EXAMINATION 1
Chemistry 3A

Name:___________________________ **SID #:**_______________________
Print first name before second!
Use capital letters!

GSI (if you are taking Chem 3AL): _______________________

Peter Vollhardt
February 28, 2017

Please provide the following information if applicable.

Making up an I Grade _____
If you are, please indicate the semester during which you took previous Chem 3A and the instructor:

________________ _____________
Semester Instructor

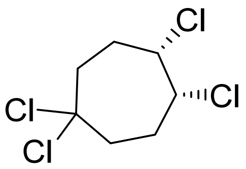
Auditor _____

Please write the answer you wish to be graded in the boxed spaces provided.

Do scratch work on the back of the pages. This test should have **16** numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy now than sorry later!** ***Good Luck*!**

I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*, *R*, *S*, or dashed/wedged lines).

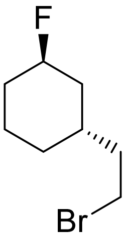
a.



b.

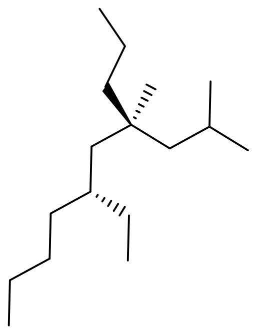
trans-1,3-Bis(1-methylethyl)cyclopentane

c.



d.

(*R*)-4-(1-Chloroethyl)-1,7-diiodoheptane e.



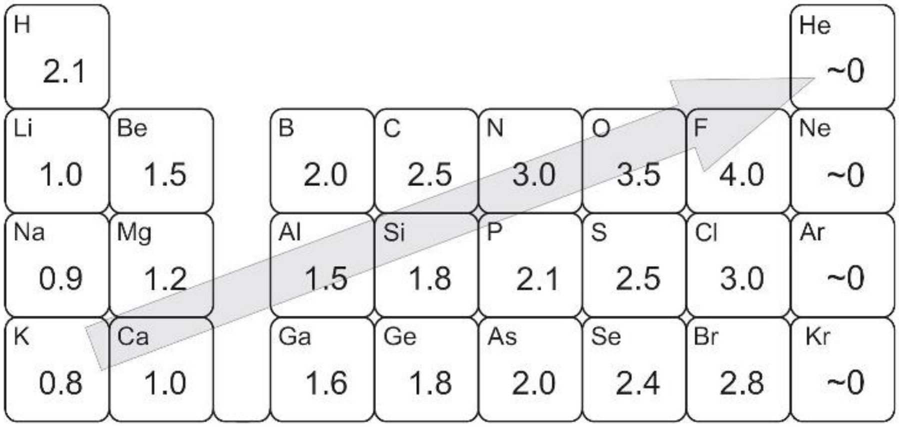
II. [30 Points] Write the best Lewis structure for each of the following molecules. **Remember to assign charges, if any, to atoms!**

TABLE 1-1 Partial Periodic Table

Period							Halogens	Noble gases
First	H^{1}							He^{2}
Second	$Li^{2,1}$	$Be^{2,2}$	$B^{2,3}$	$C^{2,4}$	$N^{2,5}$	$O^{2,6}$	$F^{2,7}$	$Ne^{2,8}$
Third	$Na^{2,8,1}$	$Mg^{2,8,2}$	$Al^{2,8,3}$	$Si^{2,8,4}$	$P^{2,8,5}$	$S^{2,8,6}$	$Cl^{2,8,7}$	$Ar^{2,8,8}$
Fourth	$K^{2,8,8,1}$						$Br^{2,8,18,7}$	$Kr^{2,8,18,8}$
Fifth							$I^{2,8,18,18,7}$	$Xe^{2,8,18,18,8}$

Note: The superscripts indicate the number of electrons in each principal shell of the atom.

Pauling Electronegativities



H 2.1							He ~0
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ~0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar ~0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr ~0

a.

What is the geometry of NON ? Place an “x” mark into the box next to your answer.

