



Washington, D.C. • USA



# Theoretical Problems

44th International  
Chemistry Olympiad  
July 26, 2012  
United States  
of America

Name:

Code: TJK-

# Instructions

- Write your name and code on each page.
- This examination has **8** problems and 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.

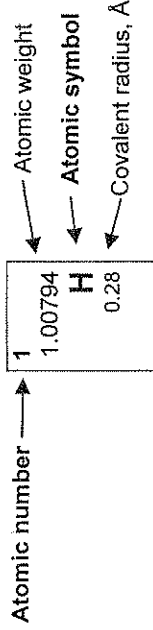
# Physical Constants, Formulas and Equations

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 ( <i>nm</i> )	$10^{-9} \text{ m}$
1 picometer ( <i>pm</i> )	$10^{-12} \text{ m}$
Equation of a circle	$x^2 + y^2 = r^2$
Area of a circle	$\pi r^2$
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	$\sin \theta = n\lambda/2d$

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1	1	1.00794 H 0.28															2	4.00260 He 1.40																		
2	3	6.941 Li	4	9.01218 Be													9	18.9984 F 0.64	10	20.1797 Ne 1.50																
3	11	22.9898 Na	12	24.3050 Mg													17	35.4527 Cl 0.99	18	39.948 Ar 1.80																
4	19	39.0983 K	20	40.078 Ca	21	44.9559 Sc	22	47.867 Ti	23	50.9415 V	24	51.9961 Cr	25	54.9381 Mn	26	55.845 Fe	27	58.9332 Co	28	58.6934 Ni	29	63.546 Cu	30	65.39 Zn	31	69.723 Ga	32	72.61 Ge	33	74.9216 As	34	78.96 Se	35	79.904 Br	36	83.80 Kr 1.90
5	37	85.4678 Rb	38	87.62 Sr	39	88.9059 Y	40	91.224 Zr	41	92.9064 Nb	42	95.94 Mo	43	(97.905) Tc	44	101.07 Ru	45	102.906 Rh	46	106.42 Pd	47	107.868 Ag	48	112.41 Cd	49	114.818 In	50	118.710 Sn	51	121.760 Sb	52	127.60 Te	53	126.904 I 1.33	54	131.29 Xe 2.10
6	55	132.905 Cs	56	137.327 Ba	57-71 La-Lu	72	178.49 Hf	73	180.948 Ta	74	183.84 W	75	186.207 Re	76	190.23 Os	77	192.217 Ir	78	195.08 Pt	79	196.967 Au	80	200.59 Hg	81	204.383 Tl	82	207.2 Pb	83	208.980 Bi	84	(208.98) Po	85	(209.99) At	86	(222.02) Rn 2.20	
7	87	(223.02) Fr	88	(226.03) Ra	89-103 Ac-Lr	104	(261.11) Rf	105	(262.11) Db	106	(263.12) Sg	107	(262.12) Bh	108	(265) Hs	109	(266) Mt	110	(271) Ds	111	(272) Rg	112	(285) Cn	113	(284) Uut	114	(289) Fl	115	(288) Uup	116	(292) Lv	117	(294) Uus	118	(294) Uuo	



57	138.906 La 1.87	58	140.115 Ce	59	140.908 Pr	60	144.24 Nd	61	(144.91) Pm	62	150.36 Sm	63	151.965 Eu	64	157.25 Gd	65	158.925 Tb	66	162.50 Dy	67	164.930 Ho	68	167.26 Er	69	168.934 Tm	70	173.04 Yb	71	174.04 Lu 1.72
89	(227.03) Ac	90	232.038 Th	91	231.036 Pa	92	238.029 U	93	(237.05) Np	94	(244.06) Pu	95	(243.06) Am	96	(247.07) Cm	97	(247.07) Bk	98	(251.08) Cf	99	(252.08) Es	100	(257.10) Fm	101	(258.10) Md	102	(259.1) No	103	(260.1) Lr

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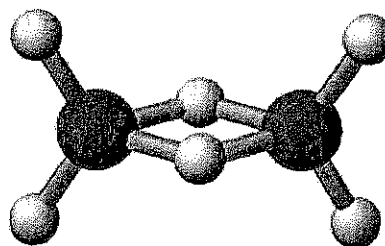
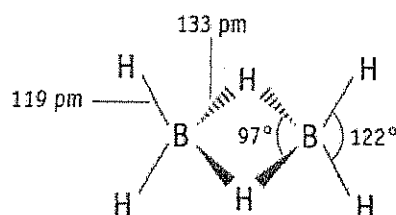
## PROBLEM 1

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** formulae for two other members of this series of boron hydrides, A and B.

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

A = \_\_\_\_\_

B = \_\_\_\_\_

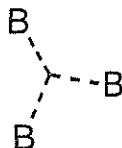
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ii. William Lipscomb received the Nobel Prize in Chemistry in 1976 for “studies on the structures of boron hydrides illuminating the problems of chemical bonding.” Lipscomb recognized that, *in all boron hydrides, each B atom has a normal 2-electron 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

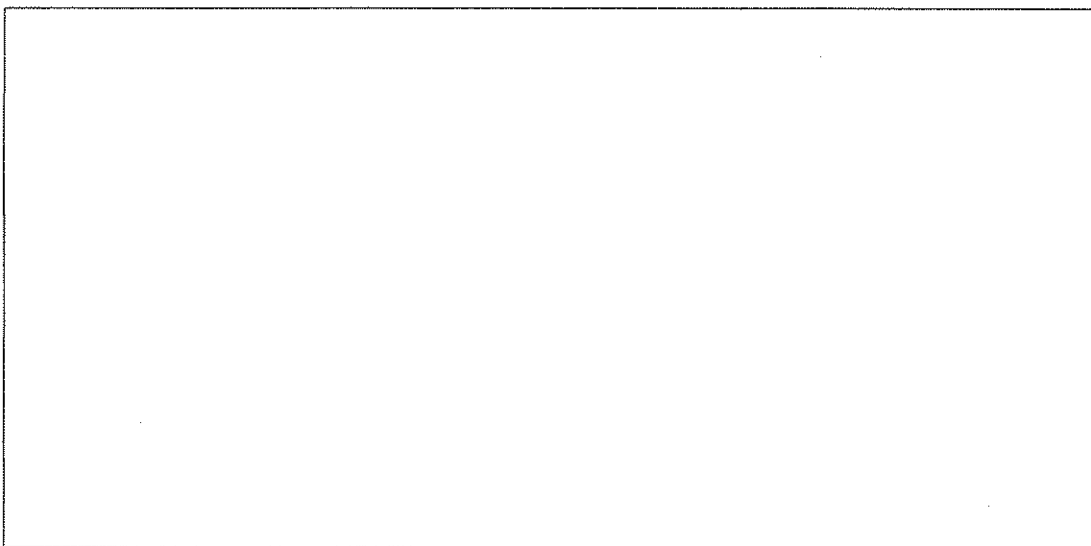
$t$  = the number of 3-center BBB bonds in the molecule



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

$x$  = the number of BH<sub>2</sub> groups in the molecule

The *styx* number for B<sub>2</sub>H<sub>6</sub> is 2002. Propose (draw) a structure for tetraborane, B<sub>4</sub>H<sub>10</sub>, with a *styx* number of 4012.

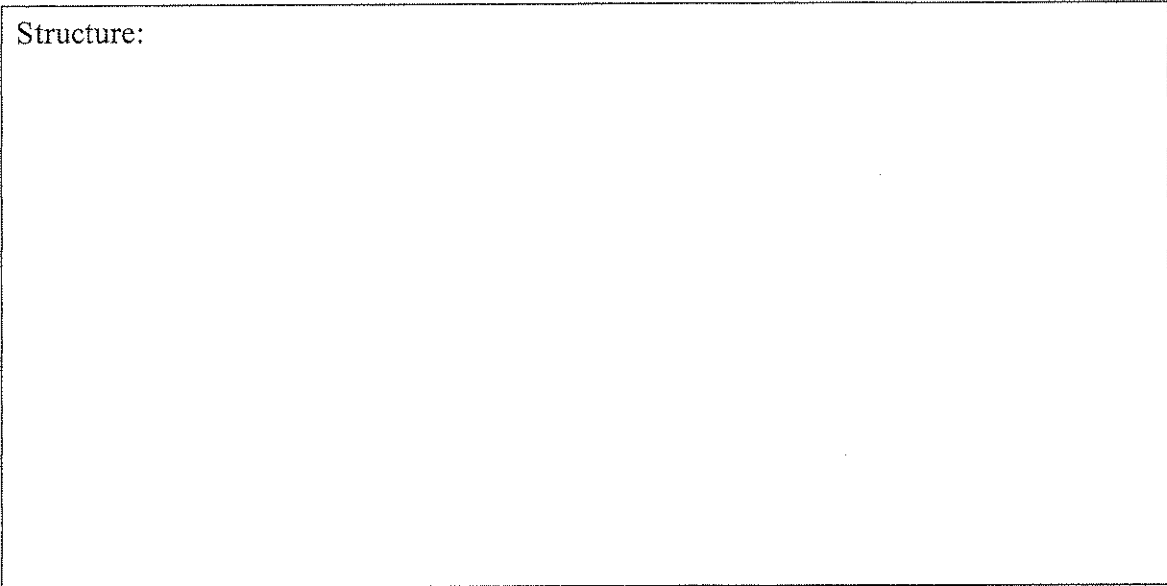


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Code: TJK

iii. A boron-based compound is composed of boron, carbon, chlorine, and oxygen ( $B_4CCl_6O$ ). Spectral measurements indicate 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  $B_4CCl_6O$ , suggest a structure for the molecule.

Structure:



Name:

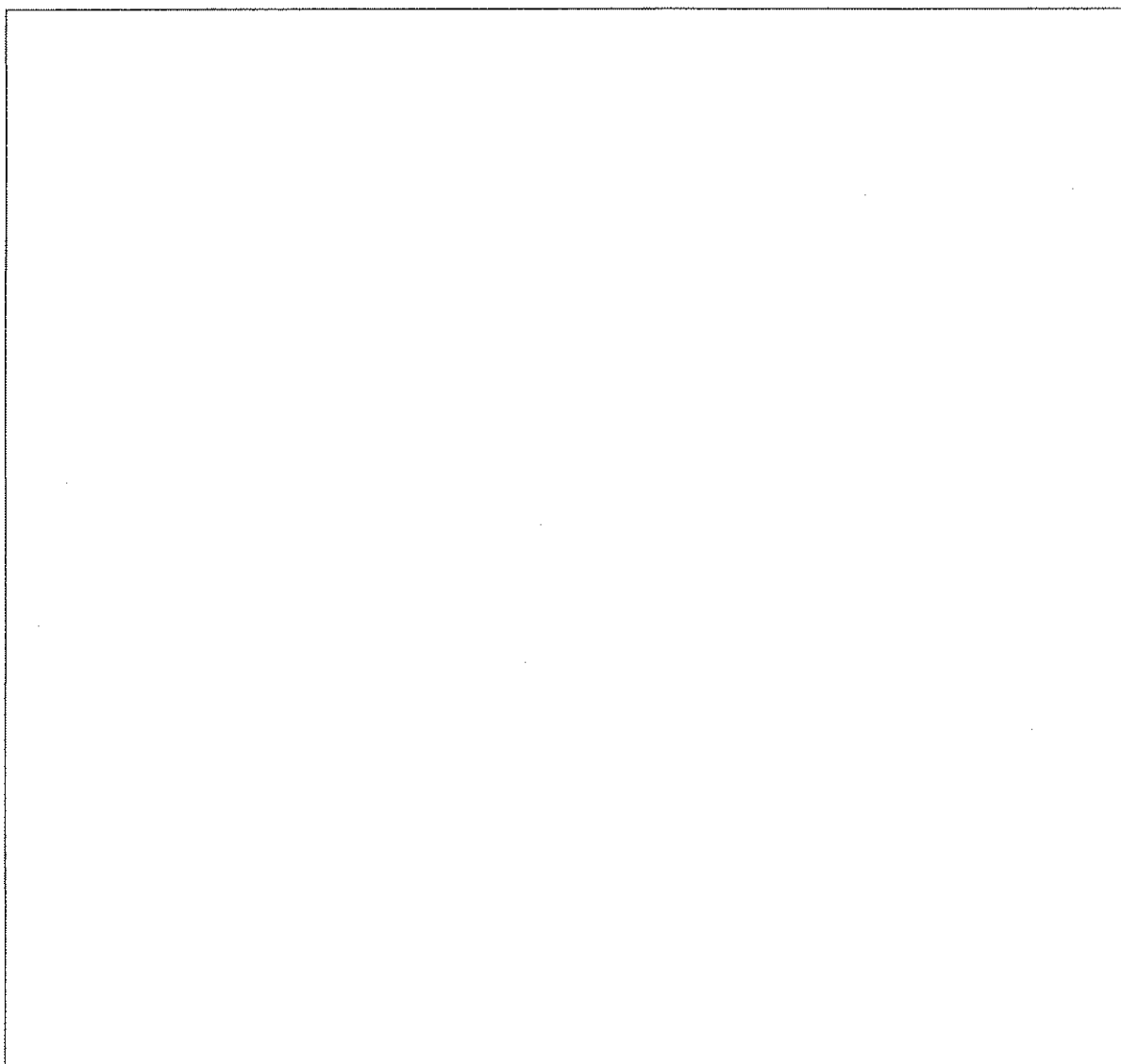
Code: TJK-

**b. Thermochemistry of Boron Compounds**

Estimate the B-B single bond dissociation enthalpy in  $B_2Cl_4(g)$  using the following information:

<b>Bond</b>	<b>Bond Dissociation Enthalpy (kJ/mol)</b>
B-Cl	443
Cl-Cl	242

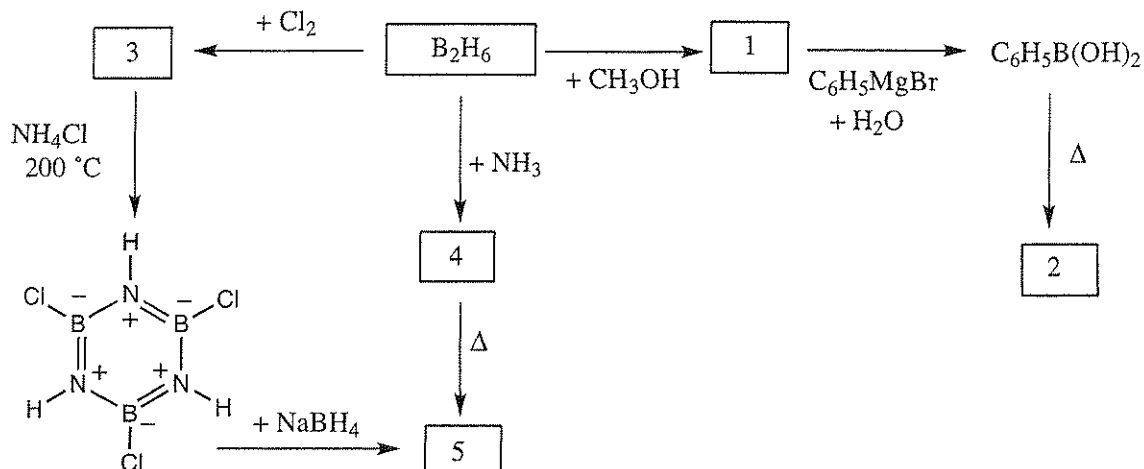
<b>Compound</b>	<b><math>\Delta_f H^\circ</math> (kJ/mol)</b>
$BCl_3(g)$	-403
$B_2Cl_4(g)$	-489





**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  $55\text{ }^\circ\text{C}$ .
- Excess reagents used in all reactions.
- The freezing point depression for  $0.312\text{ g}$  of compound **2** in  $25.0\text{ g}$  of benzene is  $0.205\text{ }^\circ\text{C}$ . The freezing point depression constant for benzene is  $5.12\text{ }^\circ\text{C/molal}$ .

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Number	Molecular Structure of Compound
1	
2	
3	
4	
5	

## PROBLEM 2

7.8% of the total

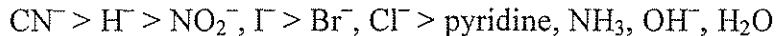
a-i	a-ii	b-i	b-ii	c	Problem 2	7.8%
4	4	6	1	5	20	

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

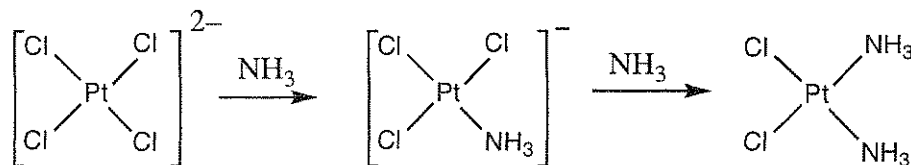
Platinum and other Group 10 metals form square planar complexes, and the mechanisms of their reactions have been studied extensively. For example, it is known that substitution reactions of these complexes proceed with retention of stereochemistry.



It is also known that the rate of substitution of ligand X by Y depends on the nature of the ligand *trans* to X, that is, on 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.



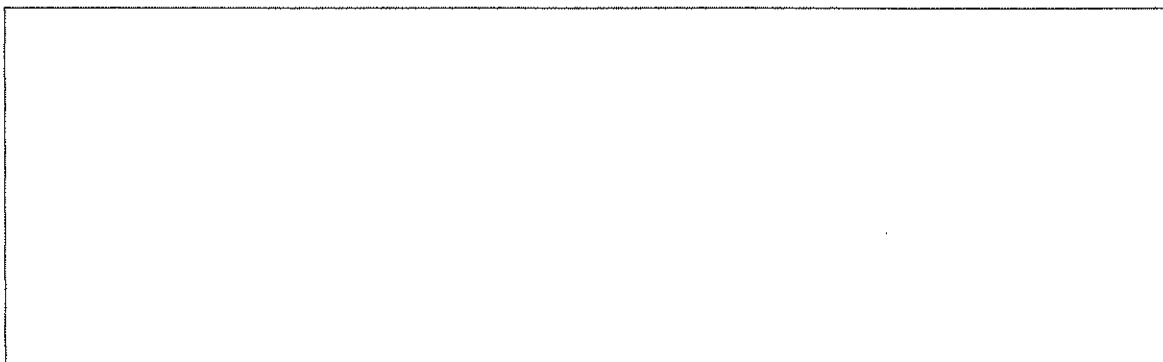
The preparations of *cis*- and *trans*-Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> depend on the *trans* effect. The preparation of the *cis* isomer, a cancer chemotherapy agent commonly called cisplatin, involves the reaction of K<sub>2</sub>PtCl<sub>4</sub> with ammonia.



Name:

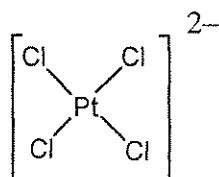
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i. Draw all possible stereoisomers for square planar platinum(II) compounds with the formula  $\text{Pt}(\text{py})(\text{NH}_3)\text{BrCl}$  (where py = pyridine,  $\text{C}_5\text{H}_5\text{N}$ ).

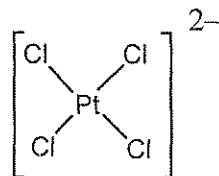


ii. Write reaction schemes including intermediate(s), if any, to show the preparation in aqueous solution for each of the stereoisomers of  $[\text{Pt}(\text{NH}_3)(\text{NO}_2)\text{Cl}_2]^-$  using, as reagents,  $\text{PtCl}_4^{2-}$ ,  $\text{NH}_3$ , and  $\text{NO}_2^-$ . The reactions are controlled kinetically by the *trans* effect.

*cis*-isomer:

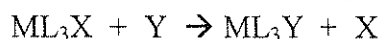


*trans*-isomer:



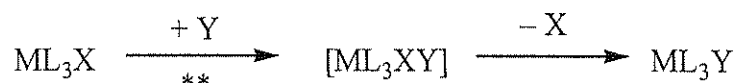
**b. Kinetic Studies of Substitution Reactions of Square Planar Complexes**

Substitutions of the ligand X by Y in square planar complexes

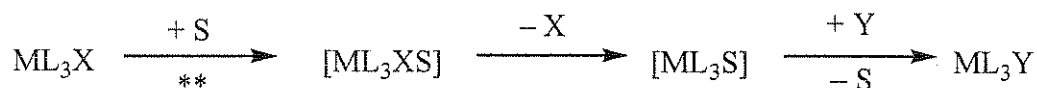


can occur in either or both of two ways:

- *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,  $\text{ML}_3\text{Y}$ .

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

- *Solvent-assisted substitution:* A solvent molecule S attaches to the central metal to give  $\text{ML}_3\text{XS}$ , which eliminates the X to give  $\text{ML}_3\text{S}$ . Y rapidly displaces S to give  $\text{ML}_3\text{Y}$ .

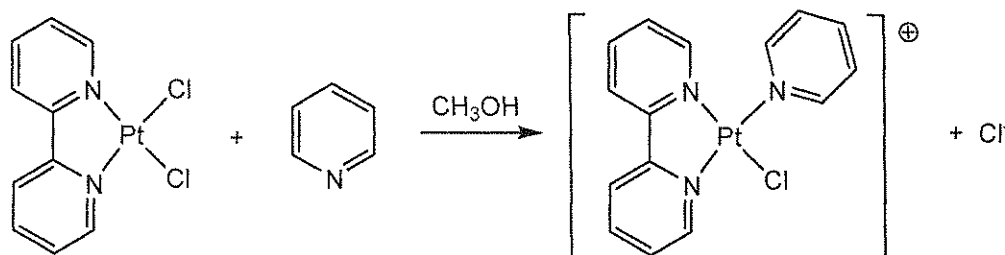
\*\* = rate determining step, Rate constant =  $k_S$ 

The overall rate law for such substitutions is

$$\text{Rate} = k_S[\text{ML}_3\text{X}] + k_Y[\text{Y}][\text{ML}_3\text{X}]$$

When  $[\text{Y}] \gg [\text{ML}_3\text{X}]$ , then  $\text{Rate} = k_{\text{obs}}[\text{ML}_3\text{X}]$ .

The values of  $k_S$  and  $k_Y$  depend on the reactants and solvent involved. One example is the displacement of the  $\text{Cl}^-$  ligand in a square planar platinum(II) complex,  $\text{ML}_2\text{X}_2$ , by pyridine ( $\text{C}_5\text{H}_5\text{N}$ ). (The  $\text{ML}_3\text{X}$  scheme above applies to  $\text{ML}_2\text{X}_2$ .)



Data for reaction at 25 °C in methanol where  $[\text{pyridine}] \gg$  the concentration of the platinum complex are given in the table below.

