EXAMINATION 1

Chemistry 3A
Kim Lavoie
Peter Vollhardt
October 4, 2001

Name:_____
[Print first name before second! Use capital letters!]

Please check the name of your TA and corresponding section number. Complete the remaining information if applicable.

111	John Antos	361	Karl Tupper
121	Jennifer Barbarow	371	Eric Schneider
161	Dennis Leung	411	Amish Patel
171	Dan Weix	421	Jennifer Prescher
211	Scheherazade Le	511	Stephany Schuck
221	Steve Pham	521	Javier Rangel
311	David Tang	561	Lianne Beltran
321	Joshua Goldberger		

Making up an I Grade _____

(If you are, please indicate the semester during which you took previous Chem 3A previously _____).

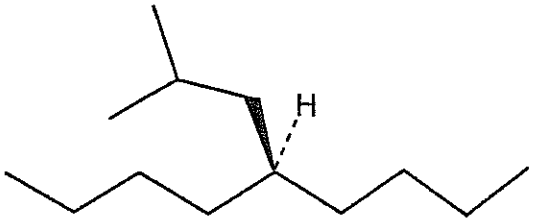
Please write the answer you wish to be graded in the spaces provided. *Do scratch work on the back of the pages.* This test should have 11 numbered pages. Check to make sure that you have received a complete exam. A good piece of advice: **read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy structures or phrases. It is better to be pedantic in accuracy! Good Luck!**

DO NOT WRITE IN THIS SPACE

I.	_____	(20)
II.	_____	(20)
III.	_____	(30)
IV.	_____	(20)
V.	_____	(30)
VI.	_____	(30)
VII.	_____	(20)
VIII.	_____	(30)
Total:	_____	(200)

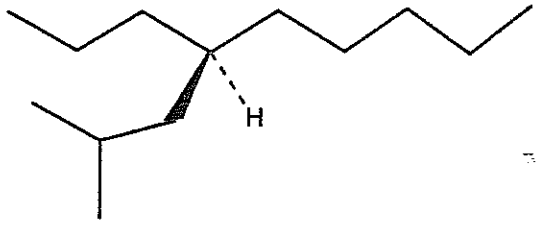
I. [20 Points] Name or draw, as appropriate, the following molecules according to the IUPAC rules. Indicate stereochemistry where necessary (*cis, trans, R, S, or meso*). Indicate with a circle whether the molecule is chiral or achiral.

a.



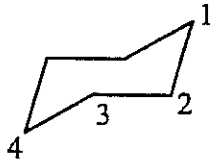
chiral achiral

b.



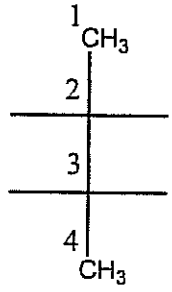
chiral achiral

c. *Meso*-1,3-dimethyl-cyclohexane



chiral achiral

d. 2*R*, 3*S*-2-Bromo-3-chlorobutane



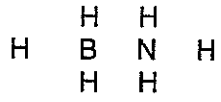
chiral achiral

II. [20 Points] Write the best Lewis resonance structure for each of the following molecules. Remember to assign charges!

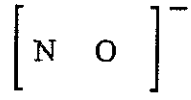
a.

F F O

b.



c.



d.

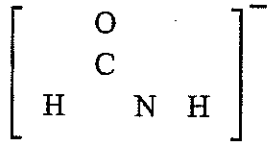


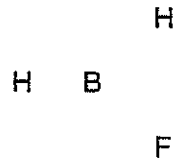
TABLE 1-1 Partial Periodic Table

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							$I^{2,8,18,18,7}$	$Xe^{2,8,18,18,8}$

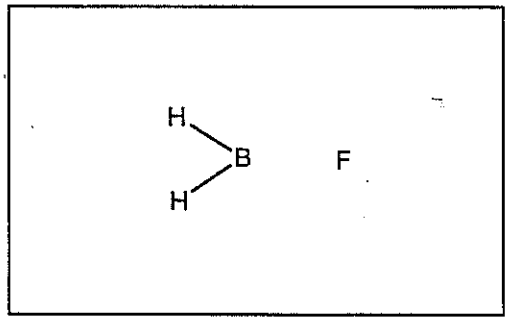
Note: The superscripts indicate the number of electrons in each principal shell of the atom.

