EXAMINATION 1
Chemistry 3A

Name:______________________________ **SID #:**______________________
Print first name before second!
Use capital letters!

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

Peter Vollhardt
February 22, 2018

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

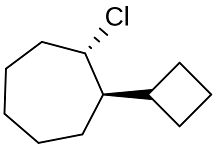
Auditor _____

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 **18** 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 (such as cis, trans, *R*, *S*, meso, hashed/wedged lines, etc.)

a.

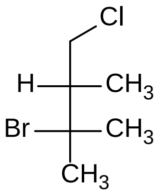


(This enantiomer)

b.

(*S*)-(1-Chloropentyl)cyclopentane

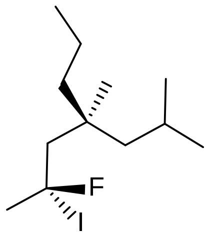
c.



(This enantiomer)

d.

4-Ethyl-3,4,5-trimethyl-5-(2-methylpropyl)-decane e.



(This enantiomer)

II. [30 Points]

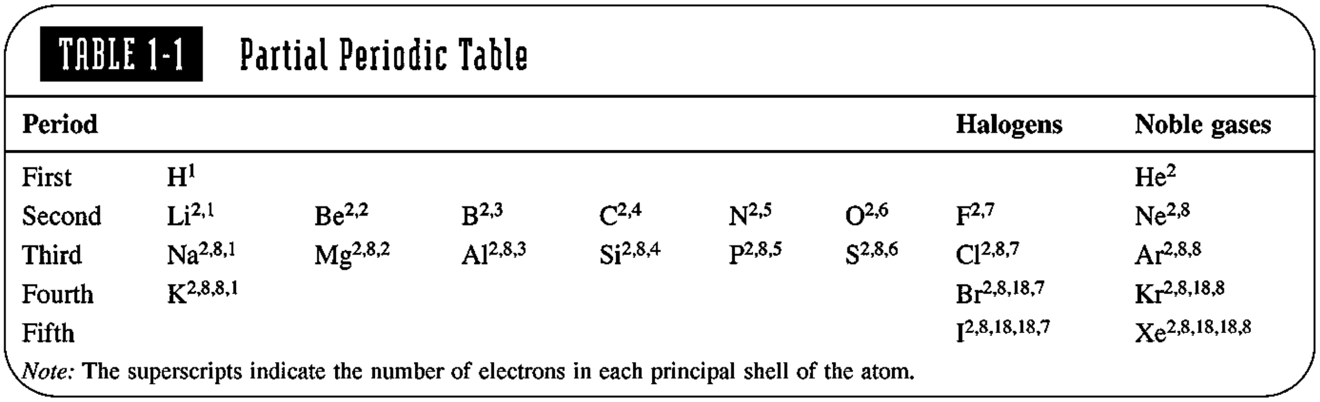
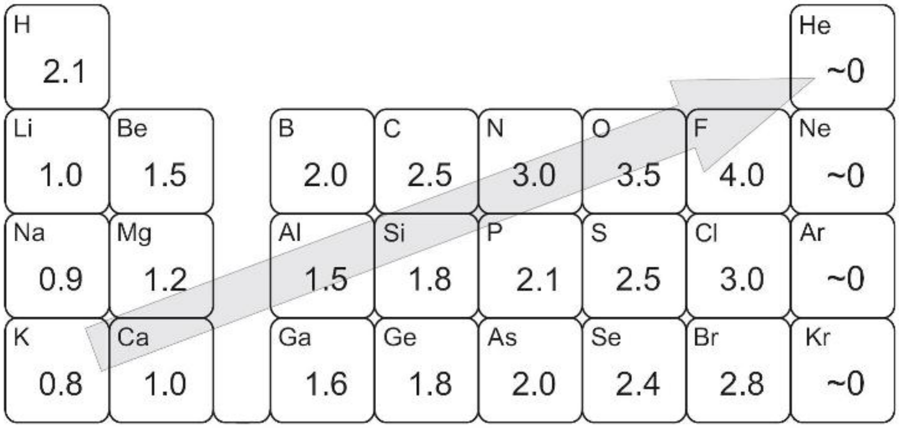


TABLE 1-1 Partial Periodic Table

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.

