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, 2020

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 _____

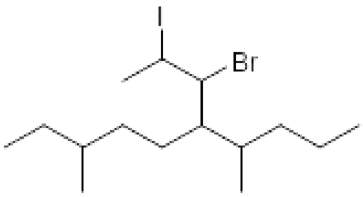
Please write the answer you wish to be graded in the boxed spaces provided.

Do scratch work on the back of the pages. This test should have **17** 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*!**

Do not unstaple and/or remove a page from the exam. It will compromise the consonance of scanned copies in Gradescope.

I. [36 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.



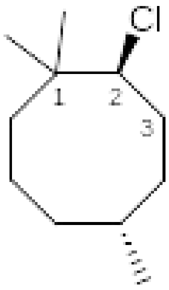
(No stereochemistry)

6-(1-Bromo-2-iodopropyl)-3,7-dimethyldecane

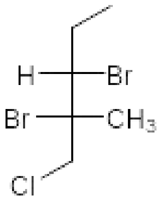
b.

(2*S*,5*R*)-2-Chloro-1,1,5-trimethylcyclooctane

(Complete the stencil in the box)



c.



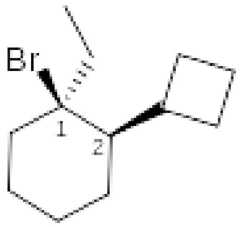
(Name this enantiomer)

(2S,3S)-2,3-Dibromo-1-chloro-2-methylpentane

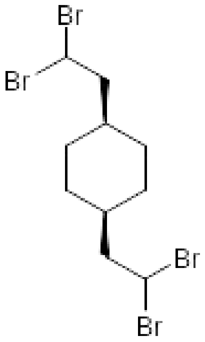
d.

(1R,2R)-1-bromo-2-cyclobutyl-1-ethylcyclohexane

(Complete the stencil in the box)



e.

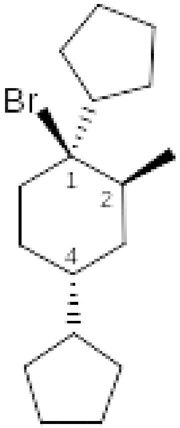


cis-1,4-Bis(2,2-dibromoethyl)cyclohexane

f.

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

(Complete the stencil in the box)



II. [30 Points]

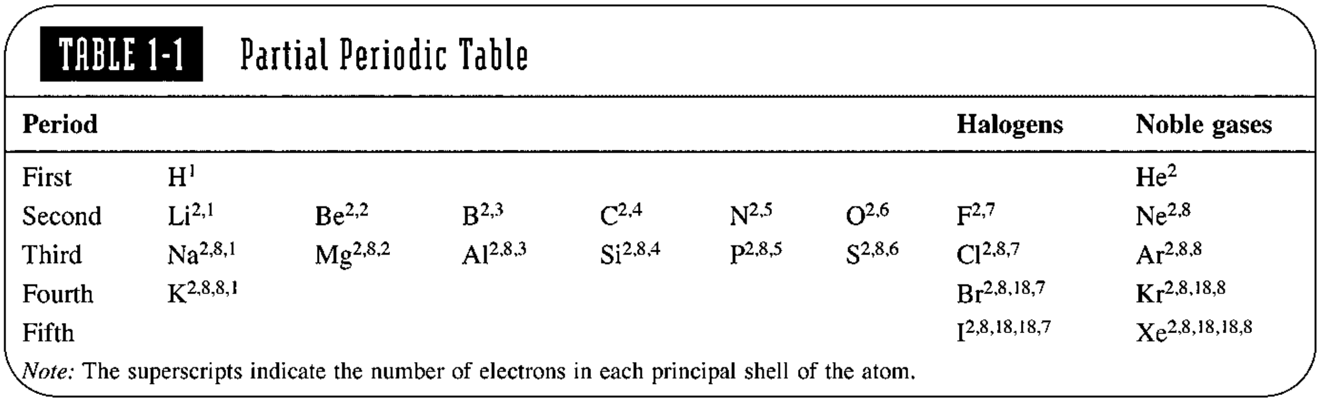
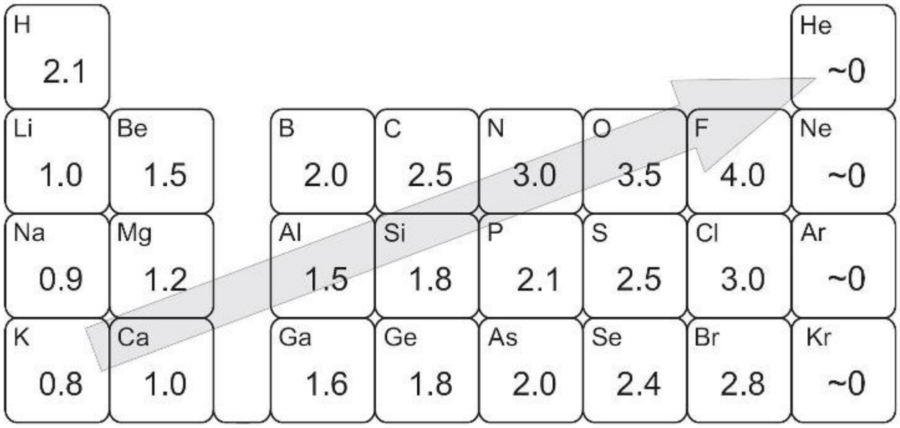


