EXAMINATION 1
Chemistry 3A

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

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

Peter Vollhardt
February 18, 2016

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

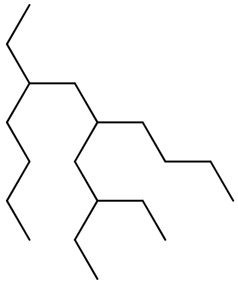
Auditor _____

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 **14** 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*!**

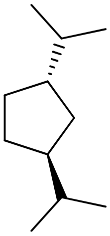
I. [30 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis*, *trans*).

a.



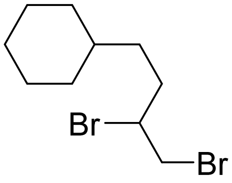
5-Butyl-3,7-diethylundecane

b.

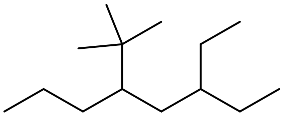


trans-1,3-Bis(1-methylethyl)cyclopentane

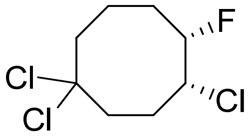
c. (3,4-Dibromobutyl)cyclohexane



d. 5-(1,1-Dimethylethyl)-3-ethyloctane



e.



cis-1,1,4-Trichloro-5-fluorocyclooctane

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

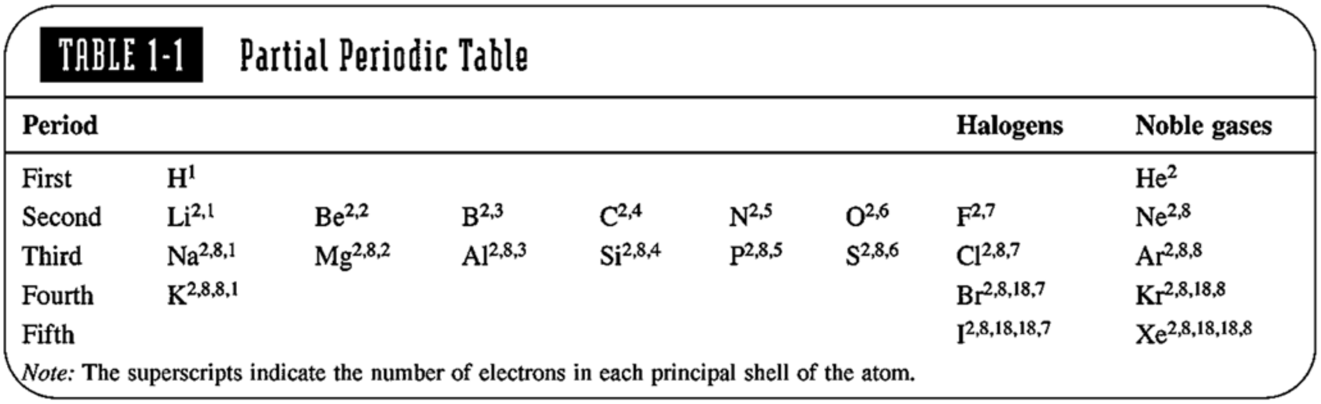
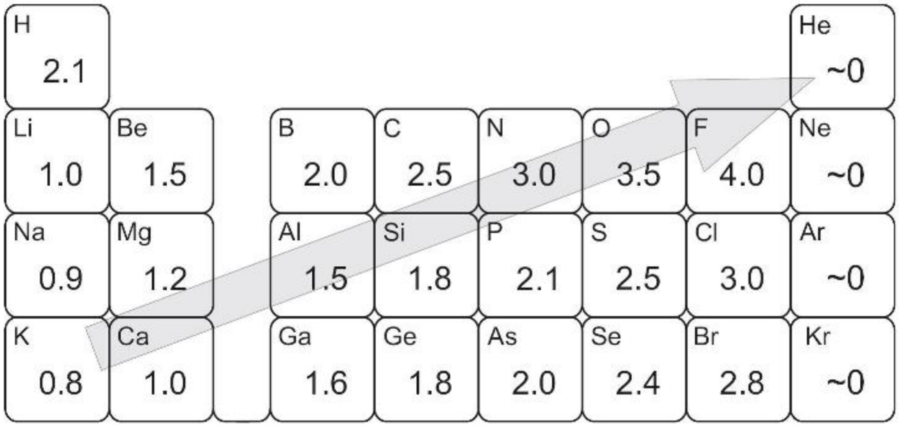