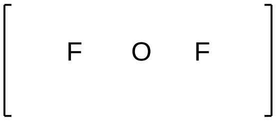
Pauling Electronegativities



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

Write the best Lewis structure for each of the following molecules. **Remember to assign charges, if any, to atoms! Don't forget to draw any lone electron pairs!**

a.

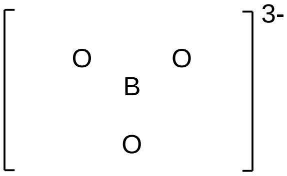


What is the geometry of FOF? Place an "x" mark into the box next to your answer.

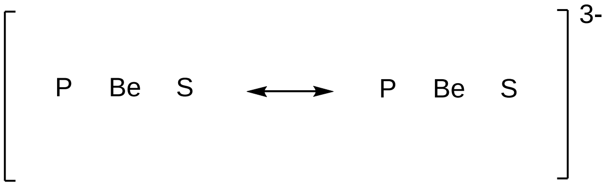
Linear ☐

Bent ☐

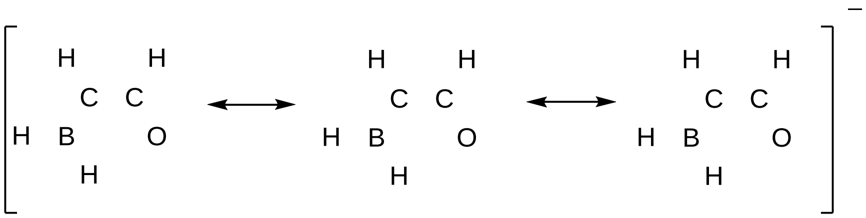
b.



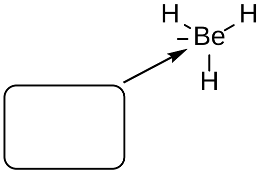
c. The following structure has two **octet** resonance forms. Circle the best one.

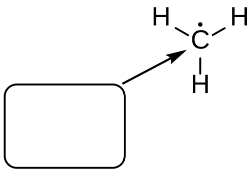


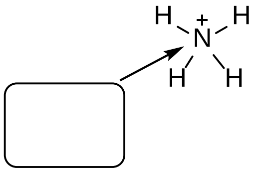
d. The following structure has three **octet** resonance forms. Circle the best one.
Note added in grading: Because of a typo (should be “one octet resonance form”, this question became intractable. Everybody got full credit on it.