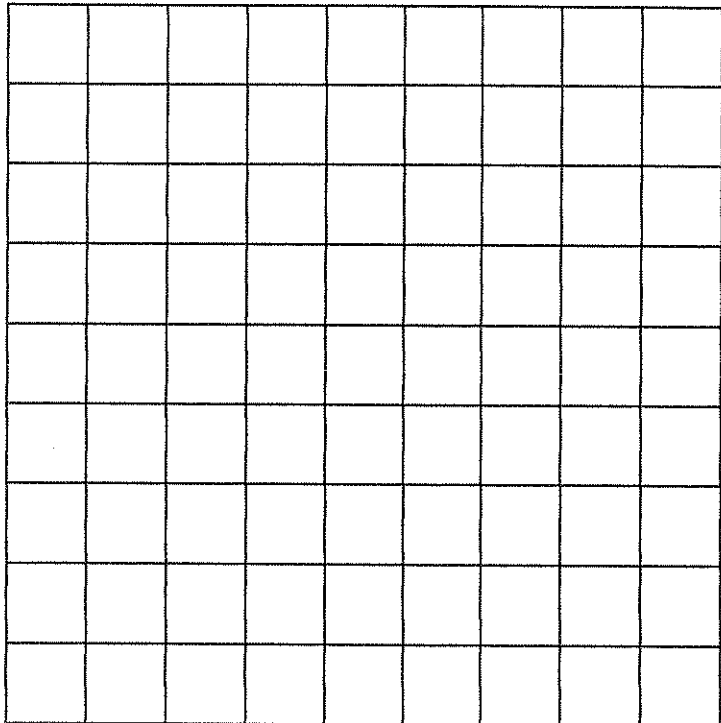
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Concentration of pyridine (mol/L)	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )
0.122	$7.20 \times 10^{-4}$
0.061	$3.45 \times 10^{-4}$
0.030	$1.75 \times 10^{-4}$

i. Calculate the values of  $k_s$  and  $k_Y$ . Give the proper unit for each constant.

A grid is given if you wish to use it.



Name:

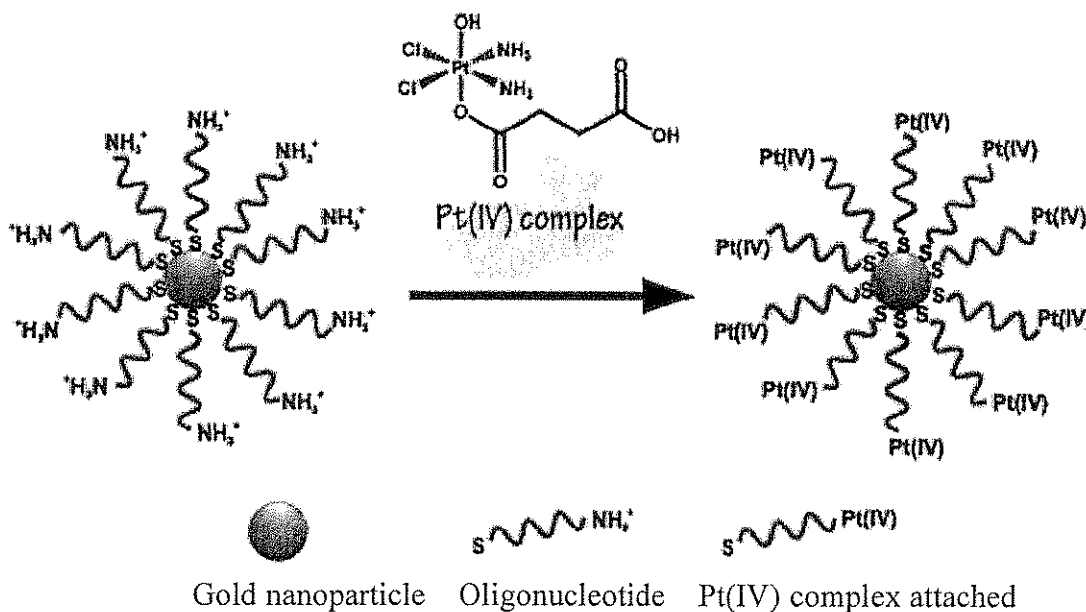
Code: TJK-

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

<input type="checkbox"/>	Most pyridine product is formed by the solvent-assisted ( $k_s$ ) substitution pathway.
<input type="checkbox"/>	Most pyridine product is formed by the direct substitution ( $k_Y$ ) pathway
<input type="checkbox"/>	Comparable amounts of product are formed by the two pathways.
<input type="checkbox"/>	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  $19.3 \text{ g/cm}^3$ )

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**Mass of platinum**

**Mass of gold**



Name:

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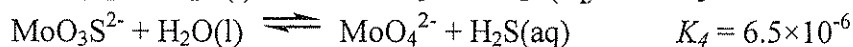
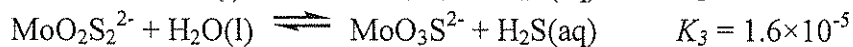
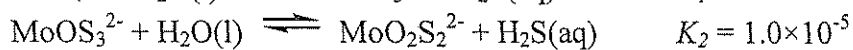
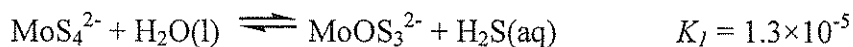
**PROBLEM 3**

**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,  $\text{MoO}_4^{2-}$ , 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  $\text{H}_2\text{S}$ . 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. If at equilibrium a solution contains  $1 \times 10^{-7}$  M  $\text{MoO}_4^{2-}$  and  $1 \times 10^{-6}$  M  $\text{H}_2\text{S}(\text{aq})$ , what would be the concentration of  $\text{MoS}_4^{2-}$ ?

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Solutions containing  $\text{MoO}_2\text{S}_2^{2-}$ ,  $\text{MoOS}_3^{2-}$  and  $\text{MoS}_4^{2-}$  display absorption peaks in the visible wavelength range at 395 and 468 nm. The other ions, as well as  $\text{H}_2\text{S}$ , absorb negligibly in the visible wavelength range. The molar absorptivities ( $\epsilon$ ) at these two wavelengths are given in the following table:

	$\epsilon$ at 468 nm $\text{L mol}^{-1} \text{cm}^{-1}$	$\epsilon$ at 395 nm $\text{L mol}^{-1} \text{cm}^{-1}$
$\text{MoS}_4^{2-}$	11870	120
$\text{MoOS}_3^{2-}$	0	9030
$\text{MoO}_2\text{S}_2^{2-}$	0	3230

b. A solution *not* at equilibrium contains a mixture of  $\text{MoS}_4^{2-}$ ,  $\text{MoOS}_3^{2-}$  and  $\text{MoO}_2\text{S}_2^{2-}$  and no other Mo-containing species. The total concentration of all species containing Mo is  $6.0 \times 10^{-6}$  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.

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

$\text{MoOS}_3^{2-}$ : \_\_\_\_\_

$\text{MoS}_4^{2-}$ : \_\_\_\_\_

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c. A solution initially containing  $2.0 \times 10^{-7}$  M  $\text{MoS}_4^{2-}$  hydrolyzes in a closed system. The  $\text{H}_2\text{S}$  product accumulates until equilibrium is reached. Calculate the final equilibrium concentrations of  $\text{H}_2\text{S}(\text{aq})$ , and all five Mo-containing anions (that is,  $\text{MoO}_4^{2-}$ ,  $\text{MoO}_3\text{S}^{2-}$ ,  $\text{MoO}_2\text{S}_2^{2-}$ ,  $\text{MoOS}_3^{2-}$  and  $\text{MoS}_4^{2-}$ ). **Ignore the possibility that  $\text{H}_2\text{S}$  might ionize to  $\text{HS}^-$  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, giving your answers to two significant figures.

$\text{H}_2\text{S}$  \_\_\_\_\_

$\text{MoO}_4^{2-}$  \_\_\_\_\_

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

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

$\text{MoOS}_3^{2-}$  \_\_\_\_\_

$\text{MoS}_4^{2-}$  \_\_\_\_\_

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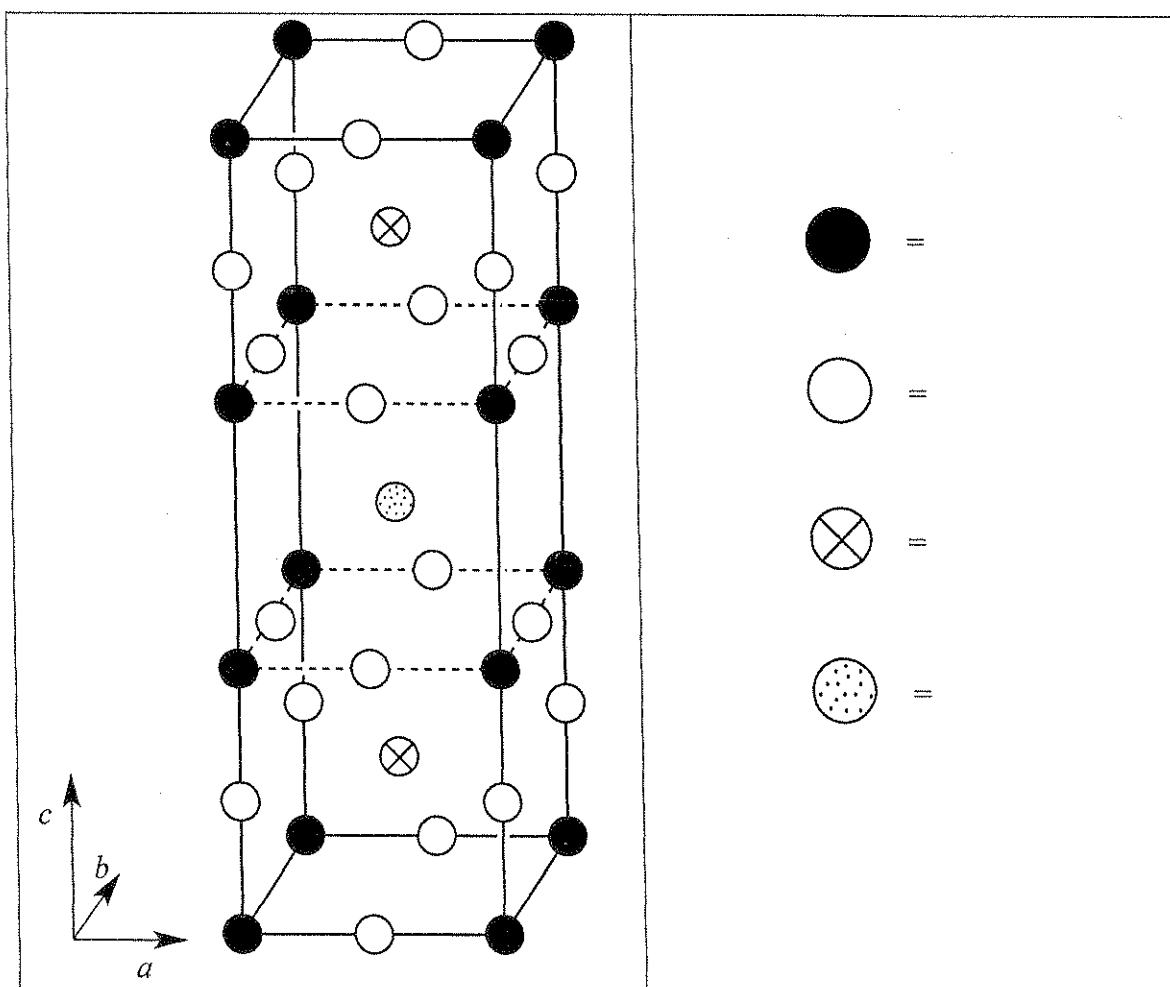
PROBLEM 4

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 1980's 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 which circles correspond to which 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  $K\alpha$  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 (calculate) the density of this sample of YBCO (with  $\delta = 0.25$ ) in  $\text{g}\cdot\text{cm}^{-3}$ . If you do not have the values for  $a$  and  $c$  from **part (b)**, then use  $a = 500$ . pm,  $c = 1500$ . pm.

