

Name:

Team Alpha Moo Mock Camp Test

Theoretical Problems Final

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 4 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
Nickel Chemistry

12% of the total

I						II				III			IV				Total	%
I.1	I.2	I.3	I.4	I.5	I.6	II.1	II.2	II.3	II.4	III.1	III.2	III.3	IV.1	IV.2	IV.3	IV.4	31	12
4	1	1	2	1	1	1	2	2	2	3	3	2	1	1	2	2		

I. Medley

Commercially important nickel ores include its sulfide, which also contains iron (II) and copper (I) sulfides. The concentrated ore is smelted in presence of silica which helps in removal of iron as slag (Step I). The upper silvery layer of Cu_2S and lower black layer of Ni_2S_3 remaining with the ore are then mechanically separated. The Ni_2S_3 is roasted in air to give a green solid (Step-II), which on subsequent treatment with water gas (mixture of CO and H_2 gas) at 50°C gives a volatile complex and other byproducts (Step-III). This complex on thermal decomposition in air at 230°C gives pure solid Ni (Step-IV).

1. Write balanced chemical equations for Steps 1-IV

Step 1	
Step 2	
Step 3	
Step 4	

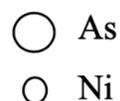
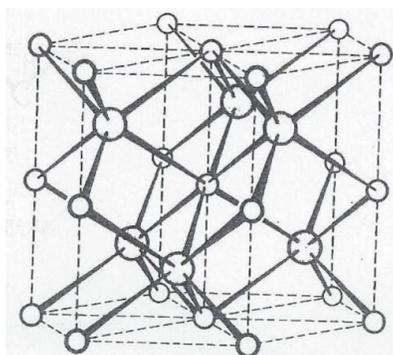
2. Which of the following statements is/are true for Step III? Circle your answer(s).

- Only H_2 from water gas reacts with Ni ions and reduces it
- H_2 from water gas reduces Ni ions and then CO complexes with the reduced form of Ni
- Only CO from water gas reduces Ni ions
- Both CO and H_2 from water gas act as reducing agents

Raney nickel is a versatile hydrogenation catalyst. It is prepared by leaching out Al selectively from Ni-Al alloy powder under controlled condition by treating it with a concentrated solution of caustic soda. The slurry of finely divided spongy nickel particles is thus obtained which is then washed with large quantities of water to make the particles free from caustic soda.

3. Write a balanced chemical equation for the leaching process.

Pure nickel forms alloys with various metals such as As, Al, Cd, Cr, Zn etc. and some of these have well defined crystal structure. The unit cell of Ni_xAs_y is shown in the following figure.



4. Using the above diagram identify the coordination number and geometries of Ni and As.

Element	Coordination Number	Coordination Geometry
Nickel		
Arsenic		

5. Find the values of x and y in Ni_xAs_y

$x =$	$y =$
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Green nickel oxide NiO can be doped with colorless lithium oxide, Li_2O , to give a black solid $\text{Li}_x\text{Ni}_{1-x}\text{O}$ which acts as a semiconductor.

6. Which of the following statement(s) is/are correct for the above observations?

	$\text{Li}_x\text{Ni}_{1-x}\text{O}$ exhibits both cationic and anionic vacancies
	$\text{Li}_x\text{Ni}_{1-x}\text{O}$ exhibits Schottky defect
	Doping of NiO with lithium induces mixed valency of nickel
	NiO becomes a p-type semiconductor

II. Nickel Complexation and Determination

Nickel forms various alloys such as stainless steel, nichrome and cupranickel which have various applications in industries.

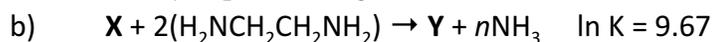
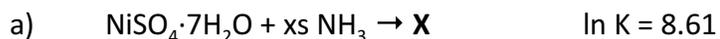
Stainless steel has the following approximate composition (w/w): 73% Fe, 18% Cr and 8% Ni. An industrial sample of stainless steel was analyzed for its nickel content using chemical methods. One of the standard quantitative methods for estimation of nickel utilizes two moles of chelating bidentate ligand, dimethylglyoxime $[\text{CH}_3\text{C}(\text{NOH})\text{C}(\text{NOH})\text{CH}_3]$. Nickel precipitates as a neutral complex $(\text{C}_8\text{H}_{14}\text{O}_4\text{N}_4\text{Ni})$, dark pink in color.

1. Draw the structure of the complex formed

1.4 g of stainless-steel sample was treated with aqua-regia to dissolve all the contents of the sample. The solution was treated for removal of iron and chromium ions and was then diluted to 100 mL using distilled water. 10 mL of this diluted solution when treated with DMG gave 0.0532 g of the precipitate of the complex.

2. Calculate the % of nickel in the sample taken for analysis. Show all important steps of calculations.

The stability of nickel complexes can be understood from their formation constant, K. The formation constants of the following Ni complexes **X** and **Y** at 25°C are



3. Draw the structure of all possible isomers of **Y** and encircle the optically active isomer/s if any exist.

4. Calculate the entropy change for the formation of **Y** in equation II at 25° C if the heat of reaction for Equation 2 at constant pressure is -12.1 kJ/mol

III. Spinel

Mixed metal oxides of transition metals often form spinels having the general formula $A^{II}B^{III}_2O_4$ where the oxide ions form a close packed cubic lattice with eight tetrahedral holes and four octahedral holes per $A^{II}B^{III}_2O_4$ unit. In a normal spinel 1/8th of the tetrahedral holes are occupied by A (II) whereas B (III) resides in octahedral sites. In inverse spinel A (II) and one half of B (III) occupy the octahedral holes while the other half of B (III) occupy the tetrahedral holes. The structure becomes 'normal' ($A^{II}B^{III}_2O_4$) or 'inverse' spinel ($B^{III}A^{II}B^{III}O_4$) depending upon the octahedral site preference energy which is the difference of the crystal field stabilization energy (CFSE) of the same cation in the corresponding octahedral and tetrahedral field of the ligand.

Metal Ion	Δ_o (cm ⁻¹)	Δ_t (cm ⁻¹)
Co ³⁺	20,760	9,226
Fe ³⁺	14,000	6,220
Ni ²⁺	8,500	3,780

Where Δ_o and Δ_t are the octahedral and tetrahedral splitting parameters for oxide ions which provide a moderately weak field similar to that of water.

1. On the basis of the above data calculate the CFSE in kJ/mol for the following ions in octahedral and tetrahedral sites respectively:

	Octahedral	Tetrahedral
Case 1	Co(III)	Co(III)
Case 2	Fe(III)	Fe(III)
Case 3	Ni(II)	Ni(II)

Case 1
Case 2
Case 3

2. Calculate the octahedral site preference energy for all the above 3 cases (how much more stable the octahedral complex is than the corresponding tetrahedral complex)

Case 1
Case 2
Case 3

3. Based on the above octahedral site preference energy calculations, classify the oxides as normal and inverse spinels. (Mark X in the correct box)

Compound	Normal	Inverse
NiFe ₂ O ₄		
NiCo ₂ O ₄		

IV. NiOOH

One of the widely used batteries of nickel is Ni-Cd battery. This battery uses high purity NiOOH (nickel oxyhydroxide) as anode. The typical synthesis of NiOOH is as follows.

In the first step, concentrated NaOH (30% w/v) is reacted with gaseous Cl₂ for sufficient time to generate hypochlorite.

1. Write the balanced chemical equation for this reaction

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The resultant reaction mixture is then treated with excess of solid NaOH with vigorous stirring which leads to precipitation of NaCl. The precipitate is filtered and the sufficient amount of Ni(OH)₂ is added to the filtrate with constant stirring. Black colored NiOOH is formed as suspension.

2. Write the balanced chemical equation that leads to the formation of NiOOH

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The NiOOH suspension thus obtained is filtered and dried appropriately. However, before its use, it needs to be analyzed for its purity.

In one such analysis, 0.520 g of NiOOH sample prepared by the above method was treated with 25 mL of acidified 0.305 M Fe (II) solution. On dissolution, Fe(II) ions get oxidized quantitatively by Ni ions. The unreacted Fe(II) was titrated with 0.0285 M of KMnO_4 under acidic condition and the observed reading was 15.1 mL.

3. Write balanced chemical equations for

- i) Reaction of NiOOH with acidified Fe(II)
- ii) Reaction involved in titration with KMnO_4

i)
ii)

4. Calculate the percentage of NiOOH in the sample taken for analysis.

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Problem 2
FUEL AND THE OTTO ENGINE

10% of the total

2a	2b	2c	2d	2e	2f	2g	2h	2i	2j	2k	2l	2m	2n	Total	%
2	3	2	2	3	3	1	1	1	2	3	2	5	4	34	10

This task is about heptane ("hep") and iso-octane (2,2,4-trimethyl pentane, "oct"). Both are playing an important role in combustion engines. A few physico-chemical data are given all for a temperature of 298 K. Due out this task in combustion reactions $\text{H}_2\text{O}(\text{g})$ should be formed.

heptane, liquid: $\rho = 0.680 \text{ g cm}^{-3}$; enthalpy of formation $\Delta_f H^\circ = -224.4 \text{ kJ mol}^{-1}$

iso-octane, liquid: $\rho = 0.692 \text{ g cm}^{-3}$; enthalpy of combustion $\Delta_c H^\circ = -44328 \text{ kJ kg}^{-1}$

further: $\Delta_f H^\circ (\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$; $\Delta_f H^\circ (\text{H}_2\text{O}(\text{g})) = -241.8 \text{ kJ mol}^{-1}$

a) Compute the molar masses of heptane and iso-octane

b) Calculate the standard enthalpy of combustion $\Delta_c H^\circ$ for heptane in kJ/mol

c) Calculate the standard enthalpy of formation $\Delta_f H^\circ$ of iso-octane in kJ/mol.

