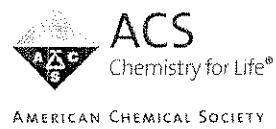


USA



Washington, D.C. • USA



Theoretical Problems

44th International
Chemistry Olympiad

July 26, 2012

United States
of America

Instructions

- Write your name and code on each page.
- This examination has 8 problems and the Periodic Table on 49 pages.
- You have 5 hours to work on the exam problems. **Begin** only when the **START** command is given.
- Use only the pen and the calculator provided.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the back side of the exam sheets if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- When you have finished the examination, put your papers into the envelope provided. Do not seal the envelope.
- You must **stop** working when the **STOP** command is given.
- Do not leave your seat until permitted by the supervisors.
- The official English version of this examination is available on request only for clarification.

Physical Constants, Formulas and Equations

Avogadro's constant, $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$

Boltzmann constant, $k_B = 1.3807 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$

Universal gas constant, $R = 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 0.08205 \text{ atm}\cdot\text{L}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Speed of light, $c = 2.9979 \times 10^8 \text{ m}\cdot\text{s}^{-1}$

Planck's constant, $h = 6.6261 \times 10^{-34} \text{ J}\cdot\text{s}$

Mass of electron, $m_e = 9.10938215 \times 10^{-31} \text{ kg}$

Standard pressure, $P = 1 \text{ bar} = 10^5 \text{ Pa}$

Atmospheric pressure, $P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ Torr}$

Zero of the Celsius scale, 273.15 K

1 nanometer (nm) = 10^{-9} m

1 picometer (pm) = 10^{-12} m

Equation of a circle, $x^2 + y^2 = r^2$

Area of a circle, πr^2

Perimeter of a circle, $2\pi r$

Volume of a sphere, $4\pi r^3/3$

Area of a sphere, $4\pi r^2$

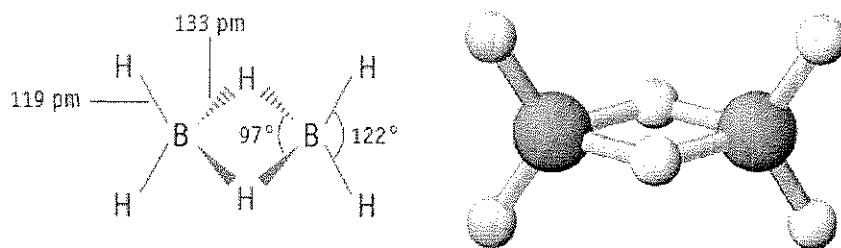
Bragg's Law of Diffraction: $\sin \theta = n\lambda/2d$

PROBLEM 1**7.5% of the total**

| a-i | a-ii | a-iii | b | c | Problem 1 | |
|-----|------|-------|---|----|-----------|------|
| 4 | 2 | 2 | 2 | 10 | 20 | |
| | | | | | | 7.5% |

a. Boron Hydrides and Other Boron Compounds

Boron hydride chemistry was first developed by Alfred Stock (1876-1946). More than 20 neutral molecular boron hydrides with the general formula B_xH_y have been characterized. The simplest boron hydride is B_2H_6 , diborane.



i. Using the data below **DERIVE** the **molecular** formulas for two other members of this series of boron hydrides, A and B.

| Substance | State (25 °C, 1 bar) | Mass Percent Boron | Molar mass (g/mol) |
|-----------|----------------------|--------------------|--------------------|
| A | Liquid | 83.1 | 65.1 |
| B | Solid | 88.5 | 122.2 |

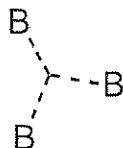
A = _____

B = _____

ii. William Lipscomb received the Nobel Prize in Chemistry in 1976 for “studies on the structures of boron hydrides illuminating the problems of chemical bonding.” Lipscomb recognized that, *in all boron hydrides, each B atom has a normal 2-electron bond to at least one H atom (B–H)*. However, additional bonds of several types occur, and he developed a scheme for describing the structure of a borane by giving it a *styx* number where:

s = number of B–H–B bridges in the molecule

t = the number of 3-center BBB bonds in the molecule



y = the number of two-center B–B bonds in the molecule

x = the number of BH_2 groups in the molecule

The *styx* number for B_2H_6 is 2002. Propose a structure for tetraborane, B_4H_{10} , with a *styx* number of 4012.

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iii. A boron-based compound is composed of boron, carbon, chlorine, and oxygen (B_4CCl_6O). Spectral measurements indicate that the molecule has two types of B atoms, with tetrahedral and trigonal planar geometry, in a 1:3 ratio, respectively. These spectra are also consistent with a CO triple bond. Given that the molecular formula of the compound is B_4CCl_6O , **DRAW** a structure for the molecule.

Structure:

Name:

Code: USA

b. Thermochemistry of Boron Compounds

ESTIMATE the B-B single bond dissociation enthalpy in $\text{B}_2\text{Cl}_4(\text{g})$ using the following information:

| Bond | Bond Dissociation Enthalpy (kJ/mol) |
|-------------|--|
|-------------|--|

| | |
|------|-----|
| B-Cl | 443 |
|------|-----|

| | |
|-------|-----|
| Cl-Cl | 242 |
|-------|-----|

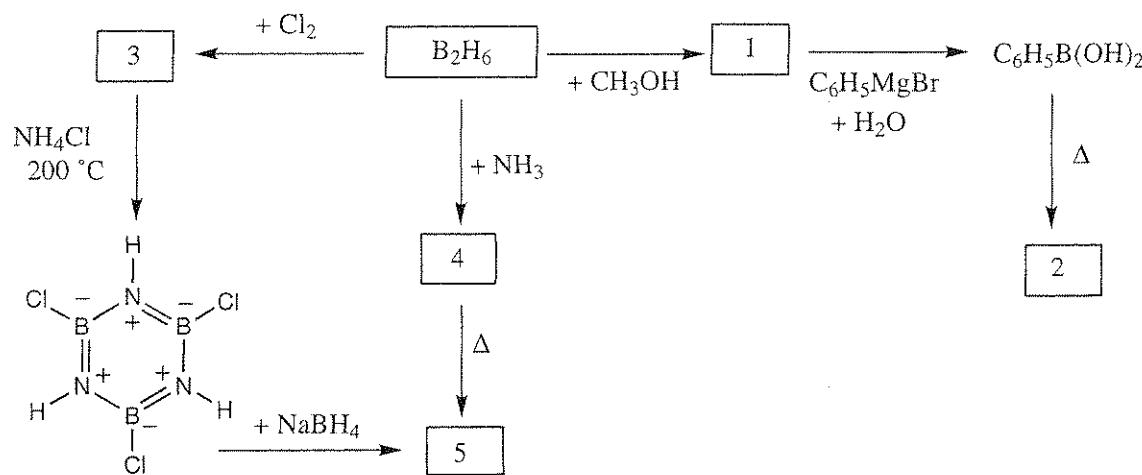
| Compound | $\Delta_f H^\circ$ (kJ/mol) |
|-----------------|---|
|-----------------|---|

| | |
|--------------------------|------|
| $\text{BCl}_3(\text{g})$ | -403 |
|--------------------------|------|

| | |
|-----------------------------------|------|
| $\text{B}_2\text{Cl}_4(\text{g})$ | -489 |
|-----------------------------------|------|

c. Chemistry of Diborane

GIVE the structure for each numbered compound in the scheme below. Each numbered compound is a boron-containing compound.



NOTES:

- The boiling point of compound 5 is 55°C .
- Excess reagents are used in all reactions.
- The freezing point depression for 0.312 g of compound 2 in 25.0 g of benzene is 0.205°C . The freezing point depression constant for benzene is 5.12°C/molal

Name:

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| Number | Molecular Structure of Compound |
|--------|---------------------------------|
| 1 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |

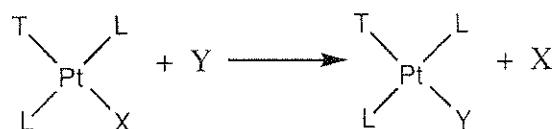
PROBLEM 2

7.8% of the total

| a-i | a-ii | b-i | b-ii | c | Problem 2 | 7.8% |
|-----|------|-----|------|---|-----------|------|
| 4 | 4 | 6 | 1 | 5 | 20 | |
| | | | | | | |

Platinum(II) Compounds, Isomers, and the *Trans* Effect.

