Code: USA-

Name:

Team Alpha Moo
Mock Camp Test

Theoretical Problems
Exam 1

You may want to consult the readme document so that you can read the protocols for how exams at camp are typically carried out: https://docs.google.com/document/d/1hV-thZ-qkU33DEkqGt-le5SVOTgkNRfHpgEjkTeNHyY/edit?usp=sharing

Instructions

- Write your name only on the cover sheet of the test
- Write your code number on each page (pages with no code will not be graded!)
- You have 2 hours to work on the problems
- Use only the pen and calculator (TI-30XIIS) provided
- All results should be written in the appropriate boxes. If you need extra space you may draw another box on the same page or on the backside of a different page and write a note telling the grader to refer to the backside of that page.
- Box your answers
- You may use the backsides of the sheets for scratch paper. You will not be provided with separate pieces of scratch paper.

Problem 1
Inorganic Chemistry **10% of the total**

1a	1b	Total	%
10	1	11	10

A sample of 2.3793 g of a crystallohydrate of the type $M_xA_y \cdot zH_2O$, where M is a metal, reacted with an excess of $SOCl_2$. Gaseous products formed by the reaction were introduced into a barium chloride solution containing hydrochloric acid and hydrogen peroxide. Small quantities of $SOCl_2$ carried by the gaseous products were removed by freezing out. The mass of the precipitate that is deposited from the solution, was 14.004 g. It was found to contain 13.74 mass % of sulfur.

In another experiment, 1.1896 g of the initial substance was dissolved in water and the solution was diluted to a volume of 100 cm^3. One fifth of this solution was required to react with 10 cm^3 of a 0.2-molar $AgNO_3$ solution. The mass of the precipitate formed by the titration was 0.28664 g. (The end point of the titration was determined by the conductometric method.)

Additionally it is known that the crystallohydrate has less than 8 moles of water per mole of crystallohydrate.

a) Calculate the formula of the crystallohydrate.

a) Give an example of another possible hydrate that cannot come into consideration due to the given limitation.

Problem 2
Copper Equilibria **14% of the total**

2a	2a	2c	2d	2e	Total	%
4	2	6	2	3	17	14

Two Copper (I) Salts of the organic acids HA and HB, slightly soluble in water, form a saturated solution in a buffer of a given pH. Consider the given equilibrium constants:

$CuA(s) \rightleftharpoons Cu^+ + A^-$ $\quad K_{spA} = 1.2 \times 10^{-3}$

$CuB(s) \rightleftharpoons Cu^+ + B^-$ $\quad K_{spB} = 6.4 \times 10^{-4}$

$HA(aq) \rightleftharpoons H^+ + A^-$ $\quad K_3 = 8.1 \times 10^{-6}$

$HB(aq) \rightleftharpoons H^+ + B^-$ $\quad K_4 = 2.7 \times 10^{-5}$

a) Find a generalized expression for $[Cu^+]$ in terms of only equilibrium constants and $[H^+]$

b) If the pH of the buffered solution is 5.00, compute $[Cu^+]$

c) Suppose instead that the solution is unbuffered. It is still possible to compute the solubility of Cu^+. Find an expression for $[Cu^+]$ in terms of only equilibrium constants and $[Cu^+]$.

d) Compute $[Cu^+]$ in this solution

e) Compute the pH of the solution

Problem 3
Mystery Molecule **9% of the total**

3a	3b	Total	%
17	3	20	9

An optical active compound **A** ($C_{12}H_{16}O$) shows a strong IR absorption at 3000 – 3500 cm^{-1}, and two medium signals at 1580 and 1500 cm^{-1}. The compound does not react with 2,4-dinitrophenylhydrazine (2,4-DNPH). Upon treatment with I_2/NaOH, **A** is oxidized and gives a positive iodoform reaction.

Ozonolysis of **A** (1. O_3; 2. Zn, H^+) gives **B** ($C_9H_{10}O$) and **C** ($C_3H_6O_2$). Both **B** and **C** give precipitation when treated with 2,4-D, and only **C** gives positive reaction with Tollens reagent. Nitration of **B** (HNO_3/H_2SO_4) may give two mono-nitro compounds **D** and **E**, but in practical work only **D** is formed.