Testing mixtures of n-heptane and iso-octane are of special importance. They are burnt in standardized test engines to get a measure for knock resistance for several fuels (engine knocking = ignitions in the motor cylinder at wrong time).

A fuel having the same knock resistance as an oct-hep-test mixture receives the volume fraction of octane of the latter as RON ("researched octane number"). Pure iso-octane has RON=100, pure heptane RON = 0.

Let us consider a test mixture with RON = 93, that means a volume fraction of 93% oct.

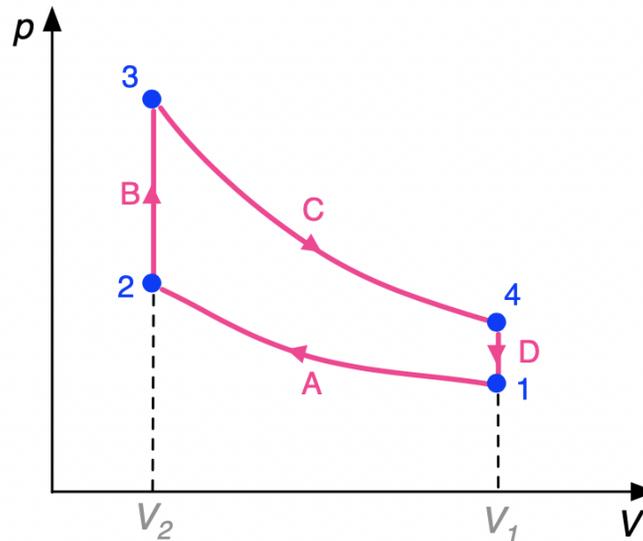
d) calculate the density of this test mixture in g/L

e) Calculate the standard enthalpy of combustion for the test mixture in kJ/mol.

f) Calculate the standard entropy and the standard Gibbs energy of mixing for 100 mL of the test mixture at 298 K.

The Otto engine, for which most of the fuels are being tested, is a heat engine. We will keep things simple and consider an idealized “thermodynamic” Otto-cycle using air as a working gas that shall behave ideal under all circumstances.

For air the molar heat capacity at constant volume is $C_{v,m} = 20.85 \text{ JK}^{-1} \text{ mol}^{-1}$, the heat capacity ratio is $\gamma = 1,40$. We take all four steps as being reversible. The pV-diagram shows the cycle:



- A (1→2) isentropic (adiabatic) compression
 B (2→3) isochoric heating
 C (3→4) isentropic (adiabatic) expansion (the power stroke of an Otto engine)
 D (4→1) isochoric cooling

g) In which of the four steps (A,B,C,D) is no work done?

h) In one of the four steps (A-B-C-D) the combustion of the fuel takes place – so fast, that the volume can be considered constant. Which step is this?

i) In which of the four steps (A,B,C, D) is the entropy of the working gas lowered?

For the four vertices in the pV-diagram the following data is known

$$T_1 = 15^\circ\text{C}, p_1 = 100\text{kPa}; \quad T_3 = 1800^\circ\text{C}$$

The cylinder has a displacement of 1.00 L. The displacement equals the difference $V_1 - V_2$. The dead volume V_2 , is 15% of the maximum volume V_1 .

j) Determine V_1 and V_2

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k) Calculate T_2 and T_4

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l) Calculate the amount of air in the cylinder in moles

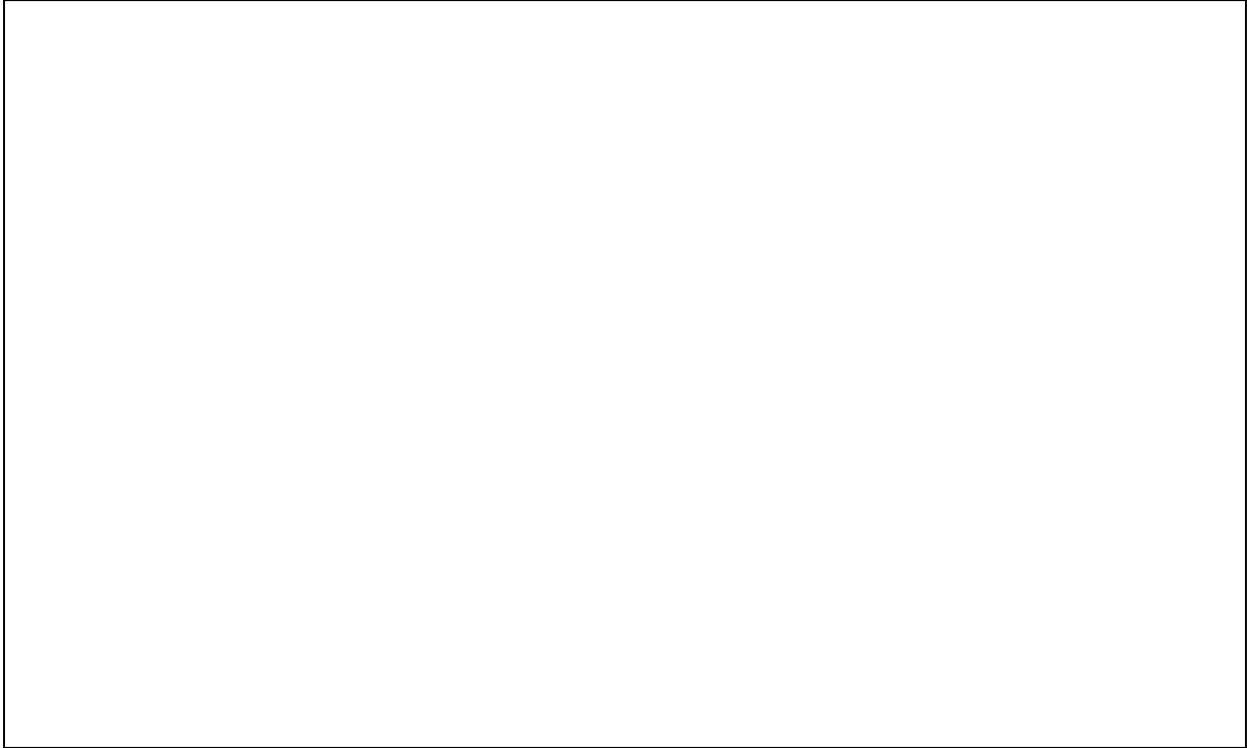
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m) Calculate the changes in internal energy for each step

Step A
Step B
Step C
Step D

The efficiency η is the ratio of heat added (q) to the total work w done by the machine.

n) Calculate the efficiency of the idealized Otto Engine

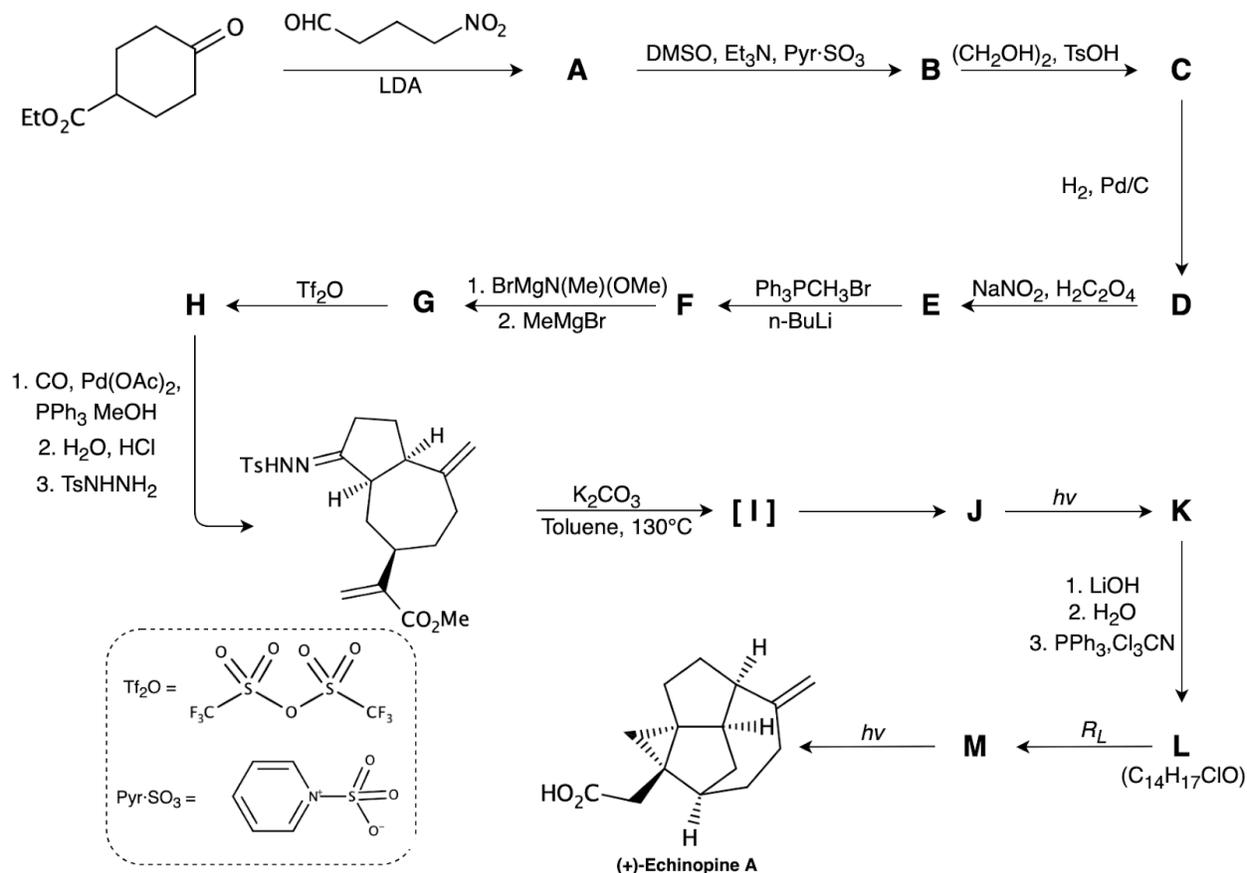


Problem 3
(+)-ECHINOPINE A

10% of the total

2a	Total	%
27	27	10

(+)-Echinopine A was synthesized as follows in 2013 by researchers from Nankai University:



- C is tricyclic
- Intermediate J was formed by a cycloaddition reaction within intermediate I.
- J→K proceeds through a paramagnetic intermediate

Note that R_L represents unknown reaction conditions which you must propose.

a. Draw the structures of intermediates A-N (no stereochemistry needed) and propose a suitable reagent for R_L . You do not need to state a solvent.

Echinopine A		
A	B	C
D	E	F
G	H	I
J	K	L
M	R_L	

Problem 4
MYSTERY METAL**8% of the total**

3.1	3.2	3.3	3.4	3.5	Total	%
6	5	4	1	4	20	8

The content of metal **A** in a solution can be determined as follows:

An excess of potassium iodide was added to the analyzed solution forming a precipitate(R1) . The precipitate was then dissolved in an excess of KI (R2). The solution was then alkalized and a 40% solution of formaldehyde was added and the flask was shaken for 3 min (R3). After that a dark suspension was formed, and formate ion was detected in the solution. The suspension was acidified with acetic acid, mixed with 5.00 ml of 0.0998 M solution of I₂ in an excess of KI (R4), and the unreacted iodine was titrated with a 0.0500 M solution of thiosulfate (R5). The volume of the thiosulfate required was 8.70 ml.

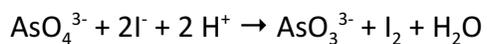
The analysis conducted above led the experimenters to conclude that the mass of **A** in the solution was $m_A = 56.6$ mg.

1. Determine the identity of metal **A**.

2. Write the equations for each step of the analysis procedure. (R1)-(R5)

R1	
R2	
R3	
R4	
R5	

In an acidic solution, arsenate can oxidize iodide to produce iodine:



When an excess of the chloride of metal **A** is present in an acidic solution, arsenite can be titrated quantitatively with Iodine.

3. Write the reaction of iodine with the chloride of **A** and the titration reaction of arsenite with iodine in the presence of the chloride of **A** in acidic solution.

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4. Which of the following indicators would be ideal for use in the titration of arsenite with iodine in the presence of **A**? (Tick all that apply)

	Diphenyl amine; forms a blue violet product upon reactions with strong oxidizers
	Starch; forms a blue complex with iodine
	Sodium sulfide; forms a colored compound with A ions
	Ammonium molybdate; forms a yellow heteropoly compound with arsenate

The quantity of **A** can also be quantitatively determined based on the reduction of **A** to its corresponding metal. Arsenite is reacted with **A** in alkaline medium, followed by titration of the excess arsenite with iodine. For this titration 7.80 ml of 0.0998 M I_2 were consumed.

5. Calculate the amounts of arsenite titrated (v_{As} , mol) and **A** reduced (v_A , mol) if 10,00 ml of 0.2020 M arsenite solution were added for the reduction of **A**. Write the equations for each reaction.

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Problem 5
MAGNETISM OF TRANSITION METAL COMPLEXES

8% of the total

4a		4b	4c	4d					Total	%
i	ii	1	1	i	ii	iii	iv	v	15	8
1	2			3	2	1	2	2		

The magnitude of paramagnetism of a metal complex is commonly reported in terms of the effective magnetic moment (μ_{eff}) which can be obtained from the experimental measurement of molar magnetic susceptibility (χ_m) and is commonly expressed in Bohr magneton (BM). Theoretically, the magnetic moment is contributed by two components, the spin angular momentum and the orbital angular momentum. For many complexes of first row d-block metal ions, however, the contribution of the second component can be ignored, and the first component depends only on the number of unpaired electrons, n.

(a) The observed effective magnetic moment of two octahedral complexes, $K_4[Mn(CN)_6] \cdot 3H_2O$ and $K_4[Mn(SCN)_6]$ are 2.18 BM and 6.06 BM, respectively.

(i) Calculate number of unpaired electrons in each complex. Which complex is low spin? Which complex is high spin?

$K_4[Mn(CN)_6] \cdot 3H_2O$	$K_4[Mn(SCN)_6]$
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(ii) Rationalize your answers by drawing the Crystal Field Theory Diagram for each.

$K_4[Mn(CN)_6] \cdot 3H_2O$	$K_4[Mn(SCN)_6]$
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(b) Calculate the μ (spin only) of complex $[Ni(H_2O)_6]Cl_2$.

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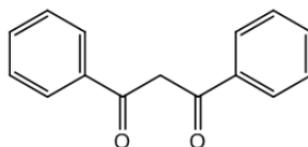
In practice, the experimentally observed μ_{eff} value of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ is 3.25 BM. This is not surprising due to the fact that the magnetic moment of octahedral complexes of Ni^{2+} (d^8) usually does not obey the spin only formula. In these cases, the contribution of orbital angular momentum should be taken into account. The simplification of spin-orbit coupling model can be applied to calculate their magnetic moment:

$$\mu_{\text{eff}} = \mu(\text{spin only}) \times \left(1 - \frac{4\lambda}{\Delta_{\text{oct}}}\right)$$

- λ is spin-orbit coupling constant of Ni^{2+} and has the value of -315 cm^{-1}
- Δ_{oct} is the crystal-field splitting parameter

(c) Calculate the effective magnetic moment of $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ taking into account spin-orbit coupling. Δ_{oct} of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is 8500 cm^{-1} .

(d) Dibenzoylmethane (DBM) is a well known chelating $\kappa\text{-O,O}$ -ligand which can form stable complexes with many transition metal ions.



DBM

Reaction of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with DBM in EtOH - H_2O solution gives light green crystalline complex **A** which loses 6.8 % of mass on heating at $210 \text{ }^\circ\text{C}$ in the air to form green solid **B**. The substance **B** is quantitatively converted to brown prismatic crystals **C** by re-crystallization in dry toluene. **B** and **C** are two polymorphic forms and their inter-conversion is reversible. The X-ray single crystal structure of **C** shows a square planar geometry with the chemical composition of $[\text{Ni}(\text{DBM})_2]$. While **B** is paramagnetic with an effective magnetic moment of 3.27 BM, the complex **C** is diamagnetic. When **B** and **C** are kept in the air, they slowly convert to **A**. This happens much faster in the presence of some organic solvents

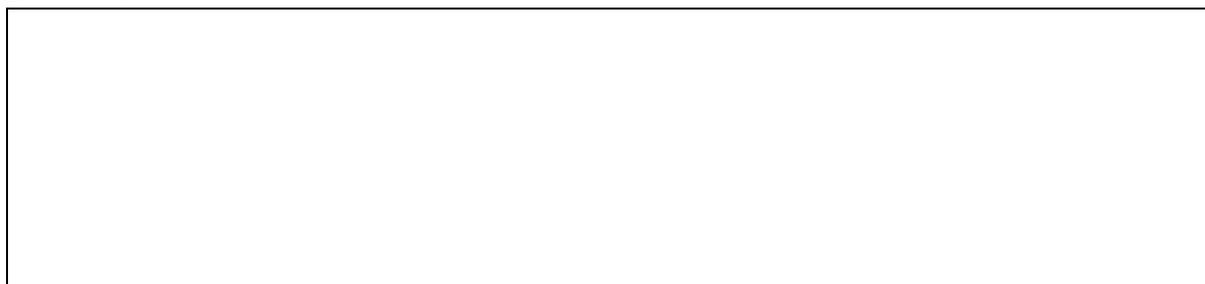
(i) Draw the splitting diagram of the d orbitals of Ni^{2+} in **C**



(ii) Determine the molecular formula of **A**



(iii) The effective magnetic moment of **A** is 3.11 BM. What is the most suitable molecular geometry of **A**?



(iv) Draw all possible isomers of **A**. (There are not necessarily 6 isomers)

(v) The geometry of **B** is not tetrahedral. Based on this information, what do you expect for the molecular geometry of **B**? Describe its structure.

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Problem 6
AQUARIUM IRON

12% of the total

2a	2b	2c	2d	2e	2f	2g	Total	%
5	2	1	3	8	1	2	22	12

Derek's hobby is keeping an aquarium (pH 7.2). He read in a book that his aquatic plants demand some soluble form of iron and its optimal concentration is $c(\text{Fe}) = 2 \mu\text{M}$.

