If you encounter any technical problems during the entire exam period, Zoom Danny Huang at https://berkeley.zoom.us/j/8716114511
Label the final pdf file with your name and the words "3AExam1" (namely: Last Name, First Name, 3AExam1) and upload it to Gradescope.

To complete this page in AcrobatPro, click on "Comments" and use the "Text" function

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EXAMINATION 1
Chemistry 3A

Name:____Key____________________ **SID #:**______________________
Print first name before second! *Make sure the number is correct!*
Use capital letters!

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

Peter Vollhardt
February 27, 2021

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 _____

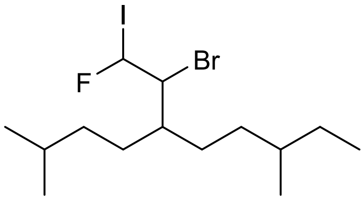
This test should have **16** numbered pages. A good piece of advice: **Read carefully over the questions (at least twice); make sure that you understand exactly what is being asked; avoid sloppy entries. *Good Luck*!**

To answer the questions in AcrobatPro, click on "Comments" and use the "Text" or "Draw" functions, as applicable. For the latter, you will only need the "Line", "Rectangle", and "Oval" options.
Keep saving your document as you complete it!

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

I. [36 Points] Name, complete the drawing, or choose one given answer, as appropriate, the following molecules according to the IUPAC rules.

a.



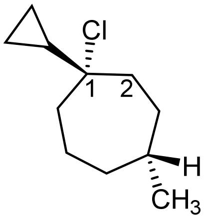
(No stereochemistry)

5-(1-Bromo-2-fluoro-2-iodoethyl)-2,8-dimethyldecane

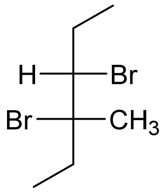
b.

(1*S*,4*R*)-1-Chloro-1-cyclopropyl-4-methylcycloheptane

[Complete the stencil in the box. Note: The hashed/wedged lines signify dangling bonds, not methyl groups. Place the four missing substituents at the end of these bonds. **For "cyclopropyl", you can use the letters "Cyc".** For methyl, you can use CH3 (no subscript)].



c.



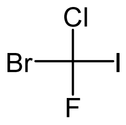
(Name this enantiomer)

(3*S*,4*S*)-3,4-Dibromo-3-methylhexane

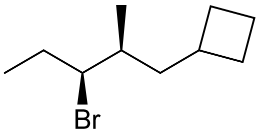
d.

(*R*)-Bromochlorofluoroiodomethane

(Complete the Fischer stencil in the box)



e.

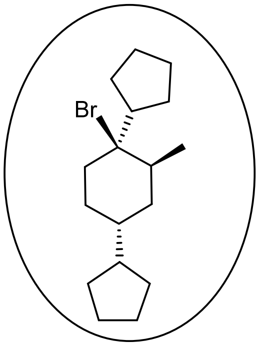


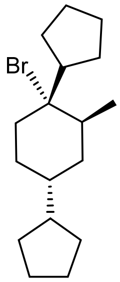
[(2*S*,3*S*)-3-Bromo-2-methylpentyl]cyclobutane

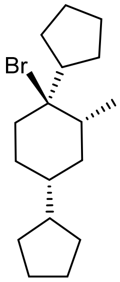
f.

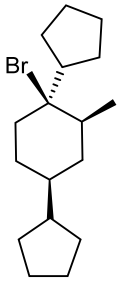
(1*R*,2*S*,4*R*)-1-Bromo-1,4-dicyclopentyl-2-methylcyclohexane

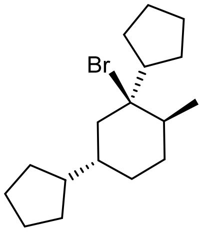
(Circle the correct answer in the box)