Acidification followed by heating of the product formed by the Tollens reaction on **C** gives compound **F** ($C_6H_8O_4$). The compound gives no absorption in IR above 3100 cm^{-1}.

a) Based on the above information draw the structure formula(e) for the compounds **A – F** and write the other mentioned reactions, including the (2,4-D) tests and the products of the Tollens and Iodoform reactions.

A	**B**	**C**
D	**E**	**F**

b) Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a D or L configuration.

Problem 4
Radical Kinetics **14% of the total**

4a	4b	4c	4d	4e	4f	Total	%
5	4	2	3	10	2	26	14

In 1934 Rice and Herzfeld proposed a mechanism for the thermal chain decomposition of ethane:

Reaction			Constant	Ea (kJ/mol)
C_2H_6	$\rightarrow$	$2CH_3\bullet$	k_1	312
$CH_3\bullet + C_2H_6$	$\rightarrow$	$CH_4 + C_2H_5\bullet$	k_2	10
$C_2H_5\bullet$	$\rightarrow$	$C_2H_4 + H\bullet$	k_3	65
$H\bullet + C_2H_6$	$\rightarrow$	$C_2H_5\bullet + H_2$	k_4	18
$H\bullet + C_2H_5\bullet$	$\rightarrow$	C_2H_6	k_5	2

a) Identify reactions 1-5 as initiation, termination, or propagation

1	
2	
3	
4	
5	

b) The decomposition of ethane can be written in 2 different reactions encompassed by the given mechanism. Write these 2 reactions.

c) Write an expression for the net rate of consumption of C_2H_6

d) Apply the steady state approximation to all radical intermediates

In practice, the rate constant k_1 is relatively small and its value decays exponentially. Thus, if two expressions containing k_1 to different powers are summed, one term can be expected to dominate.

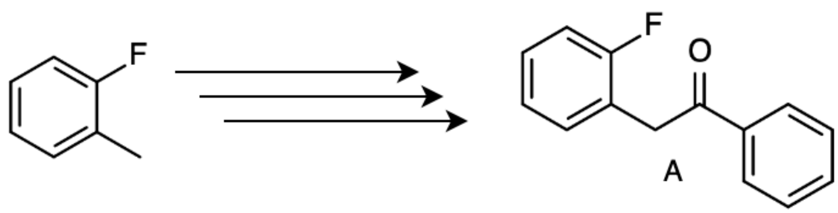
e) Express the rate law for the consumption of C_2H_6 in terms of non-intermediates and the given rate constants.

What is the overall activation energy for the consumption of C_2H_6?