TABLE 1-1 Partial Periodic Table

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.

$$\left[\quad :\mathrm{P}\equiv\mathrm{N}: \quad\right]$$

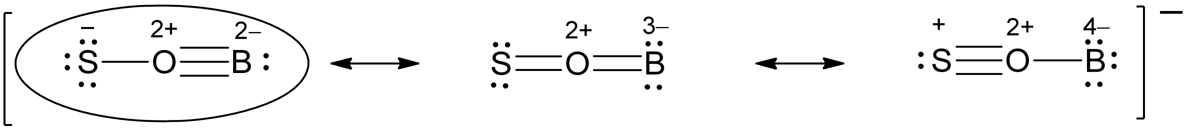
b.

What is the geometry of ClF_2^+ ? Place an “x” mark into the box next to your answer.

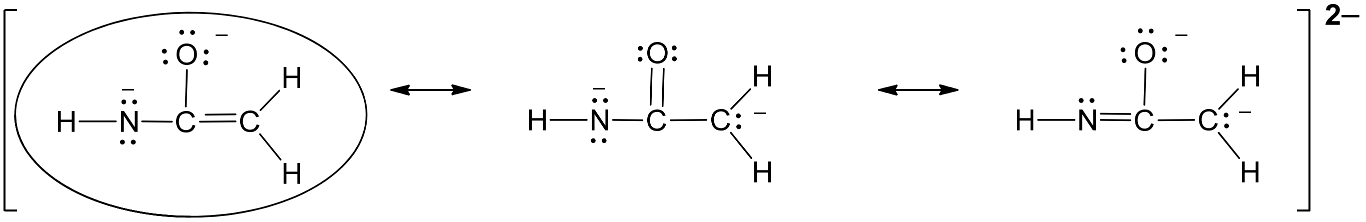
Linear ☐

Bent ☒

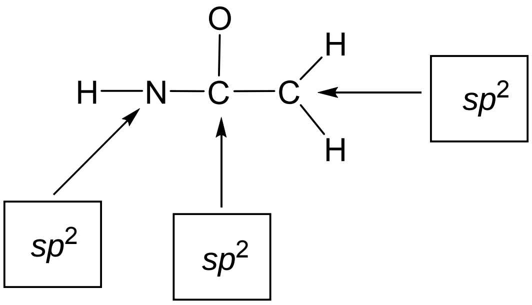
c. As the acronym implies, this one is unusual. It has three octet resonance forms. Circle the best one (remember Coulomb’s Law!).



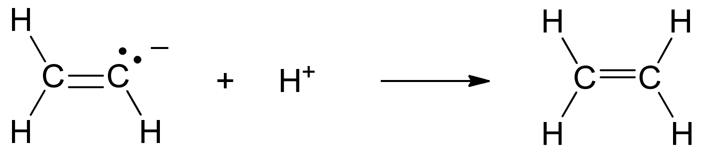
d. Note: For the following molecule, the basic connectivity is provided. Add multiple bonds, charges, electron pairs, as necessary. There are three octet resonance forms. Circle the best.



Enter in the respective boxes the hybridization of the indicated atom, i.e. *sp*, *sp*^{2}, or *sp*^{3}.