TABLE 1-1 Partial Periodic Table

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.

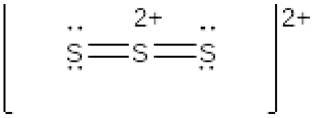
Pauling Electronegativities



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 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 lone electron pairs!**

a.

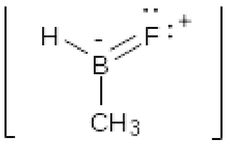


What is the geometry of S_3^{2+} ? Place an “x” mark into the box next to your answer.

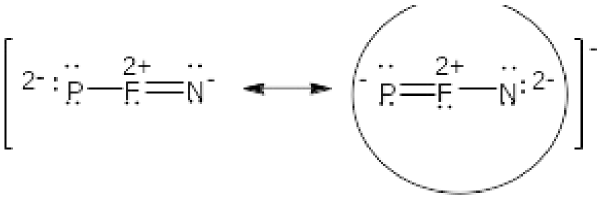
Linear ☒

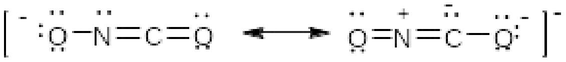
Bent ☐

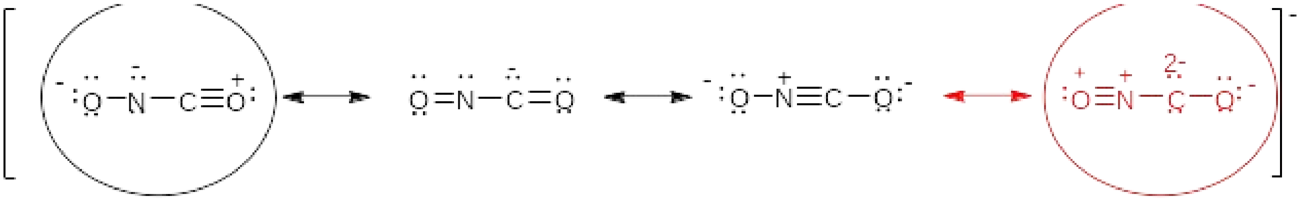
b.



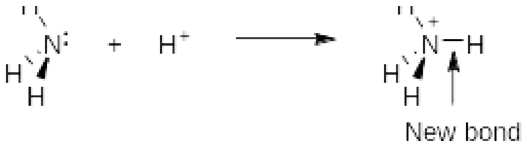
c. The following structure has two **octet** resonance forms. Circle the **best** one.



d. For  , there are three additional **octet** resonance forms. Circle the **worst** one among the new forms. Post exam fix: there is another resonance form, which is worse than that in the answer (see below). Full credit was given for either one.

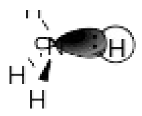


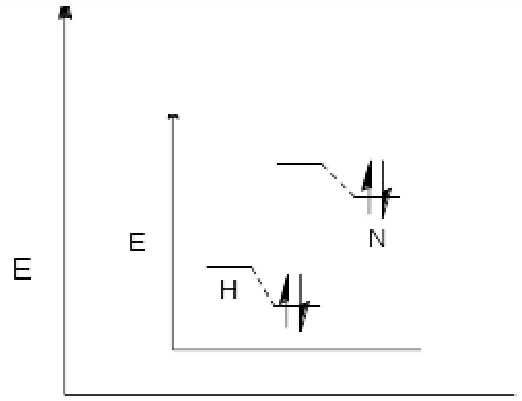
e. The protonation of ammonia, NH_3, gives ammonium ion NH_4^+.