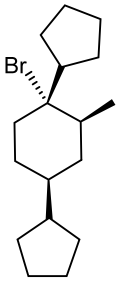












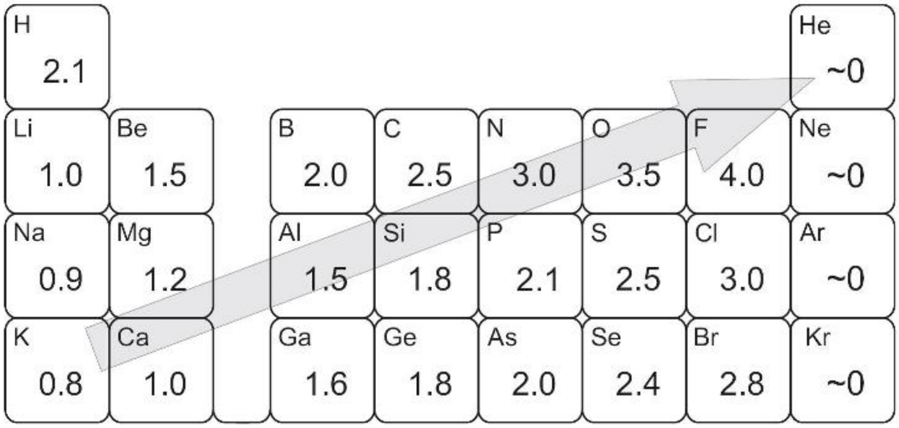
II. [30 Points]

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.

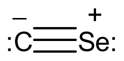
Pauling Electronegativities



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

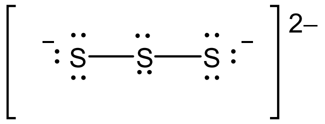
Write or complete the Lewis **octet structure** for each of the following two molecules (a. and b.). **Remember to assign charges, if any, to atoms! Do not forget to draw any (vertical) lone electron pairs (use the colon mark, as appropriate)!**

a.



$:\overset{-}{C}\equiv\overset{+}{Se}:$

b.

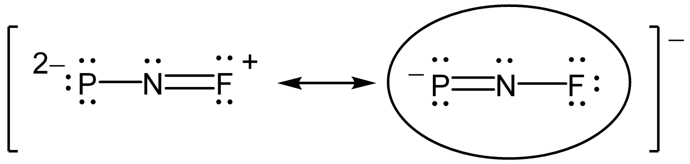


What is the geometry of S_3^{2-} ? Place an “x” mark into the box next to your answer.

Linear ☐

Bent ☒

c. The following structure has two **octet** resonance forms. Complete the partial structures below and circle the **better** one.



d. What is the origin of the octet rule for the atoms in the second row of the periodic table? Answer in one original sentence in the box. No cutting and pasting!

Atoms strive to attain a noble gas configuration with all four orbitals filled.

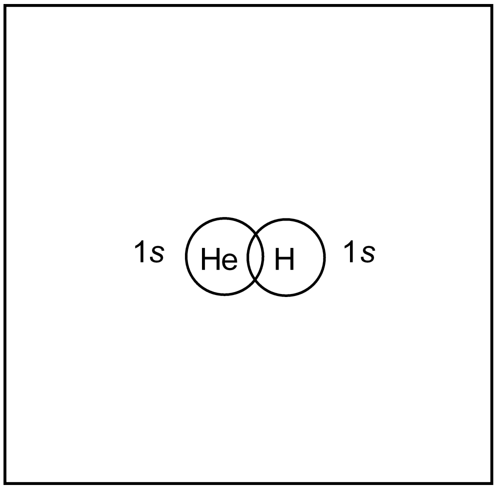
e. Helonium, HeH^+, is thought to be the first molecular species to have formed in the early universe.
Draw the Lewis structure of HeH^+.

$^{+}$He–H

In the respective boxes,

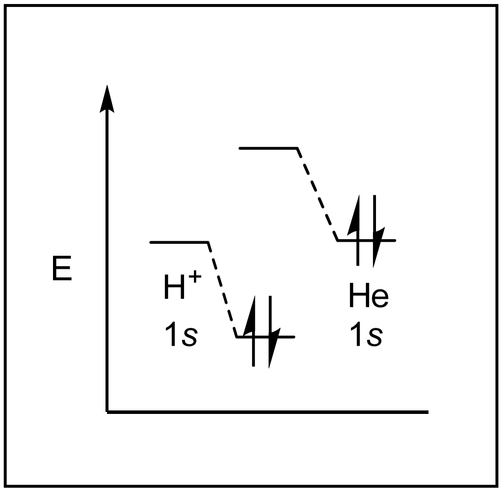
1. Box 1: Draw the overlap of the orbitals that make up the new He–H bond. Label the orbitals (e.g., 1*s*, 2*p*, etc.).
2. Box 2: Compose the energy-splitting diagram depicting the protonation of He to give helonium, starting with the energy level of the proton orbital (place on the left of your scheme). Label the starting levels only (e.g., 1*s*, 2*p*, etc.). Show the electrons. There is no need to draw the dashed lines used to picture the orbital splitting.