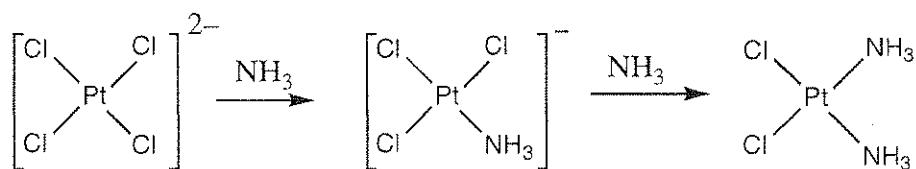
Platinum and other Group 10 metals form square planar complexes, and the mechanisms of their reactions have been studied extensively. For example, it is known that substitution reactions of these complexes proceed with retention of stereochemistry.



It is also known that the rate of substitution of ligand X by Y depends on the nature of the ligand *trans* to X (ligand T). This is known as the *trans effect*. When T is one of the molecules or ions in the following list, the rate of substitution at the *trans* position decreases from left to right.



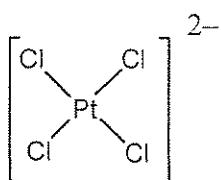
The preparations of *cis*- and *trans*-Pt(NH₃)₂Cl₂ depend on the *trans* effect. The preparation of the *cis* isomer, a cancer chemotherapy agent commonly called cisplatin, involves the reaction of K₂PtCl₄ with ammonia.



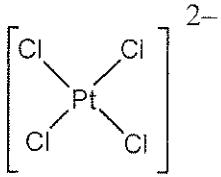
i. **DRAW** all possible stereoisomers for square planar platinum(II) compounds with the formula $\text{Pt}(\text{py})(\text{NH}_3)\text{BrCl}$ (where py = pyridine, $\text{C}_5\text{H}_5\text{N}$).

ii. **WRITE** reaction schemes including intermediate(s), if any, to show the preparation in aqueous solution for each of the stereoisomers of $[\text{Pt}(\text{NH}_3)(\text{NO}_2)\text{Cl}_2]^{2-}$ using, as reagents, PtCl_4^{2-} , NH_3 , and NO_2^- . The reactions are controlled kinetically by the *trans* effect.

cis-isomer:



trans-isomer:



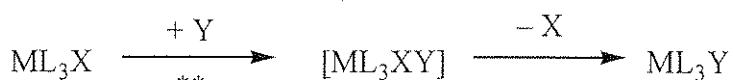
b. Kinetic Studies of Substitution Reactions of Square Planar Complexes

Substitutions of the ligand X by Y in square planar complexes



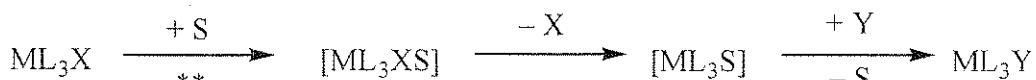
can occur in either or both of two ways:

- *Direct substitution*: The incoming ligand Y attaches to the central metal, forming a five-coordinate complex, which then rapidly eliminates a ligand, X, to give the product, ML_3Y .



$\ast\ast$ = rate determining step, Rate constant = k_Y

- *Solvent-assisted substitution*: A solvent molecule S attaches to the central metal to give ML_3XS , which eliminates the X to give ML_3S . Y rapidly displaces S to give ML_3Y .



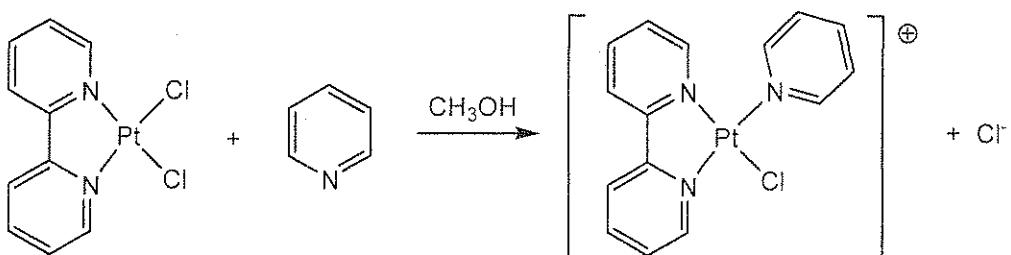
$\ast\ast$ = rate determining step, Rate constant = k_S

The overall rate law for such substitutions is

$$\text{Rate} = k_s[ML_3X] + k_Y[Y][ML_3X]$$

When $[Y] \gg [ML_3X]$, then $\text{Rate} = k_{\text{obs}}[ML_3X]$.

The values of k_s and k_Y depend on the reactants and solvent involved. One example is the displacement of the Cl^- ligand in a square planar platinum(II) complex, ML_2X_2 , by pyridine (C_5H_5N). (The ML_3X scheme above applies to ML_2X_2 .)



Data for the reaction at 25 °C in methanol where [pyridine] \gg the concentration of the platinum complex are given in the table on page 13.

| Concentration of pyridine (mol/L) | $k_{\text{obs}} (\text{s}^{-1})$ |
|-----------------------------------|----------------------------------|
| 0.122 | 7.20×10^{-4} |
| 0.061 | 3.45×10^{-4} |
| 0.030 | 1.75×10^{-4} |

i. **CALCULATE** the values of k_s and k_Y . **GIVE** the proper unit for each constant.
A grid is provided if you wish to use it.

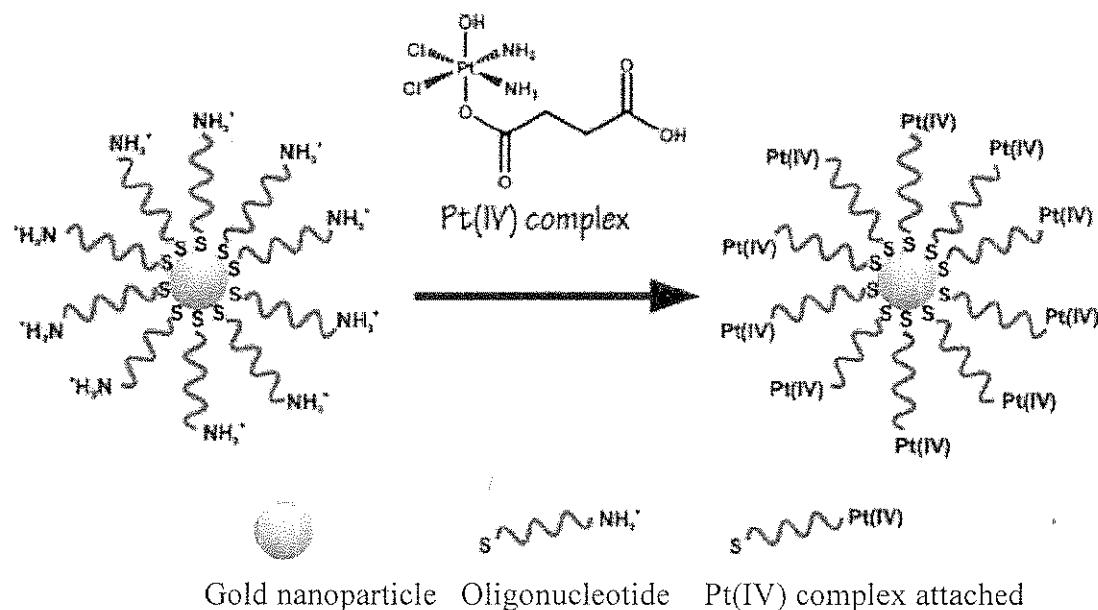
| | | | | | | | | |
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ii. When $[\text{pyridine}] = 0.10 \text{ mol/L}$, which of the following is true? (CHECK the box next to the correct answer.)

| | |
|--|---|
| | Most pyridine product is formed by the solvent-assisted (k_s) substitution pathway. |
| | Most pyridine product is formed by the direct substitution (k_Y) pathway |
| | Comparable amounts of product are formed by the two pathways. |
| | No conclusions may be drawn regarding the relative amounts of product produced by the two pathways. |

c. A chemotherapy agent

In an effort to better target cisplatin to cancer cells, Professor Lippard's group at MIT attached a platinum(IV) complex to oligonucleotides bound to gold nanoparticles.