In the respective boxes,

1. draw the overlapping orbitals that make up the new N–H bond.
2. compose the energy splitting diagram depicting the protonation of NH_3, starting with the proton orbital energy level on the left side.





Orbitals that make up the new N–H bond Energy splitting diagram

III. [20 Points]

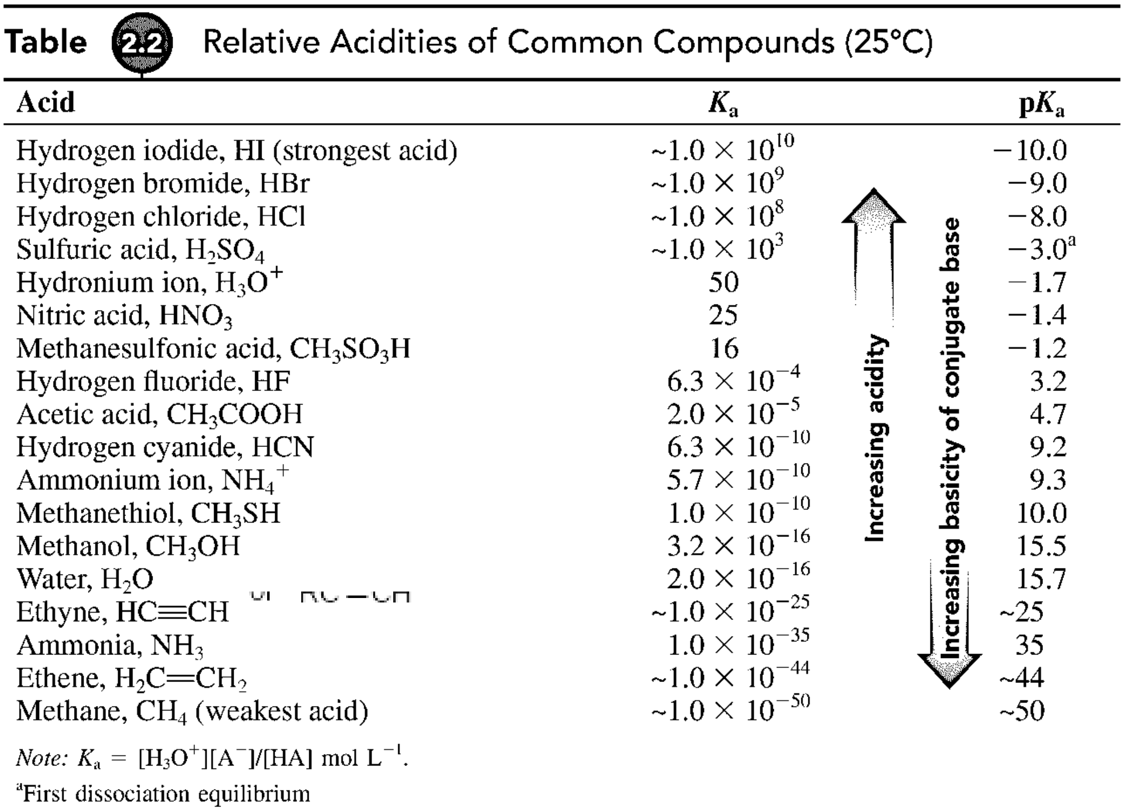


Table 2.2 Relative Acidities of Common Compounds (25°C)

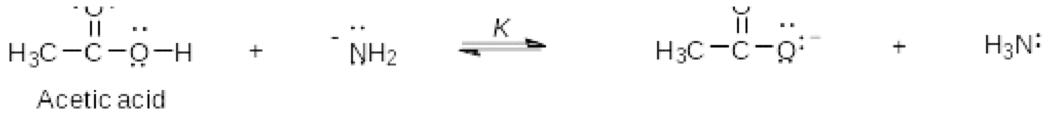
Acid	K_a	pK_a
Hydrogen iodide, HI (strongest acid)	$\sim 1.0 \times 10^{10}$	-10.0
Hydrogen bromide, HBr	$\sim 1.0 \times 10^{9}$	-9.0
Hydrogen chloride, HCl	$\sim 1.0 \times 10^{8}$	-8.0
Sulfuric acid, H_2SO_4	$\sim 1.0 \times 10^{3}$	-3.0^a
Hydronium ion, H_3O^+	50	-1.7
Nitric acid, HNO_3	25	-1.4
Methanesulfonic 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, $HC\equiv CH$	$\sim 1.0 \times 10^{-25}$	~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, 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) in the respective boxes provided.

a.



$$H_3C-\overset{O}{\overset{\|}{C}}-OH + {}^{-}NH_2 \overset{K}{\rightleftharpoons} H_3C-\overset{O}{\overset{\|}{C}}-O^{-} + H_3N:$$

Equilibrium lies to the: left [✓ right]

$K \approx \boxed{10^{29.7}}$

b.