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







III. [20 Points]

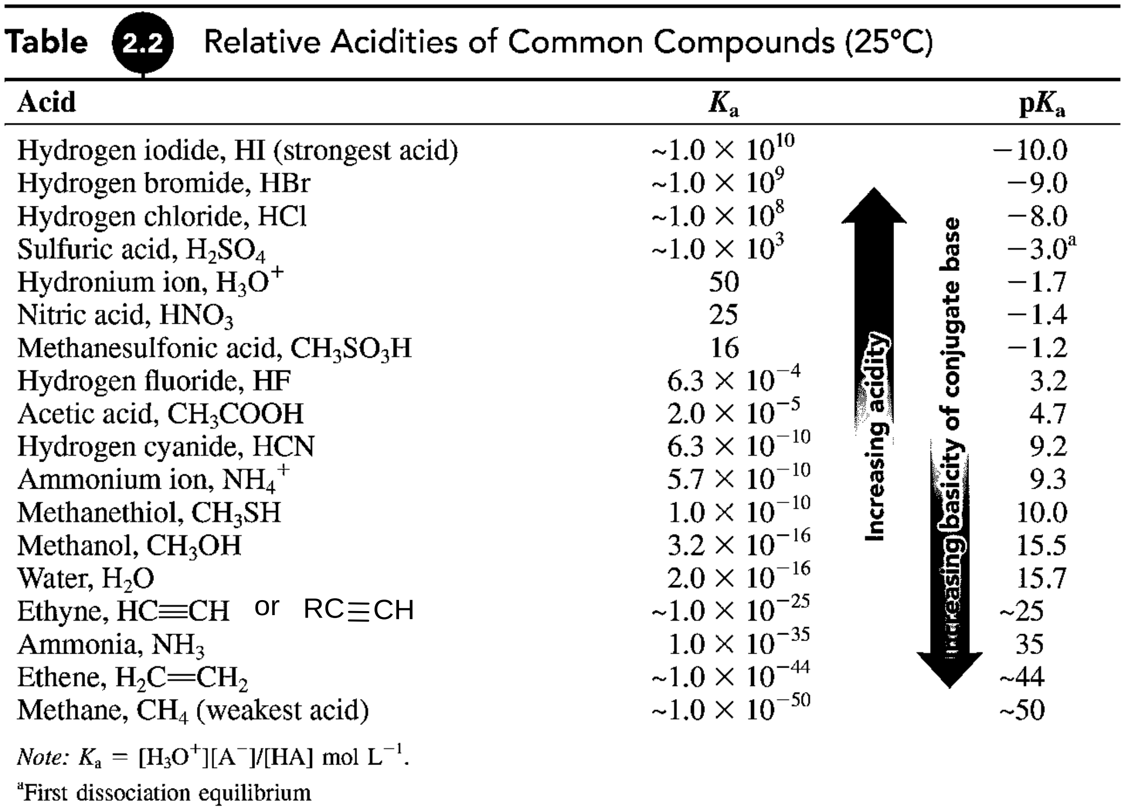


Table 2.2 Relative Acidities of Common Compounds (25°C)

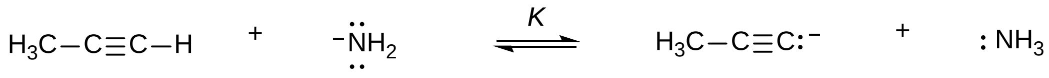
Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	$\sim 1.0 \times 10^{10}$	-10.0
Hydrogen bromide, HBr	$\sim 1.0 \times 10^{9}$	-9.0
Hydrogen chloride, HCl	$\sim 1.0 \times 10^{8}$	-8.0
Sulfuric acid, H_2SO_4	$\sim 1.0 \times 10^{3}$	-3.0^a
Hydronium ion, H_3O^+	50	-1.7
Nitric acid, HNO_3	25	-1.4
Methanesulfonic acid, CH_3SO_3H	16	-1.2
Hydrogen fluoride, HF	6.3×10^{-4}	3.2
Acetic acid, CH_3COOH	2.0×10^{-5}	4.7
Hydrogen cyanide, HCN	6.3×10^{-10}	9.2
Ammonium ion, NH_4^+	5.7×10^{-10}	9.3
Methanethiol, CH_3SH	1.0×10^{-10}	10.0
Methanol, CH_3OH	3.2×10^{-16}	15.5
Water, H_2O	2.0×10^{-16}	15.7
Ethyne, $HC{\equiv}CH$ or $RC{\equiv}CH$	$\sim 1.0 \times 10^{-25}$	~25
Ammonia, NH_3	1.0×10^{-35}	35
Ethene, $H_2C{=}CH_2$	$\sim 1.0 \times 10^{-44}$	~44
Methane, CH_4 (weakest acid)	$\sim 1.0 \times 10^{-50}$	~50

Note: $K_a = [H_3O^+][A^-]/[HA]$ mol L^{-1}.