Box 1



Orbitals that make up the He–H bond

Box 2



Energy splitting diagram

III. [20 Points]

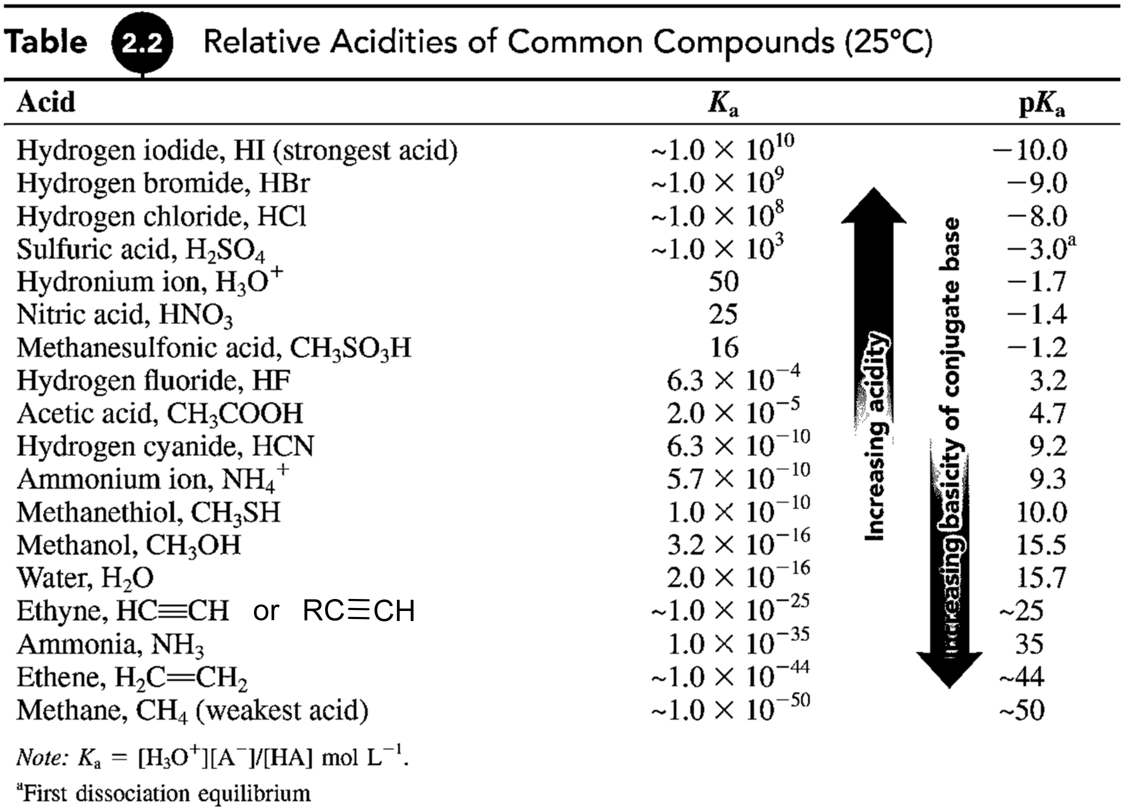


Table 2.2 Relative Acidities of Common Compounds (25°C)

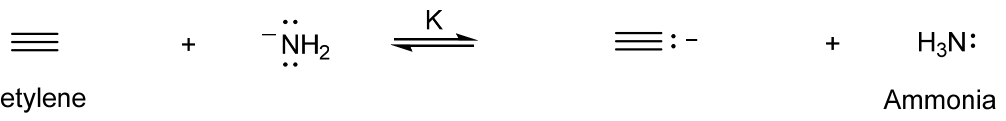
Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	~1.0×10^{10}	−10.0
Hydrogen bromide, HBr	~1.0×10^{9}	−9.0
Hydrogen chloride, HCl	~1.0×10^{8}	−8.0
Sulfuric acid, H_2SO_4	~1.0×10^{3}	−3.0[a]
Hydronium ion, H_3O^+	50	−1.7
Nitric acid, HNO_3	25	−1.4
Methanesulfonic acid, CH_3SO_3H	16	−1.2
Hydrogen fluoride, 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≡CH or RC≡CH	~1.0×10^{-25}	~25
Ammonia, NH_3	1.0×10^{-35}	35
Ethene, $H_2C{=}CH_2$	~1.0×10^{-44}	~44
Methane, CH_4 (weakest acid)	~1.0×10^{-50}	~50

