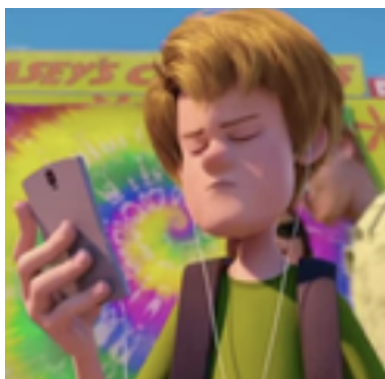


Theoretical Problems Solutions



MOCK ICHO 2021 **Chemistry Online Discord Server**

Pensive Insular and Scoob



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Instructions

- This theoretical exam booklet contains 22 pages.
- You may begin writing as soon as the **START** command is given.
- You have **5 hours** to complete the exam.
- All results and answers must be clearly written **in PEN in their respective designated areas** on the exam papers. Answers written outside the answer boxes will NOT be graded.
- You may use as much scratch paper as you want (due to the online format of this competition). Remember that nothing outside the designated areas will be graded.
- The periodic table is not part of this booklet; it is provided separately.
- Use only the pen and calculator provided.
- **This is the official English version** of the exam booklet
- The supervisor will announce a 30-minute warning before the **STOP** command.
- You must stop your work immediately when the **STOP** command is announced. Failure to stop writing within 30 seconds will lead to nullification of your theoretical exam.
- After the **STOP** command has been given, place your exam booklet back in your exam envelope and wait at your seat. The exam supervisor will come to collect the envelope.



Theoretical #1	1.	2.	3.	4.	5.	6.	7.	8.	9.	Total
13% of the total	1	2	3	1	3	3	4	3	3	23

Problem 1. Cool Chemistry

1. Calculate the standard change in internal energy and change in enthalpy for the vaporization of one mole of NKT-19.

$$\Delta U = \Delta A + \Delta(TS) = \Delta A + T\Delta S = -5100 + 298(140-20) = \mathbf{30.66 \text{ kJ/mol}}$$

$\Delta H = \Delta U + \Delta(PV)$, since the volume of the liquid is negligible:

$$\Delta H = \Delta U + RT\Delta n = 30660 + (8.314)(298)(1) = 33.1376 \approx \mathbf{33.14 \text{ kJ/mol}}$$

If you were to account for the volume of liquid, $V_l = 60 \cdot 10^{-3} / \rho = 0.01796 \text{ L}$

$$\Delta H = \Delta U + P(V_{\text{gas}} - V_{\text{liquid}}) = \Delta U + P(nRT/P - 0.044776) \cdot 0.1 \approx 33.14 \text{ kJ/mol}$$

Note: $\text{L} \cdot \text{bar} = 100 \text{ J} = 0.1 \text{ kJ}$

$$\Delta U^\circ = \mathbf{30.66 \text{ kJ/mol}}$$

$$\Delta H^\circ = \mathbf{33.14 \text{ kJ/mol}}$$

2. Calculate the boiling point of NKT-19 at $P_{\text{ext}} = 1 \text{ bar}$.

$$\Delta G = \Delta H - T\Delta S = 0 \text{ at } P = 1 \text{ bar.}$$

$$T = \Delta H / \Delta S = \mathbf{276.1 \text{ K}}$$

$$T_{\text{boil}} = \mathbf{276.1 \text{ K}}$$

3. What is the vapor pressure of the liquid?

Use the Clausius-Clapeyron equation. $\ln(P/1 \text{ bar}) = -\Delta H/R (1/270 - 1/276.1)$

$$P = \mathbf{0.7217 \text{ bar}}$$

$$P_{\text{vap}} = \mathbf{0.7217 \text{ bar}}$$

4. Which of the following should be true of a reversible process? (Choose one)

1. $P < P_{\text{ext}}$

$P = P_{\text{ext}}$ ← This is the answer

$P > P_{\text{ext}}$



5. The piston then expands isothermally and reversibly until all the liquid is vaporized, removing heat from the refrigerator. How much work is done by the expanding gas, and how much heat is absorbed?

$$w = RT\Delta n = \mathbf{2.245 \text{ kJ}} \quad (\Delta n = 0.9), \quad q \sim n \cdot \Delta H = 0.9 \cdot \Delta H = \mathbf{29.83 \text{ kJ}} \quad (\text{all or nothing})$$

$$w_{done} = \mathbf{2.020 \text{ kJ}}$$

$$q_{ads} = \mathbf{29.83 \text{ kJ}}$$

6. What is the vapor pressure of the coolant at T_H ?

Use the Clausius-Clapeyron equation. $\ln(P/1 \text{ bar}) = -\Delta H/R (1/330 - 1/276.1)$

$$\mathbf{P = 10.57 \text{ bar}}$$

Alternatively $\Delta G = \Delta H - T\Delta S = -6.426 \text{ kJ/mol}$, $\Delta G = -RT \ln K = -R(330) \ln K$

$$\mathbf{K = P_{vap} = 10.57 \text{ bar}}$$

$$\mathbf{P_{vap} = 10.57 \text{ bar}}$$

7. Calculate the work done during the compression step, and the temperature after compression.

The initial pressure is .7217 bar, and the initial volume is 31.81 L from our answer to part (3).

$$(.7217)(31.81)^{1.3} = (10.57)V^{1.3}$$

$$V = 4.2275 \text{ L}$$

$$T = PV/nR = \mathbf{537.5 \text{ K}}$$

At such a high temperature, $P_{vap} \gg \gg 10.57 \text{ bar}$.

We could integrate the adiabat, but this is hard, and Alec hates calculus, so it seems impossible (it's not actually that hard though but takes a long time so don't do it lol)

BUT WAIT! $\Delta U = q + w$, but $q = 0$, so we only need to find ΔU !

$$\Delta U = C_v \Delta T, \quad (C_v + R)/C_v = \gamma = 1.33$$

$$C_v = 24.94 \text{ J/K}, \quad \text{so } \Delta U = w = \mathbf{6.672 \text{ kJ}}$$

$$w_{done} = \mathbf{6.672 \text{ kJ}}$$

$$T_f = \mathbf{537.5 \text{ K}}$$



8. Finally, the gas must be cooled isobarically from **X** to **Y** before it begins condensing. Calculate the heat removed from the gas and work done on the gas during this step.

At $P = 10.57$ and $T = T_H = 330$ K, $V = 2.596$ L.

$$w = -P\Delta V = -(10.57)(2.596 - 4.2275) = \mathbf{1.724 \text{ kJ/mol}}$$

$$q = \Delta U - w = C_v(330 - 537.5) - w = \mathbf{-6.900 \text{ kJ/mol}}$$

$$q_{rem} = \mathbf{-6.900 \text{ kJ}}$$

$$w_{done} = \mathbf{1.724 \text{ kJ}}$$

9. Compute the refrigerator efficiencies of the NKT-19 refrigerator and that of a maximally efficient heat pump refrigerator operating between 270 K and 330 K.

The heat transfer is simply equal to $0.90 \Delta H = 29.83$ kJ

The work was found earlier to be 6.672 kJ.

Thus, efficiency = $29.83/6.672 = \mathbf{447\%}$!!!! This is why refrigerators (and heaters) are such powerful devices: they can move more heat than they use work.

Ideal efficiency = $1/(1 - T_C/T_H) = \mathbf{550\%}$.

$$\eta_{NKT-19} = \mathbf{447\%}$$

$$\eta_{Ideal} = \mathbf{550\%}$$



Theoretical #2	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	Total
15% of the total	6	2	2	2	1	1	2	1	1	2	3	6	9	38

Problem 2. Interesting Oxidation States of Copper

1. Determine the formula of **A**, and write the overall reaction for the formation of the copper (III) periodate complex **A** according to the procedure.

Ratio of Cu:I:O:H = 1:2:24:26

Leftover charge: $1(3)+2(7)+24(-2)+26(1) = -5$

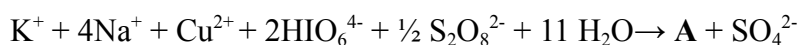
Excess mass: 131 g/mol

Possible counterions are K, Na \rightarrow 4Na, 1K

A = $\text{KNa}_4\text{Cu}(\text{HIO}_6)_2 \cdot 12\text{H}_2\text{O}$ or $\text{KNa}_4\text{Cu}(\text{IO}_4)_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ etc.

- 3 points for work
 - 1 point for finding correct ratio of Cu,I,O,H
 - 1 point for finding total mass of counterions
 - 1 point for finding corresponding charge
- 1 point for final formula

Reaction



or



- 2 points for a correct reaction
- All or nothing

No penalty for:

- Multiplying by 2,
- Using IO_4^- and OH^- instead of HIO_4^-
- Using any form of orthoperiodic acid *except* H_5IO_6 .



2. Draw the structure of the copper containing ions in the complex and draw a d-orbital splitting diagram for Cu (III) in its coordination environment. Fill in the electrons and label the orbitals.

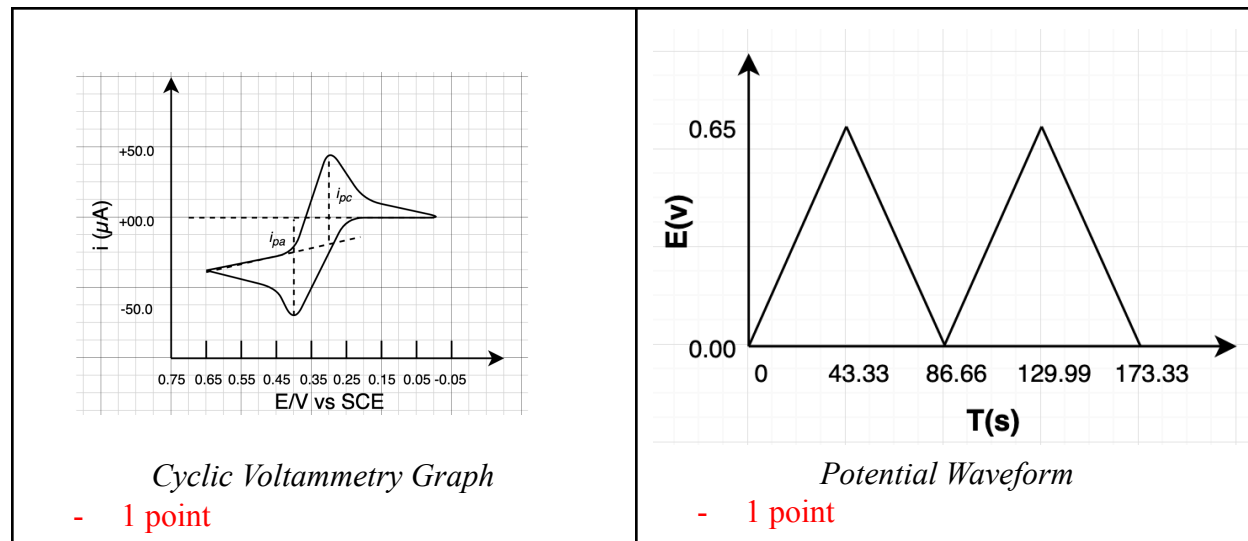
<i>Structure</i>	<i>Splitting Diagram</i>
- 1 point	- 1 point

3. Draw and fill the crystal field of A if (a) H_2O is a stronger field ligand than periodate and if (b) H_2O is weaker. Be sure to label each orbital.