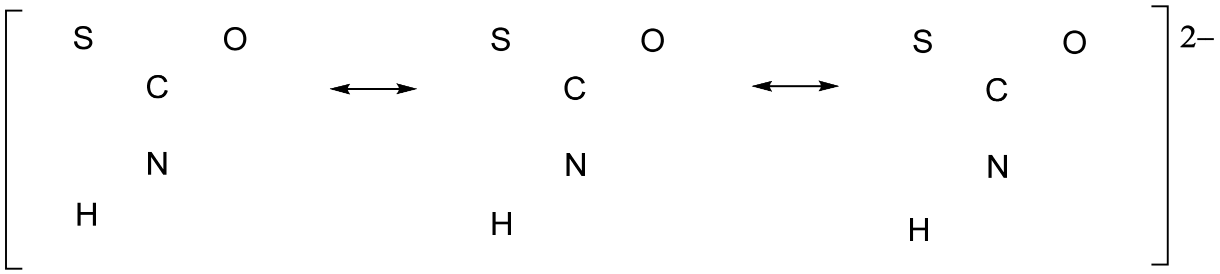
Linear ☐

Bent ☐

b.

$$\left[\ P \quad C\ \right]^{-}$$

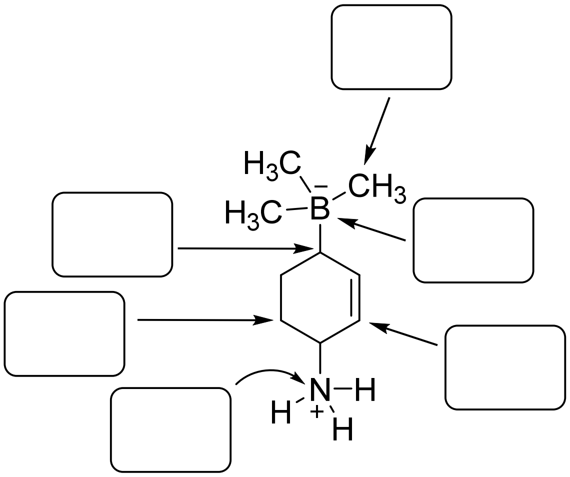
c. The following structure has three octet resonance forms. Circle the best one.



d. The following structure has three octet resonance forms. Circle the best one.

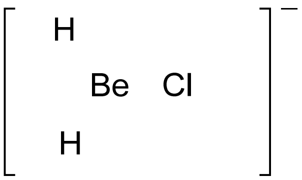
$$\left[\ \mathrm{S\quad B\quad O} \longleftrightarrow \mathrm{S\quad B\quad O} \longleftrightarrow \mathrm{S\quad B\quad O}\ \right]^{-}$$

e. Enter the hybridization (*sp*, *sp*^{2}, *sp*^{3}) of the indicated atom in the box provided.

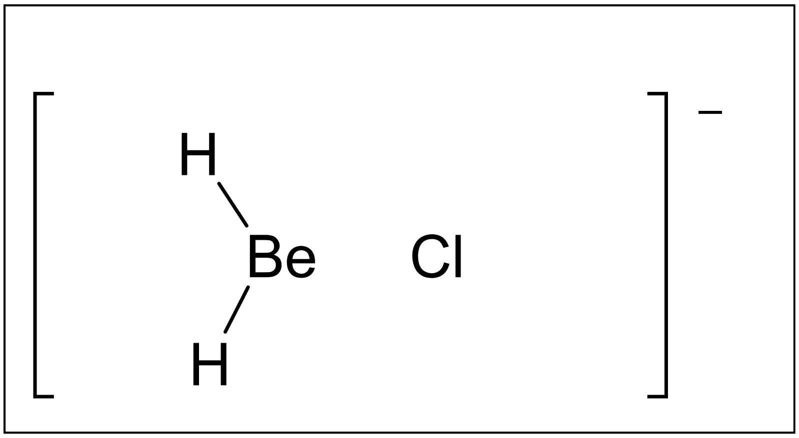


III. [30 Points]

a. Draw the octet structure of the anion shown below. **Hint:** There will be a Be-Cl double bond.