-The dissolved oxygen concentration for solutions open to the atmosphere is $3.12 \cdot 10^{-4} \text{ M}$

For reference:

$\text{Fe}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	$K_{\text{sp}} = 4 \cdot 10^{-38}$
$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2(\text{aq}) + \frac{1}{2}\text{H}_2\text{O} \rightleftharpoons \text{Fe}^{3+} + \text{OH}^-$	$K_{\text{ox}} = 10^5$

Complex	Fe^{2+}Y	Fe^{3+}Y	$\text{Fe}(\text{OH})^{2+}$	$\text{Fe}(\text{OH})_2^+$	$\text{Fe}(\text{OH})_3(\text{aq})$
Stability Constant	$\beta^{\text{II}} = \frac{[\text{FeY}^{2-}]}{[\text{Fe}^{2+}][\text{Y}^{4-}]}$	$\beta^{\text{III}} = \frac{[\text{FeY}^+]}{[\text{Fe}^{3+}][\text{Y}^{4-}]}$	$\beta_1 = \frac{[\text{FeOH}^{2+}]}{[\text{Fe}^{3+}][\text{OH}^-]}$	$\beta_2 = \frac{[\text{Fe}(\text{OH})_2^+]}{[\text{Fe}^{3+}][\text{OH}^-]^2}$	$\beta_3 = \frac{[\text{Fe}(\text{OH})_3]}{[\text{Fe}^{3+}][\text{OH}^-]^3}$
Value	10^{14}	10^{25}	10^{12}	10^{22}	10^{30}

a) Calculate the fraction $\alpha(\text{Fe}^{3+})$ of free Fe^{3+} cation at pH = 7.2

b) Compute the solubility of $\text{Fe}(\text{OH})_3$ in an aquarium solution buffered at 7.2 (disregard the formation of Fe^{2+} species)

Derek decides to try using Fe(II) instead of Fe(III) because he reads that plants consume iron more efficiently if the oxidation state is +2.

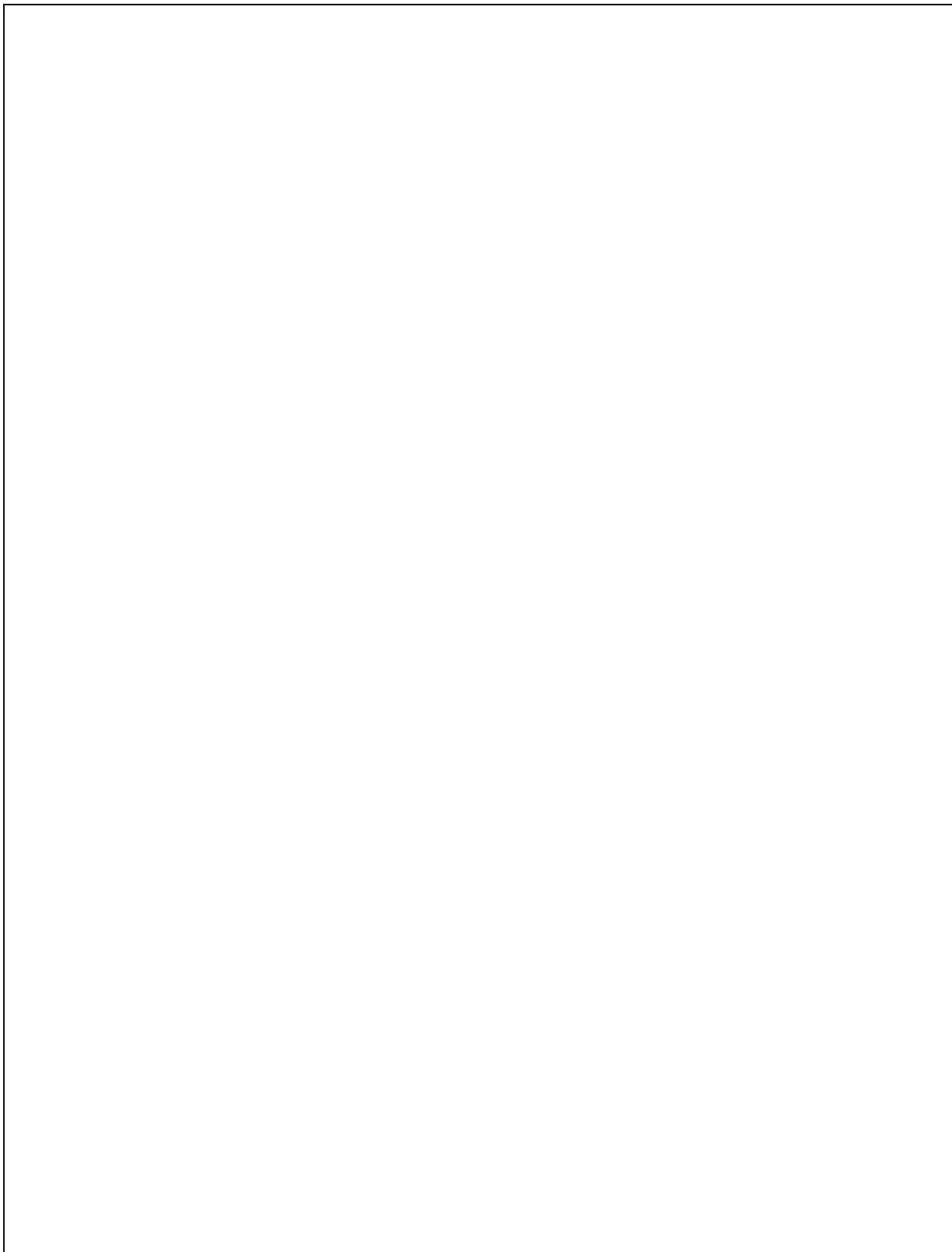
c) What reaction will occur upon the direct addition of Iron (II) Sulfate to the aquarium?

d) What percentage of dissolved iron will be present in the 2+ form at equilibrium, if 2 μM of iron(II) sulfate is added at pH 7.2 in an open atmosphere aquarium?

It is sometimes advised to increase the solubility of iron and its stability as iron(II) by adding iron as a chelate that can be prepared by mixing iron sulfate and EDTA. Derek simultaneously adds enough FeSO_4 so that the final total iron concentration in his aquarium is 2 μM , and enough EDTA so that the final total EDTA concentration in his aquarium is 3 μM .

EDTA is a tetraprotic acid. At pH = 7.2 the molar fraction of the completely deprotonated EDTA (Y^{4-} which forms complexes with Fe) relative to the various deprotonated forms equals $8 \cdot 10^{-4}$

e) Calculate the concentration of $[\text{Fe}^{3+}]$, $[\text{Fe}^{2+}]$, $[\text{Y}^{4-}]$, and $[\text{FeY}^-]$ in this solution



f) Does Iron (III) precipitate in the aquarium under these conditions?

[]

Yes

[]

No

g) Compute the percent of dissolved Iron present as Iron(II) in the aquarium at equilibrium



Problem 7
ENZYME INHIBITION

13% of the total

6a	6b	6c	6d	6e	6f	6g	6h	6i	Total	%
2	2	2	4	6	1	3	1	2	23	13

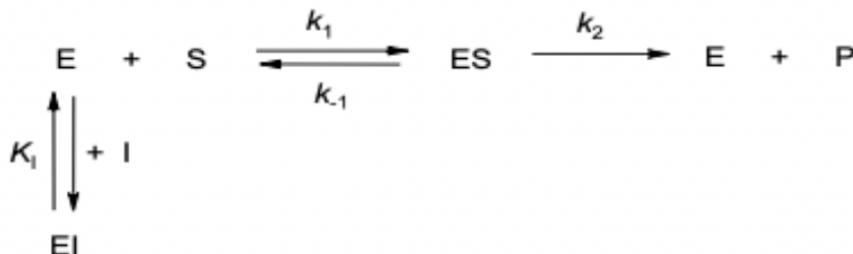
Enzymatic reactions are a very important class of catalytic reactions due to their key role in life processes. They are also widely used in biotechnology, so the course of enzymatic reactions is the subject of intensive research. A number of mechanisms for these reactions are proposed, and one of the most typical is the so-called the Michaelis-Menten mechanism, which can be represented by the following general scheme:



where E - enzyme in free form, S - substrate, ES - enzyme complex with substrate, P - product
 The initial velocity (for small degrees of conversion of substrate S) is then given by:

$$v_0 = v_{\max} [S]/(KM + [S]), \quad KM = (k_{-1} + k_2)/k_1$$

The rate of enzymatic reaction decreases after the addition of a competitive inhibitor, i.e. a substance that blocks the active site of the enzyme, thereby hindering substrate access and reaction. There are several types of inhibitors. Operation of the so-called a competitive inhibitor for the reaction following the Michaelis-Menten mechanism is shown in the diagram below:



The free enzyme is in this system in equilibrium with the form bound to the inhibitor, as described by the dissociation constant $K_1 = [E][I] / [EI]$.

The reaction speed is then given by the formula: $v_0 = v_{\max} [S]/(KM' + [S])$,
 where KM' is the so-called Michaelis constant.

The hydrolysis reaction of urea NH_2CONH_2 catalyzed by urease was measured at $T = 323 \text{ K}$. 10 mg of enzyme (molecular weight about $480 \times 10^3 \text{ g/mol}$) was added to 100 cm^{-3} of aqueous urea solution. The initial velocities of the reaction were determined based on conductometric measurements using different initial concentrations of urea [S]. The results of measurements are summarized in **Table 1**.