<i>(a) stronger</i>	<i>(b) weaker</i>
(either accepted)	(either accepted)
- 1 point	- 1 point



4. Draw approximately the shape of the cyclic voltammetry curve (i vs E) and the potential waveform (E vs time) for the $\text{pH} = 13.3$ trial. Label the axes of the potential waveform as you see fit.



5. Based on the experiment above which of the following can the researchers conclude?

(Check all that apply)

- The reaction is reversible
- The reaction is quasi-reversible ← This answer
- The reaction is irreversible
- The reaction becomes more reversible at high pH ← This answer
- The reaction becomes less reversible at high pH

- 0.5 points for each correct answer
- 0.5 point penalty for each incorrect answer

6. Which of the following best accounts for your answer to question 5? (Check only one)

- The reaction produces a Cu^{2+} periodate complex which is more stable than other possible products
- The reaction produces $\text{Cu}(\text{OH})_2$ precipitate which is more stable than other possible products
- The reaction produces a Cu^{2+} periodate complex which is more stable in acidic conditions and competes with the precipitation of $\text{Cu}(\text{OH})_2$ which is favorable at highly basic pH
- The reaction produces a Cu^{2+} periodate complex which is more stable in basic conditions and competes with the precipitation of $\text{Cu}(\text{OH})_2$ which is favorable at intermediate high pH . ← This answer

- 1 points for correct answer
- 1 point penalty for each incorrect answer



7. Construct a mathematical equation for the calibration curve.

Perform a linear regression.

$$C_0 = 0.1032 i_{pa} - 0.2593, r^2 = 1.000$$

or

$$i_{pa} = 9.690C_0 + 2.513$$

(This plot is linear as we were told in the preceding paragraph. For more details see Randles-Sevcik equation)

- 2 points for a correct linear equation (either acceptable)

8. Determine the concentration of copper (III) periodate in the sample.

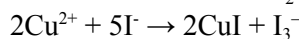
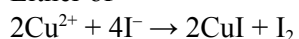
Plug into formula.

$$C_{Cu} = 4.729 \text{ mM}$$

- 1 points for correct answer

9. Write the balanced equation for the reaction of Cu^{2+} and I^- .

Either of



- 1 points for correct answer
 - Fractional coefficients acceptable
 - I_3^- acceptable for this equation

10. Calculate standard reduction potentials of Cu^{2+} and I_2 with respect to the SCE.

Simply add the potential of the reverse SCE equation, i.e. subtract 0.25.

$$E^\circ(\text{Cu}) = -0.1 \text{ V}, E^\circ(\text{I}_2) = 0.29 \text{ V}$$

$$E(\text{Cu}^{2+})/\text{SCE} = -0.1 \text{ V}$$

$$E(\text{I}_2)/\text{SCE} = 0.29 \text{ V}$$

- 1 points for correct answer
- Each is all or nothing



11. Calculate the voltage read by the indicator electrode in the beaker with 30 mmol added KI.

Overall reaction: $\text{Cu}^{2+} + 2\text{I}^- \rightarrow \text{CuI} + \frac{1}{2} \text{I}_2$

We use the simplified reaction $\text{Cu}^{2+} + \text{I}^- \rightarrow \text{Cu}^+ + \frac{1}{2} \text{I}_2$
has $E^\circ = -0.39\text{V}$, so $K = 2.529 \times 10^{-7}$, K/K_{sp} is a huge number!

Thus, it is not hard to see that the reaction goes to completion.

Thus, past the endpoint the dominant species are I_2 and I^- , with concentrations of 5 mM and 10 mM. These can be plugged directly into the Nernst equation.

$E = E^\circ(\text{I}_2) - \frac{RT}{nF} \ln\left(\frac{[\text{I}^-]}{[\text{I}_2]^{0.5}}\right) = 0.5902 \rightarrow \mathbf{0.340 \text{ V}}$ vs. SCE (Note that if the student forgets to give with respect to SCE, only one point will be deducted from problems 11, 12, and 13.)

$E_{30} = \mathbf{0.340 \text{ V}}$

- 2 points for setup
 - 1 point for determining $[\text{I}^-] = C_1 - 2C_{\text{Cu}}$
 - 1 point for determining $[\text{I}_2] = 0.5 C_{\text{Cu}}$
- 1 point for final answer
- Each is all or nothing



12. Calculate the voltage read by the indicator electrode in the beaker with 10 mmol added KI.

This is before the equivalence point. Since the reaction goes to completion, $[I_2]$ can be considered to be ≈ 2.5 mM and $[Cu^{2+}] \approx 5$ mM.

$$[I_2]^{0.5}[Cu^+]/([I^-][Cu^{2+}]) = 2.529E-7, \text{ hence } [Cu^+]/[I^-] = 2.529E-8$$

$$\text{Since } [Cu^+][I^-] = K_{sp} = 1.1E-16, [I^-]^2 = 4.34955E-9$$

$$[I^-] = 6.59511E-5 \text{ M}$$

$$E = E^\circ(I_2) - RT/nF \ln([I^-]/[I_2]^{0.5}) = \mathbf{0.460 \text{ V}} \text{ vs. SCE}$$

$$E_{10} = \mathbf{0.460 \text{ V}}$$

- 5 points for setup
 - 1 point for assuming $[I_2] = 2.5$ mM
 - 1 point for assuming $[Cu^{2+}] = 5$ mM
 - 1 point for setting up a first equation with Cu^+ and I^- (i.e. K_{sp})
 - 1 point for setting up a second equation with Cu^+ and I^-
 - 1 point for setting up nernst
- 1 point for final answer
- If $[I^-] = [Cu^+]$ is assumed
 - If computation is done correctly ($E = 0.69 \text{ V}$), 2 points
 - If computation is incorrect max score is 1 point
- Each is all or nothing



13. Calculate the voltage read by the indicator electrode in the beaker with 20 mmol added KI.

Again, since the reaction goes to completion, assume $[I_2] = 5 \text{ mM}$.

There is a bunch of CuI, and we don't know exactly how much there is, so mass balance is useless. However, we can still use charge balance. The NO_3^- and K^+ exactly cancel out, so we have the following charge balance:

$$[I^-] = [Cu^+] + 2[Cu^{2+}]$$

$$[Cu^+] = K_{sp}/[I^-]$$

$$[Cu^{2+}] = [I_2]^{0.5}[Cu^+]/[I^-]/2.529E-7 = 3.0759E-11/[I^-]^2$$

Solve:

$$x = K_{sp}/x + 2*3.0759E-11/x^2, \text{ assume the } K_{sp}/x \text{ term is negligible.}$$

$$x = (2*3.0759E-11)^{1/3}$$

$$= 3.947E-4M \ll [I_2] \text{ so our assumption worked.}$$

$$E = E^\circ(I_2) - RT/nF \ln([I^-]/[I_2]^{0.5}) = \mathbf{0.423 \text{ V}}$$

$$E_{20} = \mathbf{0.423 \text{ V}}$$

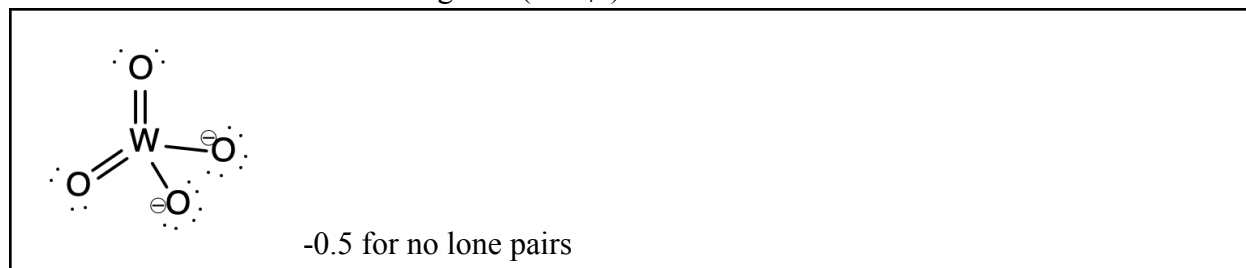
- 8 points for setup
 - 1 point for assuming $[I_2] = 5 \text{ mM}$
 - 2 points for charge balance $[I^-] = [Cu^+] + 2[Cu^{2+}]$
 - 1 point for using $[Cu^{2+}] = [I_2]^{0.5}[Cu^+]/[I^-]/2.529E-7$
 - 1 point for $[Cu^+] = K_{sp}/[I^-]$
 - 2 point for setting up equation and computing $[I^-]$ with method of choice
 - 1 point for Nernst Equation
- 1 point for final answer
- 0 points overall if $[I^-] = [Cu^+]$ is assumed
- Each is all or nothing