The experiments use gold nanoparticles with a diameter of 13 nm. Attached to each nanoparticle are 90 oligonucleotide groups, with 98% of them being bound to a Pt(IV) complex. Suppose that the reaction vessel used for treating cells with the Pt(IV) nanoparticle reagent has a volume of 1.0 mL and that the solution is $1.0 \times 10^{-6} \text{ M}$ in Pt. **CALCULATE the mass of gold and of platinum used in this experiment.** (The density of gold is 19.3 g/cm^3)

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Mass of platinum

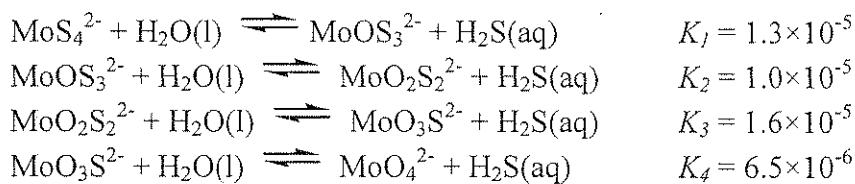
Mass of gold

PROBLEM 3**7.5 % of the Total**

| a | b | c-i | c-ii | Problem 3 | |
|---|----|-----|------|-----------|------|
| 4 | 12 | 6 | 12 | 34 | 7.5% |
| | | | | | |

Thiomolybdate ions are derived from molybdate ions, MoO_4^{2-} , by replacing oxygen atoms with sulfur atoms. In nature, thiomolybdate ions are found in such places as the deep waters of the Black Sea, where biological sulfate reduction generates H_2S . The molybdate to thiomolybdate transformation leads to rapid loss of dissolved Mo from seawater to underlying sediments, depleting the ocean in Mo, a trace element essential for life.

The following equilibria control the relative concentrations of molybdate and thiomolybdate ions in dilute aqueous solution.



a. At equilibrium a solution contains 1×10^{-7} M MoO_4^{2-} and 1×10^{-6} M $\text{H}_2\text{S(aq)}$.
CALCULATE the concentration of MoS_4^{2-} .

Solutions containing $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-} display absorption peaks in the visible wavelength range at 395 and 468 nm. The other ions, as well as H_2S , absorb negligibly in the visible wavelength range. The molar absorptivities (ϵ) at these two wavelengths are given in the following table:

| | ϵ at 468 nm $\text{L mol}^{-1} \text{cm}^{-1}$ | ϵ at 395 nm $\text{L mol}^{-1} \text{cm}^{-1}$ |
|-------------------------------|--|--|
| MoS_4^{2-} | 11870 | 120 |
| MoOS_3^{2-} | 0 | 9030 |
| $\text{MoO}_2\text{S}_2^{2-}$ | 0 | 3230 |

b. A solution *not* at equilibrium contains a mixture of MoS_4^{2-} , MoOS_3^{2-} and $\text{MoO}_2\text{S}_2^{2-}$ and no other Mo-containing species. The total concentration of all species containing Mo is 6.0×10^{-6} M. In a 10.0 cm absorption cell, the absorbance of the solution at 468 nm is 0.365 and at 395 nm is 0.213. **CALCULATE** the concentrations of all three Mo-containing anions in this mixture.

$\text{MoO}_2\text{S}_2^{2-}$: _____

MoOS_3^{2-} : _____

MoS_4^{2-} : _____

Name:

Code: USA

c. A solution initially containing 2.0×10^{-7} M MoS_4^{2-} hydrolyzes in a closed system. The H_2S product accumulates until equilibrium is reached. Calculate the final, equilibrium concentrations of H_2S (aq), and all five Mo-containing anions (that is, MoO_4^{2-} , $\text{MoO}_3\text{S}^{2-}$, $\text{MoO}_2\text{S}_2^{2-}$, MoOS_3^{2-} and MoS_4^{2-}). Ignore the possibility that H_2S might ionize to HS^- under certain pH conditions. *(One-third credit is given for writing the six independent equations that constrain the problem, and two-thirds credit is given for the correct concentrations.)*

i. **WRITE** the six independent equations that determine the system.

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ii. **CALCULATE** the six concentrations, making reasonable approximations. **GIVE** your answers to two significant figures.

H_2S _____

MoO_4^{2-} _____

$\text{MoO}_3\text{S}^{2-}$ _____

$\text{MoO}_2\text{S}_2^{2-}$ _____

MoOS_3^{2-} _____

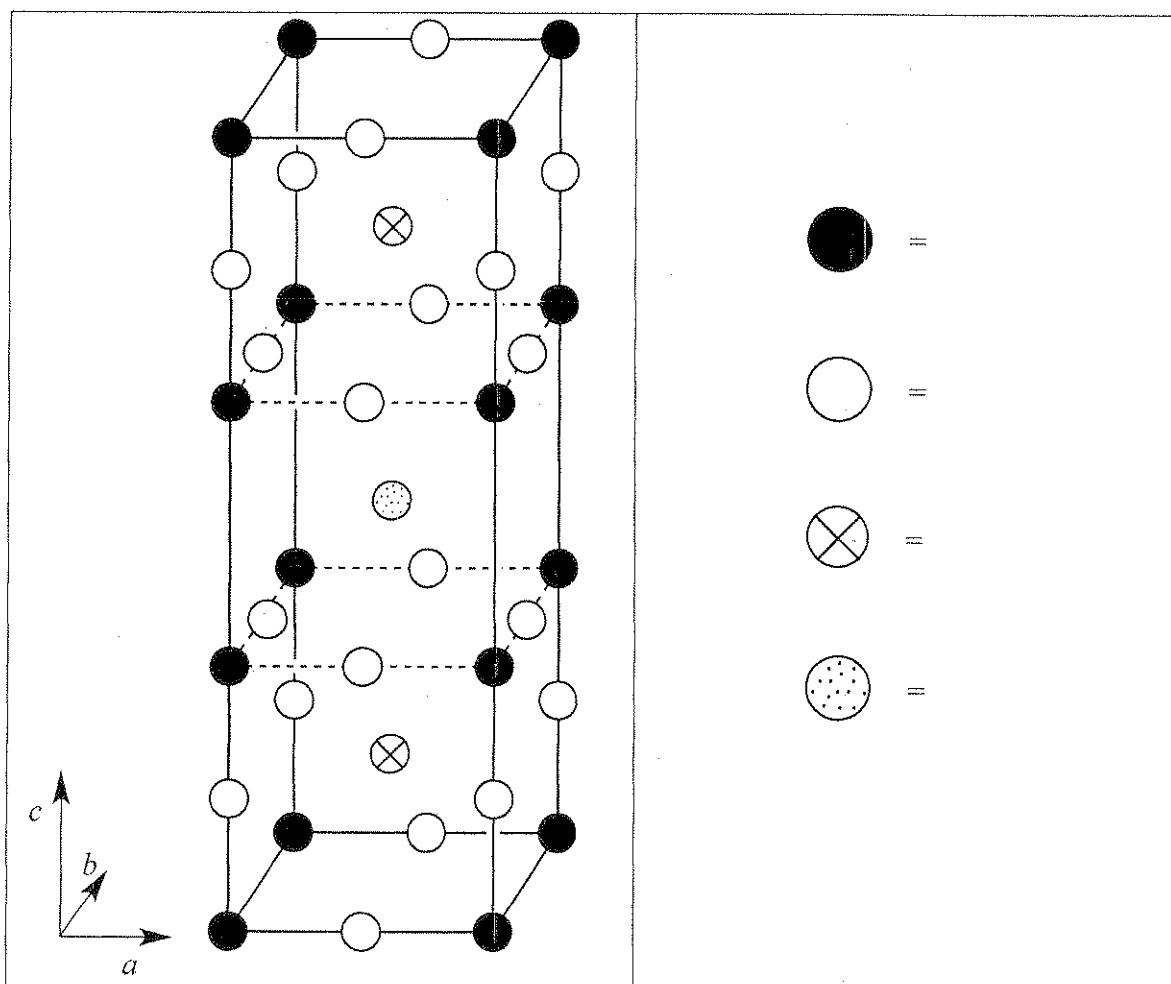
MoS_4^{2-} _____

PROBLEM 4**7.8% of the Total**

| a | b | c | d-i | d-ii | d-iii | d-iv | e-i | e-ii | Problem 4 | |
|----|----|----|-----|------|-------|------|-----|------|-----------|------|
| 12 | 14 | 10 | 4 | 2 | 2 | 4 | 4 | 8 | 60 | 7.8% |
| | | | | | | | | | | |

In the 1980s a class of ceramic materials was discovered that exhibits superconductivity at the unusually high temperature of 90 K. One such material contains yttrium, barium, copper and oxygen and is called "YBCO". It has a nominal composition of $\text{YBa}_2\text{Cu}_3\text{O}_7$, but its actual composition is variable according to the formula $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 < \delta < 0.5$).

a. One unit cell of the idealized crystal structure of YBCO is shown below. **IDENTIFY** the circles that correspond to the elements in the structure.