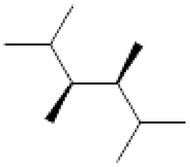
$$H_3C{-}\ddot{S}{:}^{-} + H_3C{-}\ddot{O}{-}H \overset{K}{\rightleftharpoons} H_3C{-}S{-}H + H_3C{-}\ddot{O}{:}^{-}$$

Equilibrium lies to the: [✓ left]

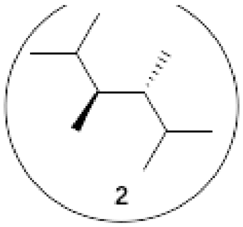
right

$K \approx \boxed{10^{-5.5}}$

IV. [36 Points] Consider the two diastereomers of 2,3,4,5-tetramethylhexane, **1** and **2**, shown below.



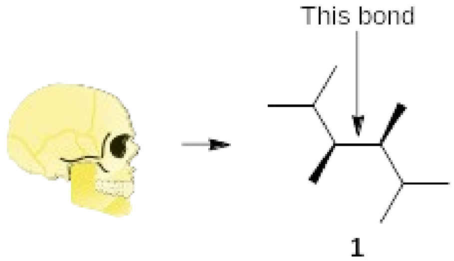
1



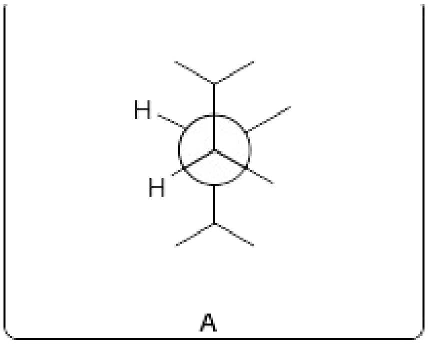
2

a. One of them has a meso structure. Circle which one.

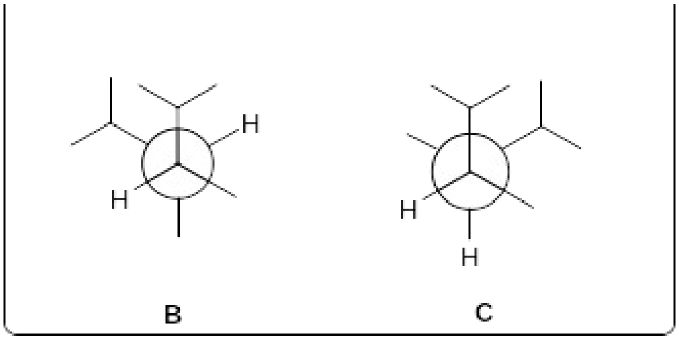
b. Draw the Newman projection **A** of **1** along the view depicted by the skull below by completing the Newman stencil in the box provided.



Newman projection of **1**:



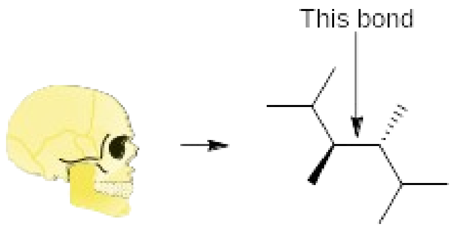
c. Draw the Newman projections **B** and **C** arising from the **clockwise** rotation of the back carbon by successive 120°.



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

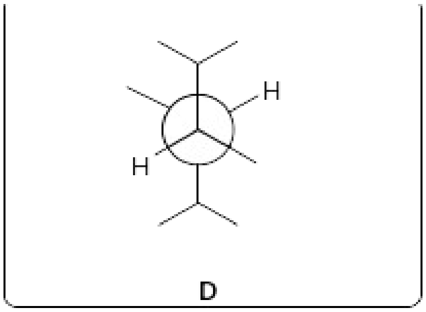
A **B** [✓ **C**]

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.