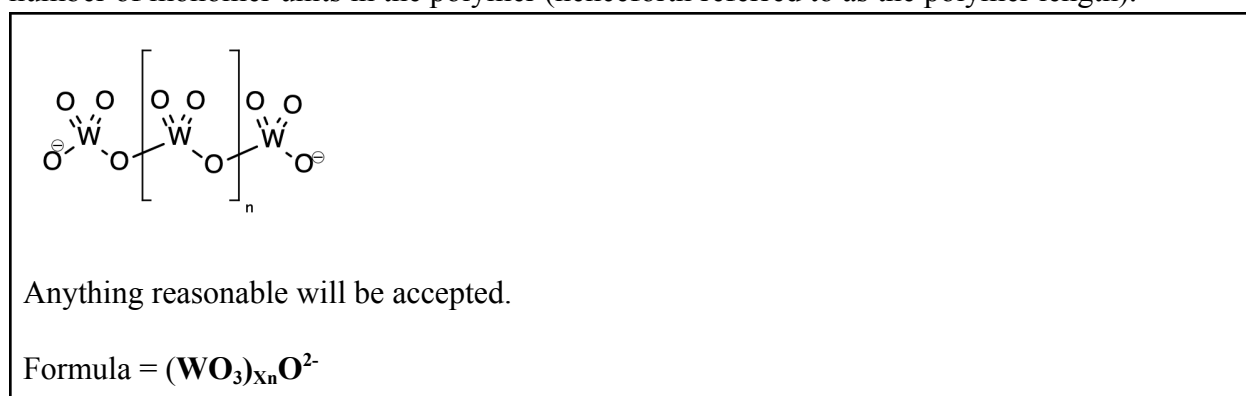
Theoretical #3	1.	2.	3.	4.	5.	6.	7.	8.	Total
8% of the total	1	2	3	5	1	7	8	2	29

Problem 3. Wolfram, 钨, вольфрама, التنغستن

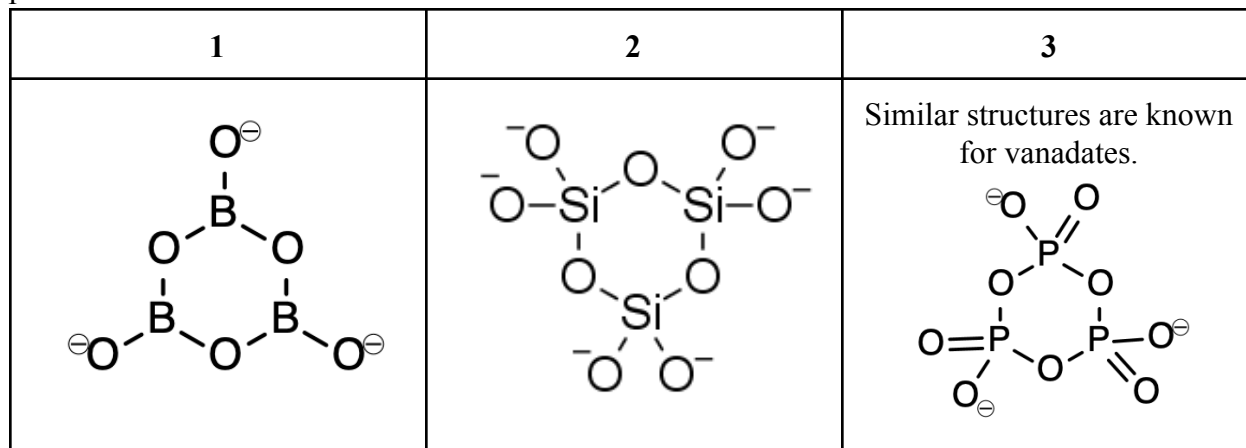
1. Draw the lewis structure of tungstate (WO_4^{2-}).



2. Draw the structure of a tungstate polymer, and write a generic formula in terms of X_n , the number of monomer units in the polymer (henceforth referred to as the polymer length).



3. Many cyclic oxyanions are known. Draw 3 examples, each based on a different group of the periodic table.





4. Calculate the value of the equilibrium constant K_{eq} .

General formula of polymer is $[(WO_3)_xO]^{2-}$

$$X_n = (2200-16)/(183.81+16*3) = 9.4219. \text{ 1pt}$$

The number of polymer molecules = $100 \text{ mmol}/X_n = 10.614 \text{ mmol}$. 1pt

This corresponds to 21.228 mmol of terminal groups (since each polymer molecule has two terminal groups). Note that we start off with 200 mmol of terminal groups.

This means that $200-21.228 = 178.772 \text{ mmol}$ of terminal groups have reacted to form linkages, so there are $178.772/2 = 89.386 \text{ mmol}$ of linkages (each linkage requires two terminal groups).

1pt

And through this line of thinking, we get the mass balance:

$$n(\text{terminal}) + 2n(\text{linkage}) = n(\text{terminal})_i = 200 \text{ mmol}$$

$$K_{eq} = [\text{Linkages}]/([\text{Terminal}]^2[\text{H}^+]^2) = 1.984 \cdot 10^{10} \text{ 2pt}$$

We can also apply Carothers equation to get the same answer once we have X_n :

$X_n = 1/(1-p)$ where p is the degree of conversion which is defined in this case as the number of ends that have reacted to form linkages divided by the initial total number of linkages.

$$X_n = 9.4219 = 1/(1-p) \rightarrow p = 0.8918$$

$$p = (n_{i, \text{terminal}} - n_{\text{terminal}})/n_{i, \text{terminal}} = (200 - n(\text{terminal}))/200 = 0.8918$$

$$n(\text{terminal}) = 21.227 \rightarrow [\text{terminal}] = 0.021227 \text{ M}$$

$$\text{from mass balance, } [\text{linkages}] = 0.0893 \text{ M}$$

$$K_{eq} = [\text{Linkages}]/([\text{Terminal}]^2[\text{H}^+]^2) = 1.984 \cdot 10^{10}$$

$$K_{eq} = \mathbf{1.984 \cdot 10^{10}}$$

5. Pick the statements that are true regarding reaction (1). (Check all that apply)

$\Delta H_{298} > 0$

$\Delta H_{298} < 0$

$\Delta G_{298} > 0$

$\Delta G_{298} < 0$



6. Compute the statistical average molecular mass of tungstate species in this new system.

Note that the overall initial concentration of linkages for 100 mmol added to 1 L of water is 0.1 M. We can thus set up the mass balance:

$$[\text{terminal}] + 2[\text{linkage}] = 2[\text{terminal}]_i = 0.2 \text{ M}$$

From K_{eq}

$$[\text{linkage}] = K_{\text{eq}}[\text{H}^+]^2[\text{terminal}]^2 = 12 [\text{terminal}]^2$$

Plugging this into mass balance, we get a quadratic which we can solve

$$24x^2 + x - 0.2 = 0, \text{ where } [\text{terminal}] = x$$

$$[\text{terminal}] = 0.07280 \text{ M} \rightarrow [\text{linkage}] = 0.0636 \text{ M}$$

$$X_n = C_i(\text{WO}_4^{2-})/[\text{polymers}], [\text{polymers}] = [\text{end}]/2, X_n = 2.74$$

$$\text{Thus the final molecular mass is } X_n(183.8 + 3 \cdot 16) + 16 = \mathbf{652.81 \text{ g/mol}}$$

I'll demonstrate the solution using Carothers equation as well just for completeness

Once we have $[\text{terminal}]$ from the above methods, we can apply Carothers:

$X_n = 1/(1-p)$ where p is the degree of conversion which is defined in this case as the number of ends that have reacted to form linkages divided by the initial total number of linkages.

$$\text{Thus } p = (n_{i, \text{terminal}} - n_{\text{terminal}})/n_{i, \text{terminal}} = (200 - 72.80)/(200) = 0.636$$

$$\text{And so, } X_n = 1/(1-0.636) = 2.74 \rightarrow \text{MW}_{\text{avg}} = \mathbf{652.81 \text{ g/mol}}$$



7. Determine the weight % of Tungsten in the alloy sample and write balanced chemical equations for steps (1)-(5).

The white precipitate is WO_3 . 8.3 mg corresponds to $\approx 36 \mu\text{mol}$ of W in the 20 ml aliquot. Scaling up from 15 ml to 20 ml aliquot, $n(\text{Cr}^{\text{VI}}) = 2 * 20/15 * 0.000765 * 0.01723 = 35.15 \mu\text{mol}$.

The 5 ml aliquot contains the same precipitate as before. Thus the ion exchange column removes nickel, but preserves W^{VI} .

Since there is a 1:1 redox ratio of W to Cr, lead must reduce W^{VI} to W^{III} . (Using the approximate error bounds for WO_3 precipitate given confirms that the reduction step produces W^{III} and not W^{IV} or W^{II} etc.)

We obtain $35.15 \mu\text{mol}$ of W in the 20 ml aliquot, so there is $70.30 \mu\text{mol}$ in the sample.

This corresponds to 12.92 mg of W, i.e. **4.74%**.

1)	$6\text{NO}_3^- + \text{W} + 6\text{H}^+ \rightarrow 6\text{NO}_2 + \text{WO}_3 + 3\text{H}_2\text{O}$ ($\frac{1}{2}$ credit for forming NO)
2)	$\text{WO}_3 + 2\text{OH}^- \rightarrow \text{WO}_4^{2-} + \text{H}_2\text{O}$ (HWO_4^- is also acceptable)
3)	$\text{WO}_4^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{WO}_3$
4)	$3\text{Pb} + 2\text{WO}_4^{2-} + 6\text{Cl}^- + 16\text{H}^+ \rightarrow 2\text{W}^{3+} + 3\text{PbCl}_2 + 8\text{H}_2\text{O}$ (NH_4^+ is also fine, $\frac{1}{2}$ if Pb^{2+})
5)	$2\text{W}^{3+} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{W}_2\text{O}_7^{2-} + 2\text{Cr}^{3+}$ (either tungstate or ditungstate is fine)

8. Propose a reason why the titration procedure is less accurate without ammonium chloride.

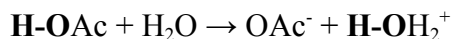
Ammonium chloride is both an acid and a source of chloride. The ammonium is a source of acid, which makes dichromate a stronger reducing agent, as well as producing H_2 . The chloride precipitates the Pb^{2+} formed, preventing it from interfering with the titration with tungsten (if for example it was oxidized).