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The true structure is actually orthorhombic ($a \neq b \neq c$), but it is approximately tetragonal, with $a \approx b \approx (c/3)$.

b. A sample of YBCO with $\delta = 0.25$ was subjected to X-ray diffraction using Cu K α radiation ($\lambda = 154.2$ pm). The lowest-angle diffraction peak was observed at $2\theta = 7.450^\circ$. Assuming that $a = b = (c/3)$, **CALCULATE** the values of a and c .

$a =$

$c =$

c. ESTIMATE the density of this sample of YBCO (with $\delta = 0.25$) in g cm^{-3} . If you do not have the values for a and c from part (b), then use $a = 500$ pm, $c = 1500$ pm.

Density =

d. When YBCO is dissolved in 1.0 M aqueous HCl, bubbles of gas are observed (identified as O₂ by gas chromatography). After boiling for 10 min to expel the dissolved gases, the solution reacts with excess KI solution, turning yellow-brown. This solution can be titrated with thiosulfate solution to a starch endpoint. If YBCO is added directly to a solution that is 1.0 M in both KI and HCl under Ar, the solution turns yellow-brown but no gas evolution is observed.

i. **WRITE** a balanced net ionic equation for the reaction when solid YBa₂Cu₃O_{7-δ} dissolves in aqueous HCl with the evolution of O₂.

ii. **WRITE** a balanced net ionic equation for the reaction when the solution from (i) reacts with excess KI in acidic solution after the dissolved oxygen is expelled.

iii. **WRITE** a balanced net ionic equation for the reaction when the solution from (ii) is titrated with thiosulfate ($S_2O_3^{2-}$).

iv. **WRITE** a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl containing excess KI in an Ar atmosphere.

e. Two identical samples of YBCO with an unknown value of δ were prepared. The first sample was dissolved in 5 mL of 1.0 M aqueous HCl, evolving O₂. After boiling to expel gases, cooling, and adding 10 mL of 0.7 M KI solution under Ar; titration with thiosulfate to the starch endpoint required 1.542×10^{-4} mol thiosulfate. The second sample of YBCO was added directly to 7 mL of a solution that was 1.0 M in KI and 0.7 M in HCl under Ar; titration of this solution required 1.696×10^{-4} mol thiosulfate to reach the endpoint.

i. **CALCULATE** the number of moles of Cu in each of the samples of YBCO.

ii. **CALCULATE** the value of δ for the samples of YBCO.

 $\delta =$

PROBLEM 5

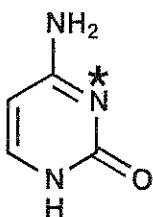
7.0 % of the Total

| a-i | a-ii | b | c | d | e | f | Problem 5 | |
|-----|------|---|---|----|---|---|-----------|------|
| 2 | 4 | 4 | 2 | 12 | 6 | 4 | 34 | |
| | | | | | | | | 7.0% |

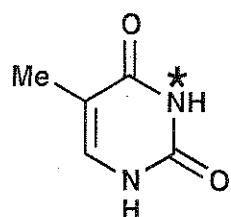
Deoxyribonucleic Acid (DNA) is one of the fundamental molecules of life. This question will consider ways that DNA's molecular structure may be modified, both naturally and in ways devised by humankind.

a. Consider the pyrimidine bases, cytosine (C) and thymine (T). The N-3 atom (indicated by *) of one of these bases is a common nucleophilic site in single strand DNA alkylation, while the other is not.

i. SELECT (circle) which base, C or T, has the more nucleophilic N-3 atom.



C



T

(i)

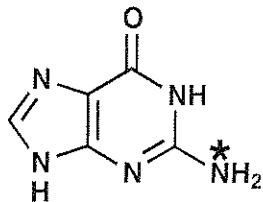
C

T

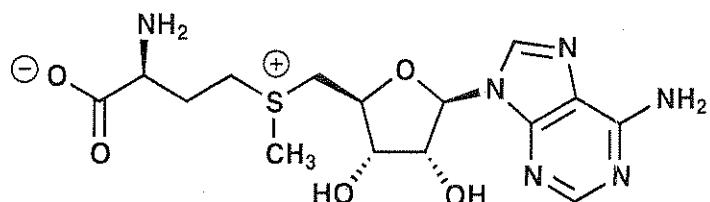
ii. DRAW two complementary resonance structures of the molecule you select to justify your answer. Indicate all non-zero formal charges on the atoms in the resonance structures that you draw.

(ii)

b. One common modification of DNA in nature is methylation of the indicated (*) position of guanine (G) by S-adenosyl methionine (SAM). **DRAW** the structures of both of the products of the reaction between guanine and SAM.



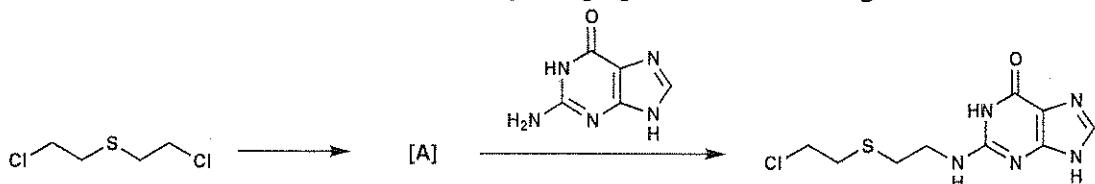
G



SAM

| | |
|--|--|
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c. One of the earliest man-made DNA alkylating agents was mustard gas.

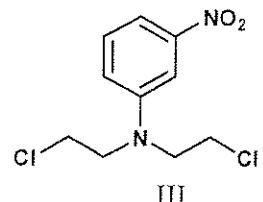
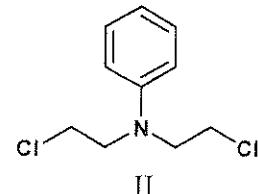
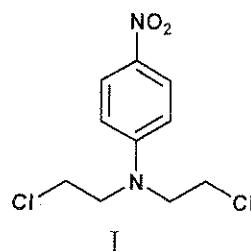


Mustard gas acts by first undergoing an intramolecular reaction to form intermediate A, which directly alkylates DNA to give a nucleic acid product such as that shown in the equation above. **DRAW** a structure for reactive intermediate A.

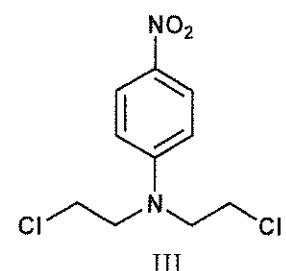
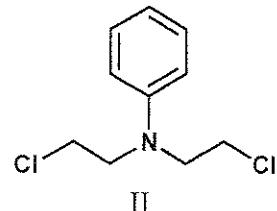
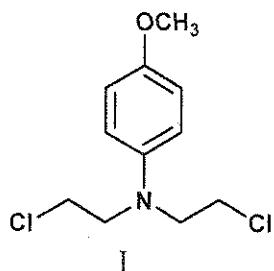
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d. The nitrogen mustards react via an analogous pathway to the sulfur mustard of part c. The reactivity of the compound may be modified depending on the third substituent on the nitrogen atom. The reactivity of nitrogen mustards increases with increasing nucleophilicity of the central nitrogen atom. **SELECT** the most and least reactive from each of following groups of nitrogen mustards.

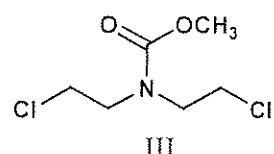
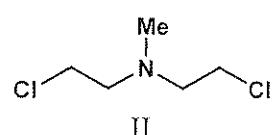
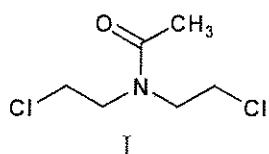
i.