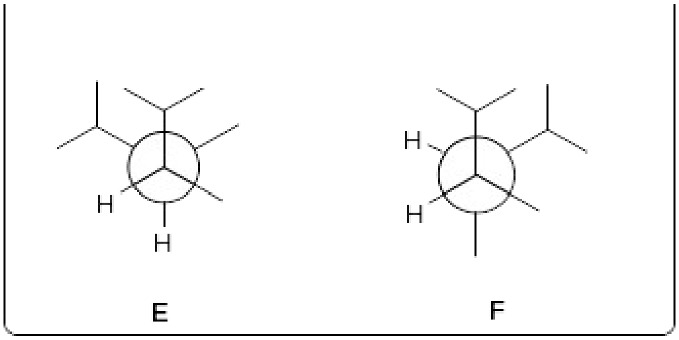
2

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°.



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. [30 Points]

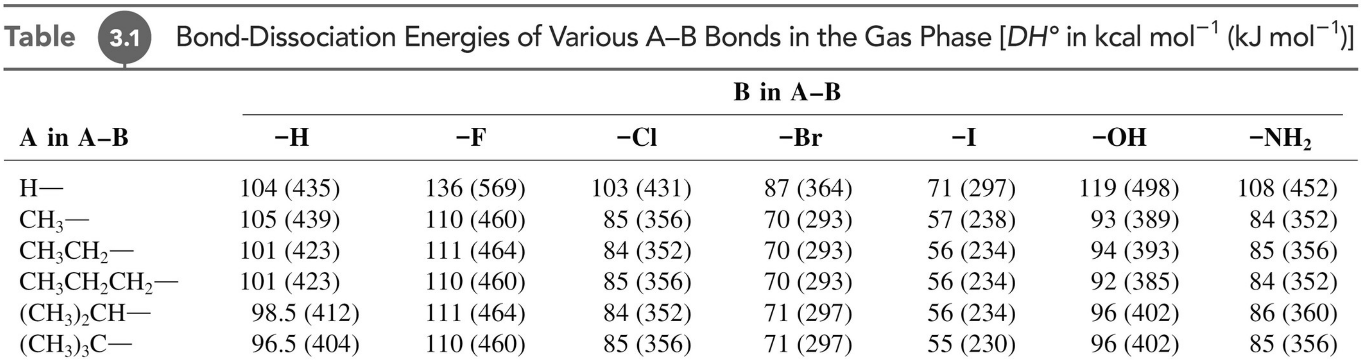
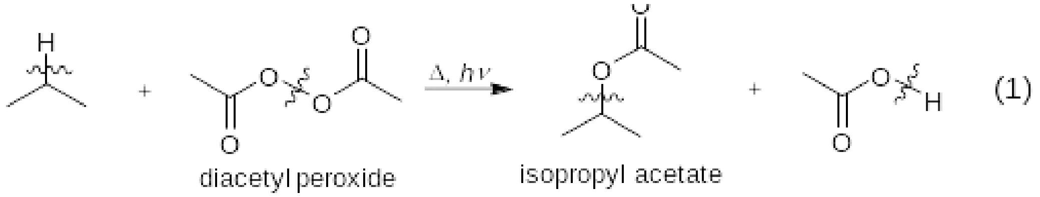


Table 3.1 Bond-Dissociation Energies of Various A–B Bonds in the Gas Phase [$DH°$ in kcal mol^{-1} (kJ mol^{-1})]

	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 attempted the radical bromination of propane in the presence of the radical initiator diacetyl peroxide. Hoping to speed up the reaction, the person used 1 equivalent of the peroxide, leading to large quantities of the ester isopropyl acetate [equation (1)].

a. The O–O D$H°$ for diacetyl peroxide is given below (37 kcal mol^{-1}). Give the missing bond dissociation energies in the equation below in the three boxes provided, using the relevant data in the Table at the top of the page.



$\boxed{98.5}$ 37 $\boxed{96}$ $\boxed{119}$ kcal mol^{-1}

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

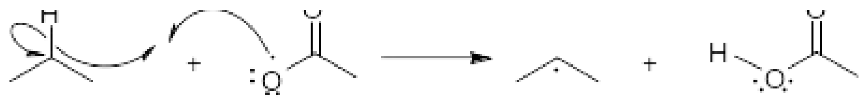
$\Delta H°$ (1) : 135.5 – 215 = –79.5 kcal mol^{-1}

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

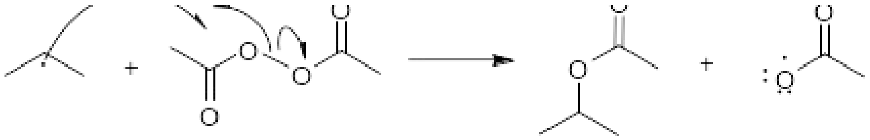
Answer: [✓ Yes] No

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.