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

[a] First dissociation equilibrium

Using the data in the Table above, circle "left" or "right" to indicate the position of the following acid-base equilibria and give the approximate equilibrium constants (namely in the form of 10^x; you can write "10^x" or "10 to the x") in the respective boxes provided.

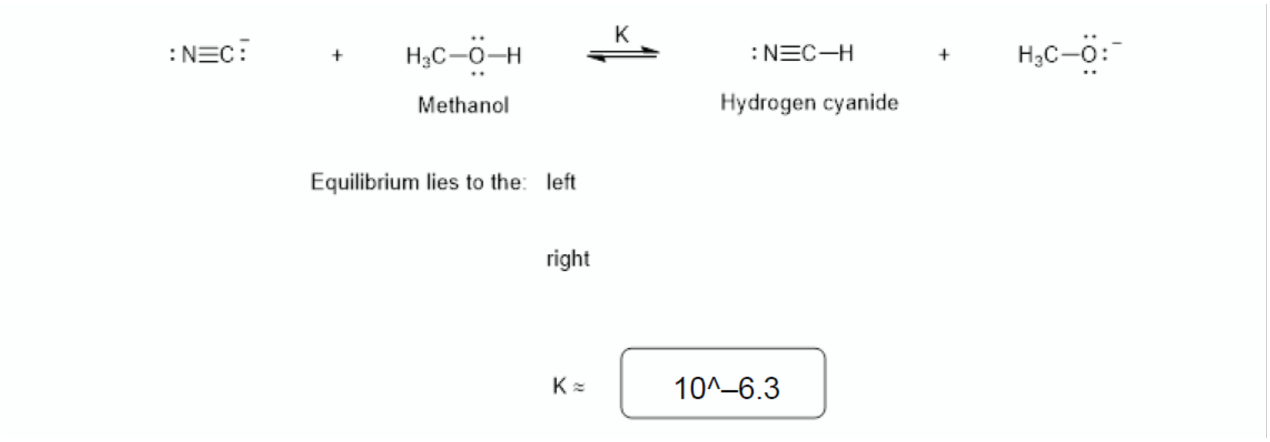
a.



Equilibrium lies to the: left [✓ right]

K ≈ $\boxed{10^{10}}$

b.



Equilibrium lies to the: left

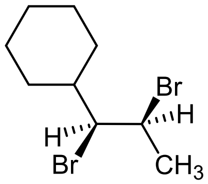
right

K ≈ 10^–6.3

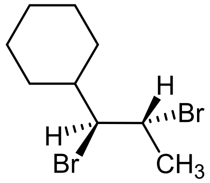
c. What is a Lewis base? Answer in one original sentence in the box. No cutting and pasting!

A Lewis base is an electron-pair donor.

IV. [36 Points] Consider the two isomers of 1,2-dibromopropyl)cyclohexane, **1** and **2**, shown below.



1



2

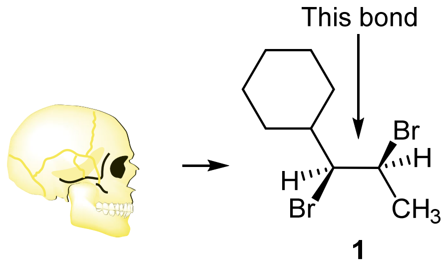
a. What is the relationship between these two compounds? Place an X mark next to the correct answer.

☐ Constitutional isomers

☐ Enantiomers

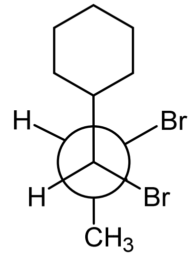
☒ Diastereomers

b. Draw the Newman projection **A** of **1** along the view depicted by the skull below by completing the Newman stencil in the box provided. You can use the abbreviation "Cy" for the cyclohexyl substituent and CH3 (no subscript) for the methyl group.