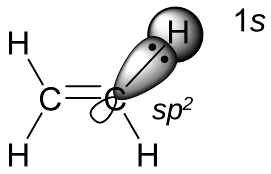
III. [30 Points] The ethenyl anion, H_2CCH^-, is a strong base that is protonated by H^+ (e.g., from water) to give ethane (ethylene), H_2CCH_2.



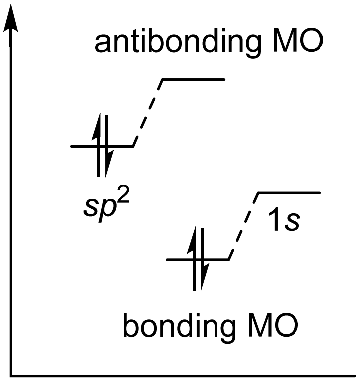
Ethenyl anion

Ethene; pK_a = 44

a. Draw the orbital on H_2CCH^- involved in this bond formation and show its overlap with the appropriate atomic orbital of H^+. Clearly label these orbitals (e.g. 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, *sp*, *sp*^{2}, *sp*^{3}, etc.)



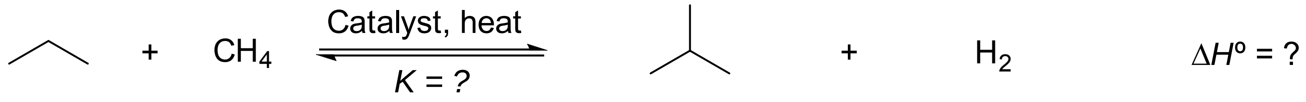
b. Draw the orbital energy splitting diagram for the formation of C_2H_4 by the reaction of H_2CCH^- with H^+. Clearly depict the energy levels of the orbitals entering into overlap and label them, and show the resulting bonding and antibonding molecular orbital levels. Place the relevant electrons into the various levels.



c. In view of the above, would you consider that hydride addition (e.g. reaction with H^-) to H_2CCH^- would give a stable bond? Explain (one sentence).

No, because the antibonding orbital is filled.

IV. [20 Points] A petroleum researcher wants to explore the possibility of the catalytic transformation of propane + methane to give 2-methylpropane and hydrogen shown below.



Propane 2-Methylpropane $DH^\circ_{H-H} = 104$ kcal mol^{-1}

a. Determine the feasibility of this transformation by calculating its ΔH^o. Enter your answer in to box provided below and show your work.

$\Delta H^o = (98.5 + 105) - (88 + 104) = +11.5$ kcal mol^{-1}

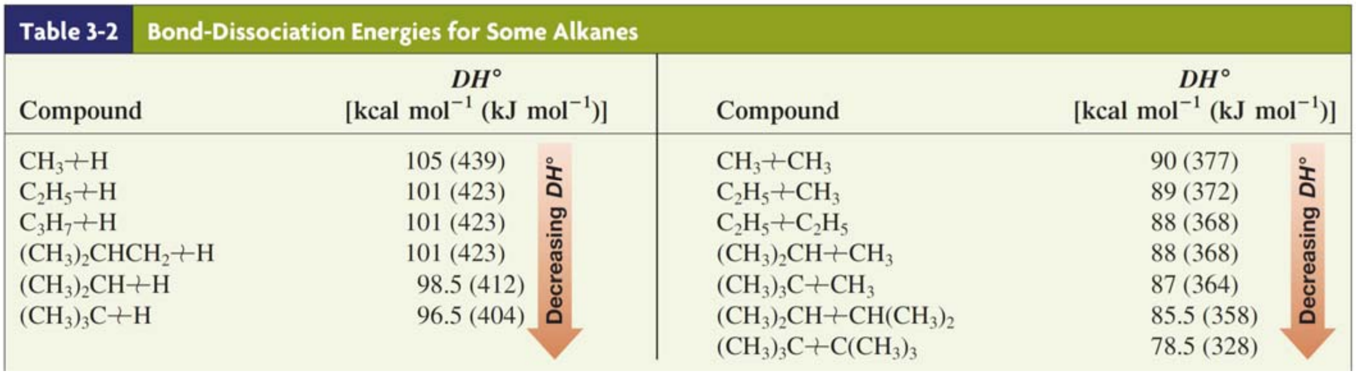


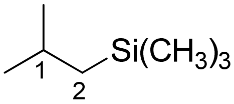
Table 3-2 Bond-Dissociation Energies for Some Alkanes