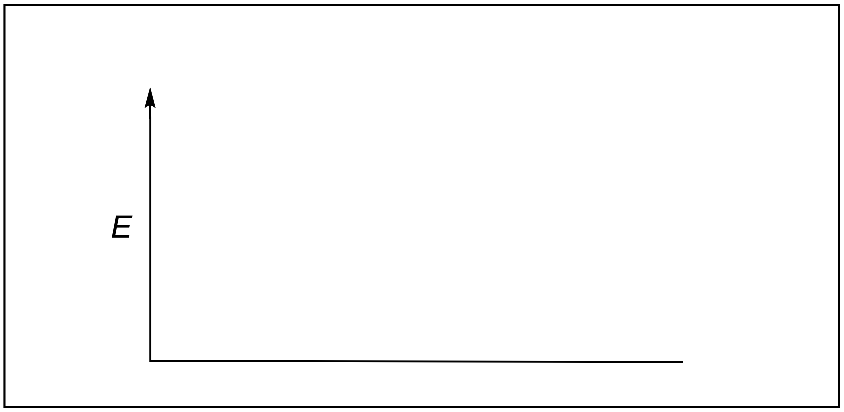


b. Draw the orbitals on Be and Cl that give rise to the double bond and draw the location of the bonding electrons using dots. Clearly label these orbitals (e.g. 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, *sp*, sp^2, sp^3, etc.)

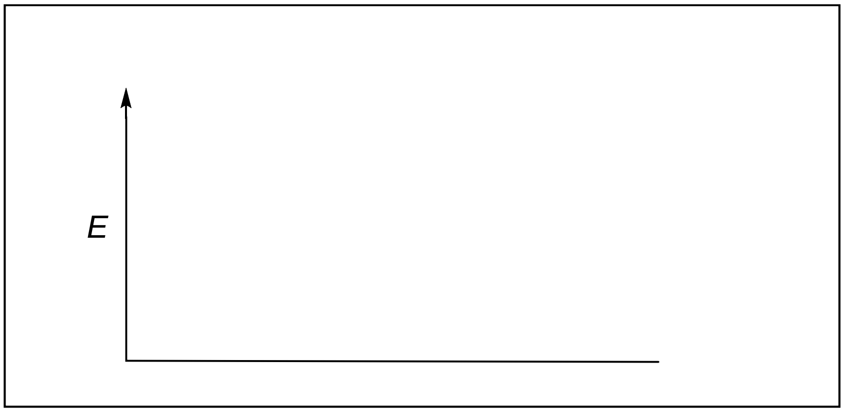


c. Draw (separately) orbital energy splitting diagrams for the formation of each part of the double bond: σ and π. Clearly depict the energy levels of the orbitals entering into overlap and label them (Be on the left, Cl on the right), and label the resulting bonding and antibonding molecular orbital levels. Place the relevant electrons into the various levels.

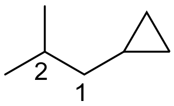
σ Part of the double bond



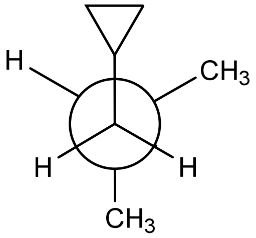
π Part of the double bond



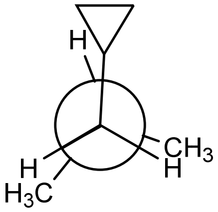
IV. [30 Points] Consider the rotation about the C1–C2 bond in the cyclopropane derivative shown.



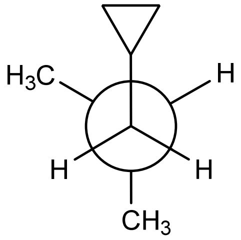
The Newman projections **A–F** below illustrate the sequential clockwise motion of the back-carbon (C1) in increments of 60°.