^{a}First dissociation equilibrium

Using the data in the Table above, indicate the position of the following acid-base equilibria and give the approximate equilibrium constants in the boxes provided.

a.



$$H_3C{-}C{\equiv}C{-}H + {}^{-}\ddot{N}H_2 \overset{K}{\rightleftharpoons} H_3C{-}C{\equiv}C{:}^{-} + {:}NH_3$$

Equilibrium lies to the: left ☐

right ☐

$K \approx$ ☐

b.

$$H_3C-C\equiv C-H \quad + \quad :NH_3 \quad \overset{K}{\rightleftharpoons} \quad H_3C-C\equiv C:^- \quad + \quad {}^+NH_4$$

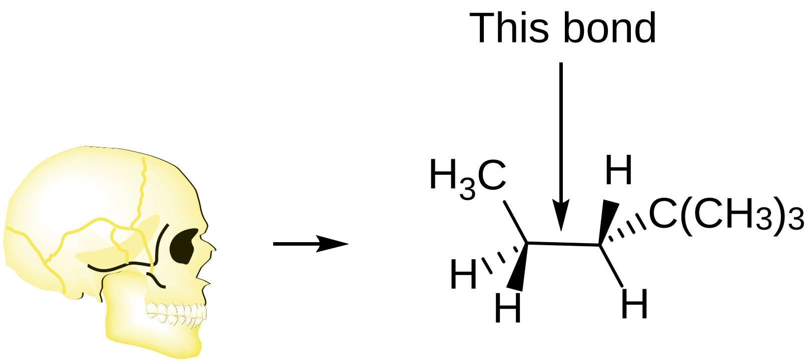
Equilibrium lies to the: left ☐

right ☐

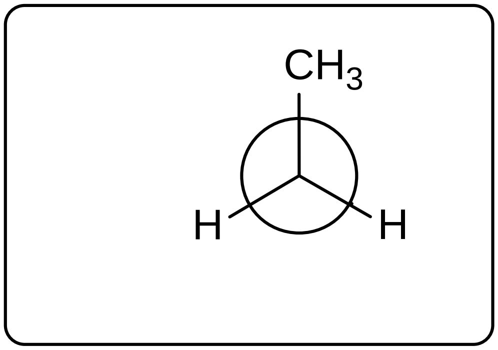
$K \approx$ ☐

IV. [20 Points] Consider the rotation about the indicated bond in the alkane shown.

a. Complete the Newman projection along the view depicted by the skull below in the box provided. Note: You will need to supply the bonds to the back carbon (circle).



Newman projection

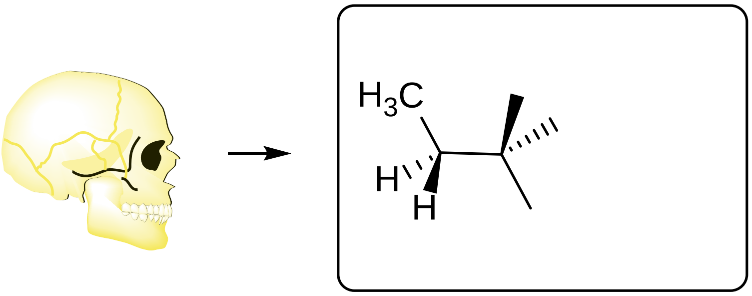


This rotamer is (circle all correct statements):

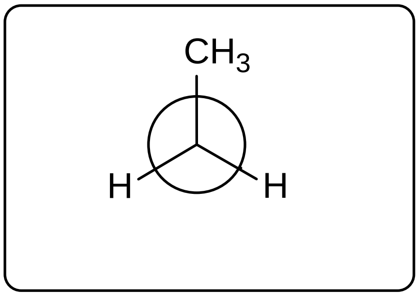
1. Staggered 2. Eclipsed 3. Equatorial 4. Gauche

5. Encumbered by transannular strain 6. Anti

b. Draw the most stable rotamer of the above molecule by completing the two stencils provided in the boxes.