Compound	DH° [kcal mol^{-1} (kJ mol^{-1})]	Compound	DH° [kcal mol^{-1} (kJ mol^{-1})]
CH_3-H	105 (439)	CH_3-CH_3	90 (377)
C_2H_5-H	101 (423)	$C_2H_5-CH_3$	89 (372)
C_3H_7-H	101 (423)	$C_2H_5-C_2H_5$	88 (368)
$(CH_3)_2CHCH_2-H$	101 (423)	$(CH_3)_2CH-CH_3$	88 (368)
$(CH_3)_2CH-H$	98.5 (412)	$(CH_3)_3C-CH_3$	87 (364)
$(CH_3)_3C-H$	96.5 (404)	$(CH_3)_2CH-CH(CH_3)_2$	85.5 (358)
		$(CH_3)_3C-C(CH_3)_3$	78.5 (328)

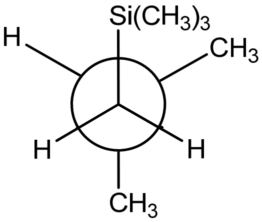
b. Estimate *roughly* the equilibrium constant for the equilibrium above at room temperature, using the equation $\Delta G^o = -1.36 \log K$ and judging that the ΔS^o term is negligible. By "roughly" is meant a range, for example, 10^{-1} to 10^{2}.
Mark the box next to your choice of an answer with an X.

1. $K \sim 10^{-7} - 10^{-9}$ ☒
2. $K \sim 10^{-1} - 10^{-3}$ ☐
3. $K \sim 10^{5} - 10^{9}$ ☐

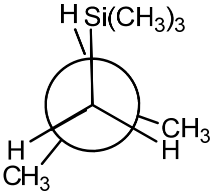
V. [50 Points] Consider the rotation about the C2–C1 bond in 1-methyl-2-(trimethylsilyl)propane, a molecule we mentioned in class:



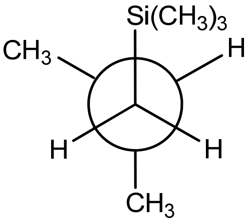
The Newman projections **A–F** below illustrate the sequential clockwise motion of the back-carbon (C1) in increments of 60°.



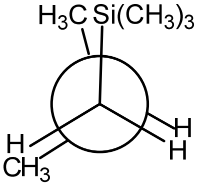
A



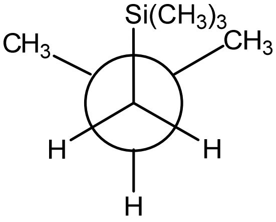
B



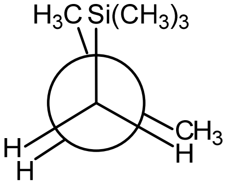
C



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:

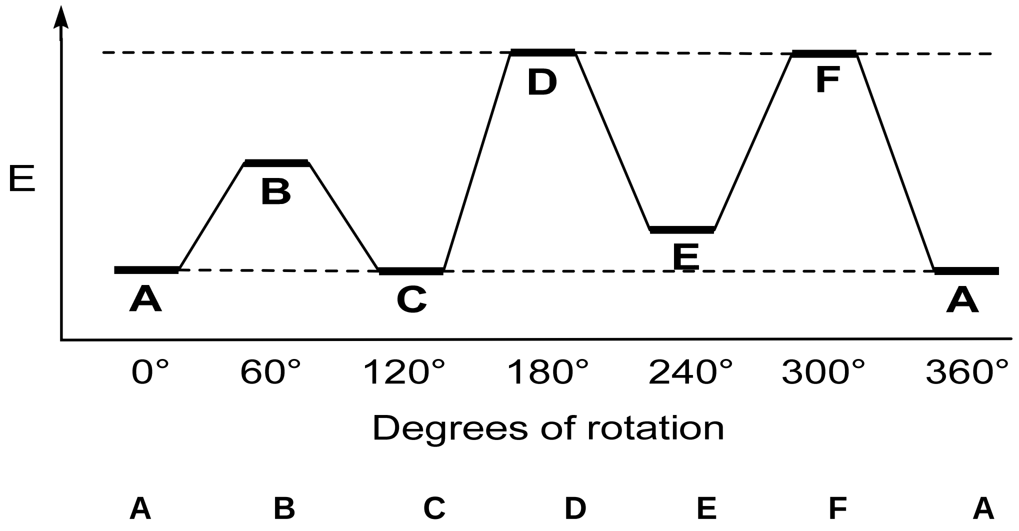
anti: [✓ A] B [✓ C] D E F

gauche: [✓ A] B [✓ C] D [✓ E] F

eclipsed: A [✓ B] C [✓ D] E [✓ F]

staggered: [✓ A] B [✓ C] D [✓ E] 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.

A, C

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

D, F

VI. [50 Points] An alternative to Cl_2 in radical halogenations of alkanes is chloramine, $ClNH_2$, as exemplified below for the chlorination of methane.

$$CH_4 + \underset{60\ \text{kcal mol}^{-1}}{H_2N\!-\!\wr\!-\!Cl} \xrightarrow{h\nu} CH_3Cl + H_2N\!-\!H \qquad (1)$$

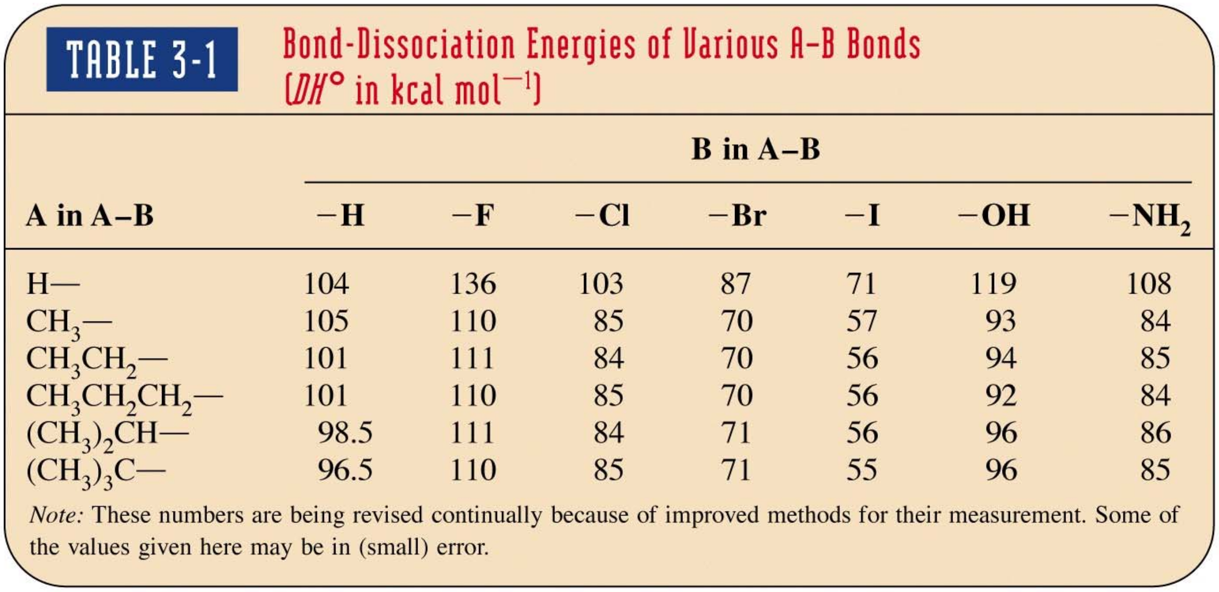


TABLE 3-1 Bond-Dissociation Energies of Various A–B Bonds ($DH°$ in kcal mol^{-1})