Then, analogous studies of the kinetics of the reaction in the presence of thiourea NH_2CSNH_2 were carried out, which acts as a competitive inhibitor in this reaction. The concentration of thiourea was $[\text{I}] = 0.0100 \text{ mol dm}^{-3}$. The measurement results are presented in **Table 2**.

Table 1			
[S] (M)	0.0100	0.0070	0.0040
t/min	$\kappa/\text{mS cm}^{-1}$		
0	0.090	0.080	0.080
1	0.320	0.250	0.190
2	0.550	0.420	0.300

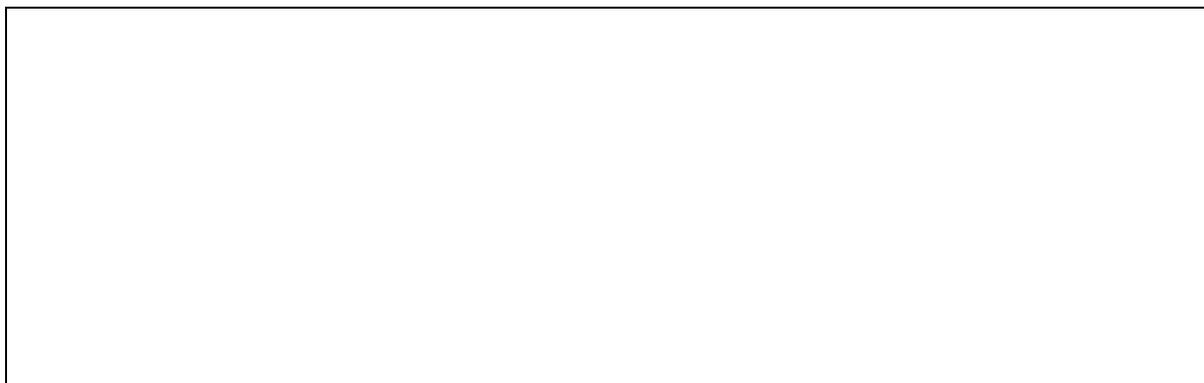
Table 2			
[S] (M)	0.0100	0.0070	0.0040
t/min	$\kappa/\text{mS cm}^{-1}$		
0	0.070	0.070	0.070
1	0.222	0.180	0.138
2	0.374	0.290	0.206

Electrolytic conductivity κ is a physicochemical quantity that determines the electrolyte's ability to conduct an electric charge. The fundamental unit of κ is $\text{S} \cdot \text{m}^{-1}$ ($\text{S} = \Omega^{-1}$). For dilute solutions of strong (completely dissociated) electrolytes interactions between ions can be neglected and then the κ value is directly proportional to the concentration. With this assumption, the reaction rate v may be expressed alternatively as a change in κ as a function of time. It is equivalent to a change in concentration as a function of time, i.e. a classically defined reaction rate. This definition of v will be used in further parts of the question ($v = \Delta\kappa/\Delta t$). Use the units for conductivity given in the table for convenience.

It should be assumed that the urea hydrolysis reaction to urease occurs according to the Michaelis-Menten mechanism. The reaction runs in a dilute aqueous solution, so the water is so large that its concentration is practically unchanged and can be excluded from kinetic considerations.

a. Write an equation for the urea hydrolysis reaction which justifies how its kinetics can be measured via conductometric measurements and briefly explain.

b. Determine the initial rates of the reaction without inhibitor in each trial



c. Sketch a simple graph of the concentration of product [P] versus time in the first trial ($[S]_i = 0.0100 \text{ mol dm}^{-3}$) and designate the phase of enzymatic reaction it describes. Explain also why the rates computed in part (b) correspond to initial rate v_i despite them being averaged values.



d. Calculate the values of v_{\max} and K_M , specifying units.



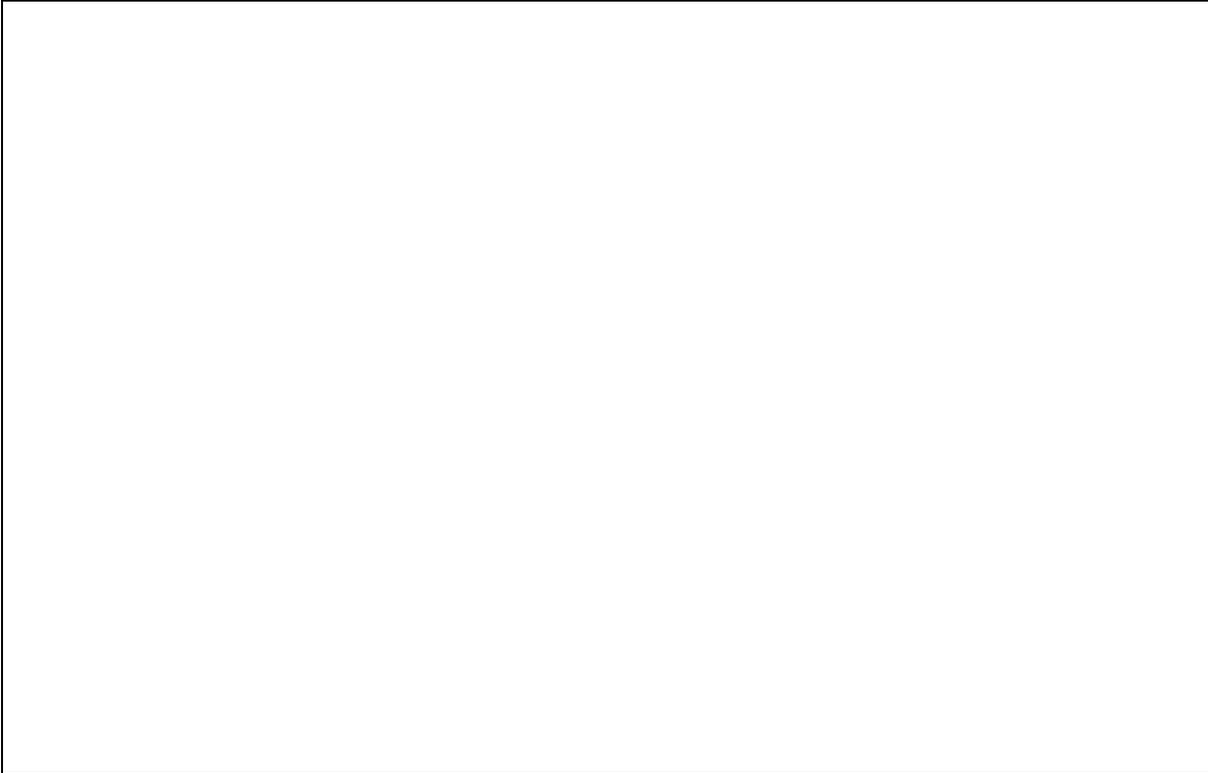
e. Derive the standard Michaelis Menten equation and then the equation for competitive inhibition, thereby deriving the value of KM'

Standard Derivation

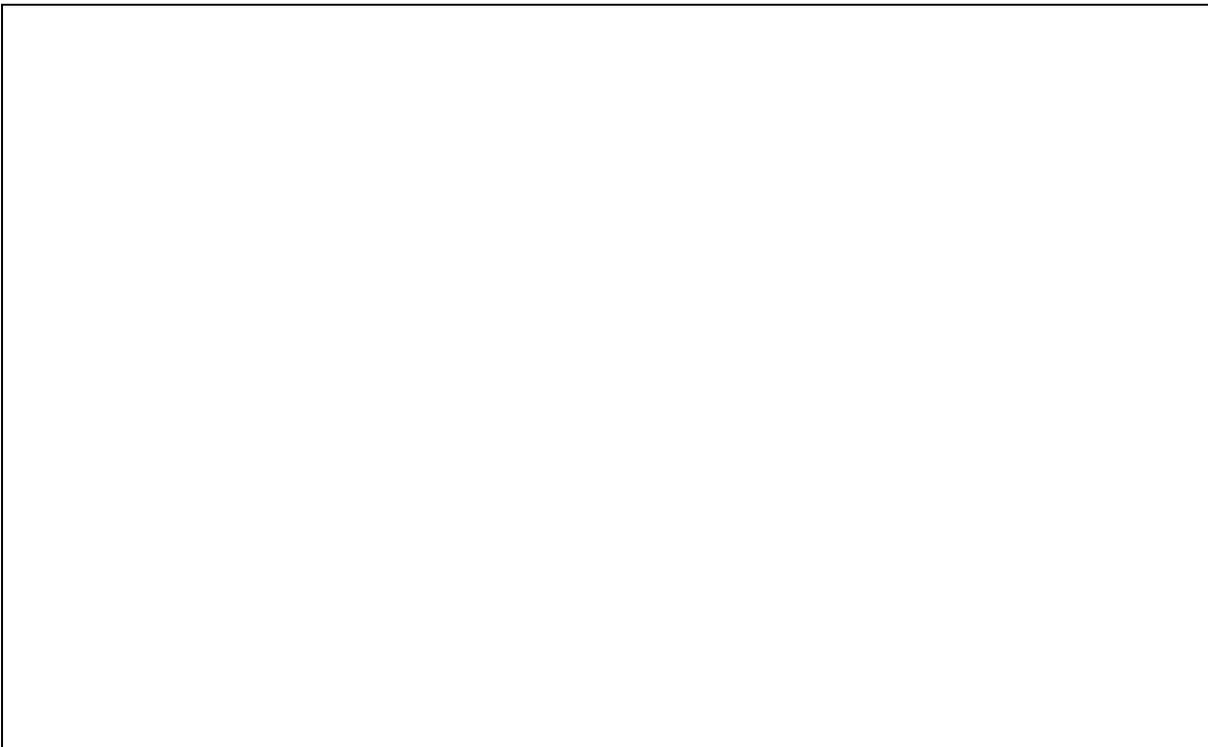
Competitive Inhibition

KM'

f. Compute the initial reaction rates of reaction v_o for the inhibitor at all 3 concentrations of urea