Density =

Name:

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d. When YBCO is dissolved in 1.0 M aqueous HCl, bubbles of gas are observed (identified as O<sub>2</sub> by gas chromatography). After boiling for 10 min to expel (remove) 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 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 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> dissolves in aqueous HCl with evolution of O<sub>2</sub>.

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.

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Code: TJK-

iii. Write a balanced net ionic equation for the reaction when the solution from (ii) is titrated with thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ).

iv. Write a balanced net ionic equation for the reaction when solid  $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$  dissolves in aqueous HCl containing excess KI in an Ar atmosphere.



Name:

Code: TJK-

e. Two identical samples of YBCO with an unknown value of  $\delta$  were prepared. The first sample was dissolved in 5 mL of 1.0 M aqueous HCl, evolving  $O_2$ . After boiling to expel (remove) gases, cooling, and addition of 10 mL of 0.7 M KI solution under Ar, titration with thiosulfate to the starch endpoint required  $1.542 \times 10^{-4}$  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  $1.696 \times 10^{-4}$  mol thiosulfate to reach the endpoint.

i. Calculate the number of moles of Cu in each of these samples of YBCO.

ii. Calculate the value of  $\delta$  for these samples of YBCO.

$\delta =$

Name:

Code: TJK-

## PROBLEM 5

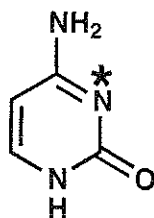
7.0 % of the Total

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

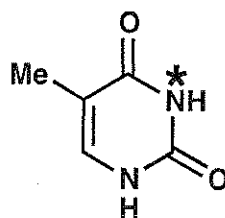
Deoxyribonucleic Acid (DNA) is one of the fundamental molecules of life. This question will consider ways that DNA's molecular structure may be modified, both naturally and in ways devised by humankind.

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

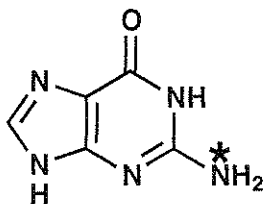
ii. Draw two complementary resonance structures of the molecule you select to justify your answer. Indicate all non-zero formal charges on the atoms in the resonance structures that you draw.

(ii)

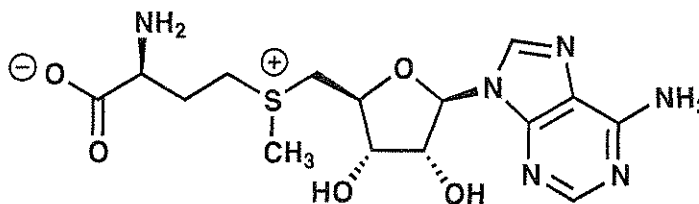
Name:

Code: TJK-

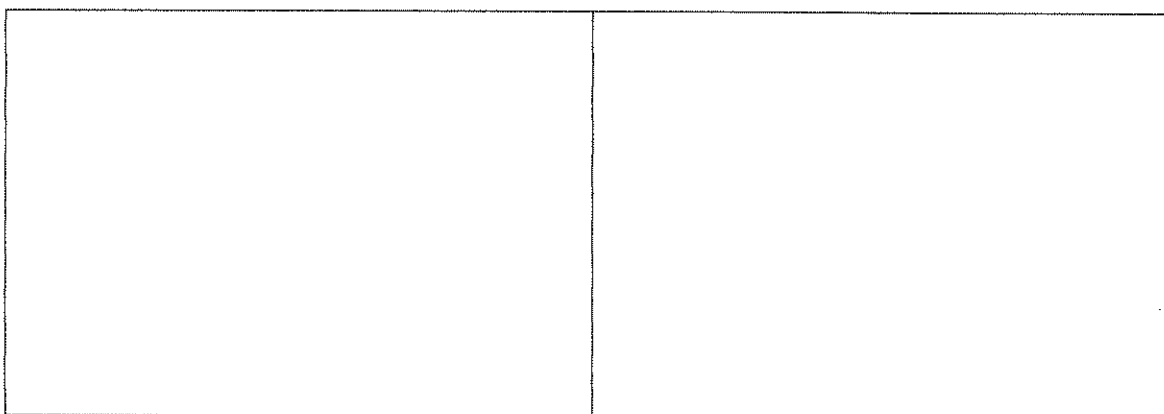
b. One common modification of DNA in nature is methylation of the indicated (\*) position of guanine (G) by S-adenosyl methionine (SAM). **Draw** the structures of both of the products of the reaction between guanine and SAM.



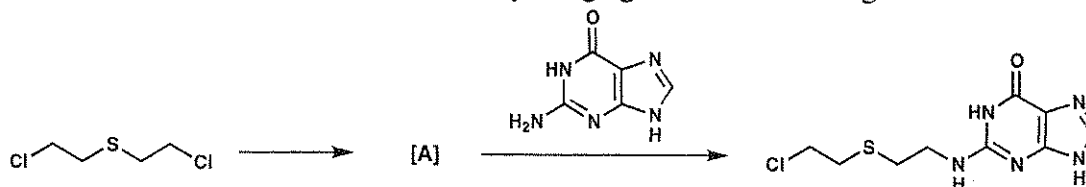
G



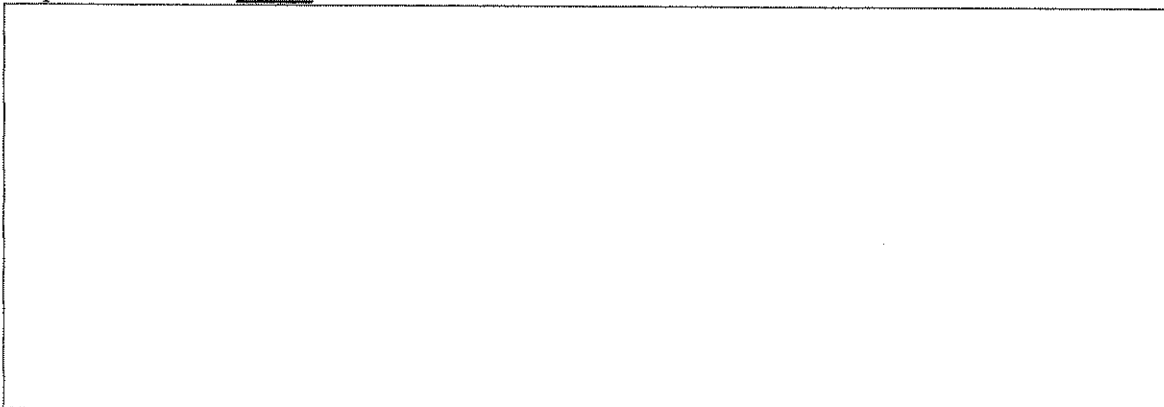
SAM



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.

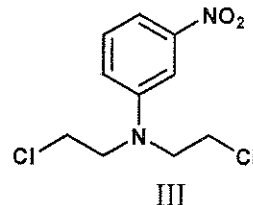
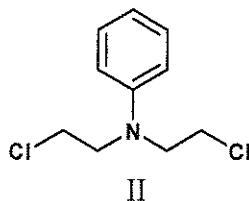
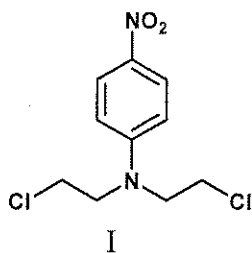


Name:

Code: TJK-

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.

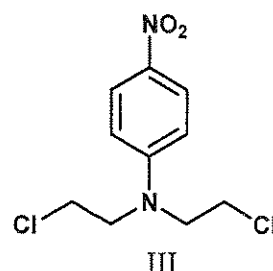
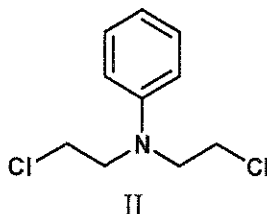
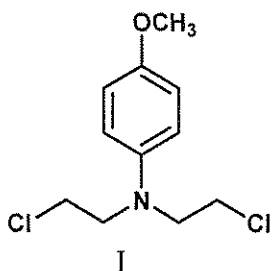
i.



**MOST REACTIVE:**

**LEAST REACTIVE:**

ii.



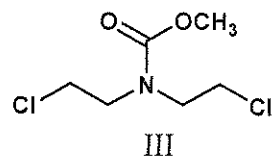
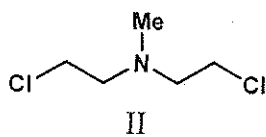
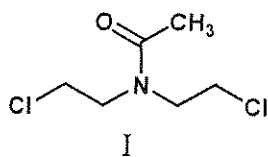
**MOST REACTIVE:**

**LEAST REACTIVE:**

Name:

Code: TJK

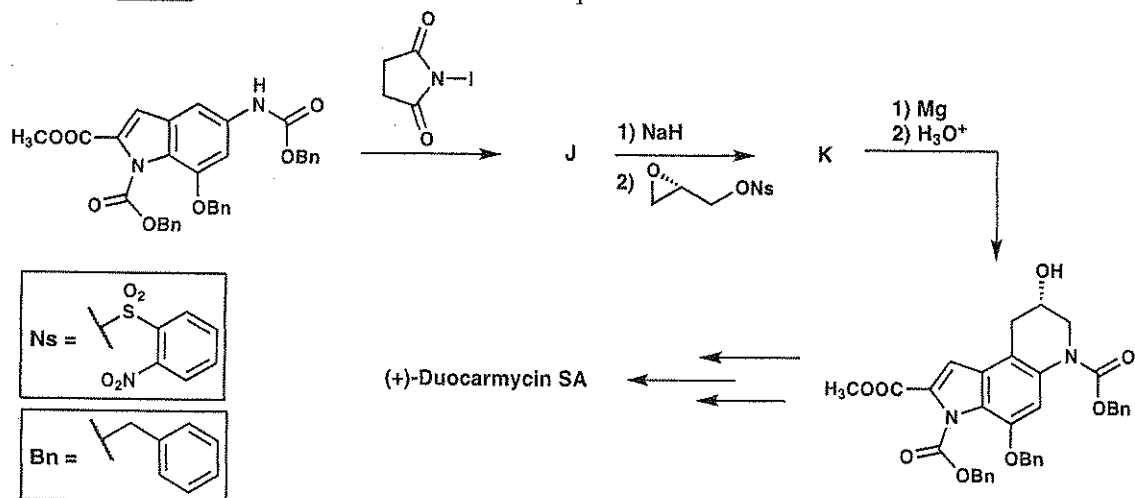
iii.