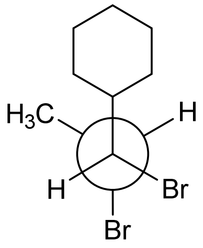
1

Newman projection of **1**:

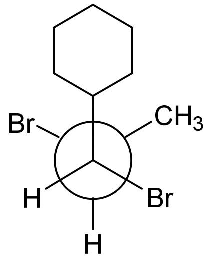


A

c. Draw the Newman projections **B** and **C** arising from the **clockwise** rotation of the back carbon by successive 120°.



B



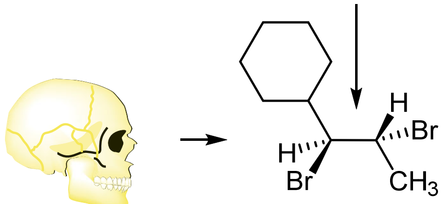
C

d. Which one of these staggered rotamers would you consider to be the **most** hindered and therefore of highest energy? Circle your answer below.

A **B** [✓ **C**]

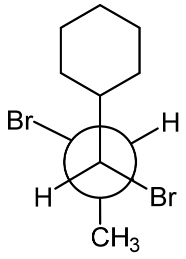
e. Draw the Newman projection **D** of **2** along the view depicted by the skull below by completing the Newman stencil in the box provided.

This bond



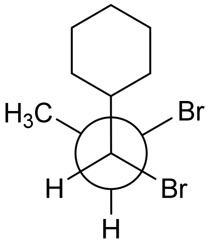
2

Newman projection of **2**:

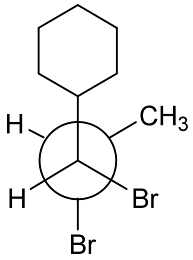


D

f. Draw the Newman projections **E** and **F** arising from the **clockwise** rotation of the back carbon by successive 120°.



E



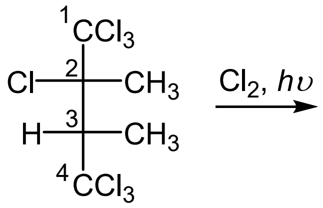
F

g. Which one of these staggered rotamers would you consider to be the **least** hindered and therefore of lowest energy? Circle your answer below.

[✓ **D**] **E** **F**

V. [38 Points]

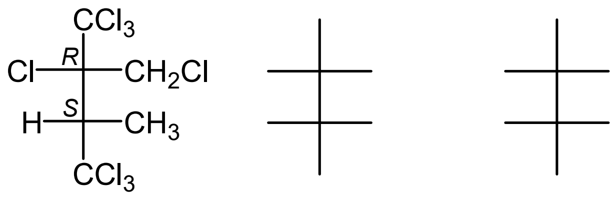
a. Draw the products of the **mono**chlorination of enantiomer **A** in the boxes below. The boxes are organized by location of attack. Add all missing substituents to the Fischer stencils provided (again, no subscripts needed, i.e. CH3, CCl3, etc.) **Caution**: In each box, there are more stencils than you will need. You will lose points for writing more products than required.



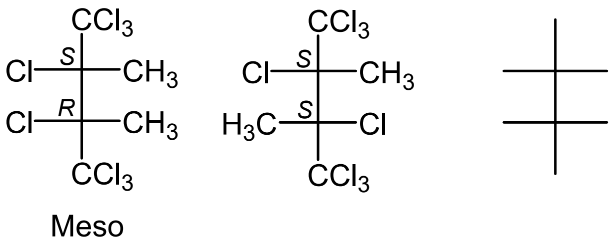
A

(2*S*,3*S*)-1,1,1,2,4,4,4-Heptachloro-2,3-dimethylbutane

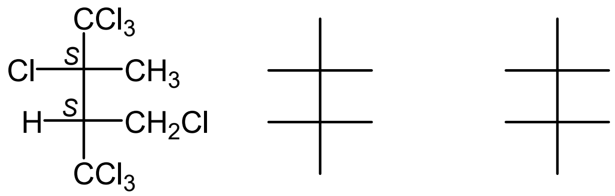
At C_2 methyl



At C_3



At C_3 methyl



b. Once you have completed part a., add the R or S designation to any stereocenters in your products.

c. Does the preceding radical chlorination of **A** give any optically **inactive** (namely achiral or racemic) products? Circle your answer.