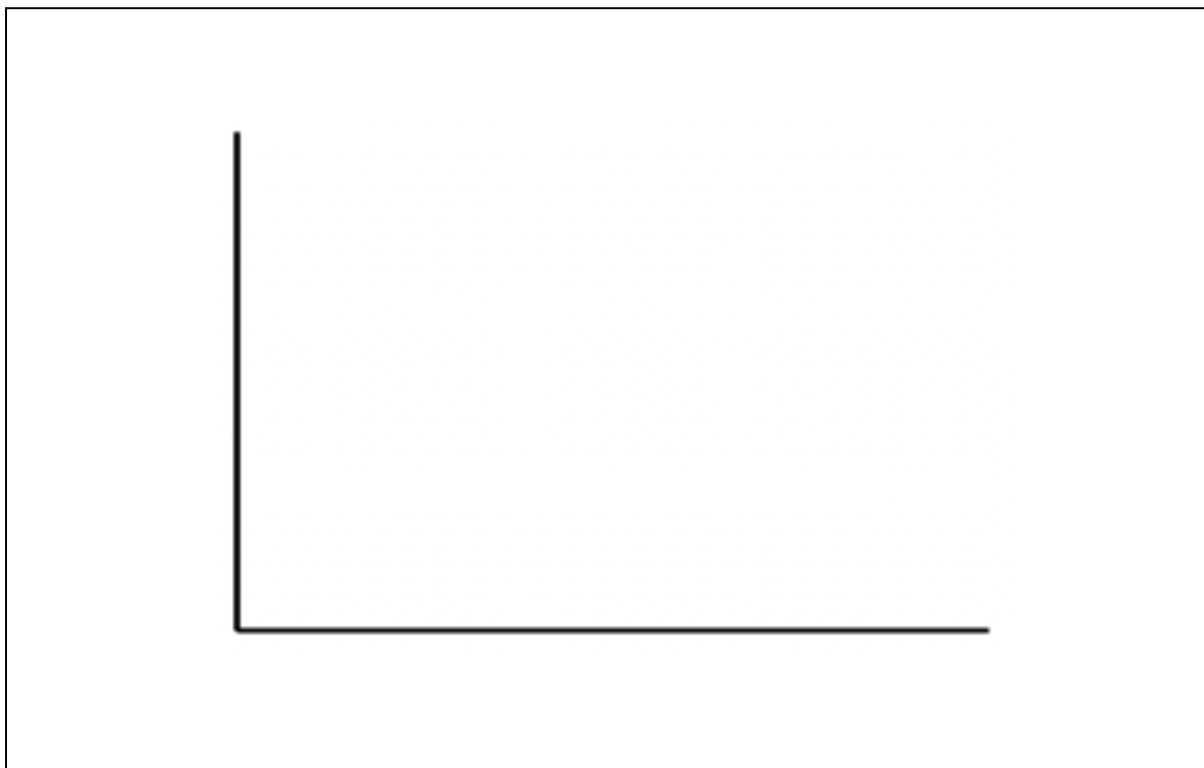


g. Calculate the dissociation constant K_I of the enzyme complex with the EI inhibitor. Specify units.



h. Compute the value of k_2 and specify its units.

i. Draw a rough sketch of $[S]$ versus rate v , identifying V_{\max} , $1/2V_{\max}$ and the value of $[S]$ that makes $v=1/2 V_{\max}$ in terms of K_M and K_M' on the same axes:

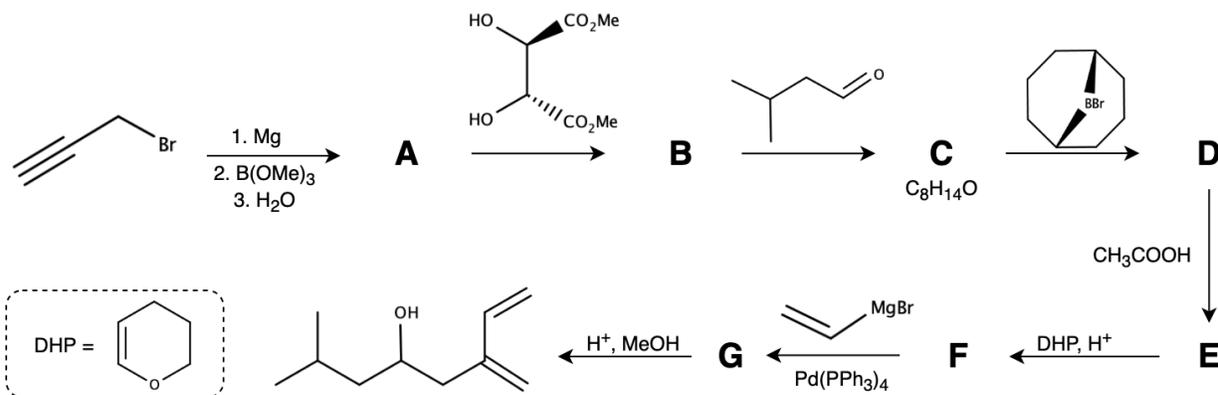


Problem 8
ORGANIC BORON

6% of the total

6a	6b	Total	%
21	3	24	6

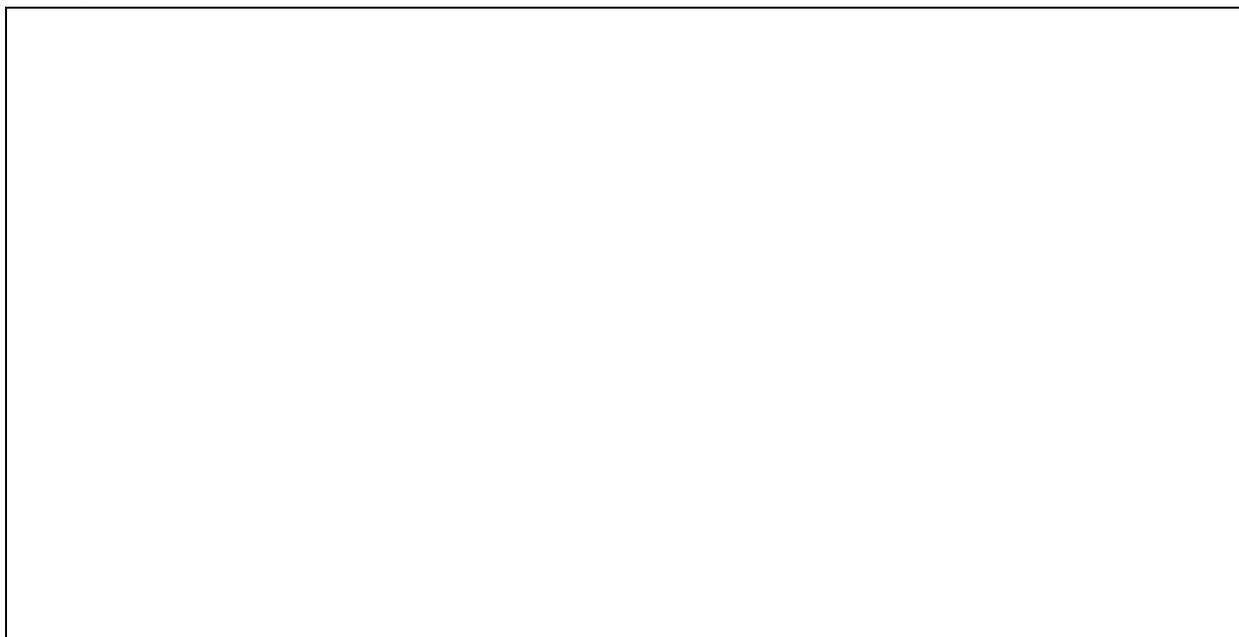
The synthesis below is an interesting application of organoboron chemistry.