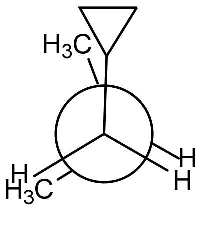
A



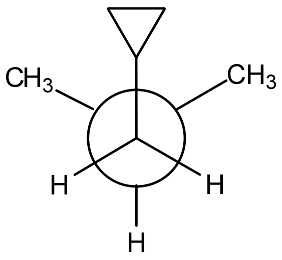
B



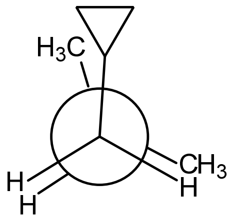
C



D



E

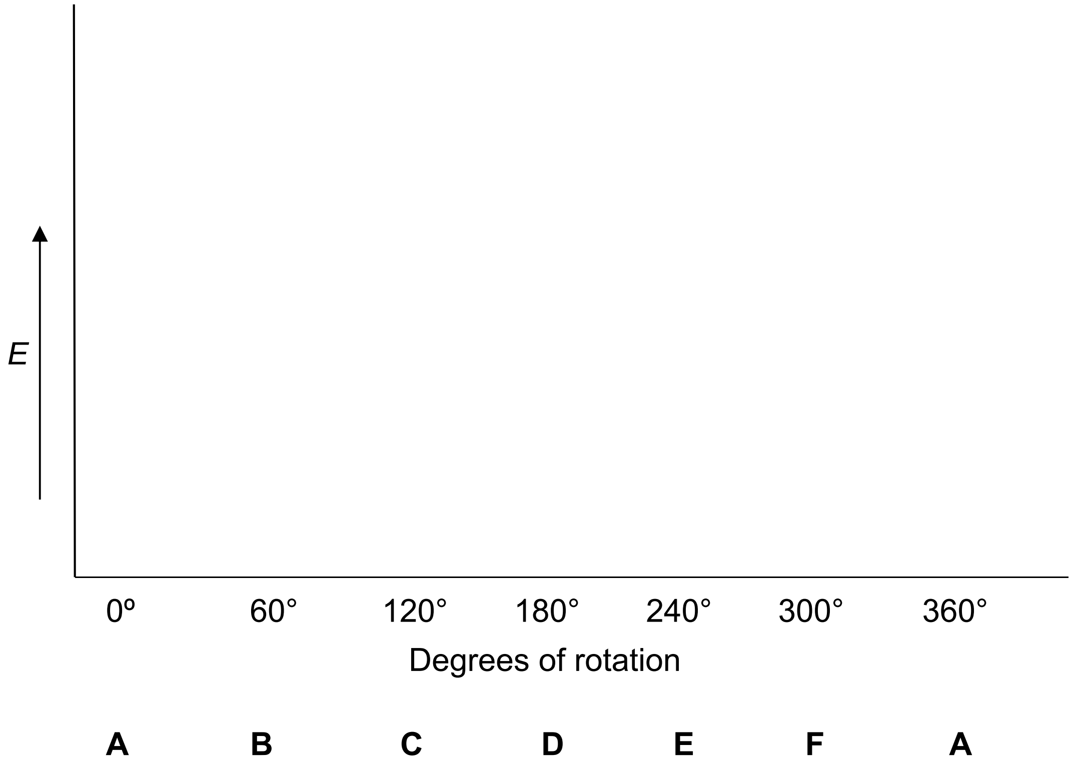


F

a. Indicate, by circling the appropriate letter, the rotamers that contain substituents that are (with respect to each other) anti or gauche, or rotamers that are eclipsed or staggered:

anti:	gauche:	eclipsed:	staggered:
A	A	A	A
B	B	B	B
C	C	C	C
D	D	D	D
E	E	E	E
F	F	F	F

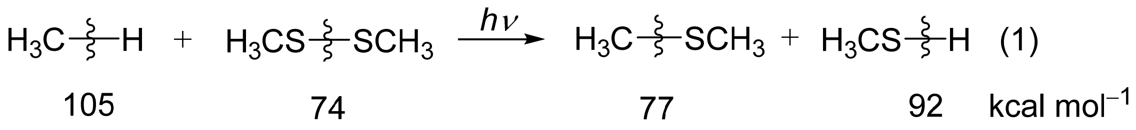
b. Draw a potential energy diagram for this movement. Start by assigning a relative energy to each rotamer on the diagram below, before drawing the interconnecting curve.



c. Two of the staggered rotamers have the same energy. Show which ones, by placing the appropriate letters in the box.

d. Two of the eclipsed rotamers have the same energy. Show which ones by placing the appropriate letters in the box.