Theoretical #4	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Total
16% of the total	1	2	2	7	2	2	2	3	2	4	2	6	35

Problem 4. Quantum Kinetics

1. Write down the acid-base reaction between HOAc and H₂O. Draw structures indicating the relevant bonds being broken and formed.



- 1 point
- All or nothing

2. Calculate, in amu, the reduced mass of the O-H bond and the O-D bond respectively. You should use integer molar masses: $m(\text{H}) = 1$ amu, $m(\text{O}) = 16$ amu.

$$\mu(\text{O-H}) = (1 \cdot 16)/(1+16) = \mathbf{.94118 \text{ amu}}, \quad \mu(\text{O-D}) = 2 \cdot 16/(2+16) = \mathbf{1.7778 \text{ amu}}$$

$$\mu(\text{O-H}) = \mathbf{.94118 \text{ amu}}$$

$$\mu(\text{O-D}) = \mathbf{1.7778 \text{ amu}}$$

- 1 point each
- Each is all or nothing

3. Calculate the stretching frequency of the O-D bond in DOAc and D₃O⁺, respectively.

$\tilde{\nu}$ is proportional to $\sqrt{1/\mu}$, and we may assume force constants don't change with isotopic substitution.

$$\tilde{\nu}(\text{O-D, DOAc}) = \tilde{\nu}(\text{O-H, HOAc}) \cdot \sqrt{.94118/1.7778} = \mathbf{2037.3 \text{ cm}^{-1}}$$

$$\tilde{\nu}(\text{O-D, D}_3\text{O}^+) = \tilde{\nu}(\text{O-H, H}_3\text{O}^+) \cdot \sqrt{.94118/1.7778} = \mathbf{2182.8 \text{ cm}^{-1}}$$

$$\tilde{\nu}\text{O-D(D}_3\text{O}^+) = \mathbf{2182.8 \text{ cm}^{-1}}$$

$$\tilde{\nu}\text{O-H (DOAc)} = \mathbf{2037.3 \text{ cm}^{-1}}$$

- 1 point each
- Each is all or nothing



4. Compute the approximate pK_a of DOAc in D_2O using the harmonic oscillator model.

$$\Delta G_H = -RT \ln K_{eq} = -RT / \log(e) * \log K_{eq} = RT / \log(e) * pK_a = \mathbf{27.0408 \text{ kJ/mol}}$$

The difference in Gibbs free change is equal to the change in ZPE (this can be proved using the general approach of description for the other solution presented below this one)

$$\Delta \Delta \tilde{\nu} = [\tilde{\nu}(\text{O-D}, D_3O^+) - \tilde{\nu}(\text{O-D}, \text{DOAc})] - [\tilde{\nu}(\text{O-H}, H_3O^+) - \tilde{\nu}(\text{O-H}, \text{HOAc})] = -54.5 \text{ cm}^{-1}$$

$$\Delta \Delta ZPE = \frac{1}{2} hc N_a * \Delta \Delta \tilde{\nu} = -326.197 \text{ J/mol} = \Delta \Delta G$$

$$\Delta G_D = \Delta G_H + \Delta \Delta G = 26.7146 \text{ kJ/mol}$$

$$pK_a = \Delta G * \log(e) / RT = \mathbf{4.6828}$$

Another acceptable (and more intuitive/less handwavey!) solution is to just apply $K = k_f/k_r$, and $K_H/K_D = KIE_f/KIE_r$. You can't necessarily assume that the transition states of the protium and deuterium reactions are the same, but this ends up not being an issue since the TS terms in $E_a = TS - ZPE$ parts of KIE_f cancel with the TS terms in the $E_a = TS - ZPE$ parts of KIE_r ! (all praise exponentials for having nice rules)

$$pK_a(\text{DOAc}) = \mathbf{4.6828}$$

- 7 points total
- 2 points if $\Delta G = \Delta ZPE$ is used (incorrect)
- 5 points for correct setup but incorrect computation

5. Determine the rate law and rate constant for this reaction.

First order in $[H]^+$, first order in $[K]$, zeroth order in $[Br_2]$.

$$\text{Rate} = k[H^+][K], k = \mathbf{1.1527 * 10^2 \text{ M}^{-1} \text{h}^{-1}}$$

$$R = k[H^+][K]$$

$$k = \mathbf{1.1527 * 10^2 \text{ M}^{-1} \text{h}^{-1}}$$

- 1 point each
- Each is all or nothing



6. Using the steady state approximation, derive the rate law for the proposed mechanism. Under what conditions does it match the experimental rate law? What step of the mechanism do you think is rate-limiting? Justify your answers.

$$\text{Rate} = k_3[\text{Br}_2][\text{enol}] = k_2[\text{HK}^+]$$

$$k_1[\text{K}][\text{H}^+] = k_2[\text{HK}^+] + k_{-1}[\text{HK}^+]$$

$$[\text{HK}^+] = k_1[\text{H}^+][\text{K}]/(k_2+k_{-1})$$

Rate = $k_2k_1[\text{H}^+][\text{K}]/(k_2+k_{-1})$. This is actually valid for all values of k_2 , k_1 , and k_{-1} .

BUT WAIT!

A proton transfer should be very rapid (most proton transfers are diffusion limited), whereas the second step of the mechanism involves breaking a C-H bond. Thus it is likely that $k_2 \lll k_1$ or k_{-1} .

$$R = k_2k_1[\text{H}^+][\text{K}]/(k_2+k_{-1})$$

The rate law matches under **all conditions**

Rate Limiting Step: **2nd step**

Justification: A proton transfer should be very rapid (most proton transfers are diffusion limited), whereas the second step of the mechanism involves breaking a C-H bond. Thus it is likely that $k_2 \lll k_1$ or k_{-1} .

- 1 point for rate law
- 1 point for justification
- All or nothing

**Points should be awarded for leaving the k_2 on the denominator, however the logic given above is needed to solve the remaining parts.*

7. K has a pK_b of approximately 21. Estimate the value of the rate constant of the rate limiting step.

$$k_{\text{eff}} = k_2k_1/(k_2+k_{-1}). \text{ Since } k_2 \lll k_{-1}, \text{ this becomes } k_2(k_1/k_{-1}) = k_2K_{\text{eq}}$$

$$\text{pK}_{\text{eq}} = \text{pK}_b - \text{pK}_w = 7. \text{ Thus, } k_2 = k_{\text{eff}}/10^{-7} = 1.1527 \cdot 10^9 \text{ M}^{-1}\text{h}^{-1}$$

$$k_{\text{rds}} = 1.1527 \cdot 10^9 \text{ M}^{-1}\text{h}^{-1}$$

- 1 point for setup
- 1 point for correct computation
- 2 points total



- 1 point only if pK_b is used instead of pK_a, producing $k = 1.1527 \cdot 10^{23}$



8. The reaction $K + H^+ \rightarrow HK^+$ has $\Delta H \sim 30$ kJ/mol. If the rate of bromination doubles at 308 K, maintaining the same buffer pH, estimate the activation energy and pre-exponential factor of the rate limiting step.

$$k_{\text{eff}}(308 \text{ K})/k_{\text{eff}}(298 \text{ K}) = k_2(308 \text{ K}) \cdot K_{\text{eq}}(308 \text{ K})/[k_2(298 \text{ K}) \cdot K_{\text{eq}}(298 \text{ K})]$$

$$\ln(K_{\text{eq}}(308 \text{ K})/K_{\text{eq}}(298 \text{ K})) = -\Delta H/R \cdot (1/308 - 1/298) = .393137, K_{\text{eq}}(308 \text{ K})/K_{\text{eq}}(298 \text{ K}) = 1.48162$$

$$\text{Hence } k_2(308 \text{ K})/k_2(298 \text{ K}) = 1.34987$$

$$\ln(k_2(308 \text{ K})/k_2(298 \text{ K})) = -E_a/R \cdot (1/308 - 1/298)$$

$$E_a = \mathbf{22.894 \text{ kJ/mol}}, k_2 = Ae^{(-E_a/RT)} = 1.1527 \cdot 10^9 \text{ M}^{-1}\text{h}^{-1} \text{ at } T = 298$$

$$A = \mathbf{1.188 \cdot 10^{13}}$$

$$E_a = \mathbf{22.894 \text{ kJ/mol}}$$

$$A = \mathbf{1.188 \cdot 10^9}$$

- 1 point for setup for E_a
- 1 point for E_a value
- 1 point for A
 - ECF if $k = 1.1527 \cdot 10^{23}$ is used, producing $A = 1.188 \cdot 10^{27}$
- Each is all or nothing

9. Calculate initial rate of bromination in H_2O solution containing 1M HOAc, 0.1M NaOAc, 0.001M K, and 0.001M Br_2 .

$$\text{pH} = \text{p}K_a + \log(.1/10) = 3.74, [\text{H}^+] = 1.8197 \cdot 10^{-4}$$

$$\text{Rate} = k_{\text{eff}}[\text{H}^+][\text{K}] = \mathbf{2.098 \cdot 10^{-5} \text{ M/h}}$$

- 1 point each for setup and final answer
- Each is all or nothing



10. Calculate initial rate of bromination in a D₂O solution containing 1M DOAc, 0.1M NaOAc, 0.001M K-D, and 0.001M Br₂. $\tilde{\nu}(\text{C-H}) = 2950 \text{ cm}^{-1}$.

$$\text{pH} = \text{pK}_a + \log(.1/10) = 3.6828, [\text{D}^+] = 2.07587 \cdot 10^{-4}$$

$$\tilde{\nu}(\text{C-D}) = \tilde{\nu}(\text{C-H}) \cdot \sqrt{.94118/1.7778} = 2146.4$$

Assume $-\Delta E_a$ is equal to change in ZPE

$$\Delta E_a = -\frac{1}{2} hc \cdot N_a \Delta \tilde{\nu} = 4.810 \text{ kJ/mol}$$

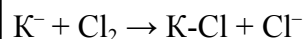
$$k_D = k_H \cdot k_D/k_H = 1.1527 \cdot 10^9 \cdot e^{(-4810/RT)} = 1.654 \cdot 10^8$$

$$\text{Rate} = k_D \cdot K_{\text{eq}}[\text{D}^+][\text{K-D}] = 3.434 \cdot 10^{-6} \text{ M/h}$$

$$R = 3.434 \cdot 10^{-6} \text{ M/h}$$

- 3 points for setup (numerical results can be wrong as long as set up correct)
 - 1 point for computation of $[\text{D}^+]$
 - 1 point for computation of $\tilde{\nu}(\text{C-D})$
 - 1 point for computation of E_a
- 1 point for final answer
- Each is all or nothing

11. Write the mechanism for this reaction. Note that the step involving Cl₂ is rate limiting.



- 2 points total
- All or nothing



12. Calculate the concentrations of all isotopic variants of K and K-Cl³⁵/K-Cl³⁷ after 3 hours, ignoring species of negligible concentration.