Newman projection



This rotamer is (circle all correct statements):

1. Staggered 2. Eclipsed 3. Equatorial 4. Gauche

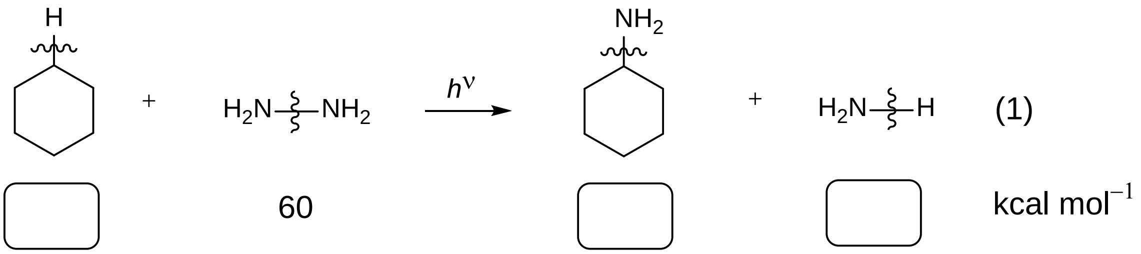
5. Encumbered by transannular strain 6. Anti

V. [40 Points]

Table 3.1 Bond-Dissociation Energies of Various A–B Bonds in the Gas Phase [$DH°$ in kcal mol^{-1} (kJ mol^{-1})]

	B in A–B						
A in A–B	**–H**	**–F**	**–Cl**	**–Br**	**–I**	**–OH**	**–NH_2**
H—	104 (435)	136 (569)	103 (431)	87 (364)	71 (297)	119 (498)	108 (452)
CH_3—	105 (439)	110 (460)	85 (356)	70 (293)	57 (238)	93 (389)	84 (352)
CH_3CH_2—	101 (423)	111 (464)	84 (352)	70 (293)	56 (234)	94 (393)	85 (356)
$CH_3CH_2CH_2$—	101 (423)	110 (460)	85 (356)	70 (293)	56 (234)	92 (385)	84 (352)
$(CH_3)_2CH$—	98.5 (412)	111 (464)	84 (352)	71 (297)	56 (234)	96 (402)	86 (360)
$(CH_3)_3C$—	96.5 (404)	110 (460)	85 (356)	71 (297)	55 (230)	96 (402)	85 (356)

A researcher wants to explore the radical amination of cyclohexane [equation (1)] using hydrazine, $H_2N–NH_2$, a cheap industrial chemical ($2,000/ton).



a. Give the missing bond dissociation energies in the equation above, using the data in the Table at the top of the page and the $H_2N–NH_2$ bond dissociation energy of 60 kcal mol^{-1}.

b. Calculate the $\Delta H°$ value for reaction (1). Show your work.

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

Answer: Yes No

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

1st Propagation step:

2nd Propagation step:

e. Calculate the respective $\Delta H°$ values for the two propagation steps. Show your work.

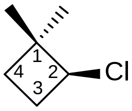
f. The first (and rate determining) propagation step in the radical *chlorination* of cyclohexane is less exothermic than that of the above amination. In comparison, would you expect aminations with hydrazine to be (circle your answer):

1. More selective?

2. Less selective?

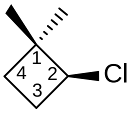
VI. [30 Points]

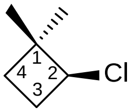
a. (*S*)-2-Chloro-1,1-dimethylcyclobutane shown below undergoes single chlorination at the methyl and 2-, 3-, and 4-positions. In the boxes and stencils provided, draw the respective products. Note: There are more stencils in each box than you will need. Add the missing chlorines and indicate stereochemistry clearly.

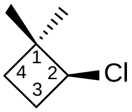


(*S*)-2-Chloro-1,1-dimethylcyclobutane

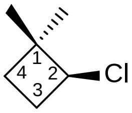
Methyls:

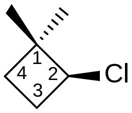


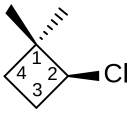




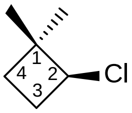
Position 2:

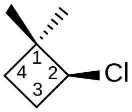


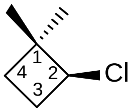




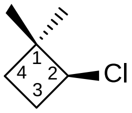
Position 3:

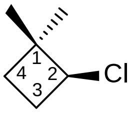


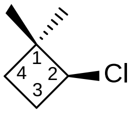




Position 4:







b. Does the above radical chlorination of (*S*)-2-chloro-1,1-dimethylcyclobutane give any optically **inactive** products? Circle your answer.