**MOST REACTIVE:****LEAST REACTIVE:**

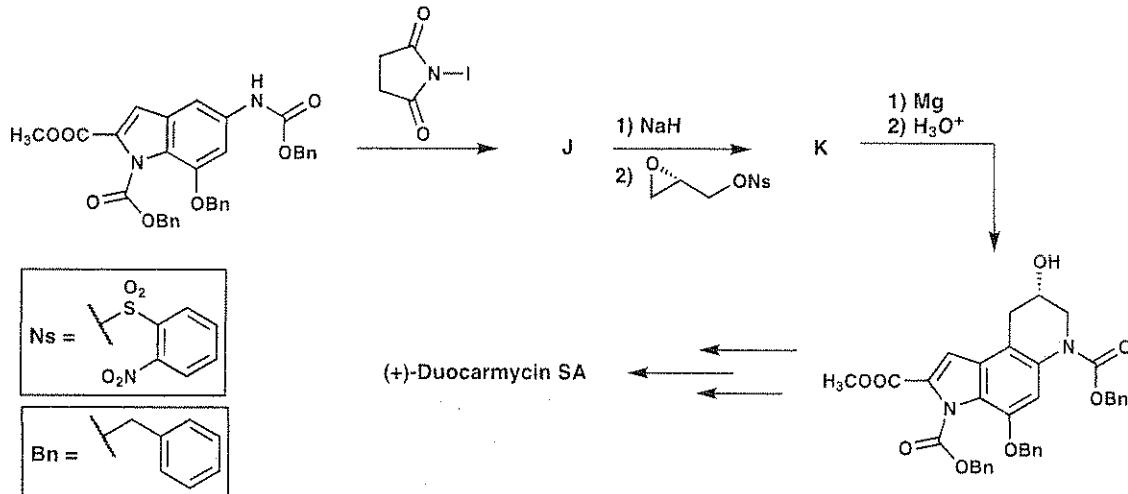
ii.

**MOST REACTIVE:****LEAST REACTIVE:**

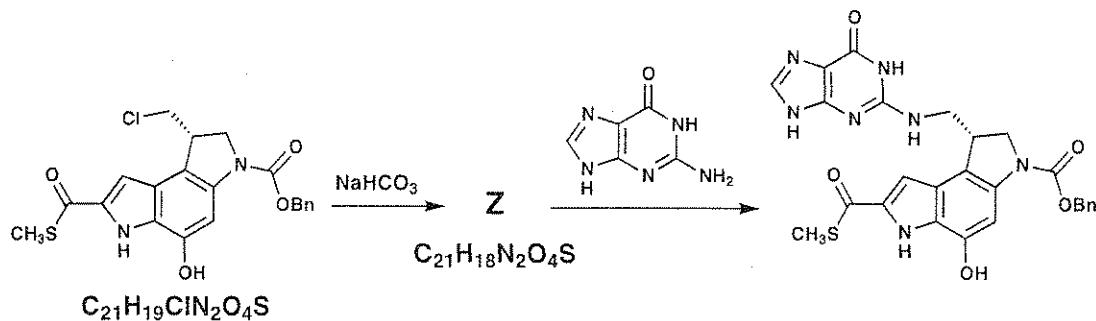
iii.

**MOST REACTIVE:****LEAST REACTIVE:**

e. Some classes of natural products act as DNA alkylators, and in this way, they have the potential to serve as cancer therapies due to their antitumor activity. One such class is the duocarmycins. Shown below are steps from an asymmetric total synthesis of the natural product. **DRAW** the structures of isolatable compounds **J** and **K**.

**J****K**

f. Related small molecules were synthesized to study the way in which the duocarmycins work. One such example is the thioester shown below. **DRAW** the structure of reactive intermediate **Z**.

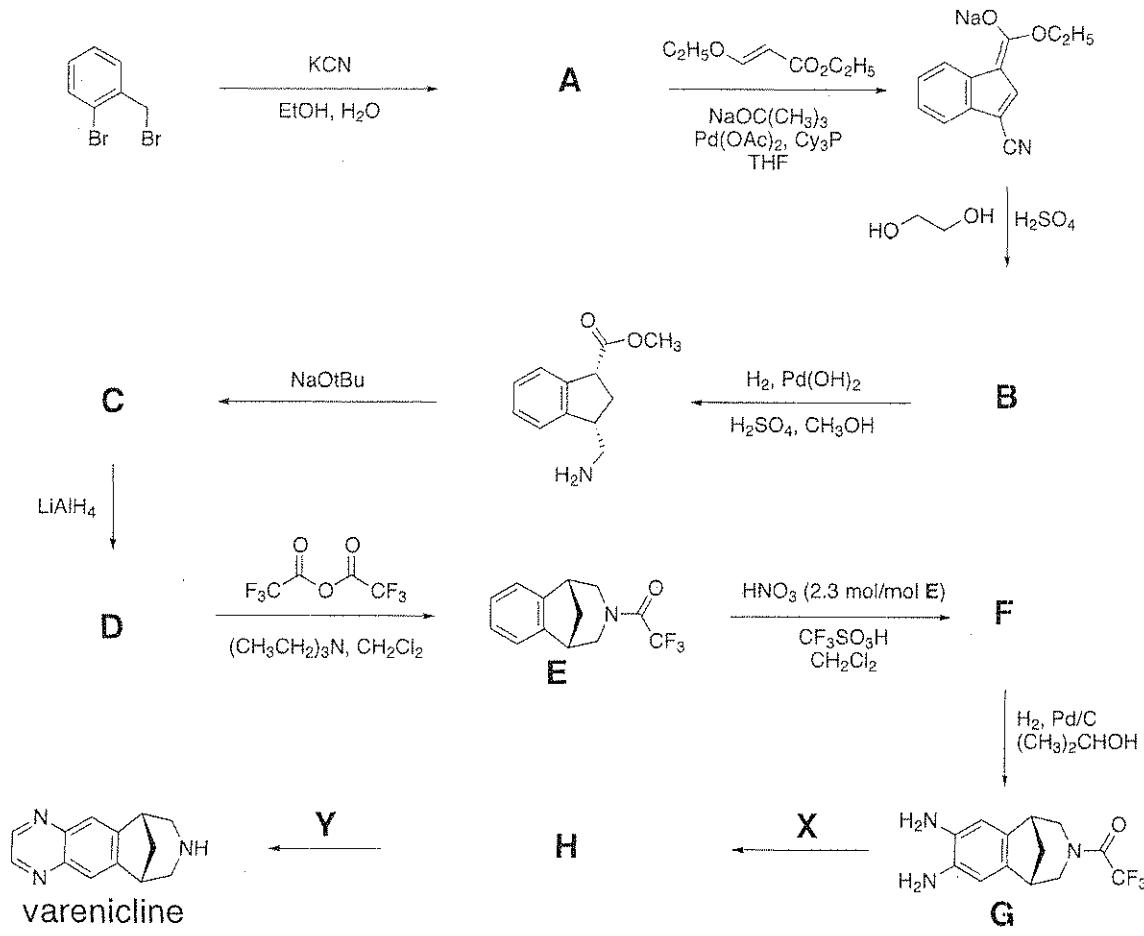


PROBLEM 6

6.6 % of the Total

| a | b | c | d | Problem 6 | |
|---|---|---|---|-----------|------|
| 2 | 4 | 6 | 8 | 20 | 6.6% |
| | | | | | |

Varenicline has been developed as an oral treatment for smoking addiction and can be synthesized by the route shown below. All compounds indicated by a letter (A – H) are uncharged, isolatable species.