Problem 5
Flunitrazepam 14% of the total

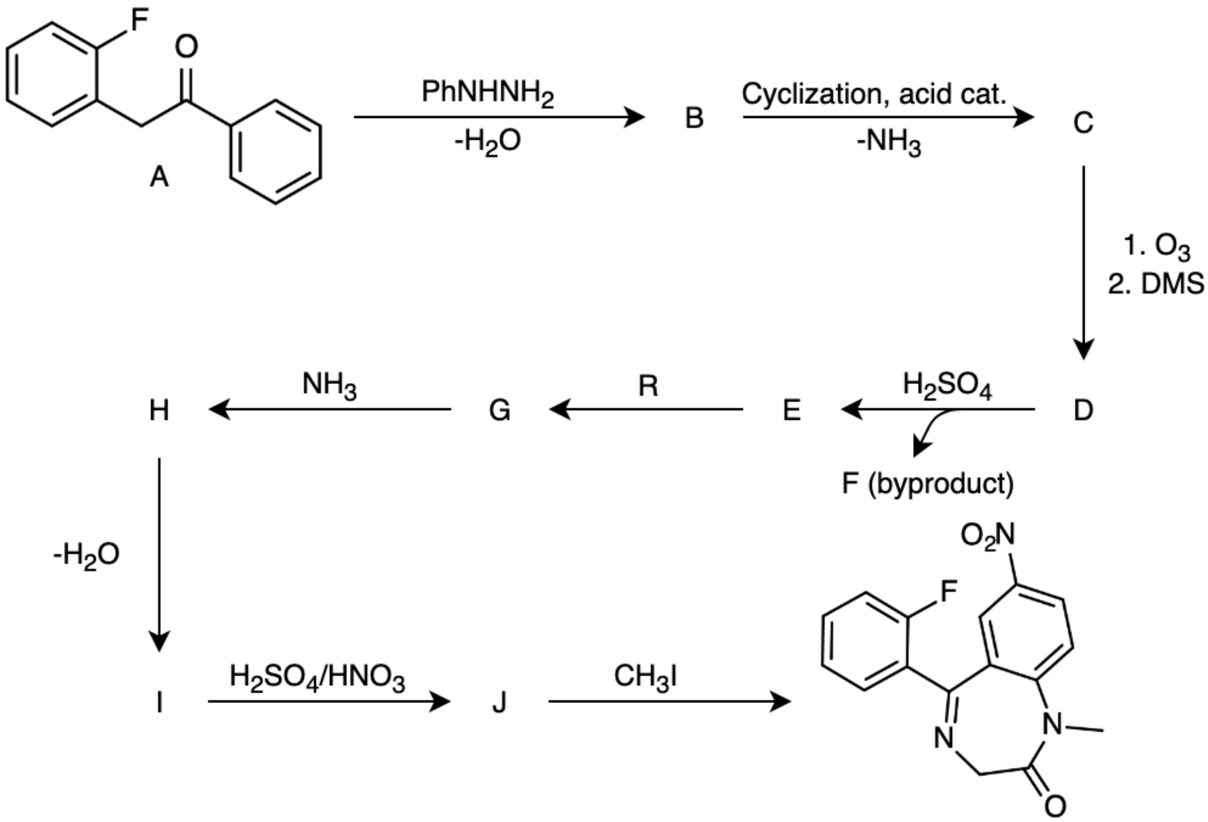
3a	3b	3c	Total	%
4	20	3	27	14

Flunitrazepam is a drug which can be synthesized starting from 2-fluorotoluene. The researchers first built up precursor **A** which was then used in the synthesis.



a) Propose a synthesis of **A** starting from 2-fluorotoluene

The rest of the synthesis was carried out as follows:



(**R** is a reagent that you must propose)

Note that B→C involves no reagents (just catalytic acid), but does release NH_3.

b) Decipher the structures of intermediates **B-J**. Also, propose a reagent **R** that could suitably carry out the transformation from **E** → **G**

B	**C**	**D**
E	**F**	**G**
H	**I**	**J**
R		

c) Propose a mechanism for the conversion of **B** → **C**

Problem 6
Gas Thermodynamics 10% of the total

6a	6b	6c	Total	%
5	2	6	13	10

Interconversion of N_2O_4 and NO_2 is a common system for discussing chemical equilibrium. The reaction is as follows:

N_2O_4 (g) $\rightleftharpoons$ 2 NO_2 (g) K_p = 0.100….(295 K)
K_p = 0.400….(315 K)

Some amount of N_2O_4/NO_2 mixture is added to a movable piston that maintains a constant pressure of 1 bar=1000 kPa.

a) Calculate the partial pressures of N_2O_4 and NO_2 in the piston at 295 K

The piston gas system is then heated up to 315 K while maintaining the total pressure of 1 bar

b) What is the value of $\Delta H°$ for the reaction (assume it is constant with respect to temperature)

c) Calculate the ratio of the total number of moles of gas at 315 K to the total number of moles of gas at 295 K in this system.