Answer: [✓ Yes] No

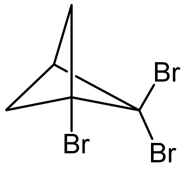
d. If your answer to c. is yes, circle the position of attack (below) that results in at least one such product.

At C_2 methyl [✓ At C_3] At C_3 methyl

VI. [15 Points]

The monobromination of hydrocarbon **1**-(*R*) gives the tribromo isomers **A**–**E**.

a. Circle the applicable properties written below each product.

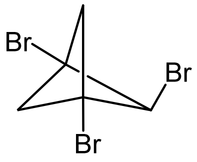


A

Chiral

[✓ Achiral]

Optically active

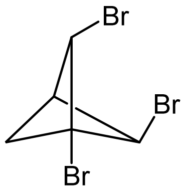


B

Chiral

[✓ Achiral]

Optically active

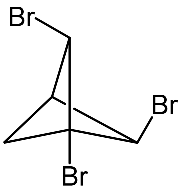


C

Chiral

[✓ Achiral]

Optically active

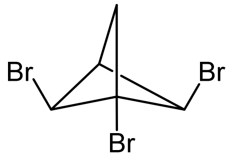


D

[✓ Chiral]

Achiral

[✓ Optically active]



E

Chiral

[✓ Achiral]

Optically active

b. The selectivity for the respective hydrogens in this bromination is tert : sec = 2 : 1. In the box below, give the expected ratio of all-tertiary to all-secondary C–H activation products in whole numbers (in other words, no need to normalize the ratio).

Ratio of (**A** + **B**) : (**C** + **D + E**) = 1:1

c. The normal selectivity in radical brominations is tert : sec ~ 20 : 1. Why are the tertiary hydrogens in **1** relatively unreactive? Answer in one sentence in the box.

The intermediate radical cannot planarize, thus impeding optimal hyperconjugation.

d. Do you expect products **C**, **D**, and **E** to be formed in equal amounts (in other words, in the ratio 1 : 1 : 1)? Circle your answer and explain it in one sentence in the box.

Yes [✓ No]

They are diastereomers.

VII. [18 Points]

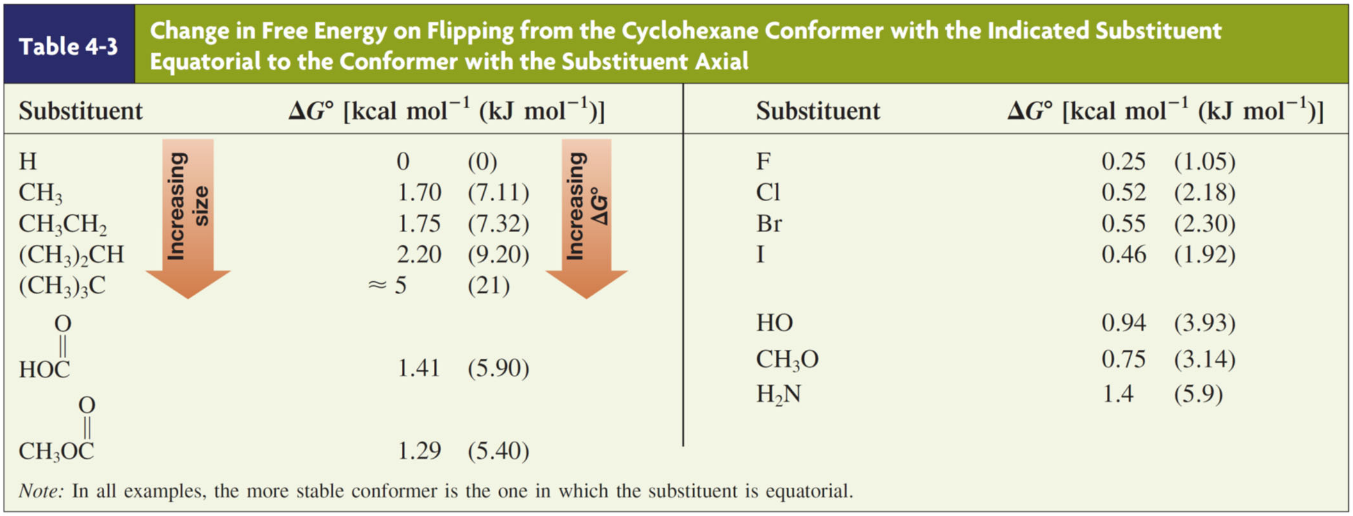


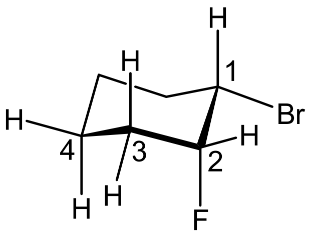
Table 4-3 **Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial**