**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 isolable compounds **J** and **K**.

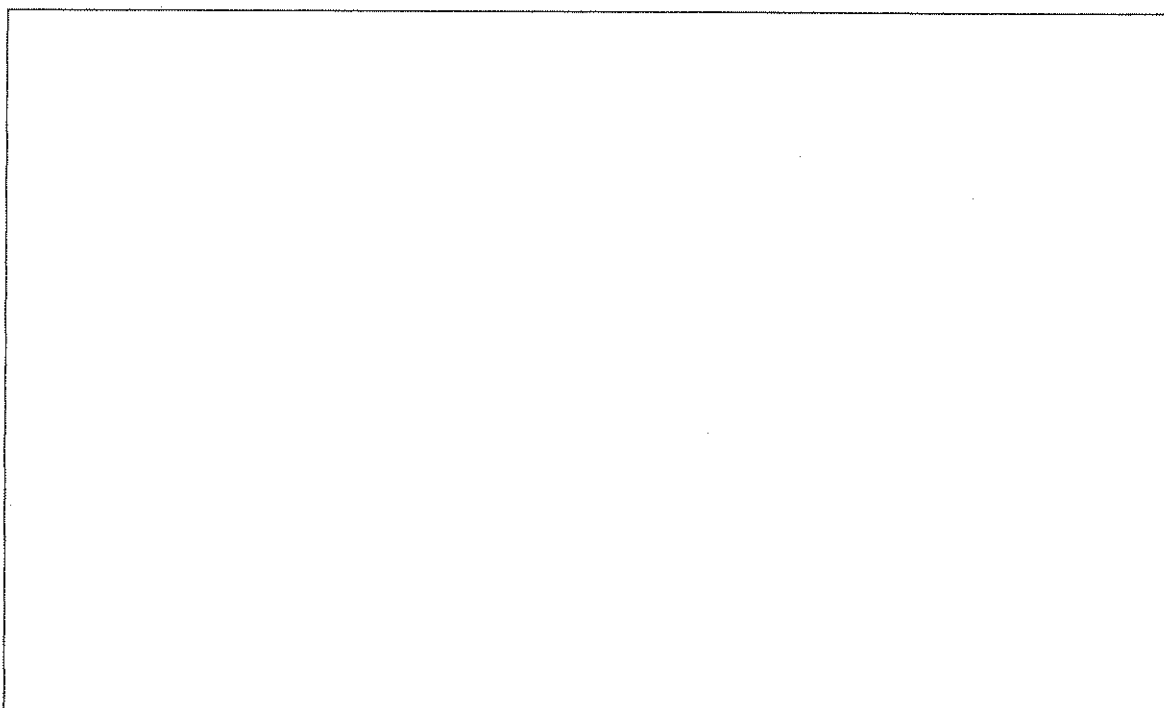
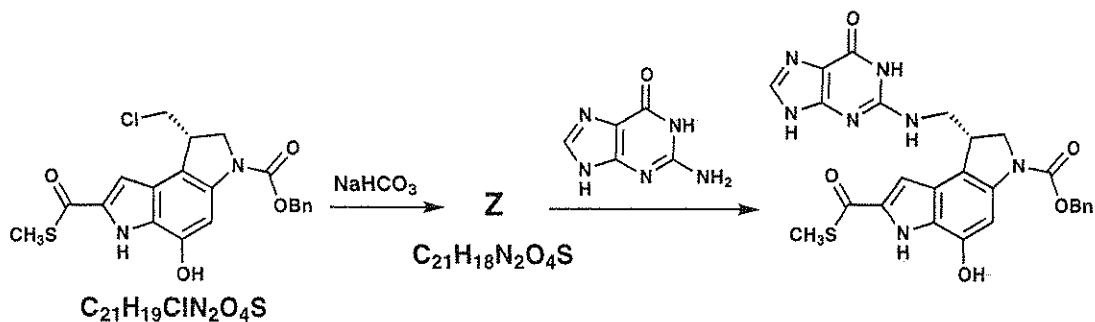


<b>J</b>	<b>K</b>
----------	----------

Name:

Code: TJK-

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**.

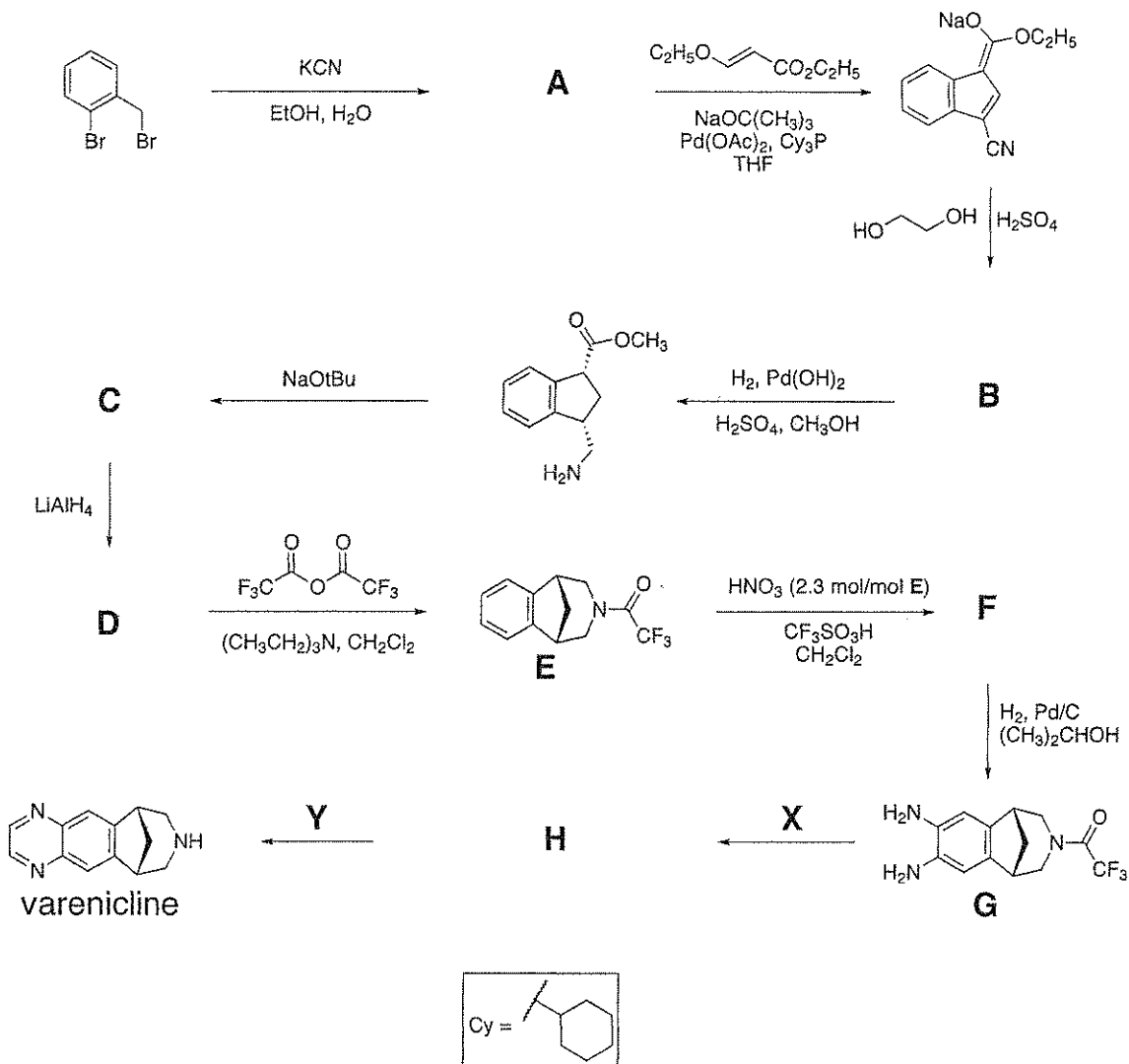


## PROBLEM 6

6.6 % of the Total

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

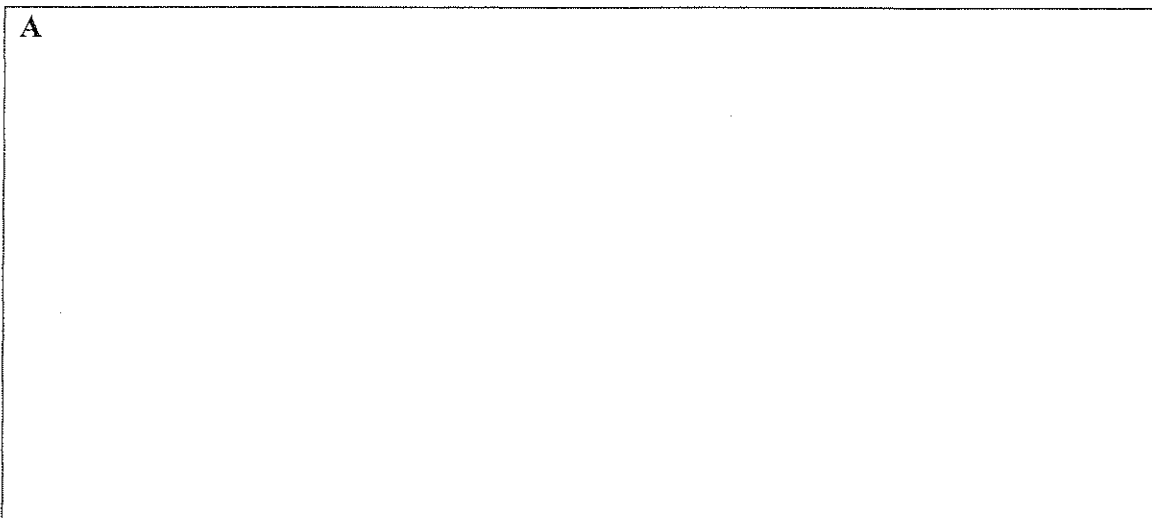
Varenicline has been developed as an oral treatment for smoking addiction and can be synthesized by the route shown below. All compounds indicated by a letter (A – H) are uncharged, isolable species.



Name:

Code: TJK-

a. Suggest a structure for compound A.



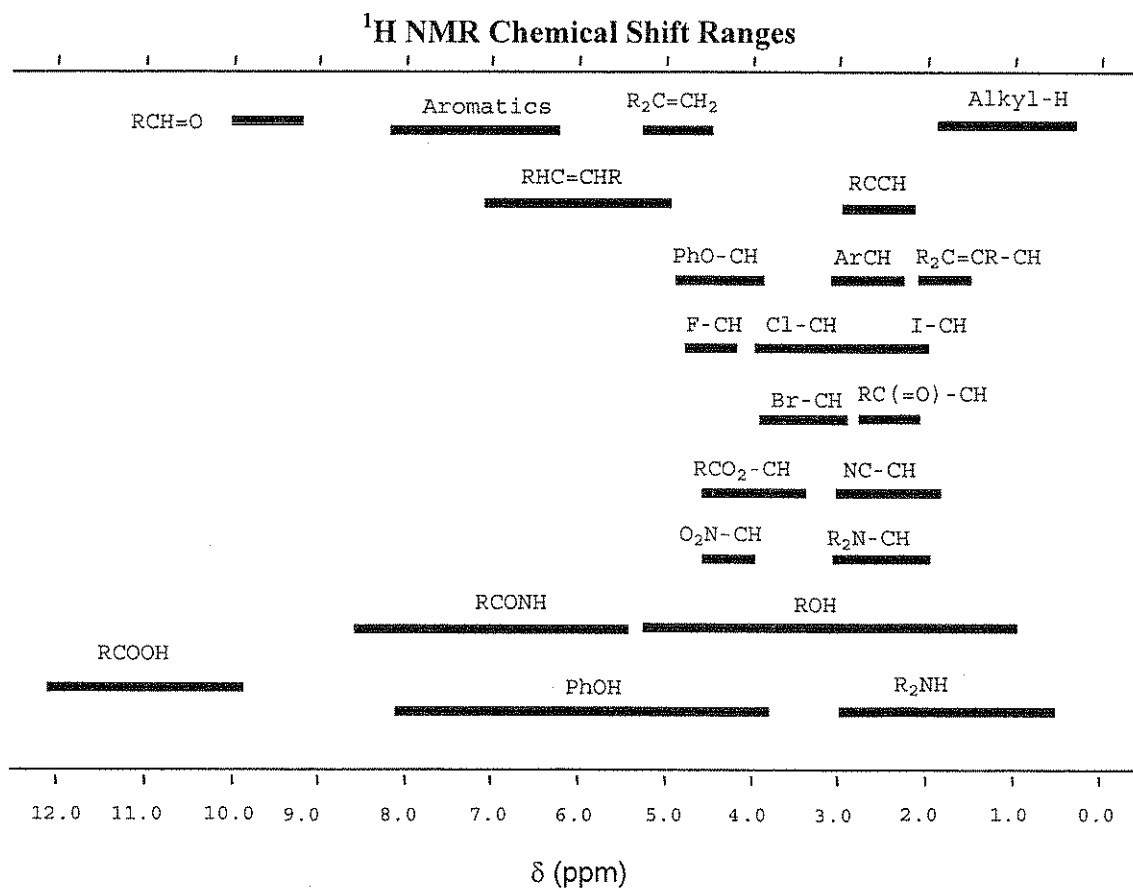


Name:

Code: TJK-

b. Suggest a structure for compound **B** consistent with the following  $^1\text{H-NMR}$  data:  
 $\delta$  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: TJK

c. Suggest a structure for compounds **C**, **D**, and **F**.