a. Draw the structures of intermediates A-G

A	B	C
D	E	F
G		

b. Propose a mechanism for the formation of **C**

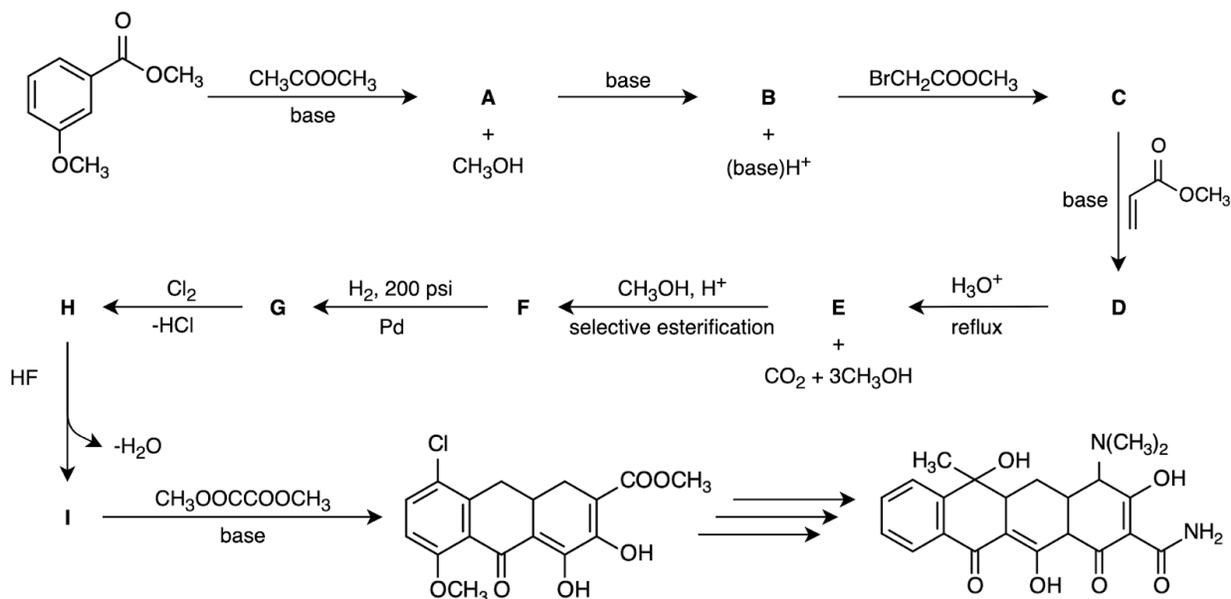


Problem 9
TETRACYCLINE

9% of the total

8a	Total	%
33	33	9

Tetracycline is a broad spectrum antibiotic that is active against penicillin-resistant Gram-positive bacterial organisms. The first synthesis of a tetracycline was reported by R. B. Woodward (Harvard University) and the Pfizer Pharmaceutical Company in 1962. Three of the four rings were synthesized by the following steps.

*Hints:*

- (1) the conversion of **E** to **F** involves only one methanol reactant;
- (2) compounds **A**, **B**, **C**, **D**, and **E** have proton NMR spectra with two hydrogen signals above 7.8 ; these absorptions are not present in compounds **G**, **H**, and **I**.

a. Draw the structures of compounds **A–I**.

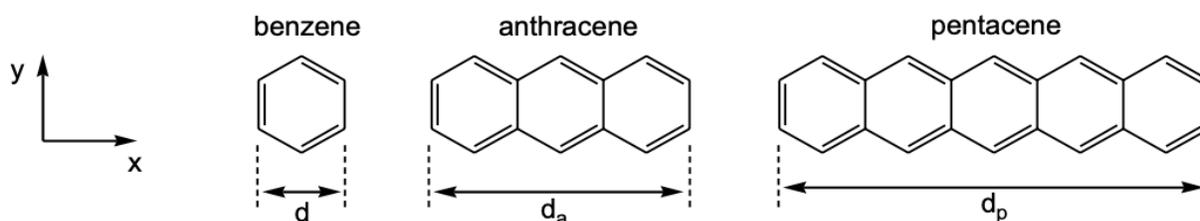
A	B
C	D
E	F
G	H
I	

Problem 10
PAHs

12% of the total

8a	8b-i	8b-ii	8b-iii	8b-iv	8b-v	8c-i	8c-ii	8c-iii	Total	%
2	3	4	6	4	2	5	8	2	36	12

Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants, components of organic light emitting diodes and components of the interstellar medium. This problem deals with so-called linear PAHs, i.e., those being just one benzene ring wide whereas the length is varied. Specific examples are benzene, anthracene and pentacene whose structures are shown below. Their physical and chemical properties depend on the extent to which the electron cloud is delocalized over the molecule.



- a) The distance across the benzene ring is $d = 240$ pm. Use this information to estimate the distances along the horizontal (x) axis for anthracene and pentacene, d_a and d_p , respectively.

- b) Assume for simplicity that the π electrons of benzene can be modeled as being confined to a square. Within this model, the conjugated π electrons of PAHs may be considered as free particles in a two dimensional rectangular box in the x - y plane.

For electrons in a two-dimensional box along the x - and y -axes, the quantized energy states of the electrons are given by

$$E = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) \frac{h^2}{8m_e}$$

In this equation, n_x and n_y are the quantum numbers for the energy state and are integers between 1 and ∞ , h is Planck's constant, m_e is the mass of the electron and L_x and L_y are the dimensions of the box.

For this problem, treat the electrons of the PAHs as particles in a two dimensional box. In this case, the quantum numbers n_x and n_y are independent.

i. For this problem, assume that the benzene unit has x and y dimensions that are each of length d . Derive a general formula for the quantized energies of linear PAHs as a function of quantum numbers n_x and n_y , the length d , the number of fused rings w , and the fundamental constants h and m_e .

ii. The energy level diagram below for pentacene shows qualitatively the energies and quantum numbers n_x, n_y for all levels occupied by π -electrons and the lowest unoccupied energy level, with the electrons of opposite spins represented as the arrows pointing up or down. The levels are labeled with quantum numbers $(n_x; n_y)$.

Pentacene:

— (3; 2)
 $\uparrow\downarrow$ (9; 1)
 $\uparrow\downarrow$ (2; 2)
 $\uparrow\downarrow$ (1; 2)
 $\uparrow\downarrow$ (8; 1)
 $\uparrow\downarrow$ (7; 1)
 $\uparrow\downarrow$ (6; 1)
 $\uparrow\downarrow$ (5; 1)
 $\uparrow\downarrow$ (4; 1)
 $\uparrow\downarrow$ (3; 1)
 $\uparrow\downarrow$ (2; 1)
 $\uparrow\downarrow$ (1; 1)

The energy level diagram for anthracene is shown below. Note that some energy levels may have the same energy. Draw the correct number of up and down arrows to represent the electrons in this diagram. Also, the blanks in parentheses within this diagram are the quantum numbers n_x , n_y for each filled and the lowest unfilled energy level(s).

Anthracene:

_ (_ ; _)
 _ (_ ; _) _ (_ ; _)
 _ (_ ; _)
 _ (_ ; _)
 _ (_ ; _)
 _ (_ ; _)
 _ (_ ; _)
 _ (_ ; _)

iii. Use this model to create an energy level diagram for benzene and fill the pertinent energy levels with electrons. Include energy levels up to and including the lowest unoccupied energy level. Label each energy level in your diagrams with the corresponding n_x , n_y . Do not assume that the particle-in-a-square-box model used here gives the same energy levels as other models.

iv. Often the reactivity of PAHs correlates inversely with the energy gap E between the highest energy level occupied by π -electrons and the lowest unoccupied energy level. Calculate the energy gap ΔE (in Joules) between the highest occupied and lowest unoccupied energy levels for benzene, anthracene and pentacene. Use your result from parts ii) and iii) for anthracene or benzene, respectively, or use (2, 2) for the highest occupied energy level and (3, 2) for the lowest unoccupied energy level for these two molecules (these may not be the true values).

ΔE for benzene

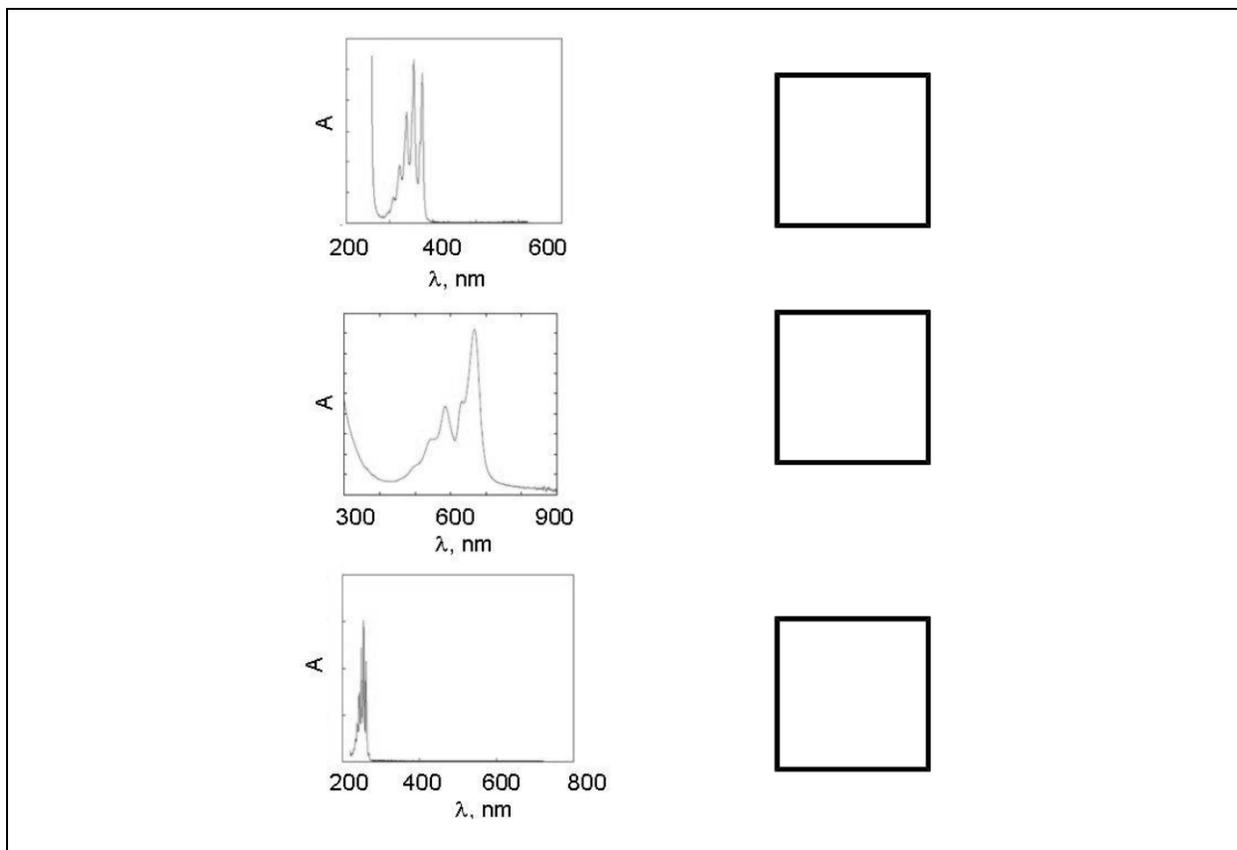
ΔE for anthracene

ΔE for pentacene

Rank benzene (**B**), anthracene (**A**), and pentacene (**P**) in order of increasing reactivity by placing the corresponding letters from left to right in the box below.