Problem 7
Peculiar Pericyclics 16% of the total

7a	7b	7c	7d	7e	Total	%
14	8	3	8	2	35	16

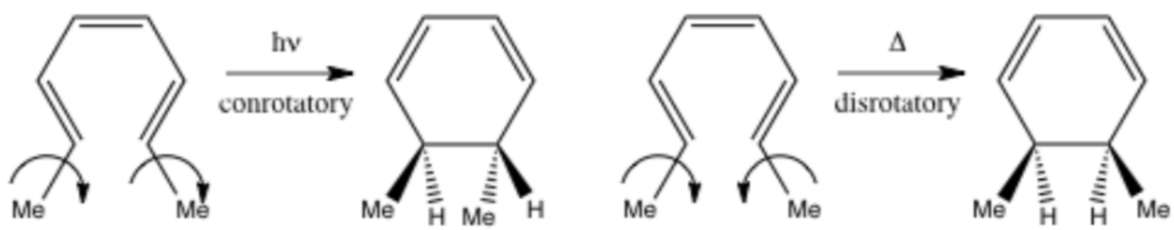
Pericyclic reactions are extremely useful for the buildup of large cyclic molecules.

Based on deductions from frontier molecular orbital theory, Woodward and Hoffmann devised a set of rules, for which Hoffmann won the Nobel Prize in Chemistry in 1981, along with Kenichi Fukui who independently reached similar rules via alternative methods. These chemists realized that for thermally–driven chemical reactions, the highest occupied molecular orbital (HOMO) was the relevant orbital; in photochemically–driven reactions, in contrast, an electron is excited from the HOMO by light to the lowest unoccupied molecular orbital (LUMO), making this the relevant orbital.

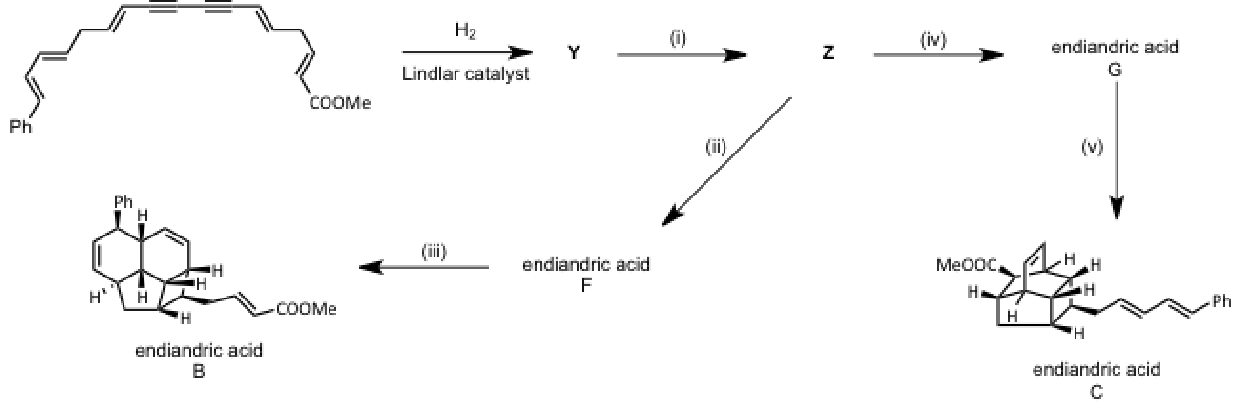
Two types of reactions governed by the rules are the Diels–Alder reaction (an example of cycloaddition) and electrocyclic reactions. For electrocyclic reactions, the Woodward–Hoffmann rules are:

Number of π-Electrons Involved in the reaction	Thermal	Photochemical
$4n$	Conrotatory	Disrotatory
$4n+2$	Disrotatory	Conrotatory

These rules predict the stereochemical course of reactions as shown:



These reactions are employed by nature in the synthesis of a class of natural products called the endiandric acids. All of the reactions shown below are either electrocyclic or cycloadditions (Diels–Alder).