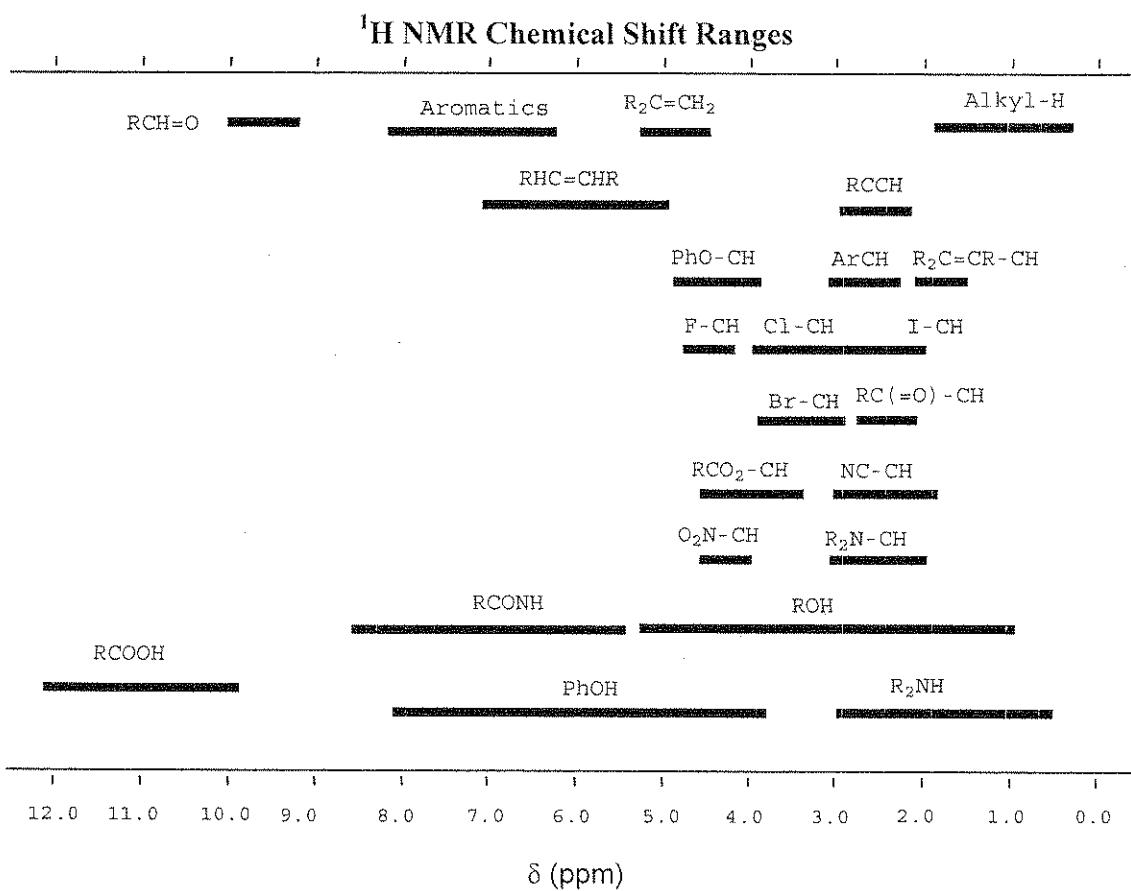
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a. **DRAW** a structure for compound A.

A

b. DRAW a structure for compound **B** consistent with the following ^1H -NMR data:
 δ 7.75 (singlet, 1H), 7.74 (doublet, 1H, $J = 7.9$ Hz), 7.50 (doublet, 1H, $J = 7.1$ Hz), 7.22 (multiplet, 2 nonequivalent H), 4.97 (triplet, 2H, $J = 7.8$ Hz), 4.85 (triplet, 2H, $J = 7.8$ Hz).

B

Name:

Code: USA

c. DRAW structures for compounds **C**, **D**, and **F**.

| | |
|----------|----------|
| C | D |
| F | |

d. SUGGEST reagents **X** and **Y** to convert compound **G** into *varenicline*, and PROVIDE the isolatable intermediate **H** along this route.

| | |
|----------|----------|
| X | Y |
| H | |

PROBLEM 7

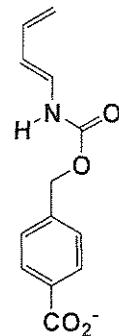
7.5 % of the Total

| a | b | c | d | e | f | Problem 7 | |
|---|----|---|---|---|---|-----------|------|
| 9 | 15 | 8 | 6 | 8 | 6 | 52 | |
| | | | | | | | 7.5% |

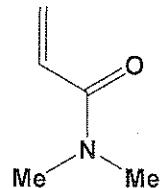
An artificial enzyme was designed to bind the two substrate molecules shown below (a diene and a dienophile) and catalyze a Diels-Alder reaction between them.

a. There are eight potential products from a Diels-Alder reaction involving these two molecules in the reaction without any enzyme.

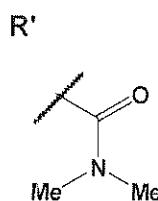
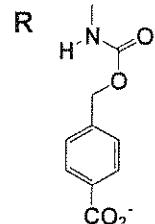
i. DRAW the structures of **any** two of the potential products that are **regioisomers** of each other, in the boxes given below. Use wedges (—) and dashes (···) to show the stereochemistry of each product in your drawings. Use **R** and **R'** shown below to represent the substituents in the molecules that are not directly involved in the reaction.



diene



dienophile



| | |
|--|--|
| | |
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Name:

Code: USA

ii. **DRAW** the structures of **any** two of the potential products that are **enantiomers** of each other, in the boxes given below. Use wedges (—) and dashes (.....) to show the stereochemistry of each product in your drawings. Use **R** and **R'** as in part (i).

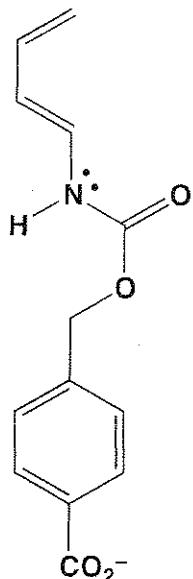
| | |
|--|--|
| | |
|--|--|

iii. **DRAW** the structures of **any** two of the potential products that are **diastereomers** of each other, in the boxes given below. Use wedges (—) and dashes (.....) to show the stereochemistry of each product in your drawings. Use **R** and **R'** as in part (i).

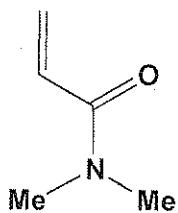
| | |
|--|--|
| | |
|--|--|

b. The rate and regioselectivity of a Diels-Alder reaction depend on the degree of electronic complementarity between the two reactants. The structures of the diene and the dienophile from part a are given below.

i. **CIRCLE** the carbon atom in the diene that has increased electron density and therefore can act as an electron donor during the reaction. **DRAW** one resonance structure of the diene in the box to support your answer. **INDICATE** all non-zero formal charges on the atoms in the resonance structure that you draw.



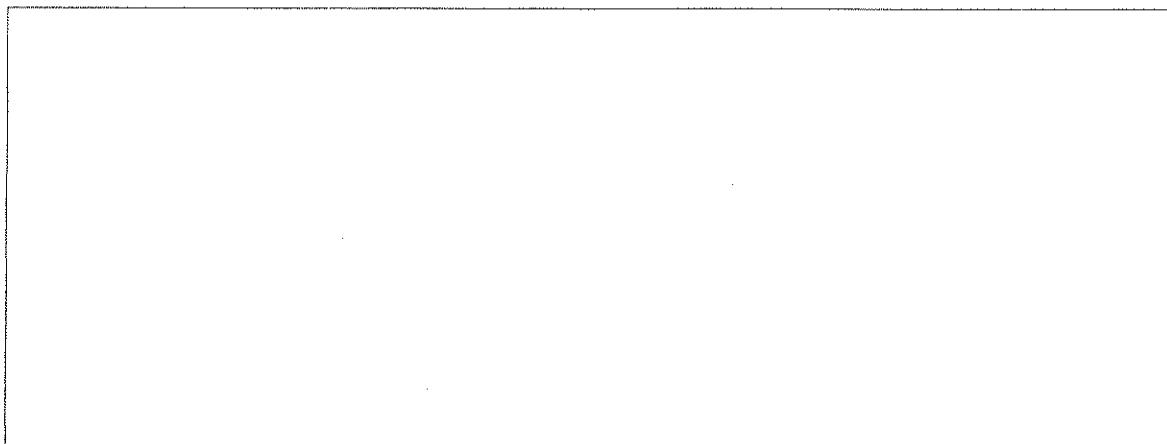
ii. **CIRCLE** the carbon atom in the dienophile that has decreased electron density and therefore can act as an electron acceptor during the reaction. **DRAW** one resonance structure of the dienophile in the box to support your answer. **INDICATE** all non-zero formal charges on the atoms in the resonance structure that you draw.