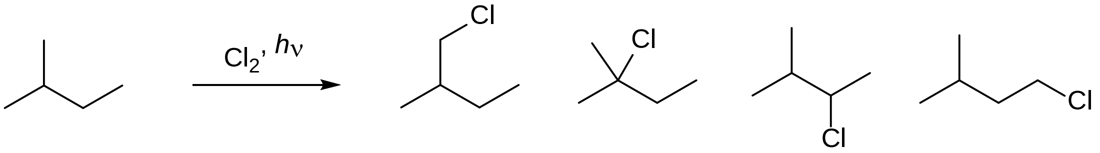
Answer: Yes No

If your answer is yes, circle the structures of the optically **inactive** substances in your boxes above.

VII. [20 Points]

The chlorination of 2-methylbutane gives products **A–D**.

a. Circle the properties written below each product molecule that are associated with it.



A	**B**	**C**	**D**
Chiral	Chiral	Chiral	Chiral
Achiral	Achiral	Achiral	Achiral
Optically active	Optically active	Optically active	Optically active

b. The selectivity for the respective hydrogens in this chlorination is tert : sec : prim = 5 : 4 : 1. In the box below, give the expected product ratio.

VIII. [15 Points]

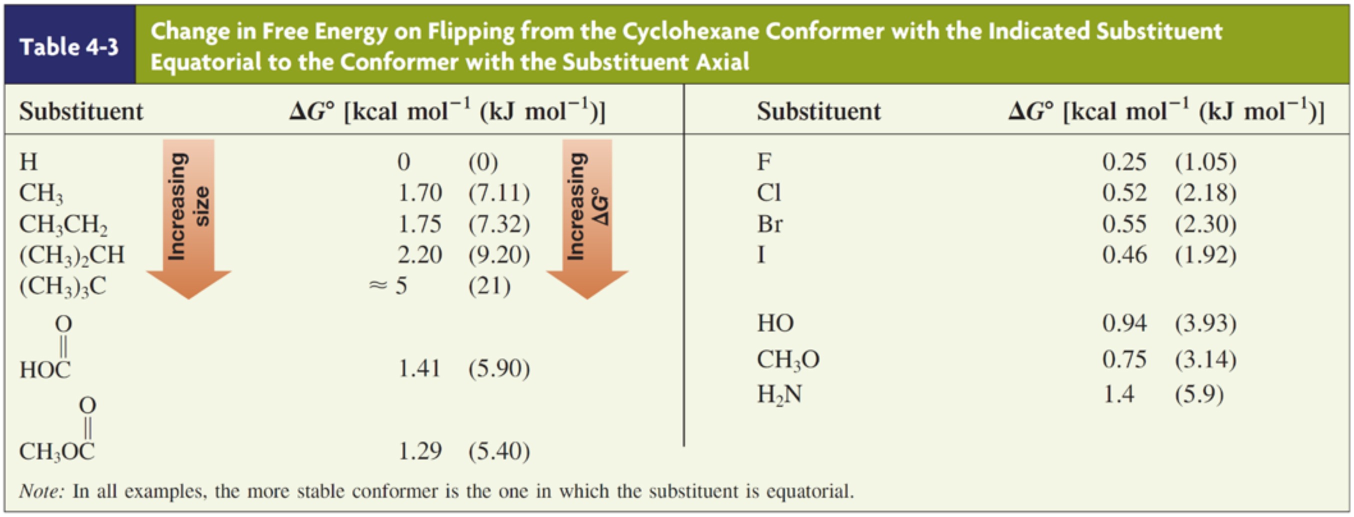


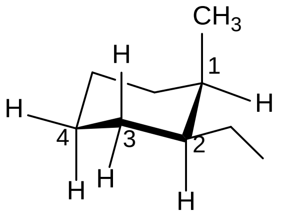
Table 4-3 **Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial**