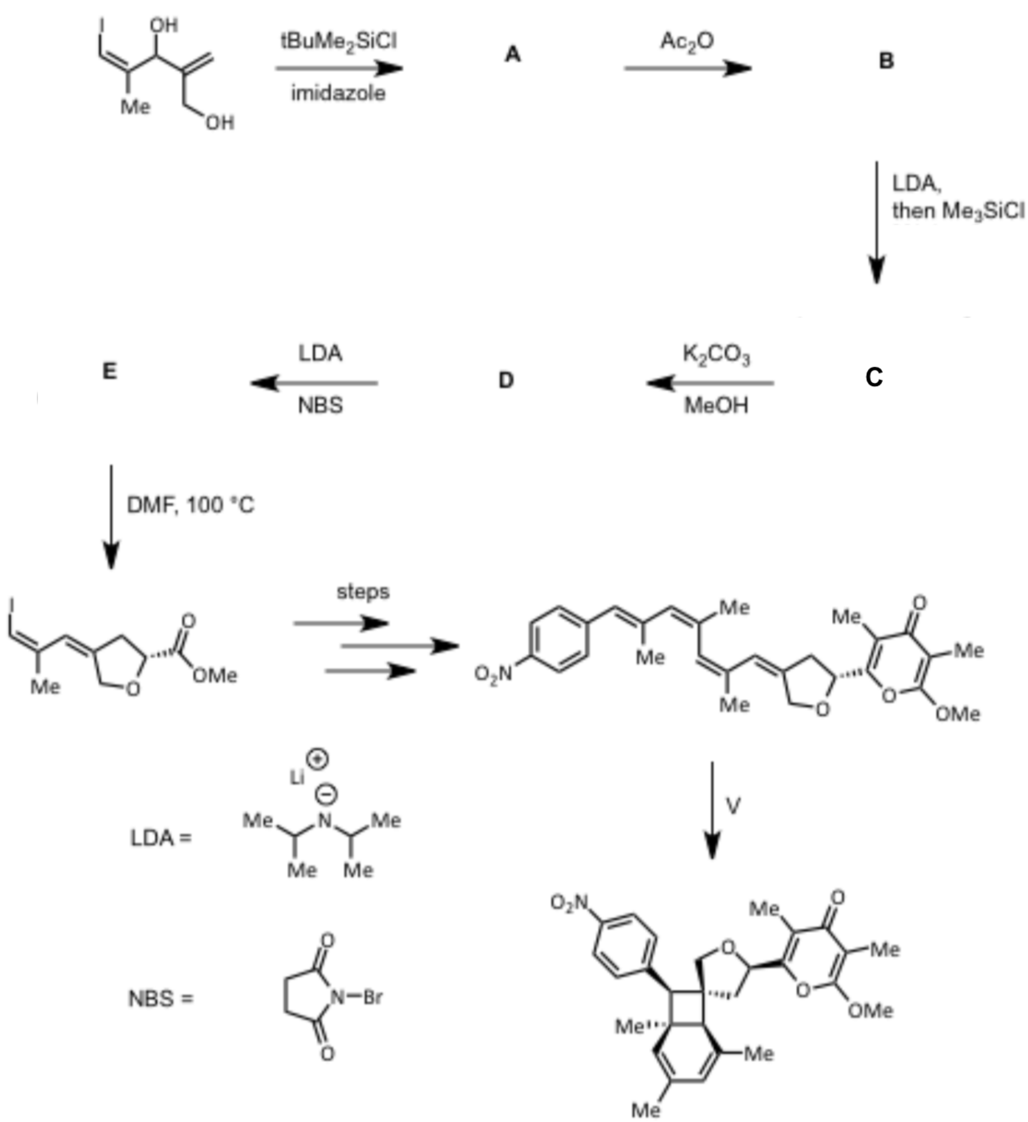
a) Draw the missing structures (**Y**, **Z**, endiandric acids **F** and **G**) in the above scheme.