The formation of the enolate is not the rate determining step, and both are treated as having the same pKa, so K and K-D behave kinetically the same in this scenario!

We can express the relative amounts of K-Cl³⁵ and K-Cl³⁷ that form according to the relative rates:

$$[\text{K-Cl}^{35}]/[\text{K-Cl}^{37}] = (1 + 0.5 \cdot 1/1.07)/(0.5 \cdot 1/1.07 + 1/1.14) = 1.0913$$

$t_{1/2} = 3400 \cdot 5 = 17000$ seconds in these conditions. Note this half life accounts for the presence of isotopically mixed Cl₂. Thus after 3 hours, $3 \cdot 3600/17000 = 0.6352$ half lives have passed.

From half life

$$[\text{K-Cl}^x]_{\text{tot}} = (1 - 0.5^{0.6352}) \cdot 0.002 \text{ M} = 7.12 \cdot 10^{-4} \text{ M}$$

$$[\text{K-Cl}^{35}] = 1.0913/(1.0913+1) \cdot [\text{K-Cl}^x]_{\text{tot}} = 3.71 \cdot 10^{-4} = [\text{K-Cl}^{35}]$$

$$[\text{K-Cl}^{37}] = 1/(1.0913+1) \cdot [\text{K-Cl}^x]_{\text{tot}} = 3.405 \cdot 10^{-4} = [\text{K-Cl}^{37}]$$

Returning to the [K-D] and [K-H] species:

Since they are both treated as having the same pKa, and being much faster than the rate determining attack on Cl₂ (i.e. a fast equilibrium), we can assume that they equilibrate with water quickly and adopt the general isotopic ratios of natural water (2000:1).

$$[\text{K-H}] + [\text{K-D}] = 0.5^{0.6352} \cdot 0.002 \text{ M} = 1.28 \cdot 10^{-3} \text{ M}$$

$$[\text{K-D}] = 6.43 \cdot 10^{-7} \text{ M}$$

$$[\text{K-H}] = 1.28 \cdot 10^{-3} \text{ M}$$

$$[\text{K-Cl}^{35}] = 3.71 \cdot 10^{-4}$$

$$[\text{K-H}] = 1.28 \cdot 10^{-3} \text{ M}$$

$$[\text{K-Cl}^{37}] = 3.41 \cdot 10^{-4}$$

$$[\text{K-D}] = 6.43 \cdot 10^{-7} \text{ M (grade leniently here)}$$

- 4 points for correct setup
 - 1 point for $[\text{K-Cl}^{35}]/[\text{K-Cl}^{37}]$
 - 1 point for $[\text{K-Cl}^x]_{\text{tot}}$ from half life
 - 1 point for set up of computation of $[\text{K-Cl}^{35}]$
 - 1 point for observation that [K-H], [K-D] adopt isotopic ratios of natural water
 - (can be taken implicitly)
- 0.5 points for each final answer
- Each is all or nothing



Theoretical #4	1.	2.	3.	4.	5.	6.	7.	8.	9.	Total
16% of the total	14	1	2	3	22	2	4	2	10	60

Problem 5. Three in One

1. Give the structures of compounds A-G.

<p>A</p>	<p>B</p>
<p>C</p>	<p>D</p>
<p>E</p>	<p>F</p>
<p>G</p>	<p>Use this area if you made a mistake, indicate the letter <i>clearly</i>.</p>

2. What is the primary purpose of HNO_3 in step **A** \rightarrow **B**:

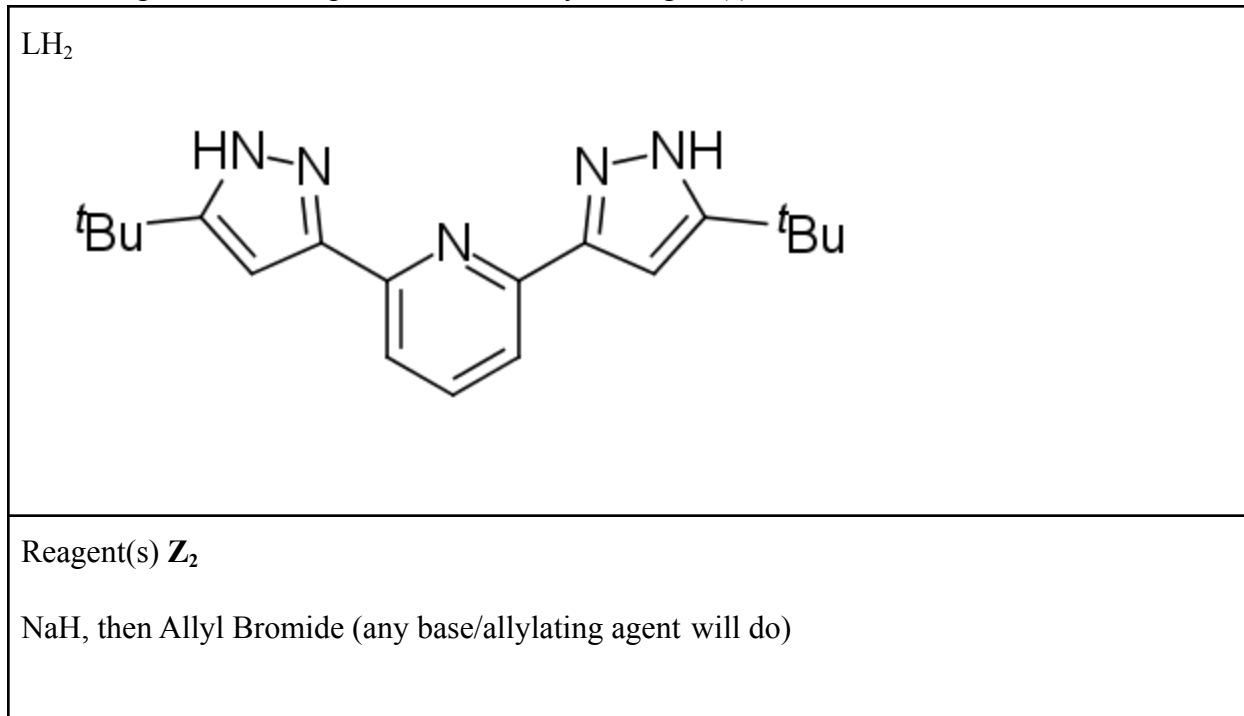
<input type="checkbox"/> Oxidant	<input type="checkbox"/> Nitration Reagent	<input type="checkbox"/> Acid Catalyst	<input type="checkbox"/> Reductant
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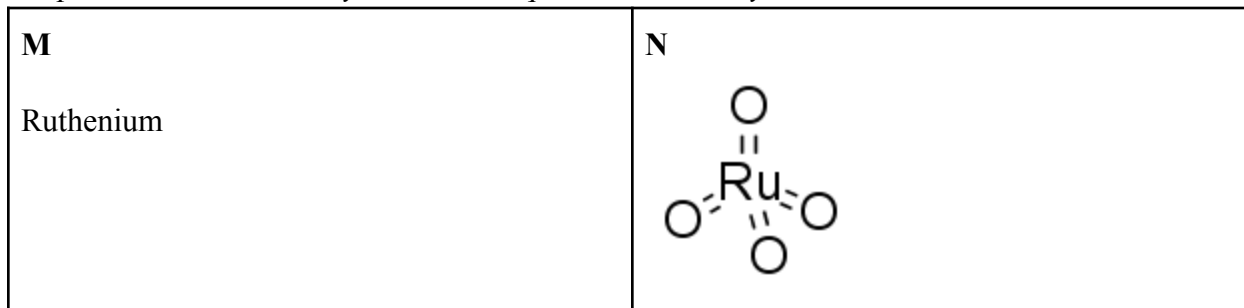
3. Reagent Z_1 is made by reaction of BH_3 in THF with cycloocta-1,5-diene. Draw its structure.



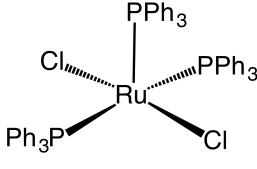
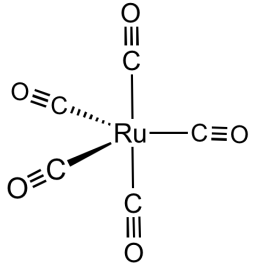
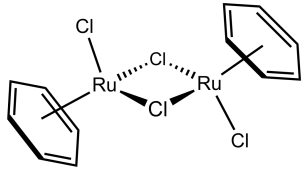
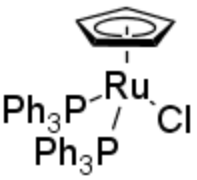
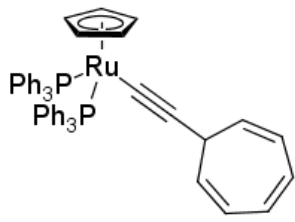
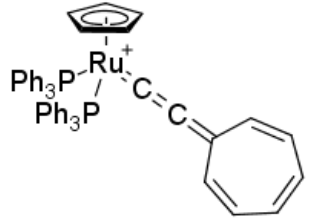
4. Draw ligand LH_2 , and provide the identity of reagent(s) Z_2 .



5. Draw structures of the compounds in the scheme, and identify metal M . Note: Some of the compounds are ionic, and you are not required to draw any counterions that do not contain M .