V. [50 Points] A researcher wants to explore the radical “methylthiolation” of alkanes, as exemplified below for reaction of methane.



$$H_3C\text{–}H + H_3CS\text{–}SCH_3 \xrightarrow{h\nu} H_3C\text{–}SCH_3 + H_3CS\text{–}H \quad (1)$$

$$105 \qquad 74 \qquad 77 \qquad 92 \quad \text{kcal mol}^{-1}$$

a. Using the bond dissociation energies provided in equation (1), calculate the $\Delta H°$ value for reaction (1). Show your work.

$\Delta H°$ (1) :

b. Is the reaction (1) thermodynamically feasible? Circle your answer.

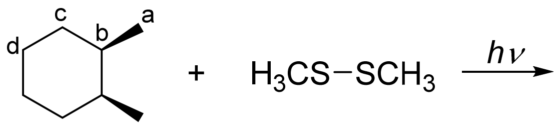
Answer: Yes No

c. Formulate the two propagation steps for reaction (1). Show electron-pushing arrows.

1st Propagation step :

2nd Propagation step :

d. The normalized selectivity tertiary : secondary : primary in methylthiolations with $CH_3S\cdot$ is 50:5:1. In the boxes provided, draw the products of single methylthiolation at the four positions of *cis*-1,2-dimethylcyclohexane (a–d), as indicated. Note: The bottom half of the molecule is the same as the top; draw only substitutions at the top. **Caution:** Watch out for diastereomers!



cis-1,2-Dimethylcyclohexane

Position a:

Position b:

Position c:

Position d:

e. Does the radical methylthiolation of *cis*-1,2-dimethylcyclohexane give any optically active products? Circle your answer.

Answer: Yes No

f. Give the ratio of all of the respective products of methylthiolation at positions a–d in the box provided. (In other words, all of the products in the box labeled “Position a” : all of the products in the box labeled “Position b” : all of the products in the box labeled “Position c” : all of the products in the box labeled “Position d”.)

Ratio of products a–d:

VI. [15 Points]

a. Using the values in the Table below and the cyclohexane stencils provided, show the structures of the most stable conformers of **A**, **B**, and **C**. For each, calculate the change in free energy on "ring flip" to the less stable conformer. Make sure to "cap off" all axial and equatorial bonds with substituents and H atoms. Enter your calculated energy of "ring flip" in the box provided.

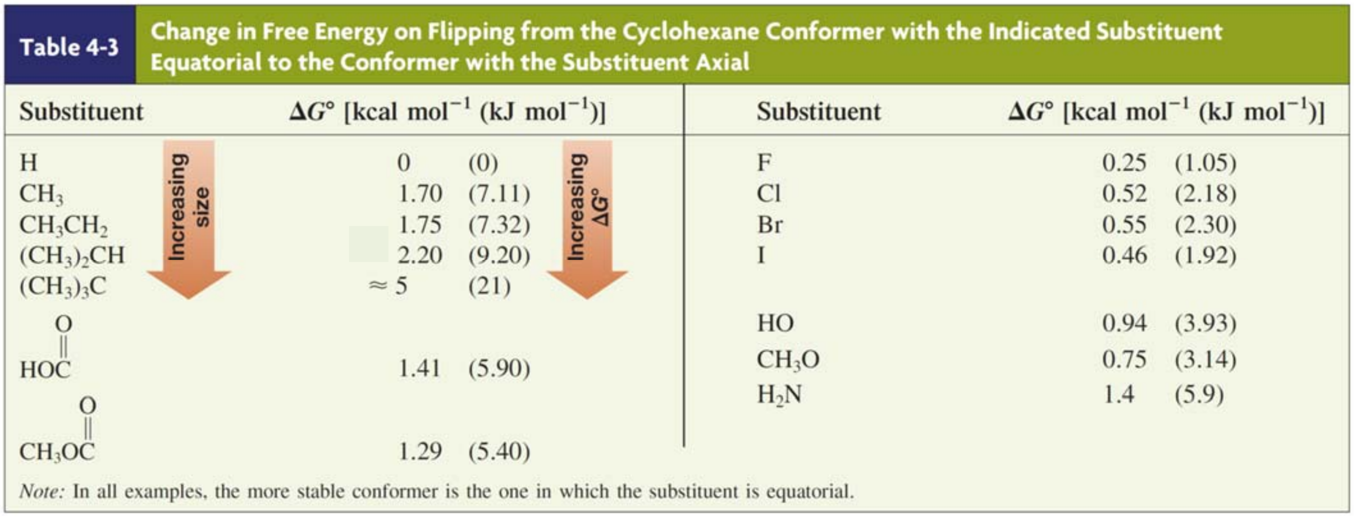
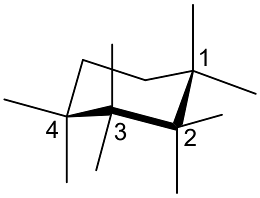