III. [30 Points] Unlike BH_3, the molecule H_2BF has an octet form.

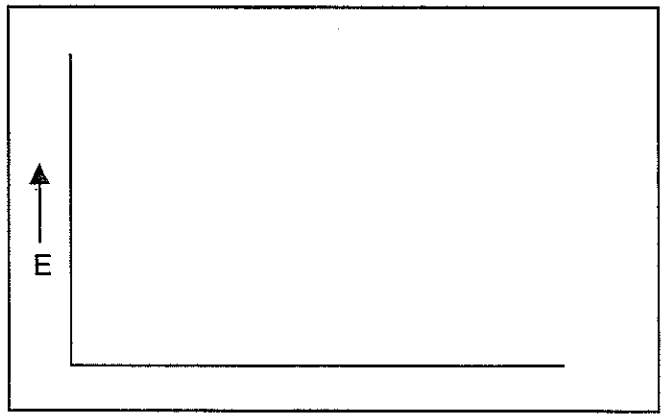
a. Draw it.



b. Show the orbital overlap picture for the bonding between B and F. Label clearly the overlapping orbitals (e.g. *s*, *p*, sp^3, etc.),

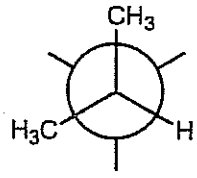


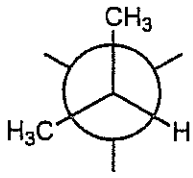
c. Show the orbital splitting associated with the B-F σ bond in an energy level diagram. Label each level clearly [e.g. *s*, *p*, sp^3, bonding molecular orbital (MO), etc.].

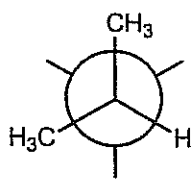


IV. [20 Points] Draw the three staggered rotamers with respect to the 2,3-bond in 2,3-dimethylbutane (fill in the blanks below).

a.







b. Circle the most stable rotamer above and explain your answer in one sentence.

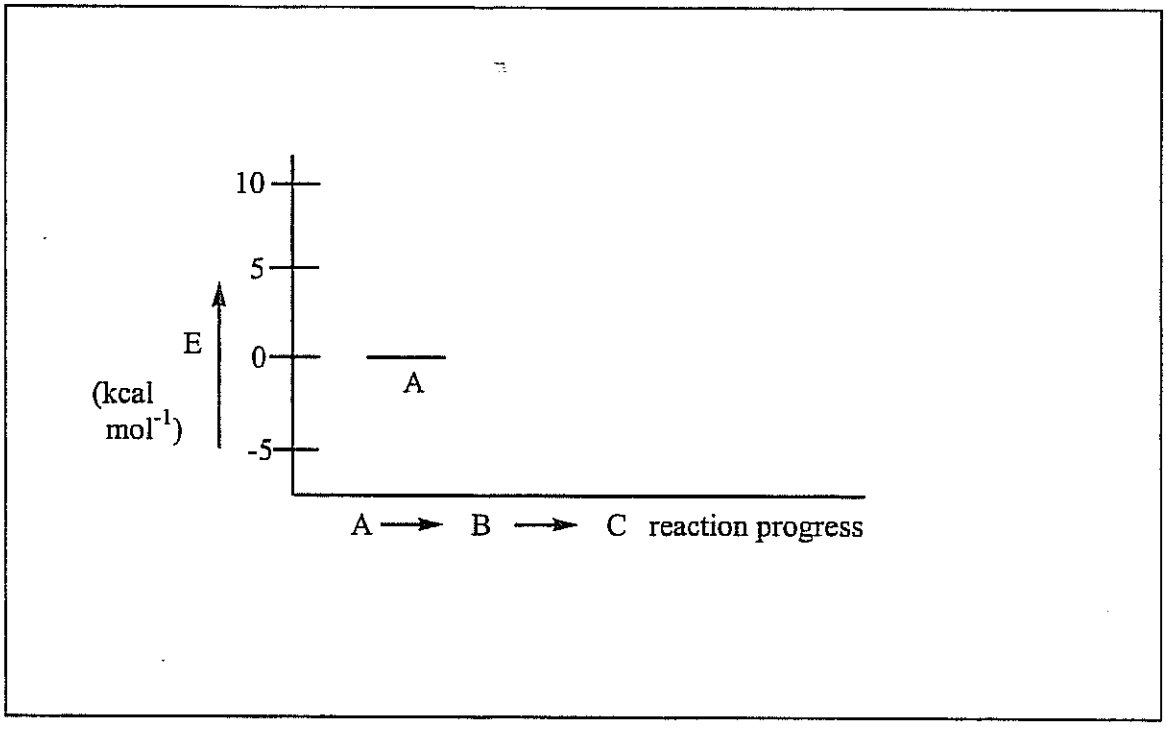
V. [30 Points] Consider the following equilibria.