Y	**Z**
F	**G**

b) Fill in the following table for reactions (i) –(v)

Reaction	Diels-Alder?	electrocyclic?	Number of π electrons	con- or dis- rotatory?
i				
ii				
iii				
iv				
v				

This synthesis of the polyketide natural product, SNF4435 C also employs pericyclic reactions.



c) How many electrocyclizations occur in the step at the end labeled “V”?

d) Determine the structures of intermediates **A-E** in the scheme

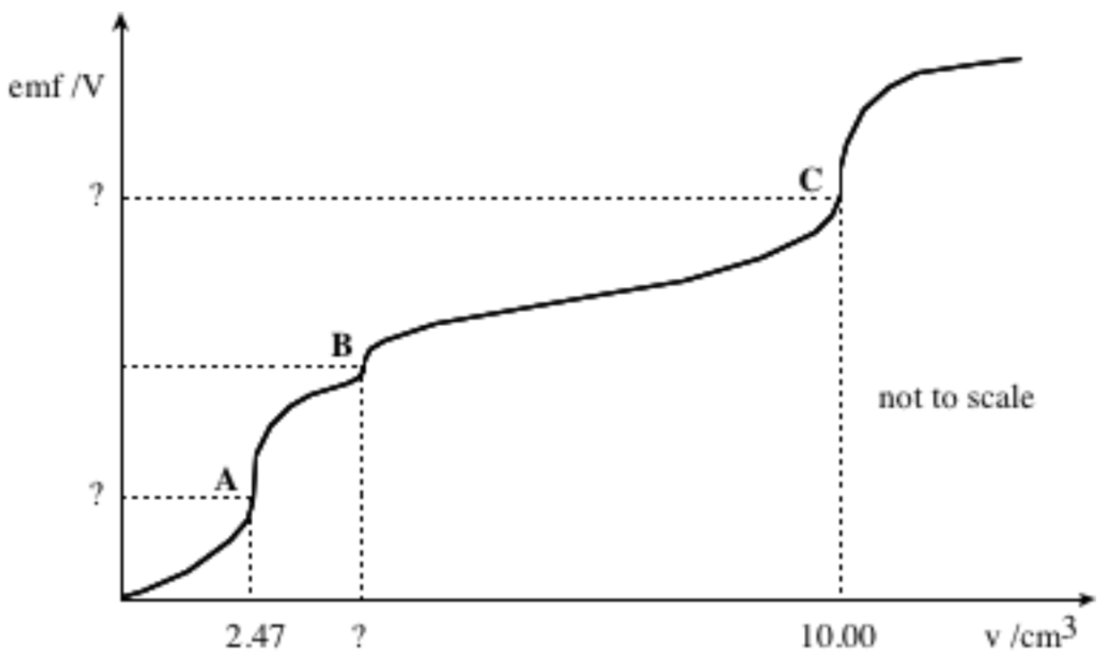
A	**B**
C	**D**
E (contains Si)	

e) Propose a mechanism for transformation **B** → **C**

Problem 8
Titrations 13% of the total

8a	8b	8c	8d	8e	Total	%
4	3	4	6	4	21	13

25.00 cm^3 of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 °C using a silver electrode and a normal calomel half-cell with KNO3 - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained is shown below. The curve plots the cell emf (V) against the volume of titrant used (cm^3).



Useful Data

$E°(Ag^+/Ag) = 0.800$ V

$E°(\text{Calomel}) = 0.285$ V

$K_{sp}(AgCN) = 10^{-15.8}$

$K_{sp}(AgCl) = 10^{-9.75}$

$\beta_2 = [Ag(CN)_2^-]/([Ag^+][CN^-]^2) = 10^{21.1}$

a) The end points of the reactions taking place during the titration, are marked with A, B, and C. Write the balanced ionic equation for each reaction.

A	
B	
C	

b) What volume of the titrant is required to reach point B?

c) Calculate the concentrations of KCl and KCN (in mol dm^{-3}) in the sample solution.

d) Calculate the emf readings at the points A and C in volts.

e) What is the molar ratio Cl^-/CN^- in the solution and in the precipitate at point C?

	Problem Sources (some were modified)
1	1976 ICHO #2
2	1977 ICHO #5
3	1994 ICHO #6
4	Engel & Reid Kinetics
5	2003 UKCHO organic
6	CCHO 2016
7	2012 ICHO prep #25
8	1987 ICHO #2