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)		
$HO\overset{\overset{O}{\|}}{C}$	1.41 (5.90)	HO	0.94 (3.93)
$CH_3O\overset{\overset{O}{\|}}{C}$	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.

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**, respectively. For each, place an “X” in the box next to the correct energy of “ring flip”. Make sure to “cap off” all axial and equatorial bonds that are explicitly shown with substituents or H atoms.

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



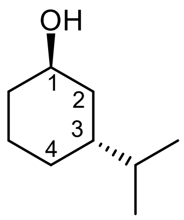
ΔG° ring flip (kcal mol^{-1})

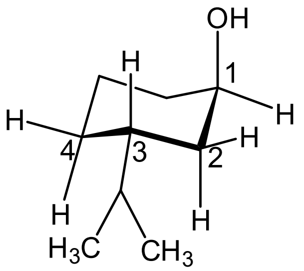
☒ 0.30

☐ +0.80

☐ –0.55

B:





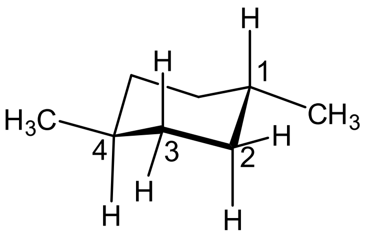
ΔG° ring flip

☐ –1.26

☒ +1.26

☐ +2.20

C: *trans*-1,4-Dimethylcyclohexane



ΔG° ring flip

☐ +1.70

☐ –1.70

☒ +3.40

VIII. [20 Points]

a. Answer the question in one sentence in the box.

1. Why is ammonia more basic than water?

Nitrogen is less electronegative than oxygen, rendering the lone pair in ammonia more easily protonated.

2. Why does the two-electron reduction of H_2 generate two hydride ions?

Two electrons will be placed into the antibonding orbital, rendering orbital overlap energetically neutral.

3. Why is methane tetrahedral and not flat?

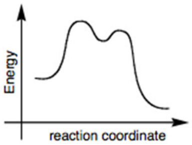
The tetrahedral geometry minimizes electron repulsion.

4. In radical halogenations, which propagation step is rate determining?

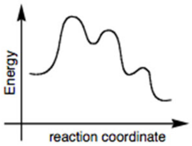
Propagation step 1.

b. Which one of the following potential-energy diagrams describes the rotation of *gauche*-butane to *anti*-butane?
Circle the correct answer: **(A)** **(B)** **(C)** [✓ **(D)**]

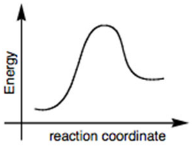
(A)



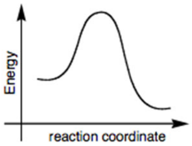
(B)



(C)



(D)



IX. [37 Points]

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

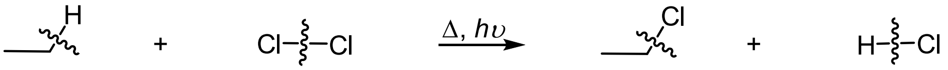
	B in A–B						
A in A–B	**–H**	**–F**	**–Cl**	**–Br**	**–I**	**–OH**	**–NH_2**
H—	104 (435)	136 (569)	103 (431)	87 (364)	71 (297)	119 (498)	108 (452)
CH_3—	105 (439)	110 (460)	85 (356)	70 (293)	57 (238)	93 (389)	84 (352)
CH_3CH_2—	101 (423)	111 (464)	84 (352)	70 (293)	56 (234)	94 (393)	85 (356)
$CH_3CH_2CH_2$—	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)

Note: (a) $DH° = \Delta H°$ for the process $A–B \rightarrow A\cdot + \cdot B$. (b) These numbers are being revised continually because of improved methods for their measurement. (c) The trends observed for A–H bonds are significantly altered for polar A–B bonds because of dipolar contributions to $DH°$.