A in A–B	–H	–F	–Cl	–Br	–I	–OH	$-NH_2$
H—	104	136	103	87	71	119	108
CH_3—	105	110	85	70	57	93	84
CH_3CH_2—	101	111	84	70	56	94	85
$CH_3CH_2CH_2$—	101	110	85	70	56	92	84
$(CH_3)_2CH$—	98.5	111	84	71	56	96	86
$(CH_3)_3C$—	96.5	110	85	71	55	96	85

Note: These numbers are being revised continually because of improved methods for their measurement. Some of the values given here may be in (small) error.

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

$\Delta H°$ (1) : (105 + 60) – (85 + 108) = – 28 kcal mol^{-1}

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

Answer: [✓ Yes] No

c. Formulate the two propagation steps for reaction (1).

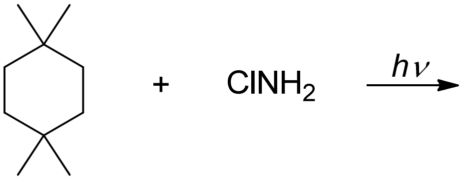
1st Propagation step :

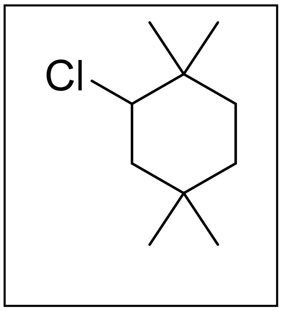
$$CH_4 + \cdot NH_2 \longrightarrow CH_3\cdot + NH_3$$

2nd Propagation step :

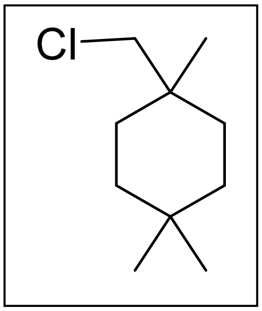
$$CH_3\cdot + Cl{-}NH_2 \longrightarrow CH_3Cl + \cdot NH_2$$

d. The normalized selectivity secondary : primary in chlorinations with $ClNH_2$ is 6:1. In the boxes provided, draw the products **A** and **B** and their ratio in the **monochlorination** of 1,1,4,4-tetramethylcyclohexane with $ClNH_2$.





A
(secondary chlorination)



B
(primary chlorination)

