>
<td><strong>34 Br</strong></td>
<td><strong>80.91</strong></td>
<td><strong>35 Kr</strong></td>
<td><strong>83.80</strong></td>
<td><strong>36 Rs</strong></td>
<td><strong>87.62</strong></td>
</tr>
<tr>
<td><strong>37 Ba</strong></td>
<td><strong>137.3</strong></td>
<td><strong>38 La</strong></td>
<td><strong>138.9</strong></td>
<td><strong>39 Hf</strong></td>
<td><strong>178.5</strong></td>
<td><strong>40 Ta</strong></td>
<td><strong>180.9</strong></td>
<td><strong>41 W</strong></td>
<td><strong>183.8</strong></td>
<td><strong>42 Re</strong></td>
<td><strong>186.2</strong></td>
</tr>
<tr>
<td><strong>43 Os</strong></td>
<td><strong>190.2</strong></td>
<td><strong>44 Ir</strong></td>
<td><strong>192.2</strong></td>
<td><strong>45 Pt</strong></td>
<td><strong>195.1</strong></td>
<td><strong>46 Au</strong></td>
<td><strong>197.0</strong></td>
<td><strong>47 Hg</strong></td>
<td><strong>200.6</strong></td>
<td><strong>48 Th</strong></td>
<td><strong>204.4</strong></td>
</tr>
<tr>
<td><strong>49 Pa</strong></td>
<td><strong>207.2</strong></td>
<td><strong>50 U</strong></td>
<td><strong>209.0</strong></td>
<td><strong>51 Np</strong></td>
<td><strong>237.1</strong></td>
<td><strong>52 Pu</strong></td>
<td><strong>244.1</strong></td>
<td><strong>53 Am</strong></td>
<td><strong>247.1</strong></td>
<td><strong>54 Cm</strong></td>
<td><strong>247.1</strong></td>
</tr>
<tr>
<td><strong>55 Bk</strong></td>
<td><strong>251.1</strong></td>
<td><strong>56 Cf</strong></td>
<td><strong>252.1</strong></td>
<td><strong>57 Es</strong></td>
<td><strong>252.1</strong></td>
<td><strong>58 Fm</strong></td>
<td><strong>257.1</strong></td>
<td><strong>59 Md</strong></td>
<td><strong>258.1</strong></td>
<td><strong>60 No</strong></td>
<td><strong>259.1</strong></td>
</tr>
<tr>
<td><strong>61 Lr</strong></td>
<td><strong>260.1</strong></td>
<td><strong>62 Hf</strong></td>
<td><strong>178.6</strong></td>
<td><strong>63 Ta</strong></td>
<td><strong>180.9</strong></td>
<td><strong>64 W</strong></td>
<td><strong>183.8</strong></td>
<td><strong>65 Re</strong></td>
<td><strong>186.2</strong></td>
<td><strong>66 Os</strong></td>
<td><strong>190.2</strong></td>
</tr>
<tr>
<td><strong>67 Ir</strong></td>
<td><strong>192.2</strong></td>
<td><strong>68 Pt</strong></td>
<td><strong>195.1</strong></td>
<td><strong>69 Au</strong></td>
<td><strong>197.0</strong></td>
<td><strong>70 Hg</strong></td>
<td><strong>200.6</strong></td>
<td><strong>71 Tl</strong></td>
<td><strong>204.4</strong></td>
<td><strong>72 Pb</strong></td>
<td><strong>207.2</strong></td>
</tr>
<tr>
<td><strong>73 Bi</strong></td>
<td><strong>209.0</strong></td>
<td><strong>74 Po</strong></td>
<td><strong>210.0</strong></td>
<td><strong>75 At</strong></td>
<td><strong>211.0</strong></td>
<td><strong>76 Rn</strong></td>
<td><strong>221.0</strong></td>
<td><strong>77 Fr</strong></td>
<td><strong>222.0</strong></td>
<td><strong>78 Ra</strong></td>
<td><strong>226.0</strong></td>
</tr>
<tr>
<td><strong>79 Ac</strong></td>
<td><strong>227.0</strong></td>
<td><strong>80 Th</strong></td>
<td><strong>232.0</strong></td>
<td><strong>81 Pa</strong></td>
<td><strong>231.0</strong></td>
<td><strong>82 U</strong></td>
<td><strong>238.0</strong></td>
<td><strong>83 Np</strong></td>
<td><strong>237.1</strong></td>
<td><strong>84 Pu</strong></td>
<td><strong>244.1</strong></td>
</tr>
<tr>
<td><strong>85 Am</strong></td>
<td><strong>243.1</strong></td>
<td><strong>86 Cm</strong></td>
<td><strong>247.1</strong></td>
<td><strong>87 Bk</strong></td>
<td><strong>247.1</strong></td>
<td><strong>88 Cf</strong></td>
<td><strong>251.1</strong></td>
<td><strong>89 Es</strong></td>
<td><strong>252.1</strong></td>
<td><strong>90 Fm</strong></td>
<td><strong>257.1</strong></td>
</tr>
<tr>
<td><strong>91 Md</strong></td>
<td><strong>258.1</strong></td>
<td><strong>92 No</strong></td>
<td><strong>259.1</strong></td>
<td><strong>93 Lr</strong></td>
<td><strong>260.1</strong></td>
<td><strong>94 Hf</strong></td>
<td><strong>178.6</strong></td>
<td><strong>95 Ta</strong></td>
<td><strong>180.9</strong></td>
<td><strong>96 W</strong></td>
<td><strong>183.8</strong></td>
</tr>
<tr>
<td><strong>97 Re</strong></td>
<td><strong>186.2</strong></td>
<td><strong>98 Os</strong></td>
<td><strong>190.2</strong></td>
<td><strong>99 Ir</strong></td>
<td><strong>192.2</strong></td>
<td><strong>100 Pt</strong></td>
<td><strong>195.1</strong></td>
<td><strong>101 Au</strong></td>
<td><strong>197.0</strong></td>
<td><strong>102 Hg</strong></td>
<td><strong>200.6</strong></td>
</tr>
<tr>
<td><strong>103 Tl</strong></td>
<td><strong>204.4</strong></td>
<td><strong>104 Pb</strong></td>
<td><strong>207.2</strong></td>
<td><strong>105 Bi</strong></td>
<td><strong>209.0</strong></td>
<td><strong>106 Po</strong></td>
<td><strong>210.0</strong></td>
<td><strong>107 At</strong></td>
<td><strong>211.0</strong></td>
<td><strong>108 Rn</strong></td>
<td><strong>222.0</strong></td>
</tr>
</tbody>
</table>

### Lanthanides

| 58 Ce | 140.1 |
| 59 Pr | 140.9 |
| 60 Nd | 144.2 |
| 61 Pm | (144.9) |
| 62 Sm | 150.4 |
| 63 Eu | 152.0 |
| 64 Gd | 157.3 |
| 65 Tb | 158.9 |
| 66 Dy | 162.5 |
| 67 Ho | 164.9 |
| 68 Er | 167.3 |
| 69 Tm | 168.9 |
| 70 Yb | 173.0 |
| 71 Lu | 174.0 |

### Actinides

| 89 Th | 232.0 |
| 90 Pa | 231.0 |
| 91 U | 238.0 |
| 92 Np | (237.1) |
| 93 Pu | (244.1) |
| 94 Am | (243.1) |
| 95 Cm | (247.1) |
| 96 Bk | (247.1) |
| 97 Cf | (251.1) |
| 98 Es | (252.1) |
| 99 Fm | (257.1) |
| 100 Md | (258.1) |
| 101 No | (259.1) |
| 102 Lr | (260.1) |