$$A \underset{}{\overset{\Delta}{\rightleftharpoons}} B \qquad \Delta G^{\circ} = +5 \text{ kcal mol}^{-1}$$

$$B \underset{}{\overset{\Delta}{\rightleftharpoons}} C \qquad \Delta G^{\circ} = -10 \text{ kcal mol}^{-1}$$

Compound B can be made independently and, when heated, generates A and C in a 1:1 ratio, initially. On prolonged heating, the (essentially) only product is C.

Draw a potential energy diagram describing the progress of the reaction from A to B to C.



VI. [30 Points] Hydrogen, H_2, reacts, just like alkanes, with bromine to generate HBr.

$$H_2 + Br_2 \xrightarrow{h\nu} 2\ HBr \qquad \Delta H^\circ = \square$$

a. Considering the DH° (H_2) = 104 kcal mol^{-1}, DH° (Br_2) = 46 kcal mol^{-1}, and DH° (HBr) = 87 kcal mol^{-1}, calculate the ΔH° for the above reaction. Show your work below and enter the result in the box above.

b. Formulate the propagation steps for the reaction, including their ΔH° values.

Step 1 : $\square$ ΔH° = $\square$

Step 2 : $\square$ ΔH° = $\square$

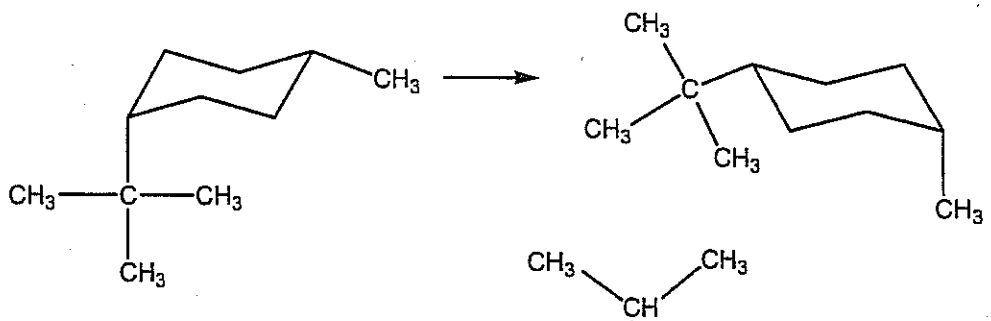
c. What is the minimum E_a for the rate determining first step?

The E_a must be larger than $\square$ kcal mol^{-1}

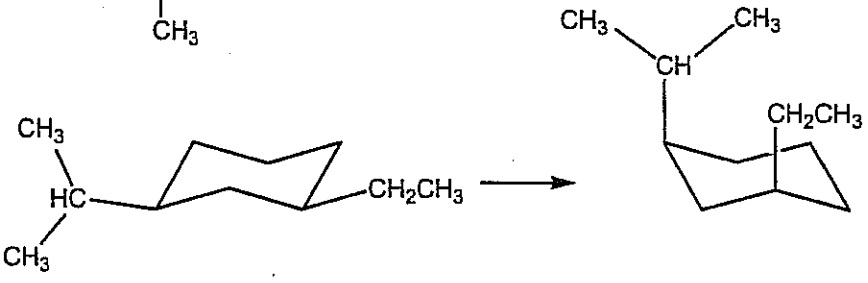
VII. [20 Points] Given below are some substituent values for the $\Delta G°$ of the equatorial - axial ring flip of cyclohexane.

	$\Delta G°$ (kcal/mole)
–H	0
$-CH_3$	1.7
$-CH_2CH_3$	1.8
$-CH(CH_3)_2$	2.2
$-C(CH_3)_3$	5.0

Calculate $\Delta G°$ for the following conversions in the large box below and enter the results in the small boxes in the margin.



$\Delta G°$ =



$\Delta G°$ =

VIII. [30 Points] Place an X mark in the box preceding the most accurate statement.

a. Fluorine (Pauling scale value 4) is more electronegative than carbon (Pauling scale value 2.6) leading to the conclusion that:

☐ all fluorinated compounds are negatively charged.

☐ the C-F bond is polarized in the sense $^{\delta+}C\text{-}F^{\delta-}$.