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)		
		HO	0.94 (3.93)
$\text{HO}\overset{\overset{\text{O}}{\|}}{\text{C}}$	1.41 (5.90)	CH_3O	0.75 (3.14)
		H_2N	1.4 (5.9)
$\text{CH}_3\text{O}\overset{\overset{\text{O}}{\|}}{\text{C}}$	1.29 (5.40)		

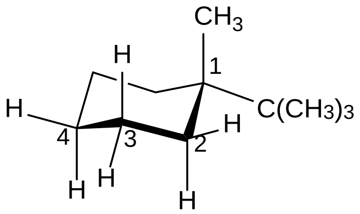
Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

Using the values in the Table above 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” (kcal mol^{-1}) in the box provided.

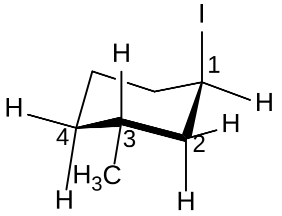
A: *cis*-2-Ethyl-1-methylcyclohexane



B: 1-(1,1-Dimethylethyl)-1-methylcyclohexane



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



VII. [45 Points]

a. Mark the box next to your choice of an answer with an X.
Acidity increases from left to right of a row in the periodic table, because

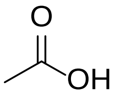
☐ steric hindrance decreases

☐ the product radicals increase in stability

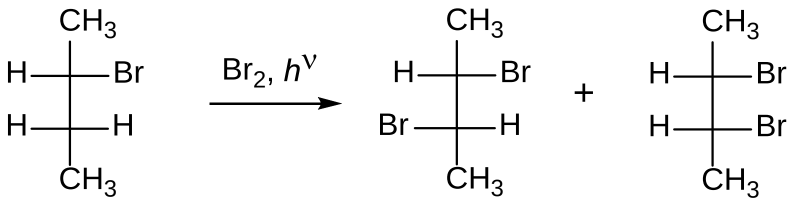
☐ the electronegativity of deprotonated atom increases

☐ hybridization changes from sp^3 to sp

b. In the following pairs of compounds, circle which one is **less** acidic.

H_2SO_4	
CH_4	NH_3
H_3O^+	H_2O
NH_3	PH_3

c. Consider the bromination of enantiomer **A** to give **B** and **C**.



A **B** **C**

(this enantiomer)

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

R *S*

2. The products are with respect to each other (circle the correct answer):

Diastereomers Enantiomers Identical A racemate

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

In equal amounts In unequal amounts

4. The products exhibit the following properties (circle the correct answer):

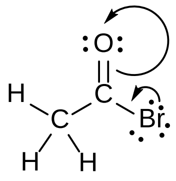
Both are optically active

Both are optically inactive

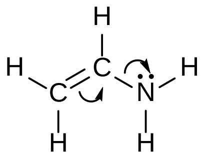
B is optically active and **C** is not

C is optically active and **B** is not

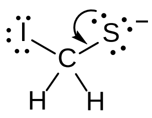
d. Does the arrow pushing in the following molecules **A**–**D** lead to an acceptable resonance form? Circle your answers.