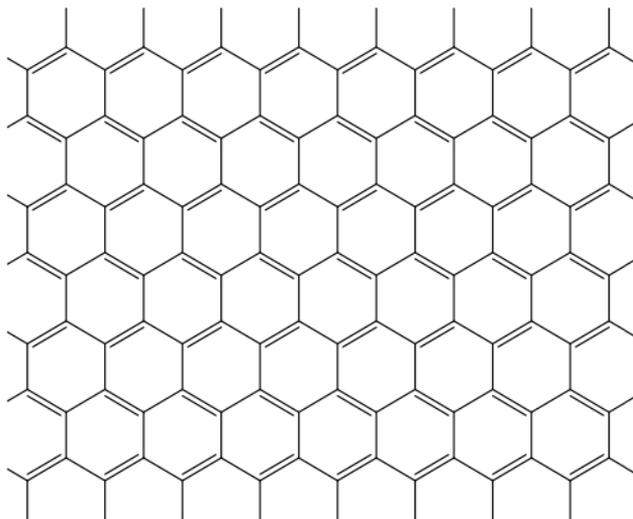
Least Reactive -----> Most Reactive

v. The electronic absorption spectra (molar absorptivity vs. wavelength) for benzene (**B**), anthracene (**A**), and pentacene (**P**) are shown below. Based on a qualitative understanding of the particle in the box model, indicate which molecule corresponds to which spectrum by writing the appropriate letter in the box to its right.



c. Graphene is a sheet of carbon atoms arranged in a two-dimensional honeycomb pattern. It can be considered as an extreme case of a polyaromatic hydrocarbon with essentially infinite length in the two dimensions. The Nobel Prize for Physics was awarded in 2010 to Andrei Geim and Konstantin Novoselov for groundbreaking experiments on graphene.

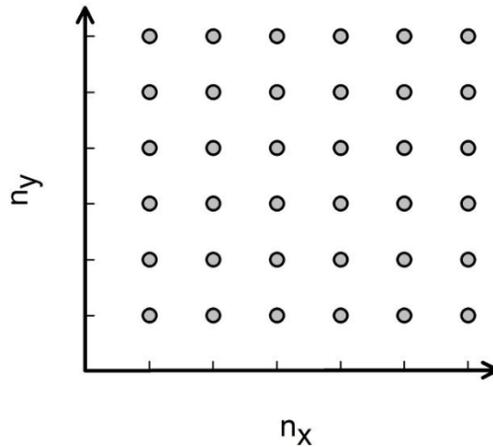
Consider a sheet of graphene with planar dimensions of $L_x=25$ nm by $L_y=25$ nm. A section of this sheet is shown below.

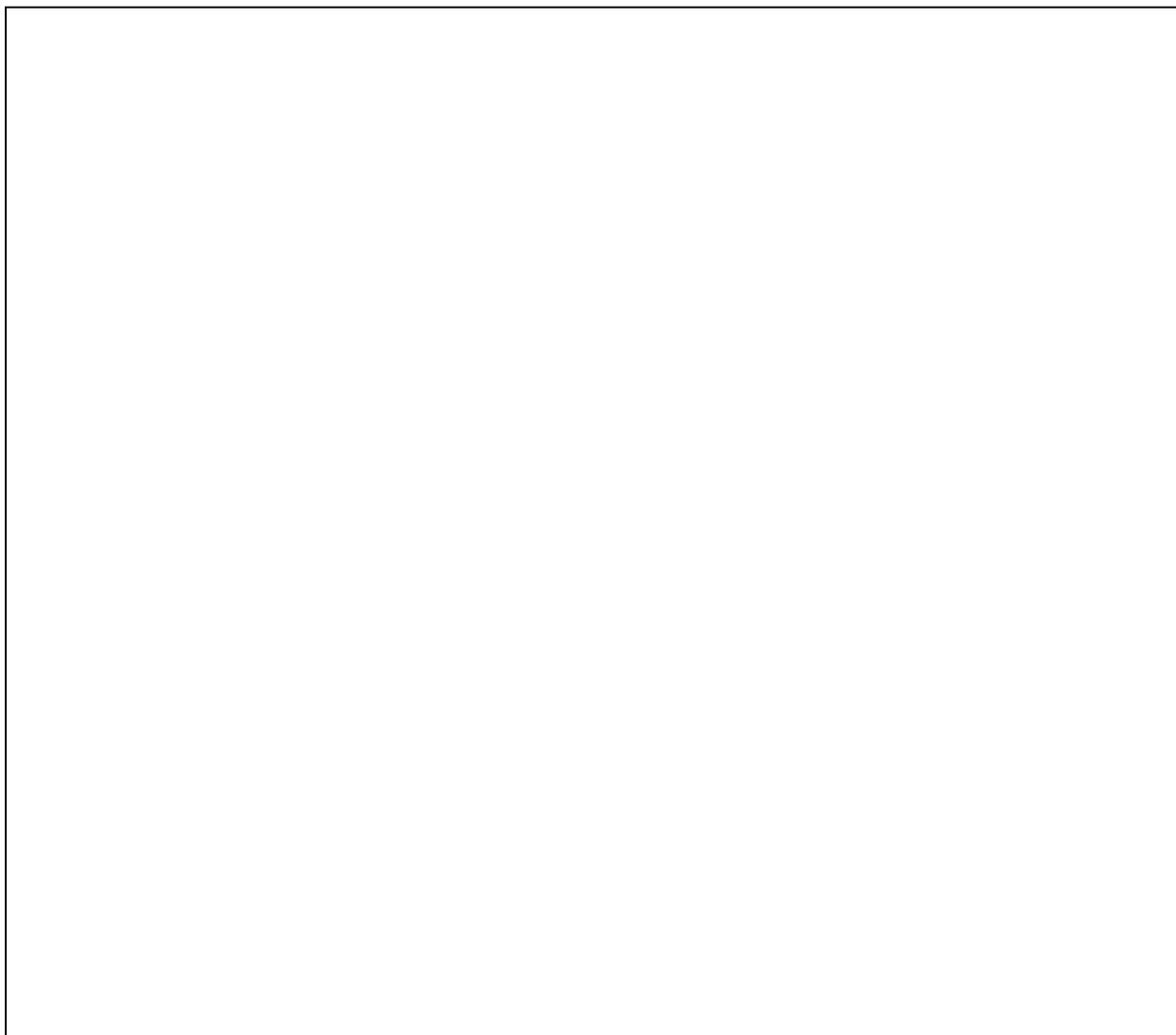


- i. The area of one hexagonal 6-carbon unit is ~ 52400 pm². Calculate the number of electrons in a (25 nm 25 nm) sheet of graphene. For this problem you can ignore edge electrons (i.e., those outside the full hexagons in the picture).

ii. We can think about the electrons in graphene as being free electrons in a 2-dimensional box.

In systems containing large numbers of electrons, there is no single highest occupied energy level. Instead, there are many states of nearly the same energy above which the remaining are empty. These highest occupied states determine the so-called Fermi level. The Fermi level in graphene consists of multiple combinations of n_x and n_y quantum numbers. Determine the energy of the Fermi level for the 25 nm \times 25 nm square of graphene relative to the lowest filled level. The lowest filled level has a non-zero energy; however, it is negligible, and can be assumed to be zero. To solve this problem it might be helpful to represent the (n_x, n_y) quantum states as points on a 2-D grid (as shown below) and consider how the energy levels are filled with pairs of electrons. For the number of electrons use your result from part i or use a value of 1000 (this may not be the true value).





iii. The conductivity of graphene-like materials correlates inversely with the energy gap between the lowest unoccupied and highest occupied energy levels. Use your analysis and understanding of electrons in PAHs and graphene to predict whether the conductivity of a $25 \text{ nm} \times 25 \text{ nm}$ square of graphene, at a given temperature, is less than, equal to or greater than the conductivity of a $1 \text{ m} \times 1 \text{ m}$ square of graphene (which is the largest obtained to date). Circle the correct answer:

Less	Equal	Greater
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Problem Sources

1	(2016 INCHO #5) Nickel spinel stuff
2	2017 Austria CHO #7
3	Original
4	2006 Mendeleev Tour 1 #3
5	2014 Prep complexes
6	2017 Mendeleev Tour 2 Analytical #2
7	2013 Polish Stage 3 #3
8	Ukraine Chemistry Olympiad
9	2012 ICHO Prep #26
10	2012 ICHO

A brief grading guide can be found here:

<https://docs.google.com/document/d/1GErzqoBnf9PYPm3zIJ5uRGTJUFY9T1UiVSLHL0kq6q4/edit?usp=sharing>