<p>O</p> <p>$[\text{NH}_4]_3[\text{RuCl}_6]$, RuCl_6^{3-} is octahedral</p>	<p>P</p> <p>RuCl_3</p>
<p>Q</p>  <p>trig. Bipyr. also accepted</p>	<p>R</p>  <p>must be trig. bipyr!</p>
<p>S</p> 	<p>T</p> <p>$[\text{Ru}(\text{Bipy})_3]\text{Cl}_2$</p>
<p>U</p> 	<p>V</p> 
<p>W</p>  <p>Resonance structures are fine</p>	<p>Use this area if you made a mistake, indicate the letter <i>clearly</i>.</p>

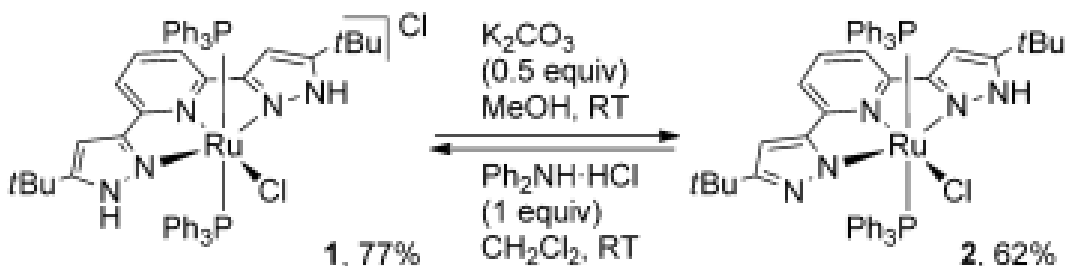


6. What is the phosphorus-containing byproduct of the reaction $\mathbf{P} \rightarrow \mathbf{Q}$? Note that this reaction is usually done in the presence of water.

Triphenylphosphine oxide

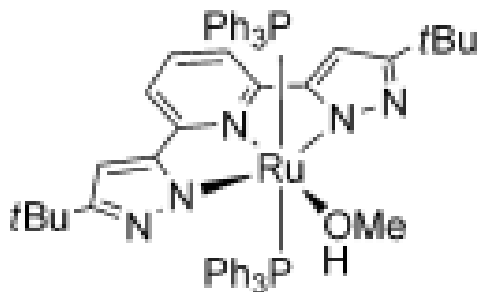
7. Reaction of \mathbf{Q} with ligand \mathbf{LH}_2 gives cationic octahedral complex \mathbf{I} (contains 1 chlorine ligand), which when treated with a suitable reagent gives neutral complex \mathbf{II} . Draw the structures of \mathbf{I} and \mathbf{II} (feel free to abbreviate the structure of \mathbf{L} as something similar to $\text{RN-N}\sim\text{N}\sim\text{N-NR}$, but draw any hydrogens bonded to nitrogen!) and propose a suitable reagent.

I and II



8. Both \mathbf{I} and \mathbf{II} react with MeOH in the presence of $\text{KN}(\text{SiMe}_3)_2$ to give \mathbf{III} . Draw the structure of \mathbf{III} ; again feel free to abbreviate the structure of \mathbf{L} .

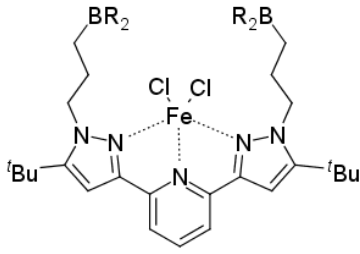
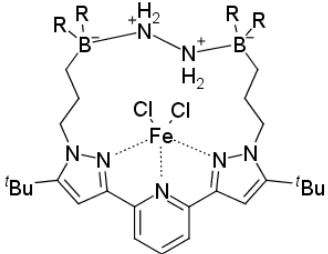
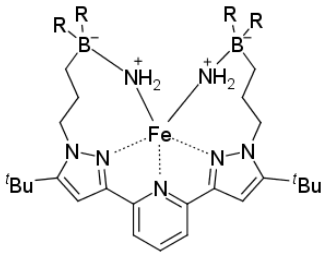
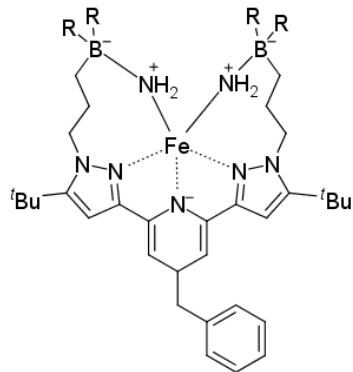
III



Use this area if you made a mistake, indicate the letter clearly.



9. Draw structures of complexes IV-VII; again feel free to abbreviate the structure of X; you do not need to draw out the -R groups.

<p>IV</p> 	<p>V</p> 
<p>VI</p> 	<p>VII</p> 
<p>Use this area if you made a mistake, indicate the letter <i>clearly</i>.</p>	<p>Use this area if you made a mistake, indicate the letter <i>clearly</i>.</p>

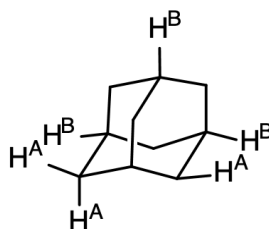


Theoretical #6	1.	2.	3.	4.	5.	6.	7.	8.	9.	Total
9% of the total	3	4	16	1	7	7	3	2	3	46

Problem 6. Adamantane, Symmetry, and NMR

1. How many hydrogen NMR signals are theoretically expected for adamantane according to its molecular symmetry? Draw in and label at least 3 of each chemically distinct hydrogen atom by environment H_a , H_b , H_c etc. (Hydrogen atoms in the same environment should have the same label). State the integration values expected for each environment.

Number of Signals: **2 (1 point)**



(3 of each environment must be shown) (1 point)

All CH_2 groups are the same (this can be seen by drawing some symmetry axes)

All CH groups are the same (same reasoning)

	H_a	H_b	H_c	H_d	H_e	H_f
Integration Values	12	4				

(There are not necessarily 6 distinct environments)

As long as integration for H_a is 3 times larger than that of H_b , full points will be awarded.

(1 point)

2. Draw the structures of **A** and **B**.

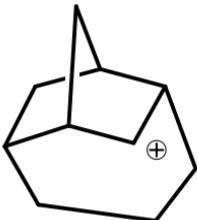
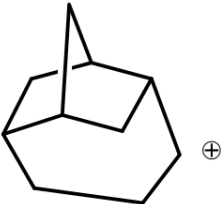
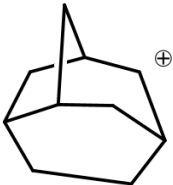
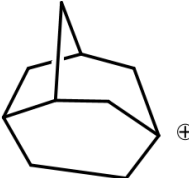
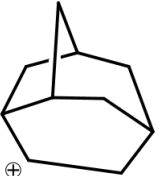
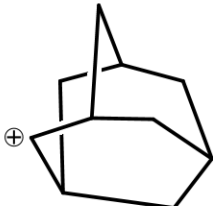
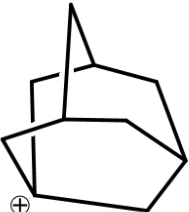
A	B
<p>- 2 points</p>	<p>- 2 points</p>



3. Draw the structures of intermediates C-I, and state whether each step Z₁-Z₄ you have proposed is a carbocation rearrangement or intramolecular hydride shift. There may be more than one unique answer, so all reasonable solutions that are consistent with the chosen Z₁-Z₄ will be accepted. A chemically reasonable answer will receive full points, while a suspect one will only obtain partial.

Note: you may abbreviate carbocation rearrangement as “CR” and intramolecular hydride shift as “intraHT” for Z₁ - Z₄.

C-I: 2 points max, 1 point for reasonable..... Z1-Z4: 1 point each

<p>C</p> 	<p>D</p> 								
<p>E</p> 	<p>F</p> 								
<p>G</p> 	<p>H</p> 								
<p>I</p> 	<table border="1"> <tbody> <tr> <td>Z₁</td> <td>CR</td> </tr> <tr> <td>Z₂</td> <td>intraHT</td> </tr> <tr> <td>Z₃</td> <td>CR</td> </tr> <tr> <td>Z₄</td> <td>intraHT</td> </tr> </tbody> </table>	Z ₁	CR	Z ₂	intraHT	Z ₃	CR	Z ₄	intraHT
Z ₁	CR								
Z ₂	intraHT								
Z ₃	CR								
Z ₄	intraHT								



4. Which solvent would 21st camper Harrison have used to carry out the reaction?

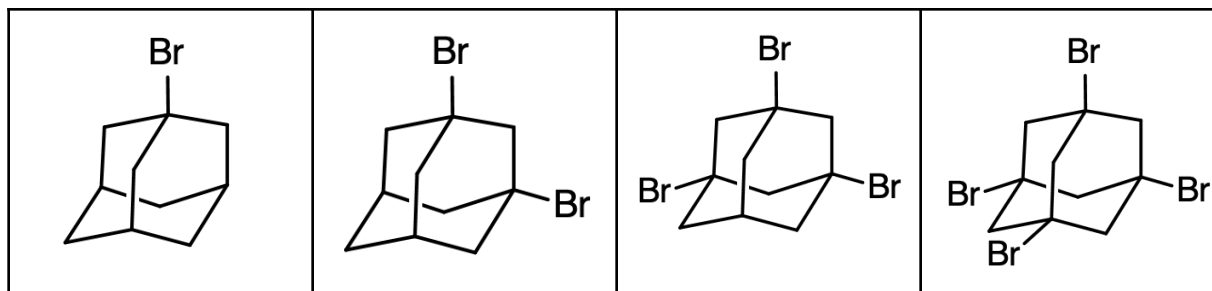
- Benzene
 Toluene
 THF
 Nitrobenzene ← This Answer
 Phenol
 Pyridine
 Pentane

(1 point)

5. Based on the data given above, draw all products formed in this reaction and their molar ratios in the NMR sample.

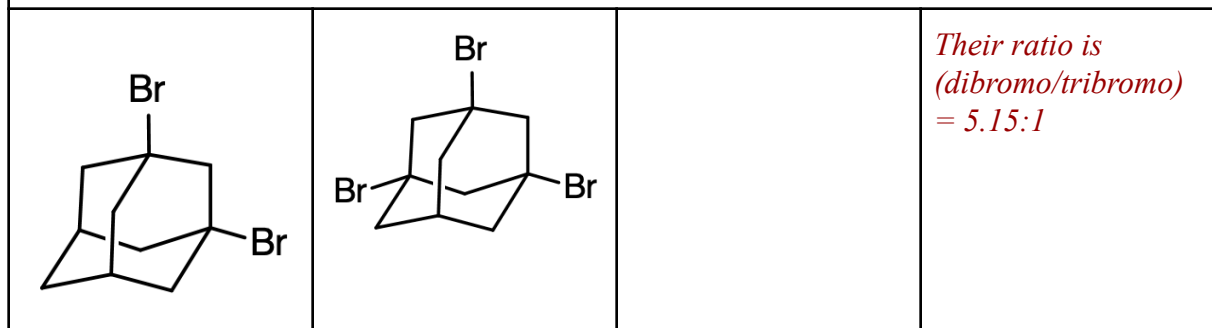
Work

Possible Products



We can figure out the integration values from the NMR data for each one to see the dibrominated and tribrominated products are present

Answer:



- 2 points for evaluating the possible products
- 2 points for using the NMR integration values to get the correct ratio
- 1.5 points for each correct final structure
 - 1.5 point penalty for each incorrect final structure drawn



6. Assign *every* NMR peak to a compound and the correct proton on that compound. You may use the letter labels from the table (i.e. label protons H_a, H_b, etc.)