<b>C</b>	<b>D</b>
<b>F</b>	

d. Suggest reagents **X** and **Y** to convert compound **G** into *varenicline*, and provide the isolable intermediate **H** along this route.

<b>X</b>	<b>Y</b>
<b>H</b>	

Name:

Code: TJK-

## PROBLEM 7

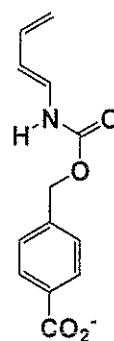
7.5 % of the Total

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

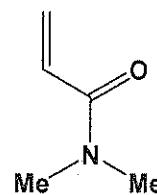
An artificial enzyme was designed to bind the two substrate molecules shown below (diene and dienophile) and catalyze a Diels-Alder reaction between them.

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

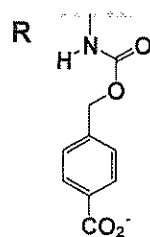
i. Draw the structures of **any two** of the potential products that are **regioisomers** of each other, in the boxes that are given below. Use wedges ( — ) and dashes ( - - - ) to show the stereochemistry of each product in your drawings. Use **R** and **R'** shown below to represent the substituents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



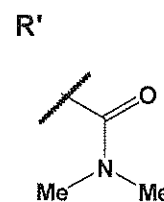
diene



dienophile



R



R'

--	--

Name:

Code: TJK-

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

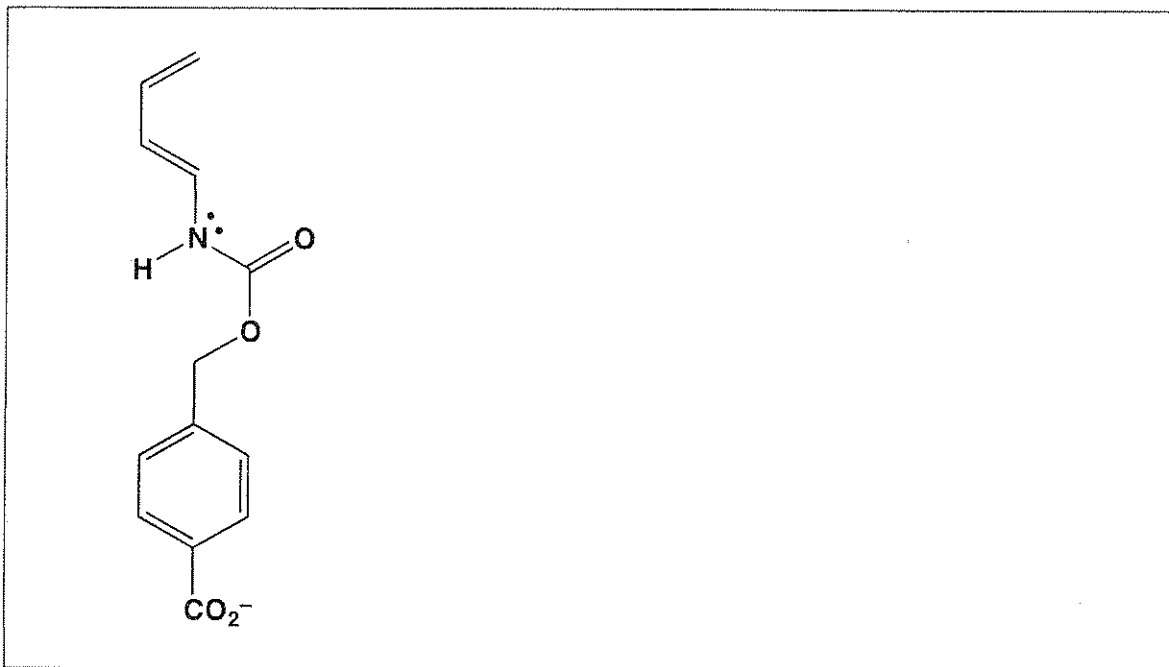
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Name:

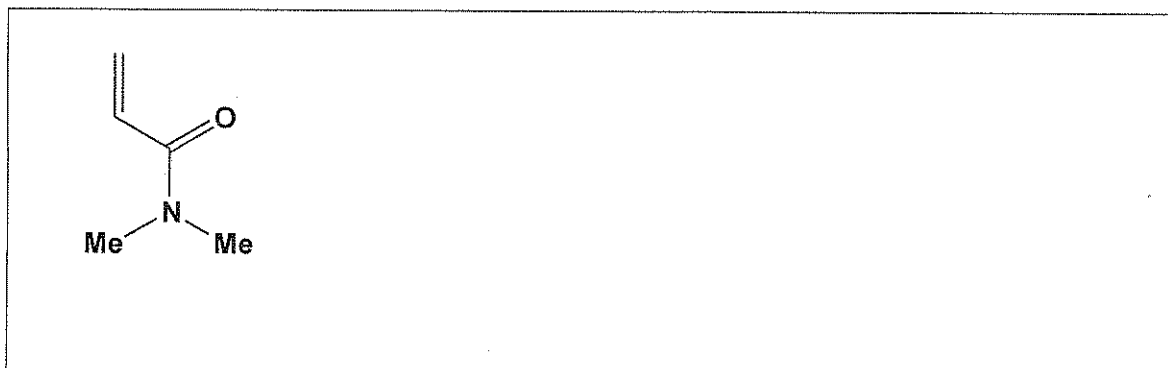
Code: TJK

b. The rate and regioselectivity of a Diels-Alder reaction depend on the degree of electronic complementarity (electronic charge opposition) 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.



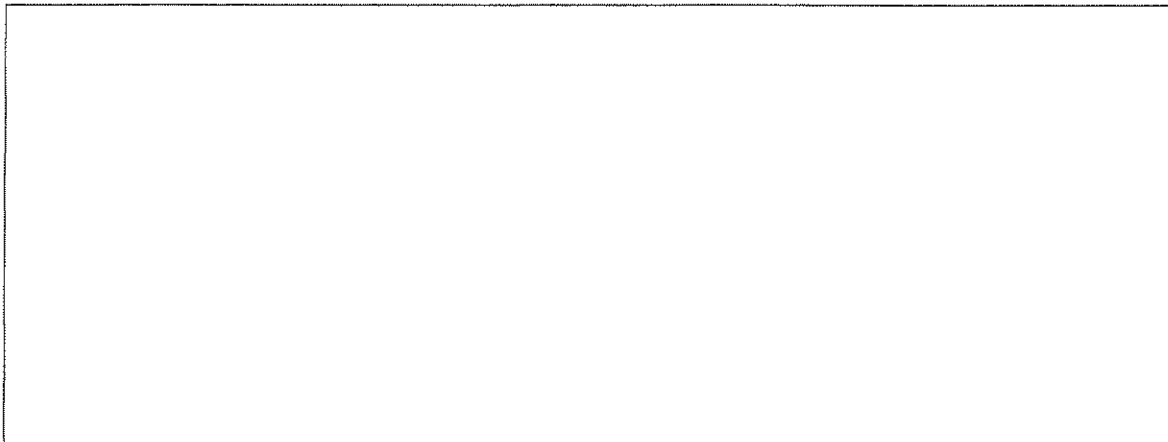
ii. **Circle** the carbon atom in the dienophile that has decreased electron density and therefore can act as an electron acceptor during the reaction. Draw one resonance structure of the dienophile in the box to support your answer. Indicate all non-zero formal charges on the atoms in the resonance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



Name:

Code: TJK-

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.

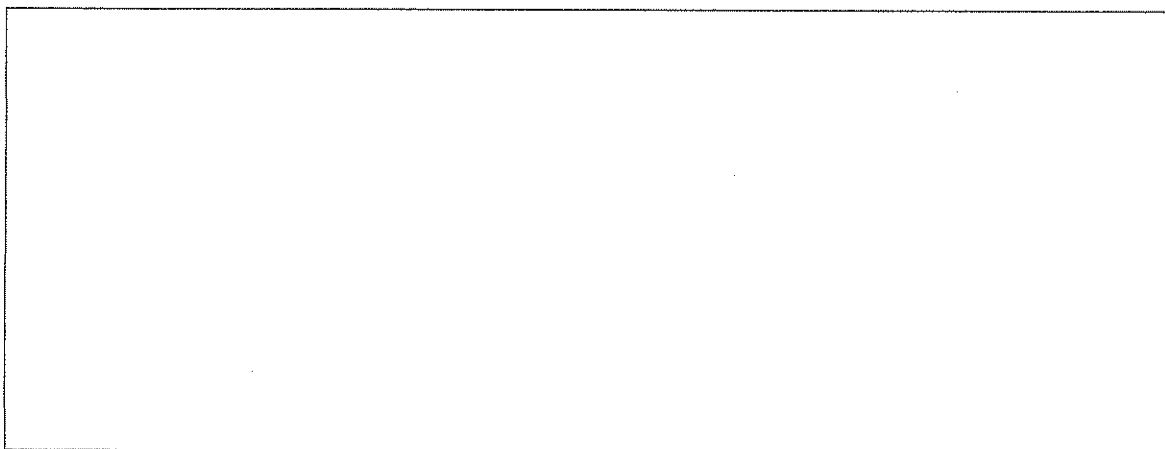
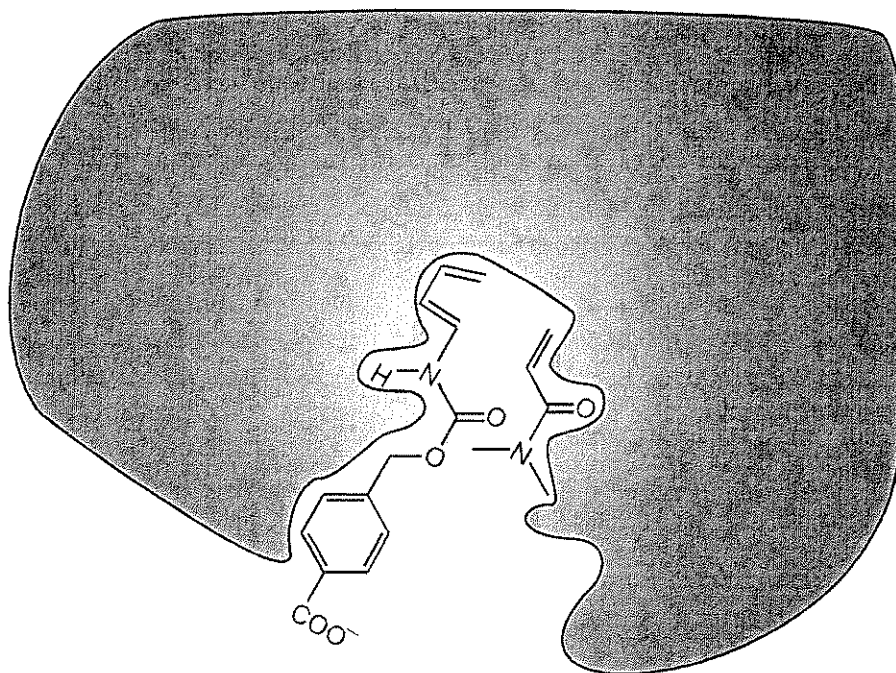


Name:

Code: TJK-

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 and use **R** and **R'** as you did for **question a**.