Name:

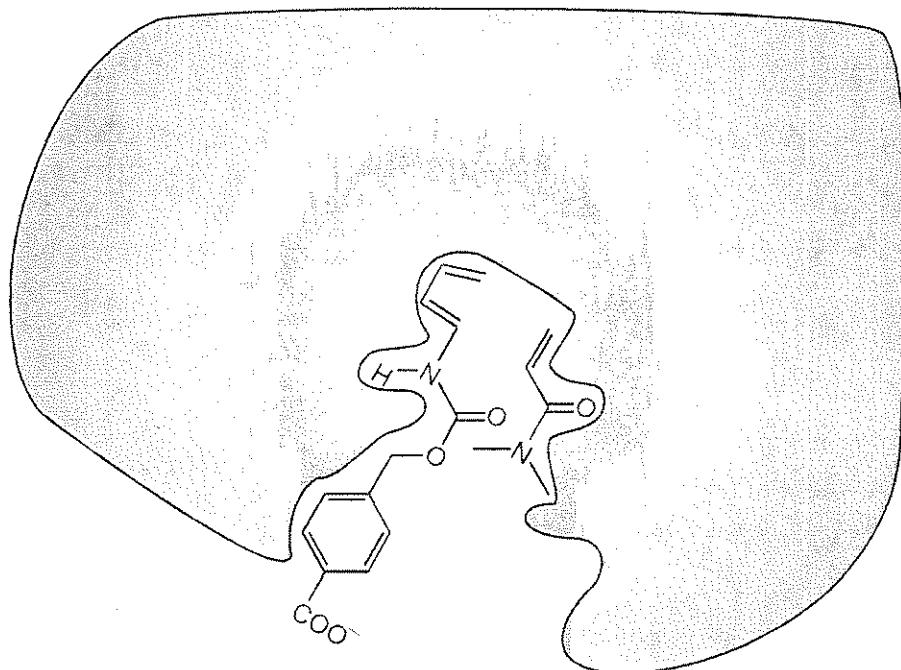
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iii. Based on your assignments in parts (i) and (ii), **PREDICT** the regiochemistry of the uncatalyzed Diels-Alder reaction of the diene and dienophile by drawing the major product. You need not show the stereochemistry of the product in your drawing.



c. The figure below shows the Diels-Alder reactants as they are bound before they enter the transition state for product formation in the active site of the artificial enzyme. The gray area represents a cross-section through the enzyme. The dienophile is **below** the cross-section plane whereas the diene is **above** the cross-section plane, when the two molecules are bound in the active site that is shown.

DRAW the structure of the product of the enzyme-catalyzed reaction in the box given below. **SHOW** the stereochemistry of the product in your drawing, using **R** and **R'** as you did for question **a**.



Name:

Code: USA

d. Consider the following statements about enzymes (artificial or natural). For each statement, **INDICATE** whether that statement is True or False (**CIRCLE** "True" or "False").

i. Enzymes bind more tightly to the transition state than to the reactants or products of the reaction.

True **False**

ii. Enzymes alter the equilibrium constant of the reaction to favor the product.

True **False**

iii. Enzymatic catalysis always increases the entropy of activation of the reaction compared to the uncatalyzed reaction.

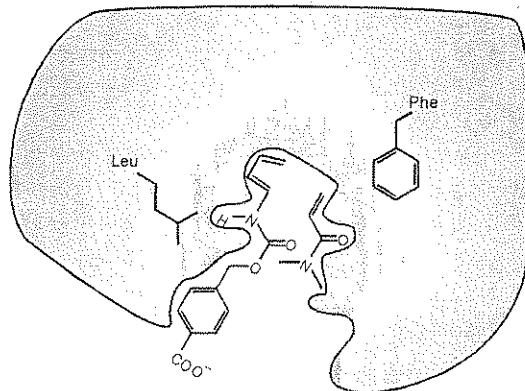
True **False**

e. Modified versions of the artificial enzymes with different catalytic activities were prepared: enzymes I, II, III, and IV (see the figure below). Two amino acid residues that differ among the different enzymes are shown. Assume that the enzyme functional groups shown are located in close proximity to the matching fragments of the reagents when they form the transition state in the enzyme active site.

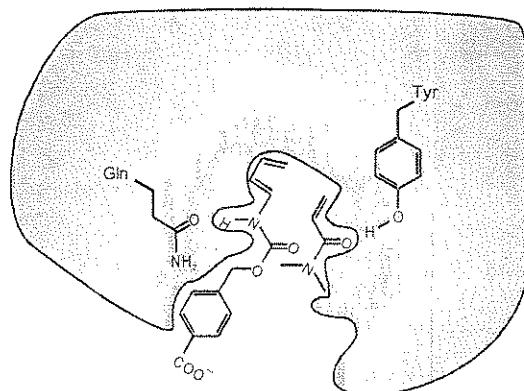
Of these four enzymes, **WHICH ONE** would cause the greatest increase in the rate of the Diels-Alder reaction compared to the uncatalyzed reaction?

Enzyme #

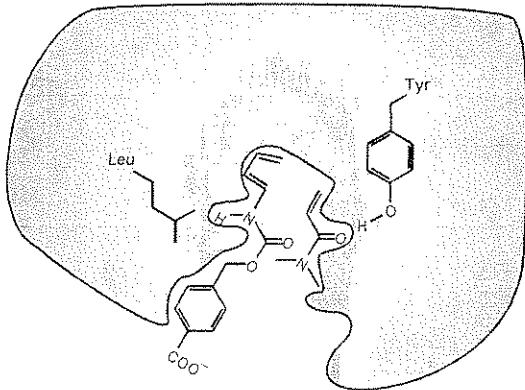
Enzyme I



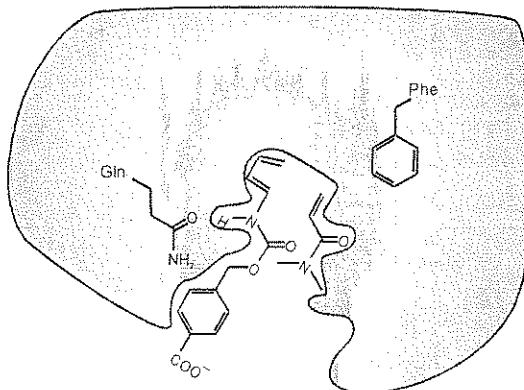
Enzyme II



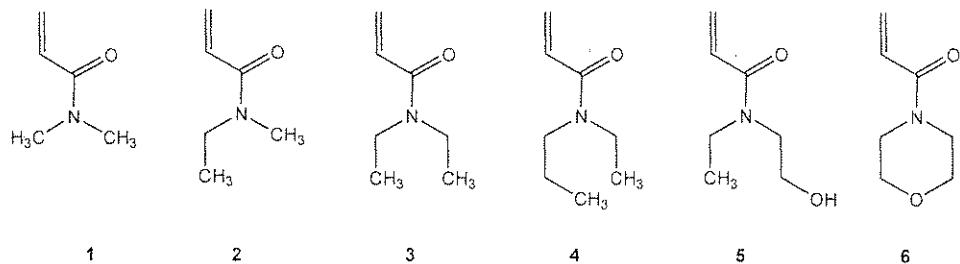
Enzyme III



Enzyme IV



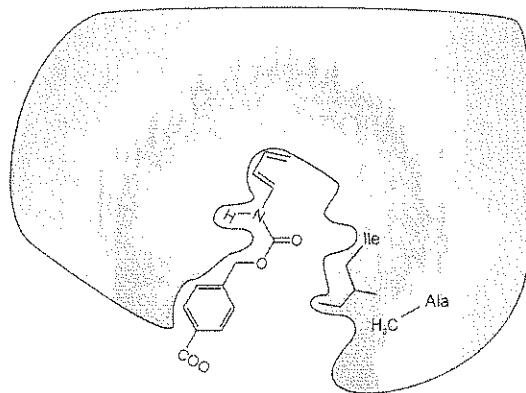
f. The substrate specificity of the artificial enzymes **V** and **VI** (see below) was tested by using the dienophile reactants **1** - **6**, shown below.



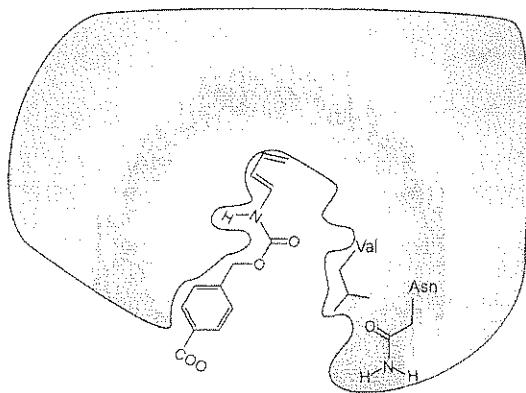
Dienophile #**1** reacted most rapidly in the reaction catalyzed by the artificial **enzyme V** (see below). However, artificial **enzyme VI** catalyzed the reaction most rapidly with a different dienophile. Of the six dienophiles shown above, **WHICH ONE** would react most rapidly in the Diels-Alder reaction catalyzed by **enzyme VI**?