Protons i and k may be swapped for no penalty, same with e and g.

Score = (# of correct protons)(7/13), round down to nearest integer.

7. How much Br₂ actually reacted with Adamantane? Explain this result, with regard to the amount (≈2 ml) of Br₂ added.

There are 14.68 mmol of adamantane. It takes 3 eq. of Br₂ to make the tribromo adamantane, and 2 eq. to make the dibromo version.

$$14.68[2(5.15/6.15) + 3(1/6.15)] = 31.45 \text{ mmol of Br}_2 \text{ consumed.}$$

However, about 39 mmol of Br₂ were added, which is much more! The extra Br₂ was consumed by reaction with Fe to form the necessary FeBr₃ catalyst *in situ*.

- 2 points for determining the amount of Br₂ reacted with adamantane
- 1 point for explanation involving reaction with Fe to form FeBr₃



8. Draw the structure of **I** with the correct orientation of atoms/stereochemistry.



(2 points, all or nothing)

The computationally derived enthalpy of activation ΔH^\ddagger for the conversion between the epimers is 81 kJ/mol at 298 K.

9. Estimate the entropy of activation ΔS^\ddagger for the conversion. Assume that conversion of the transition state to the product occurs with 100% probability.

$$k = \ln(2)/t_{1/2} = 23.1 \text{ s}^{-1} = k_b T/h e^{-\Delta G^\ddagger/RT}$$

$$\Delta G^\ddagger = 65.2 \text{ kJ/mol.}$$

$$\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger)/T = \mathbf{53 \text{ J/mol}\cdot\text{K}}$$

- 2 points for use of Eyring Equation
- 1 point for correct final answer

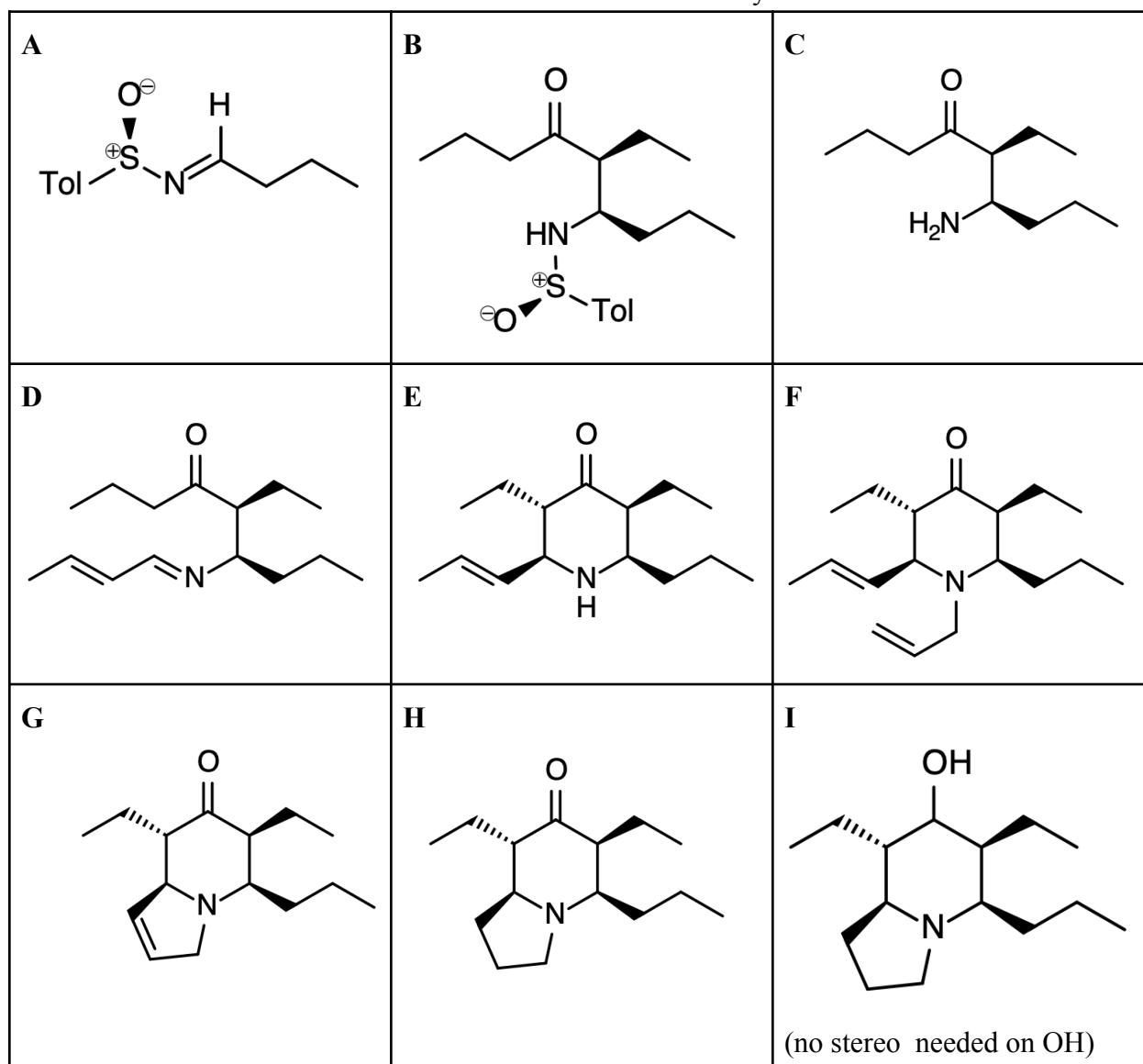


Theoretical #7	1.	2.	3.	Total
15% of the total	27	6	30	63

Problem 7. Build your own frogger

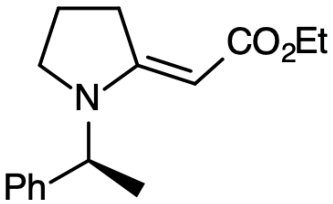
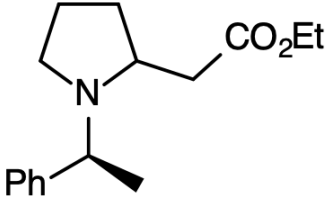
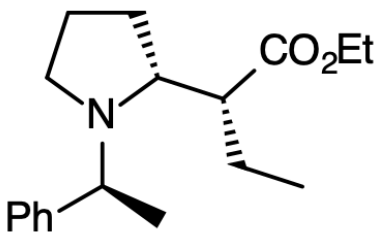
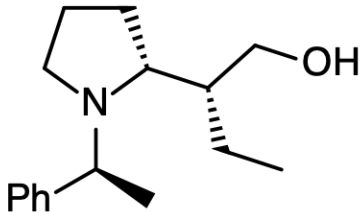
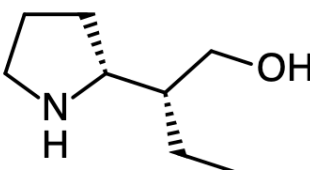
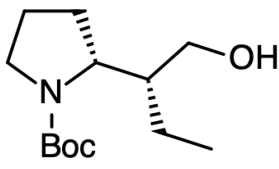
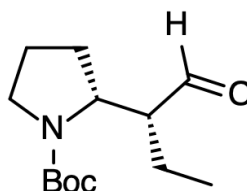
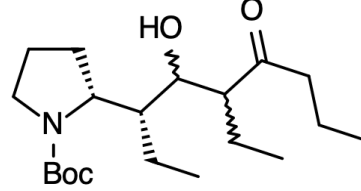
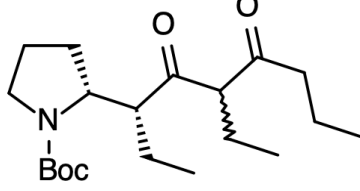
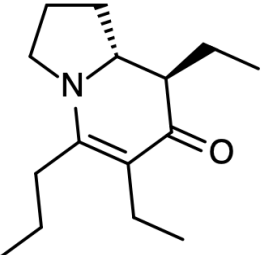
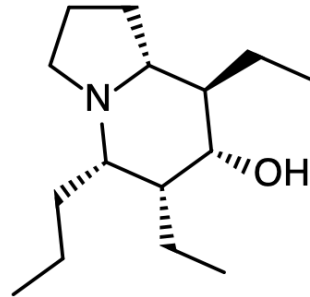
3 points each. 2 points if bad stereochem (penalized once), 1 point for the first reasonable but incorrect structure, 0 points for further. 0 points for “forcing” a solution.