☐ carbon prefers sp^3 hybridization compared to fluorine because in this way it can minimize electron repulsion.

☐ carbon is a better electron acceptor than fluorine.

b. CH_3^+ is a molecule whose carbon center is a.) sp^2-hybridized, leaving an empty p orbital aligned perpendicular to the molecular plane, and b.) electron-deficient (6e), at odds with the octet rule. Therefore:

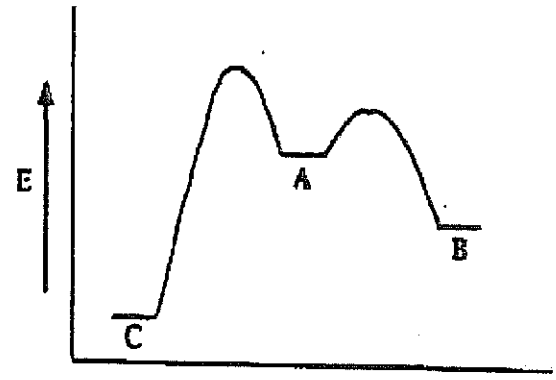
☐ to satisfy the octet rule, the molecule is readily protonated.

☐ to satisfy the octet rule, the molecule readily dimerizes.

☐ to satisfy the octet rule, the molecule readily dissociates to $CH_2 + H^+$.

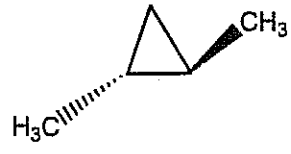
☐ to satisfy the octet rule, the molecule readily attacks electron rich species, such as water (e.g., $CH_3^+ + H_2\ddot{O} \longrightarrow CH_3\overset{+}{\ddot{O}}H_2$).

c. When considering the following potential energy diagram:



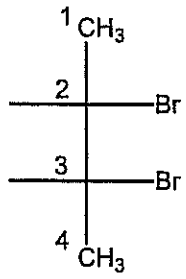
- ☐ compound **A** will convert to **B** faster than it will to **C**.
- ☐ **C** is the thermodynamically most stable component of the mixture and will form at the greatest rate from **A** or **B**.
- ☐ **B** will convert to **C** faster than **A** will.
- ☐ none of the above

d. The following molecule is



- ☐ achiral because it has a plane symmetry.
- ☐ achiral because it has rotational symmetry.
- ☐ chiral because image and mirror image are non-superimposable.
- ☐ achiral because it contains no stereocenters.

e. Radical bromination of **A** at C2 will give:



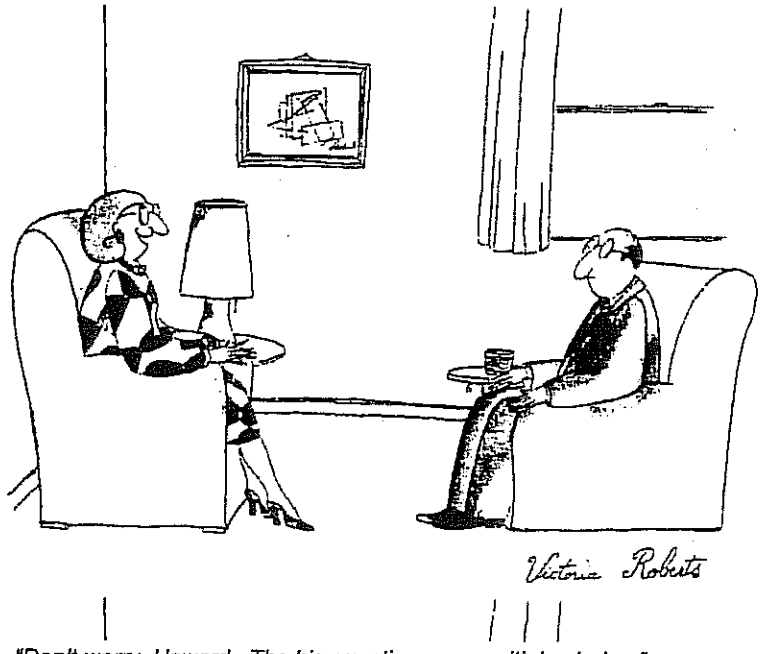
A

☐ an achiral molecule because **A** is meso.

☐ an optically active tribromide.

☐ a molecule without stereocenters.

☐ a chiral tribromide



"Don't worry, Howard. The big questions are multiple choice."

* The End *