Table 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial

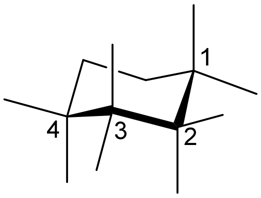
Substituent	ΔG° [kcal mol^{-1} (kJ mol^{-1})]	Substituent	ΔG° [kcal mol^{-1} (kJ mol^{-1})]
H	0 (0)	F	0.25 (1.05)
CH_3	1.70 (7.11)	Cl	0.52 (2.18)
CH_3CH_2	1.75 (7.32)	Br	0.55 (2.30)
$(CH_3)_2CH$	2.20 (9.20)	I	0.46 (1.92)
$(CH_3)_3C$	≈ 5 (21)		
$\mathrm{HO}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}$	1.41 (5.90)	HO	0.94 (3.93)
$\mathrm{CH_3O}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}$	1.29 (5.40)	CH_3O	0.75 (3.14)
		H_2N	1.4 (5.9)

Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

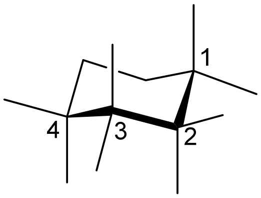
A: *cis*-1-Bromo-2-fluorocyclohexane



B: *cis*-1-Methyl-4-(1,1-dimethylethyl)cyclohexane



C: *trans*-1-Iodo-3-methylcyclohexane



VII. [65 Points]

1. Mark the box next to your choice of an answer with an X.

The C–H bond strength deceases in the order CH_4, primary, secondary, tertiary, because

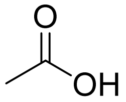
☐ steric hindrance decreases

☐ the product radicals increase in stability

☐ the product radicals decrease in stability

☐ hybridization changes from *sp*^{2} to *sp*^{3}

2. In the following pairs of compounds, circle which one is more acidic.

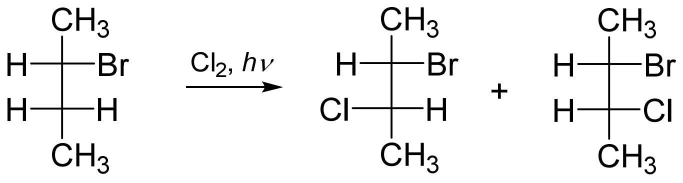
H_2SO_4 

CH_4 NH_3

H_3O^+ H_2O

NH_3 PH_3

3. Consider the following chlorination.



A

a. What is the absolute configuration of A (*R* or *S*)? Circle the correct answer.

R *S*

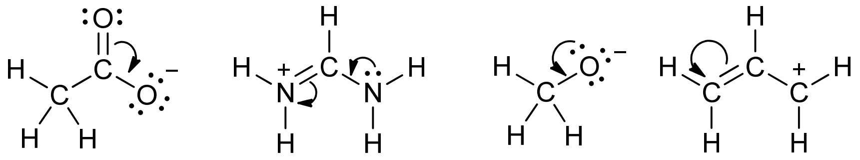
b. The products are (circle the correct answer):

Diastereomers Enantiomers Identical A racemate

c. The products are formed (circle the correct answer):