1. Draw the structures of intermediates A-I with stereochemistry





2/3. Draw the structures of **J** and intermediates **K-T** with stereochemistry
(The answer boxes for these parts were combined to save space)

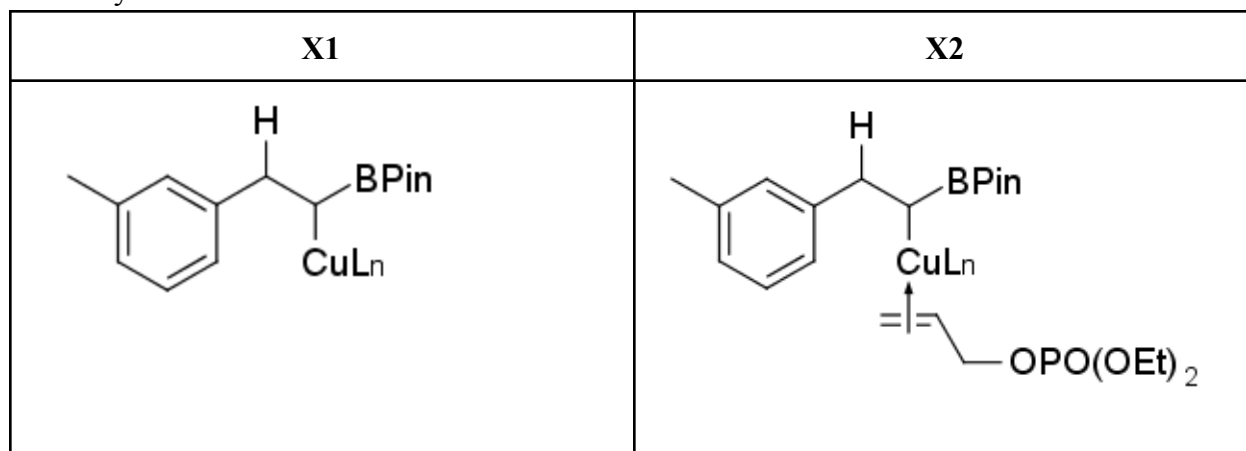
<p>J</p>  <p style="text-align: center;">4 pts for Z isomer</p>	<p>K</p> 	
<p>L</p> 	<p>M</p> 	<p>N</p> 
<p>O</p> 	<p>P</p> 	<p>Q</p>  <p>Note: ambig stereochem</p>
<p>R</p>  <p>Note: ambig stereochem</p>	<p>S</p> 	<p>T</p>  <p>(No stereo needed on OH)</p>



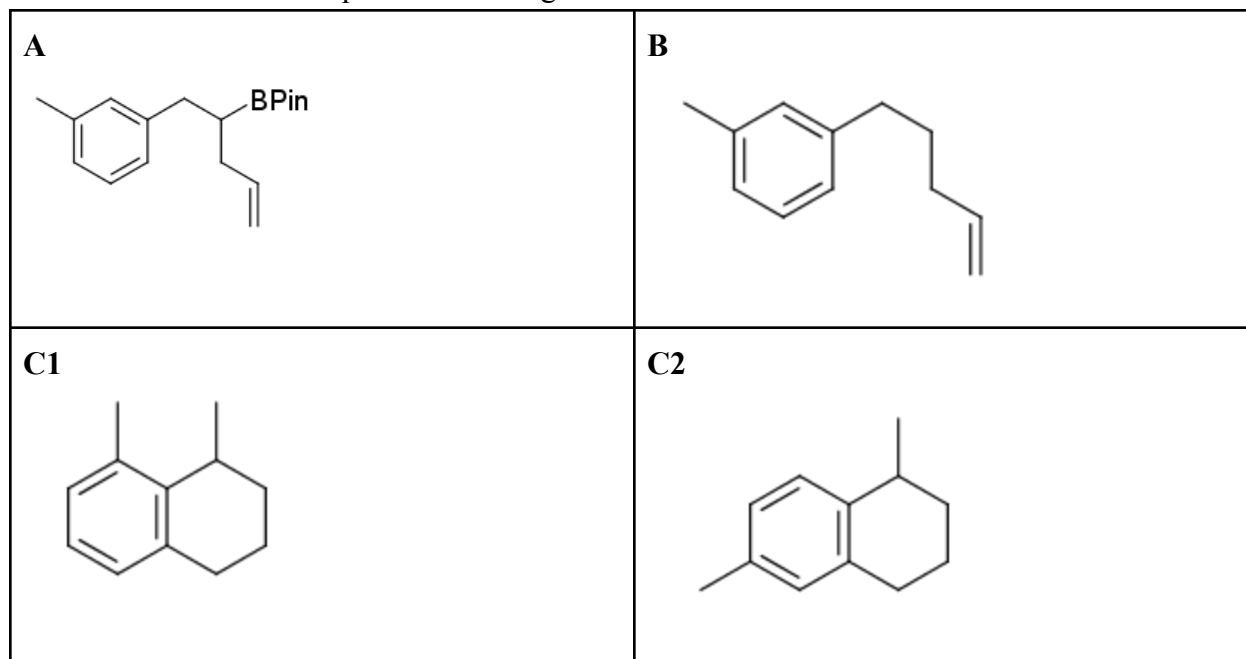
Theoretical #8	1.	2.	3.	4.	Total
8% of the total	6	10	5	9	30

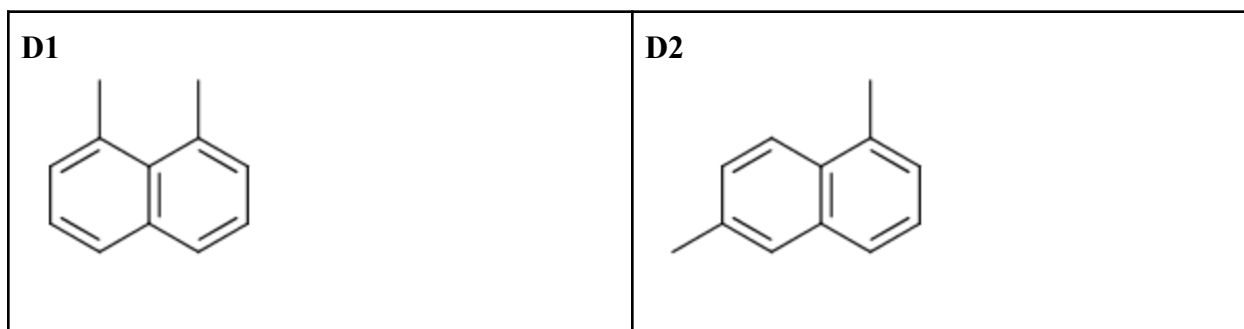
Problem 8. Non-Classical Chemistry

1. Draw the structure of intermediates of **X1** and **X2**, which are intermediates in the mechanism for the synthesis of **A**.



2. Draw structures of compounds **A** through **D1/2**.





3. Propose reagent(s) **Y** (note that reagent(s) **Y** may involve many steps).

Some examples:

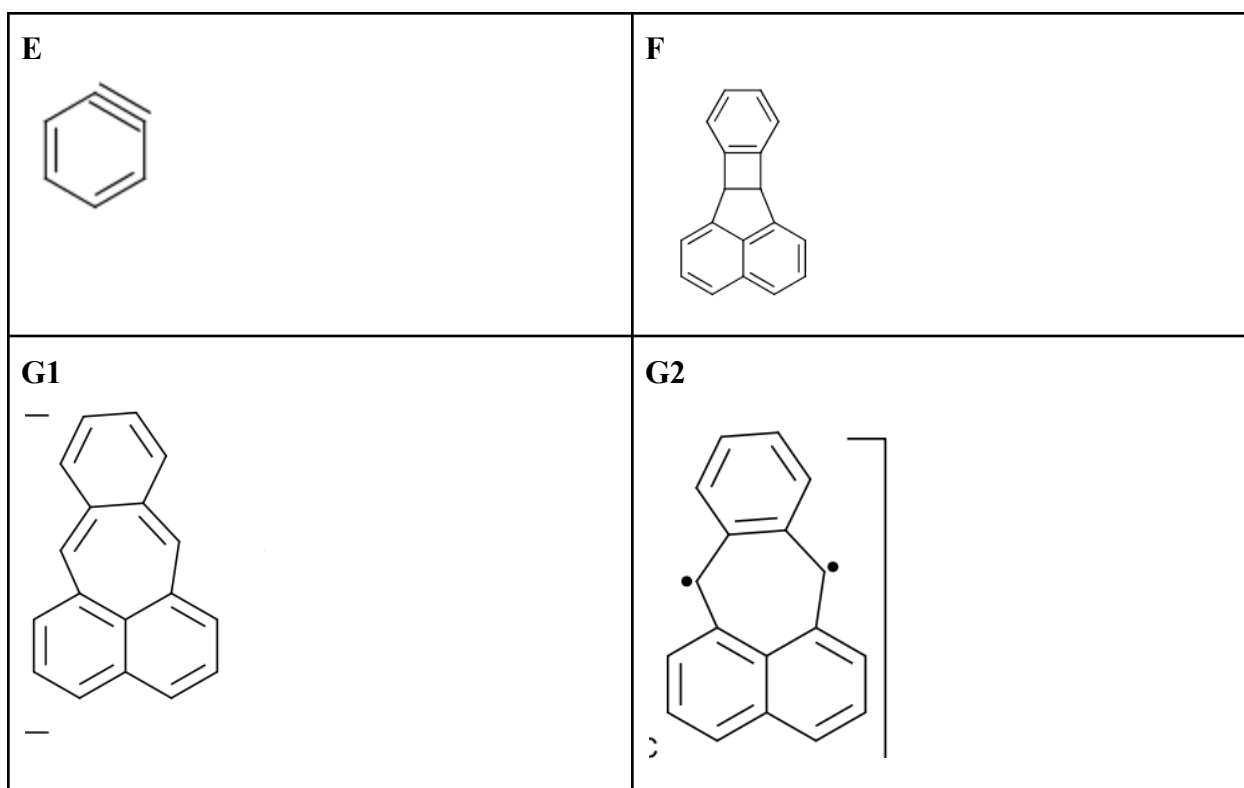
1) $\text{Br}_2/h\nu$ 2) Na 3) Pd, heat, $-\text{H}_2$

1) SeO_2 2) Pinacol Coupling 3) Corey-Winter Olefination

1) SeO_2 2) CH_2PPh_3 3) Grubbs Cat.

Use your imagination!

4. Draw the structures of reactive intermediate **E**, **F**, and the “classical” and “non-classical” resonance structures **G1** and **G2**. Draw the dimer of **G** as well.





G Dimer