Dienophile #

Enzyme V



Enzyme VI

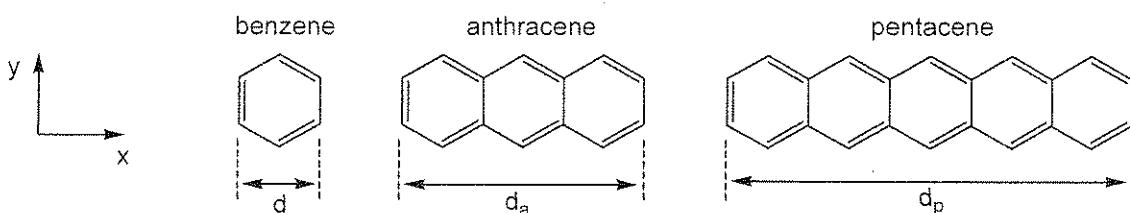


PROBLEM 8

8.3% of the Total

| a | b-i | b-ii | b-iii | b-iv | b-v | c-i | c-ii | c-iii | Problem 8 | |
|---|-----|------|-------|------|-----|-----|------|-------|-----------|------|
| 2 | 3 | 4 | 6 | 4 | 2 | 5 | 8 | 2 | 36 | 8.3% |
| | | | | | | | | | | |

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 π electron cloud is delocalized over the molecule.



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

For anthracene, $d_a =$

For pentacene, $d_p =$

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:

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

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 π 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) |
| ↑↓ (9; 1) |
| ↑↓ (2; 2) |
| ↑↓ (1; 2) |
| ↑↓ (8; 1) |
| ↑↓ (7; 1) |
| ↑↓ (6; 1) |
| ↑↓ (5; 1) |
| ↑↓ (4; 1) |
| ↑↓ (3; 1) |
| ↑↓ (2; 1) |
| ↑↓ (1; 1) |

The energy level diagram for anthracene is shown below. Note that some energy levels may have the same energy. **FILL IN** the energy level diagram with the correct number of up and down arrows to represent the π electrons in anthracene. Also, the blanks in parentheses within this diagram are the quantum numbers n_x , n_y , which you need to determine. **INDICATE** in the blanks the pertinent values of 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 diagram 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.

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Code: USA

iv. Often the reactivity of PAHs correlates inversely with the energy gap ΔE 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:

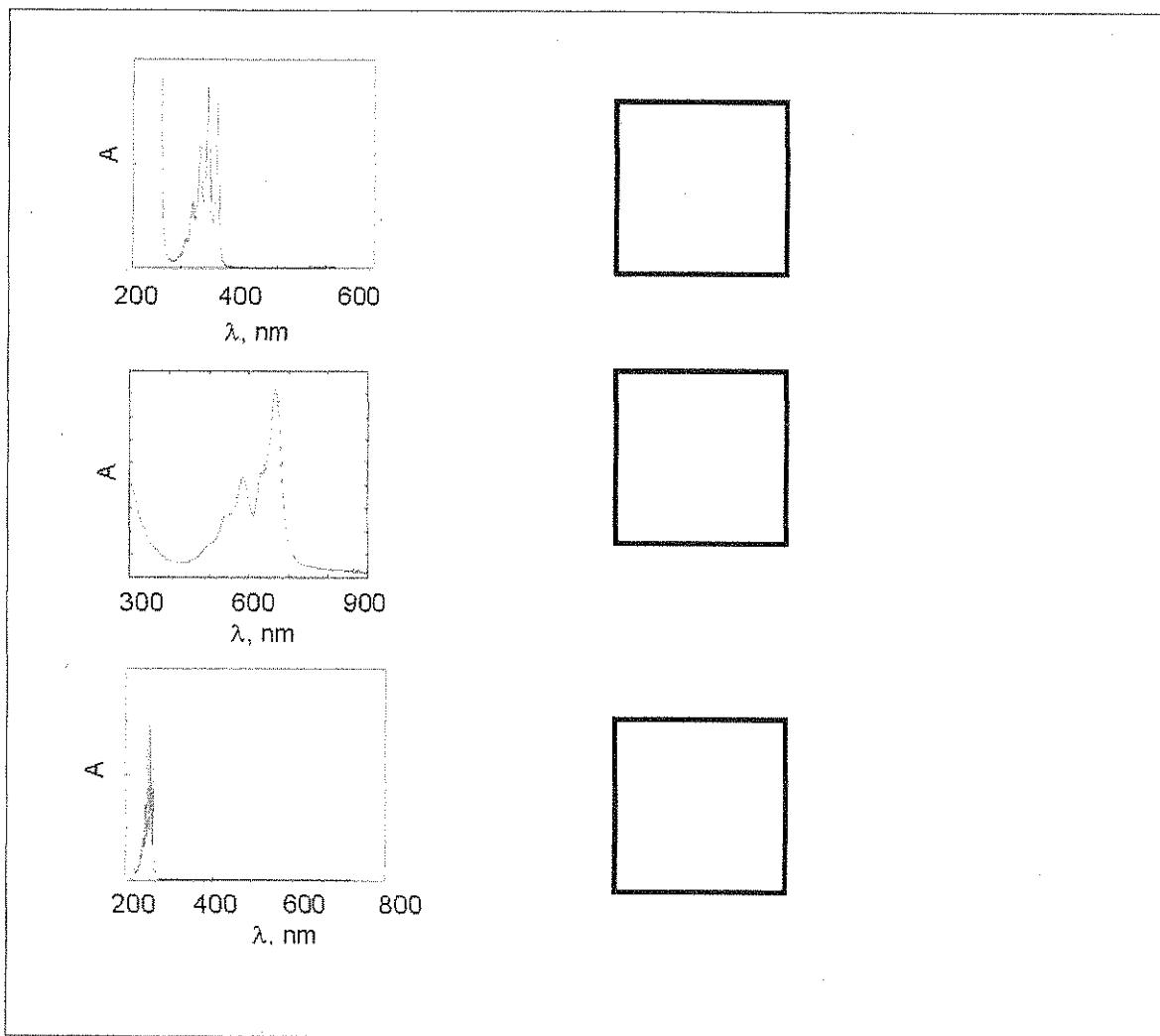
ΔE for anthracene:

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.

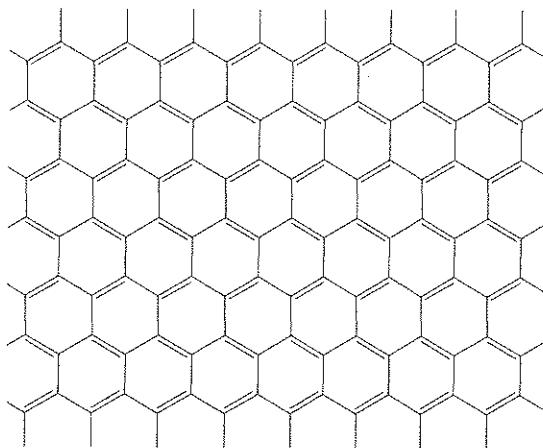
Least reactive -----> Most reactive

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 polycyclic aromatic 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.

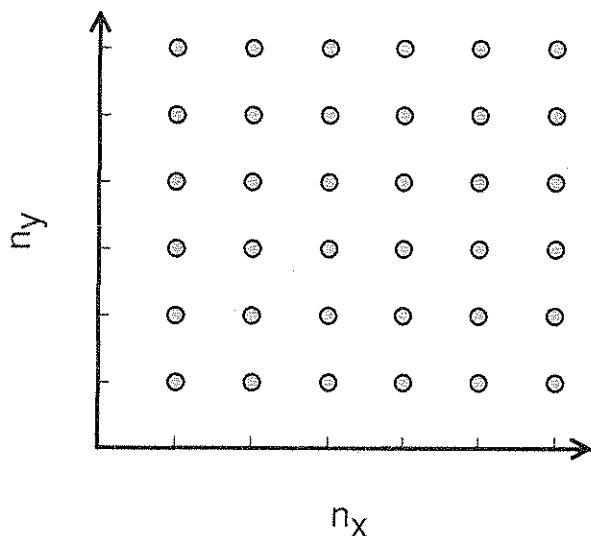
Consider a sheet of graphene with planar dimensions of $L_x=25$ nm by $L_y=25$ nm. A section of this sheet is shown below.



i. The area of one hexagonal 6-carbon unit is ~ 52400 pm 2 . **CALCULATE** the number of π electrons in a (25 nm \times 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 π 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 $25 \text{ nm} \times 25 \text{ nm}$ 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 (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).



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| |
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|--|

iii. The conductivity of graphene-like materials correlates inversely with the energy gap between the lowest unoccupied and highest occupied energy levels. Using your analysis and understanding of π electrons in PAHs and grapheme, **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 |
|------|-------|---------|