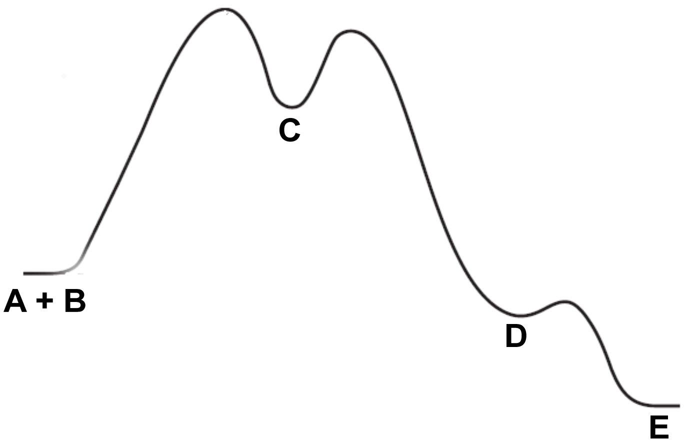
In equal amounts In unequal amounts

4. Does the arrow pushing in the following molecules **A**–**D** lead to an acceptable resonance form? Circle your answers.



A	**B**	**C**	**D**
Yes no	Yes no	Yes no	Yes no

5. The following potential-energy diagram shows the addition reaction of A to B to give E via intermediates C and D.



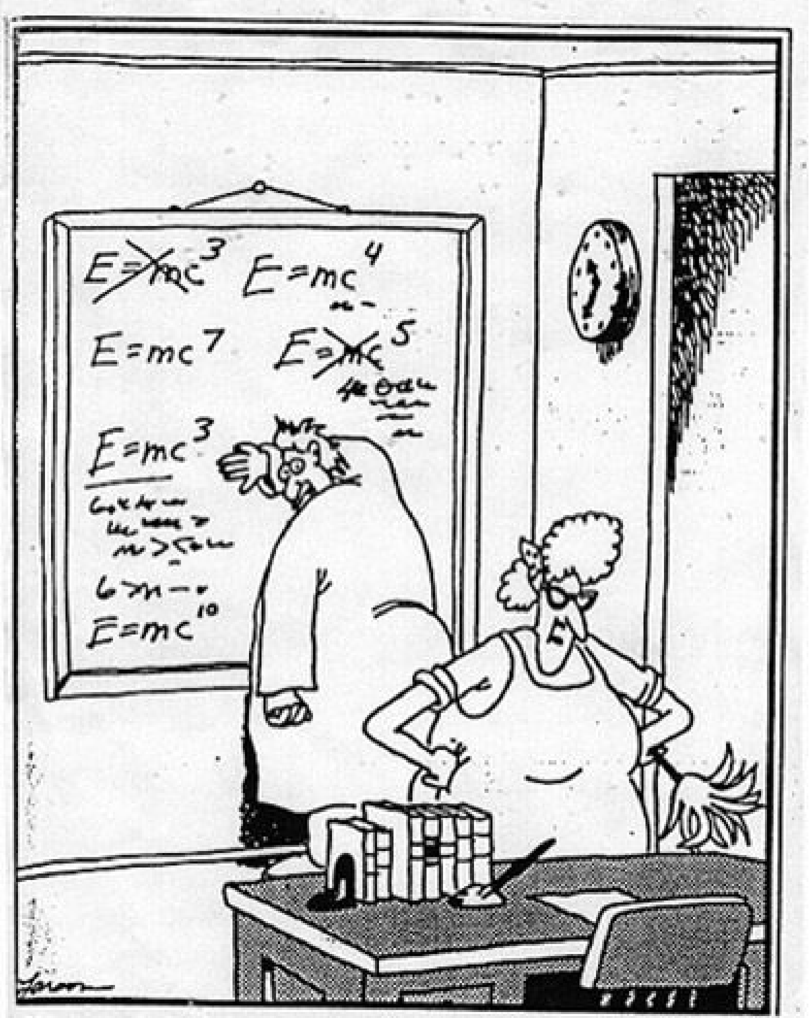
a. Mark with an "X" the rate-determining step of the transformation of A+B to D.

b. If you were to follow the progress of the transformation, would you observe sizeable amounts of C and/or D? Place an "X" mark in the appropriate box.

☐ only of C ☐ only of D ☐ yes ☐ no

c. The reaction of A with B follows second order kinetics. If you double the concentration of A and simultaneously double the concentration of B what would be the effect on the rate of the reaction? Place an "X" mark in the appropriate box.

☐ no effect ☐ the rate doubles ☐ the rate fourfolds ☐ the rate diminishes



"*Now* that desk looks better. Everything's squared away, yessir, squaaaaaared away."

♫ The End ♫