Table 3.4 $DH°$ Values for the Elemental Halogens

Halogen	**$DH°$ [kcal mol^{-1} (kJ mol^{-1})]**
F_2	38 (159)
Cl_2	58 (243)
Br_2	46 (192)
I_2	36 (151)

a. Equation (1) depicts the chlorination of ethane to chloroethane. Give the bond dissociation energies in the four boxes provided, using the relevant data in the Tables above.



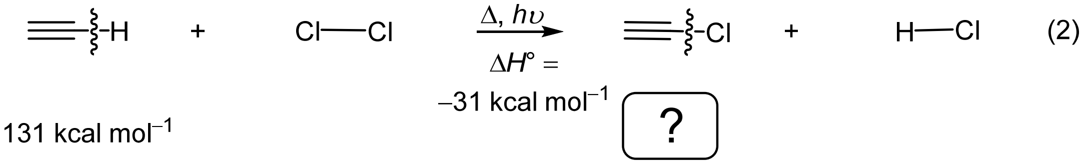
(1)

101	58	84	103	kcal mol^{-1}

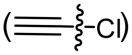
b. Calculate the $\Delta H°$ value for reaction (1). Show your work.

$\Delta H°$ (1) : (84 + 103) – (101 + 58) = –28 kcal mol^{-1}

c. Compare equation (1) with that for the hypothetical reaction of acetylene with chlorine to give chloroacetylene, equation (2). The $\Delta H°$ for this process is estimated to be –31 kcal mol^{-1}.



Given the *DH*° of the acetylenic C–H bond (131 kcal mol^{-1}), calculate the strength of the C–Cl bond in the product. Show your work.

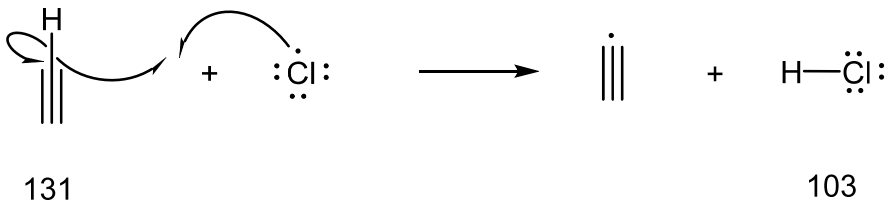
DH° () = x; $(x + 103) - (131 + 58) = -31$ kcal mol^{-1};

x = 117 kcal mol^{-1}

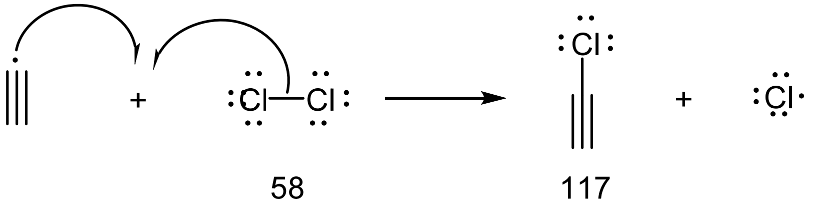
The following three problems should be answered on three consecutive separate pages of hard copy white paper using a dark (at least #2) pencil. Label these pages "IX.d, IX.e, and IX.f". Ascertain that your drawings are clearly visible. When you are finished, scan the pages on your device with a suitable scanning app (do not use CamScanner) in the order IX.d, IX.e, and IX.f, save the document as a pdf file, and add it to this file, using the "Combine Files" feature on AcrobatPro. Make sure to set up the correct order of the two; the combined file should feature your scanned pages at the end.
Label the final pdf file with your name and the words "3AExam1" (namely: Last Name, First Name, 3AExam1) and upload it to Gradescope.

IX.d. Formulate the two propagation steps for reaction (2). Show electron-pushing fishhook arrows.

Step 1



Step 2



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

Step 1: $\Delta H° = 131 - 103 = +28$ kcal mol^{-1}

Step 2: $\Delta H° = 58 - 117 = -59$ kcal mol^{-1}

IX.f. Which of the two reactions (1) and (2) would be the faster one and why? Answer in one sentence.

Reaction (1) is faster, because the ethane C–H bond is weaker than the acetylene C–H bond.

"How much is that in years of tuition?"

♫ The End ♫