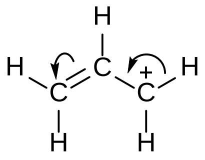
A



B



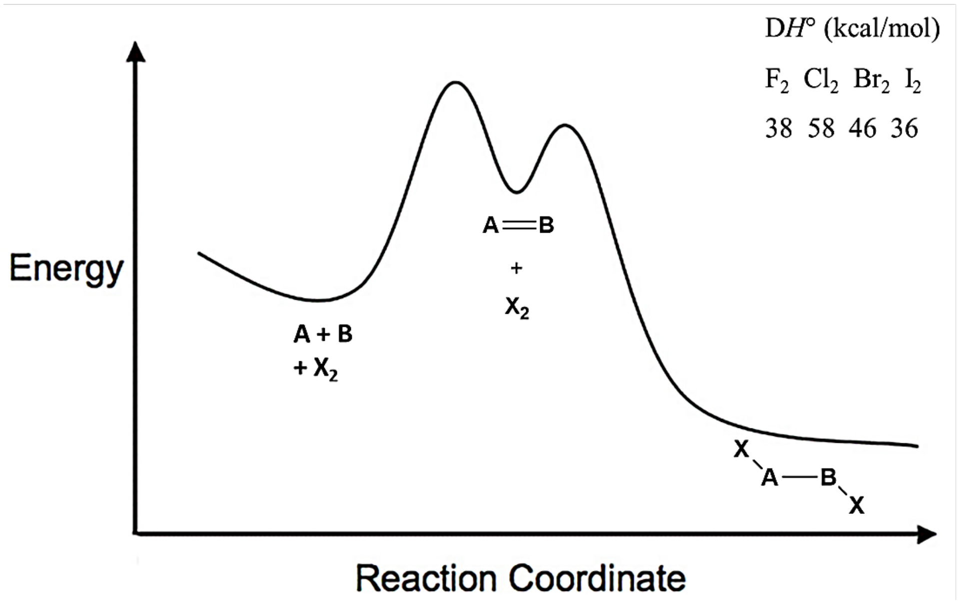
C



D

Yes No Yes No Yes No Yes No

e. The following potential-energy diagram shows the reaction of **A** + **B** in the presence of a halogen **X₂** to generate an unobserved intermediate double-bonded species **A=B**, which is trapped by the halogen to give the final product **X-A-B-X**. The profile of this transformation is the same for X = F, Cl, Br, and I.



1. Place an “X” mark into the box next to the best statement.

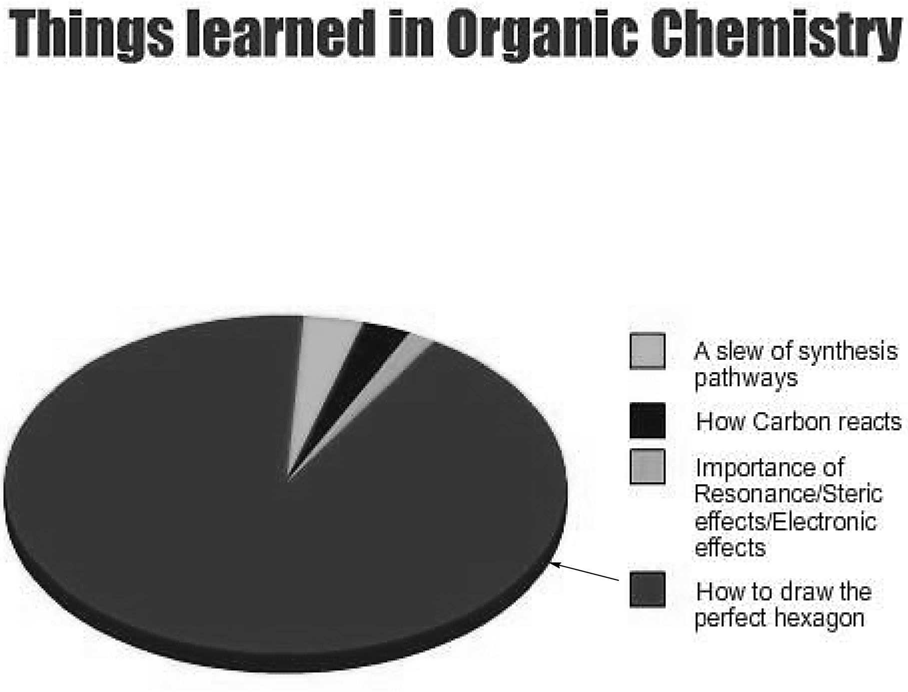
☐ The rate of the reaction increases when changing **X** from **Cl** to **Br**

☐ The rate of the reaction decreases when changing **X** from **Cl** to **Br**

☐ The rate of the reaction is unaffected when changing **X** from **Cl** to **Br**

2. 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



♫ The End ♫