**Name:**

**Code: TJK-**

**d.** Consider the following statements about enzymes (artificial or natural). For each statement, indicate whether that statement is True or False (draw a circle around “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**

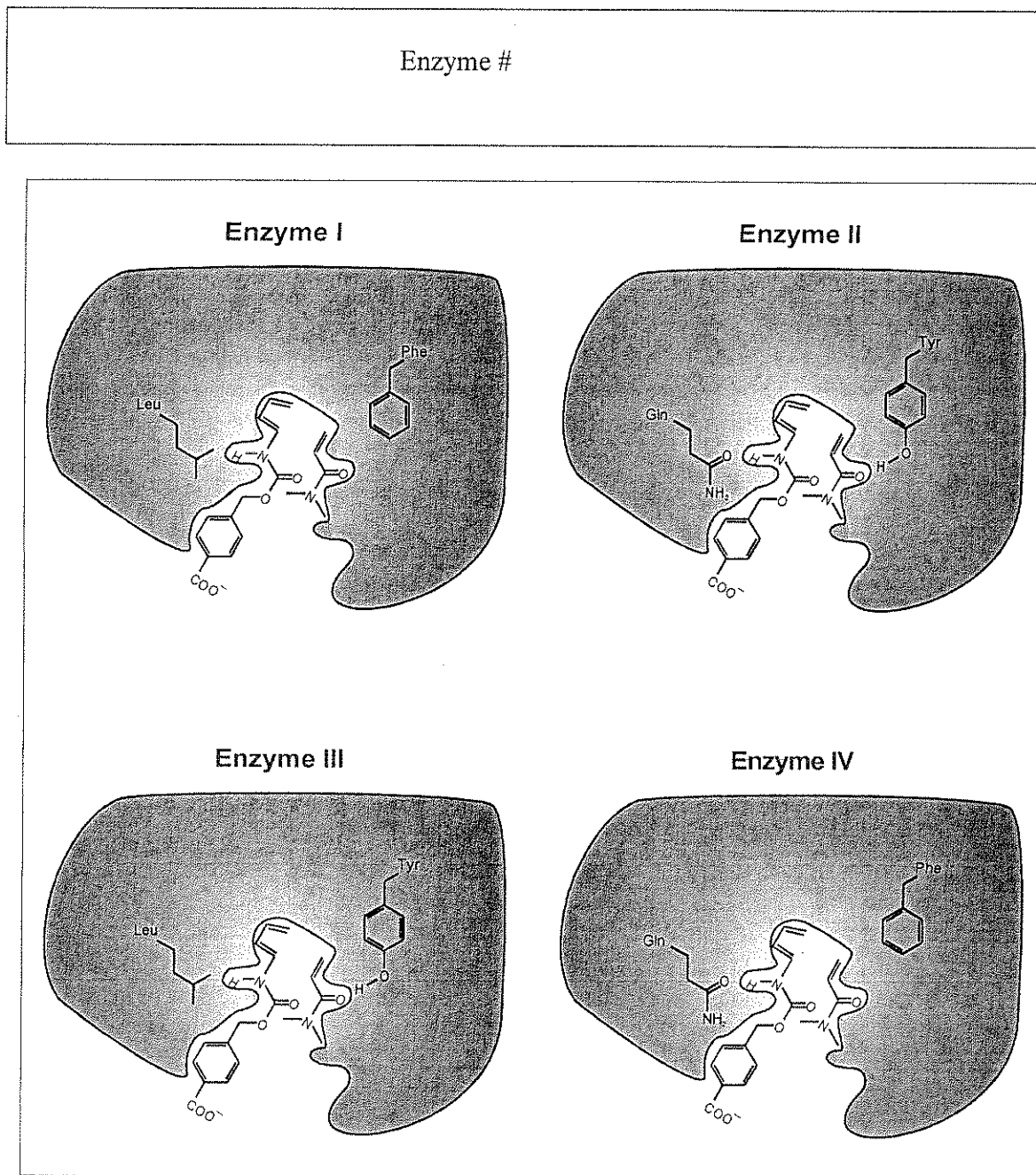


Name:

Code: TJK-

e. Modified versions of the artificial enzymes with different catalytic activities were prepared (enzymes I, II, III, and IV, shown in 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.

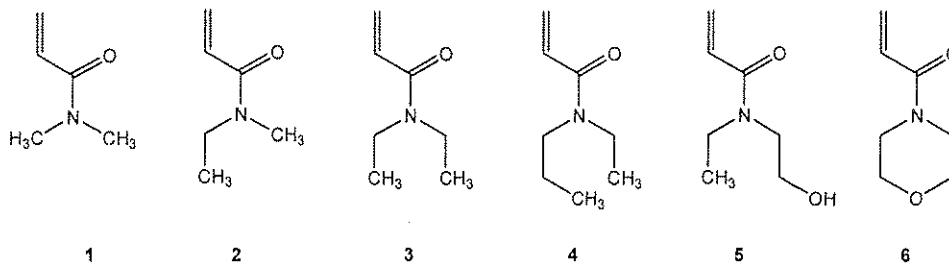
Of these four enzymes which one would cause the greatest increase in the rate of the Diels-Alder reaction compared to the uncatalyzed reaction?



Name:

Code: TJK-

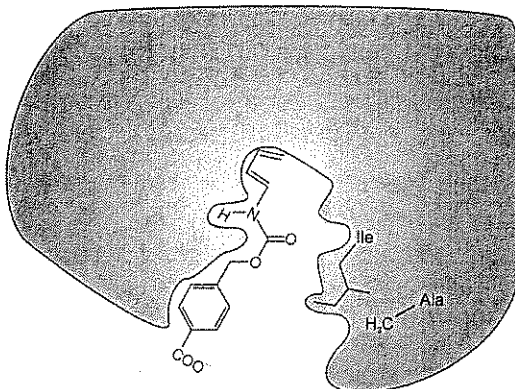
f. The substrate specificity of the artificial enzymes **V** and **VI** (see below) was tested by using the dienophile reactants **1 - 6**, shown below.



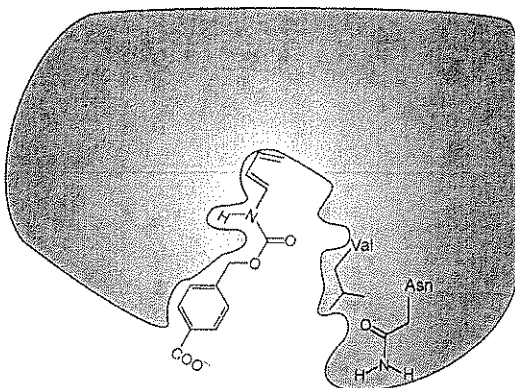
Dienophile #1 reacted most rapidly in the reaction catalyzed by artificial **enzyme V** (see below). However, artificial **enzyme VI** catalyzed the reaction most rapidly with a different dienophile. Of the six dienophiles shown above, which one would react most rapidly in the Diels-Alder reaction catalyzed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

Dienophile #

Enzyme V



Enzyme VI

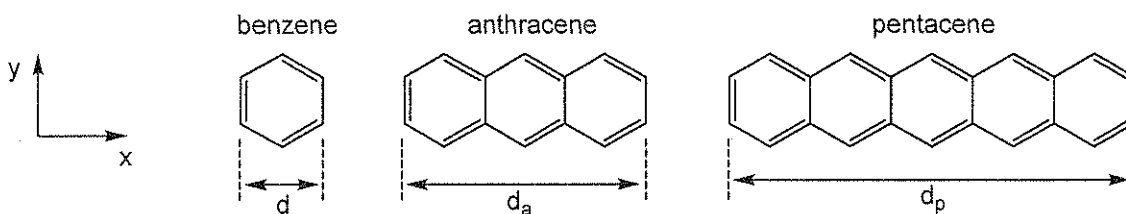


## PROBLEM 8

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 (detector). 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  $\pi$  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.

For anthracene,  $d_a =$

For pentacene,  $d_p =$

- b. Assume for simplicity that the  $\pi$  electrons of benzene can be modeled as being confined to (assumed to be) a square. Within this model, the conjugated  $\pi$  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

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

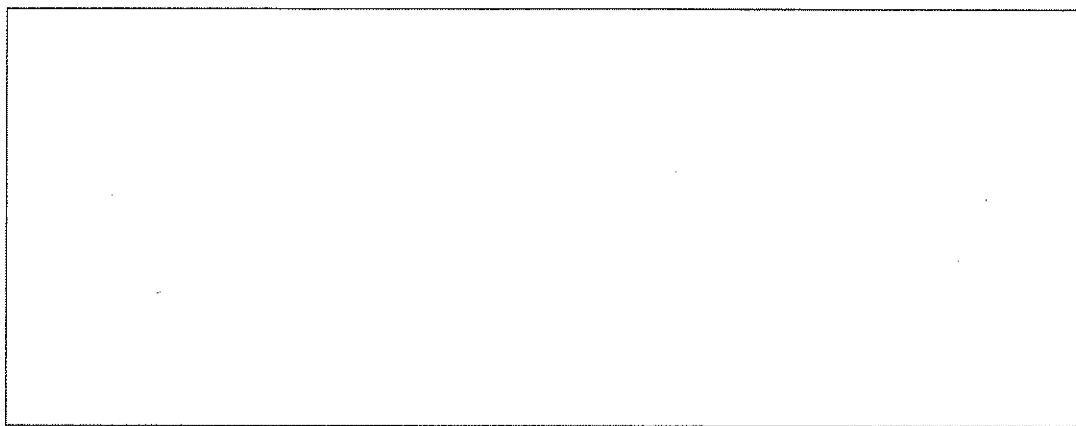
Name:

Code: TJK-

In this equation,  $n_x$  and  $n_y$  are the quantum numbers for the energy state and are integers between 1 and  $\infty$ ,  $h$  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  $\pi$  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  $\pi$ -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)

Name:

Code: TJK-

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  $\pi$  electrons in anthracene. Also, the blanks in parentheses within this diagram are the quantum numbers  $n_x, n_y$ , which you need to determine. Fill these blanks with the pertinent values of  $n_x, n_y$  for each filled and the lowest unfilled energy level(s).

Anthracene:

\_\_ ( ; )

\_\_ ( ; )    \_\_ ( ; )

\_\_ ( ; )

\_\_ ( ; )

\_\_ ( ; )

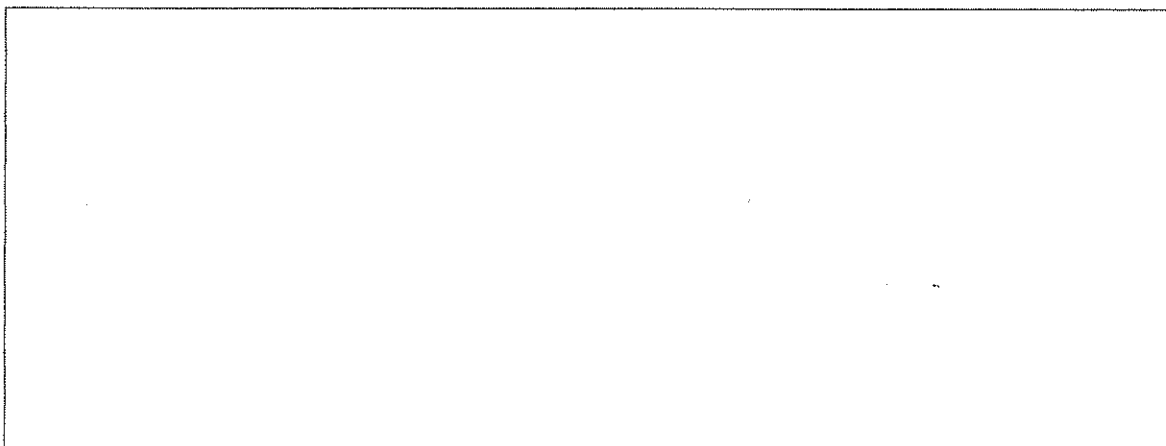
\_\_ ( ; )

\_\_ ( ; )

\_\_ ( ; )

\_\_ ( ; )

iii. Use this model to create an energy level diagram for benzene and fill the pertinent (suitable) 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.