Ratio **A** : **B** = 4:1

VII. [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.

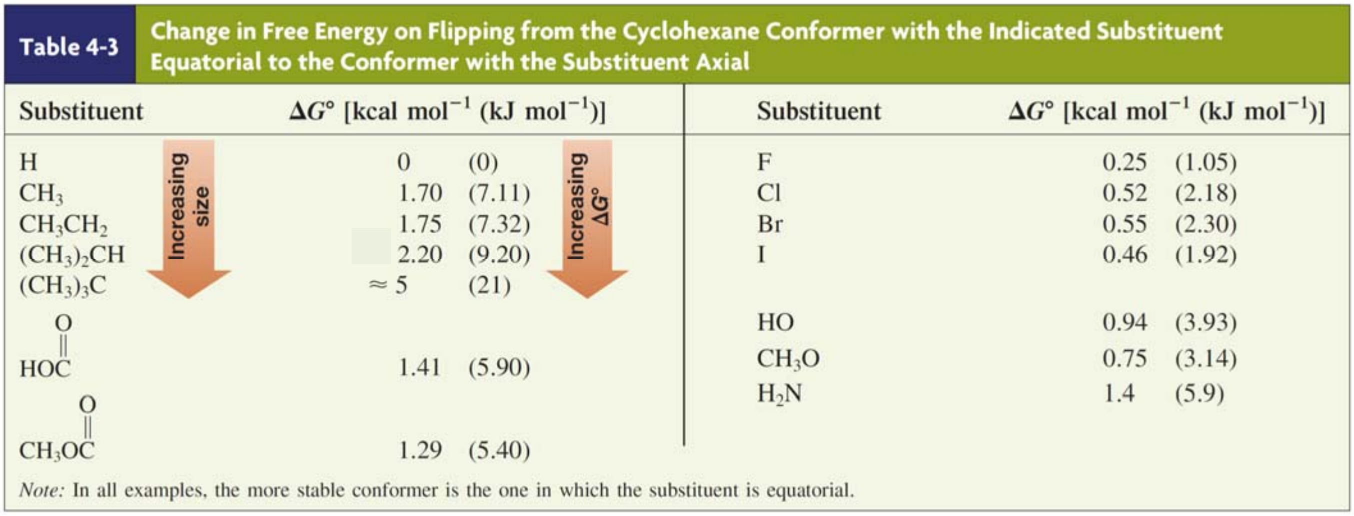
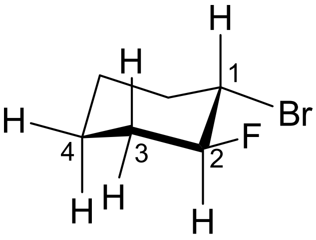


Table 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial

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

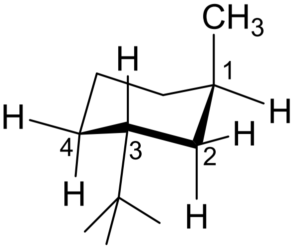
Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

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



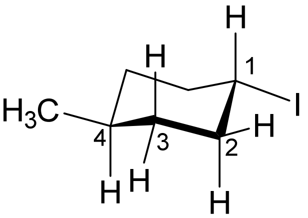
+0.8 kcal mol^{-1}

B: *trans*-1-Methyl-3-(1,1-dimethylethyl)cyclohexane



+3.3 kcal mol^{-1}

C: *trans*-1-Iodo-4-methylcyclohexane



+2.16 kcal mol^{-1}

VIII. [25 Points]

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

Radical bromination of alkanes is more selective than the corresponding chlorinations, because

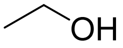
☐ HBr is a stronger acid than HCl.

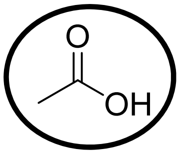
☐ the second propagation step is rate-determining.

☒ H abstraction occurs via a late transition state.

☐ the products are more stable.

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





[✓ H_2O] NH_3

[✓ H_3O^+] $^+NH_4$

H_2O [✓ H_2S]

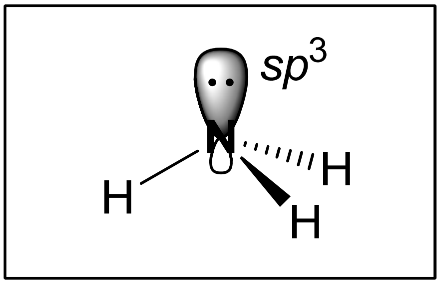
3. What are the three primary forms of strain present in cycloalkanes?

a. angle

b. eclipsing or torsional

c. transannular

4. Draw the geometry of ammonia, using the wedged-dashed line notation, and the orbital in which the lone pair resides. Label this orbital as *s*, *p*, *sp*, *sp*^{2}, or *sp*^{3}.



5. There are four primary factors that control the rates of reactions. Name three.

a. energy of activation

b. temperature

c. concentration

(d. probability factor)

He *did* pass Chem 3A

♫ The End ♫