Name: \_\_\_\_\_

Code: TJK-

iv. Often the reactivity of PAHs correlates inversely with the energy gap  $\Delta E$  between the highest energy level occupied by  $\pi$ -electrons and the lowest unoccupied energy level. Calculate the energy gap  $\Delta E$  (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).

$\Delta E$  for benzene:

$\Delta E$  for anthracene:

$\Delta E$  for pentacene:

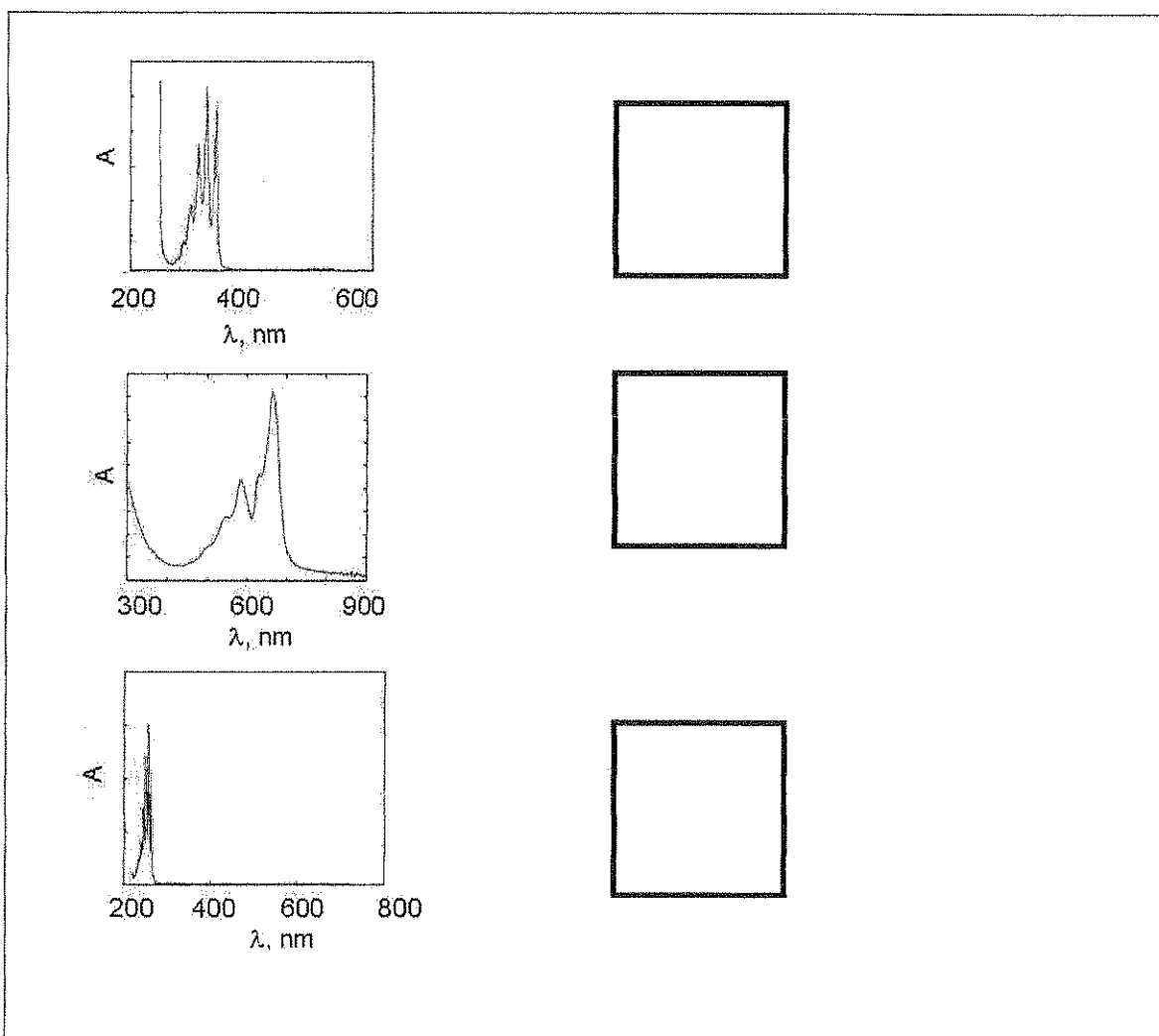
Name:

Code: TJK-

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.

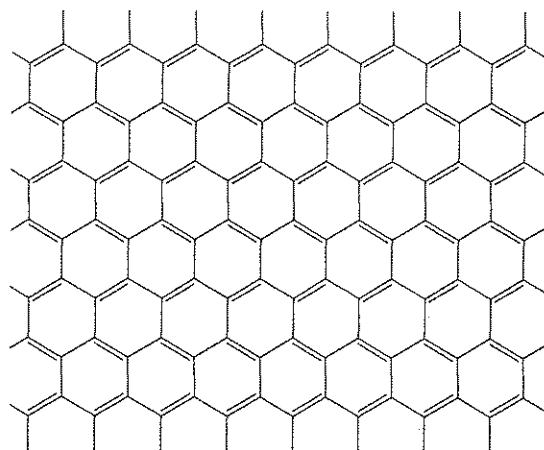


c. Graphene is a sheet of carbon atoms arranged in a two-dimensional honeycomb pattern. It can be considered as an extreme case of a polyaromatic hydrocarbon with essentially infinite length in the two dimensions. The Nobel Prize for Physics was awarded in 2010 to Andrei Geim and Konstantin Novoselov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

Name:

Code: TJK-

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  $\sim 52400$  pm<sup>2</sup>. Calculate the number of  $\pi$  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).

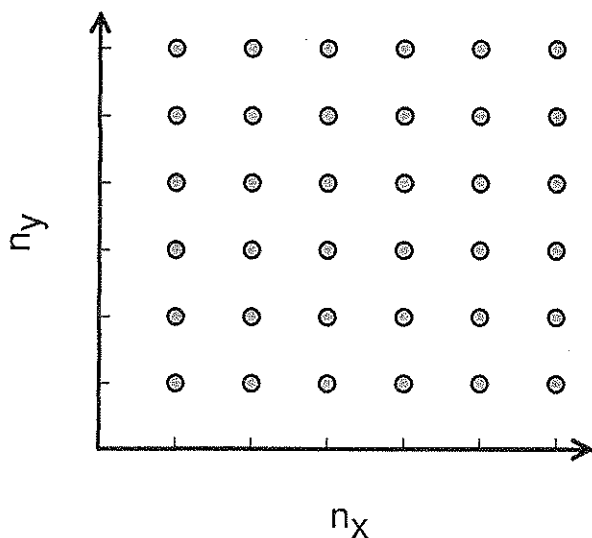


Name:

Code: TJK-

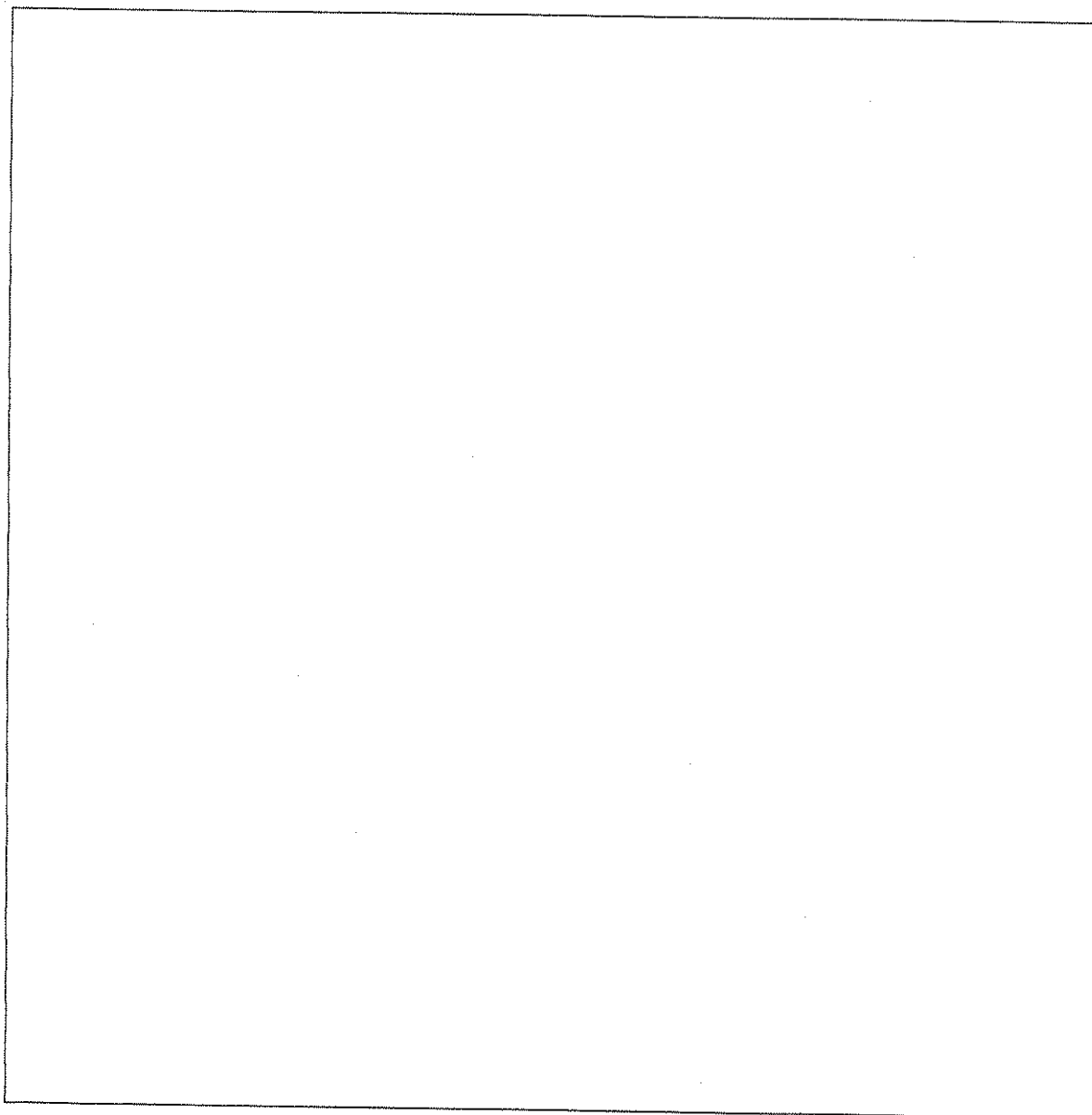
ii. We can think about the  $\pi$  electrons in graphene as being free electrons in a 2-dimensional box.

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-Dimensional 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).



Name:

Code: TJK



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  $\pi$  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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