$\Delta H°$ (1st propagation step): $98.5 - 119 = -20.5$ kcal mol^{-1}

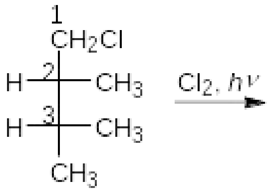
$\Delta H°$ (2nd propagation step): $37 - 96 = -59$ kcal mol^{-1}

f. The O–O $DH°$ for diacetyl peroxide (37 kcal mol^{-1}) is much lower than that for hydrogen peroxide, HO–OH (50 kcal mol^{-1}). Why? Answer in one sentence in the box.

The radical is stabilized by resonance.

VI. [38 Points]

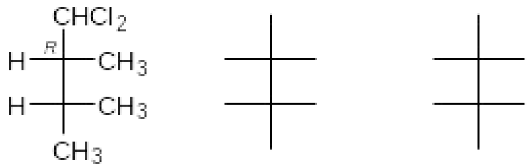
a. Draw the products of the **mono**chlorination of enantiomer **A** in the boxes below. The boxes are organized by location of attack. Add all missing substituents to the Fischer stencils provided. **Caution**: In each box, there are more stencils than you will need. You will lose points for writing more products than required.



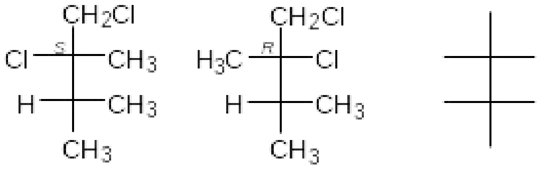
A

(*R*)-1-Chloro-2,3-dimethylbutane

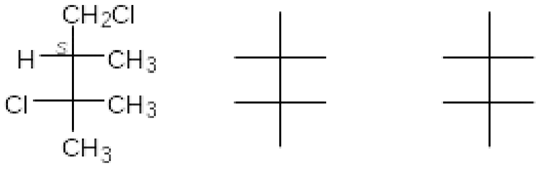
At C1



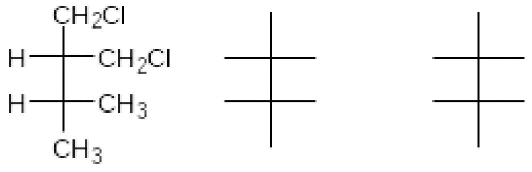
At C2



At C3



At C2 methyl



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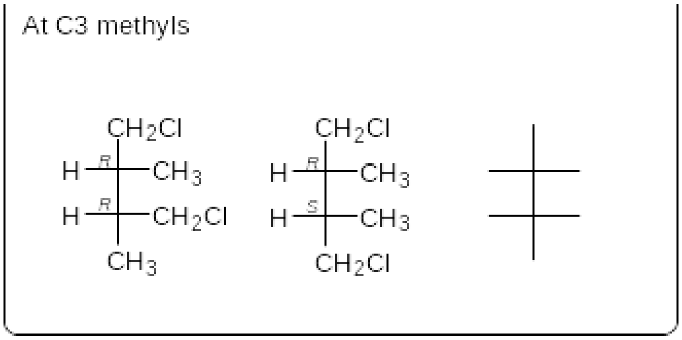


b. Once you have completed part a., add the R or S designation to any stereocenters in your products.

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

Answer: [✓ Yes] No

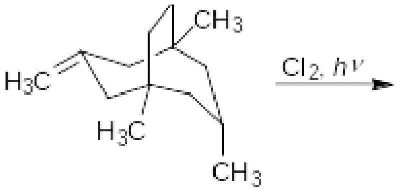
If your answer is yes, circle the position of attack (below) that results in at least one such product (there may be several correct answers):

At C1 [✓ At C2] At C3 [✓ At C2 methyl] [✓ At C3 methyls]

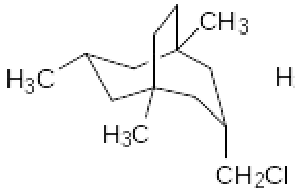
VII. [15 Points]

The monochlorination of hydrocarbon **1** gives constitutional isomers **A**–**E** (do not worry about stereocenters).

a. Circle the applicable properties written below each product.

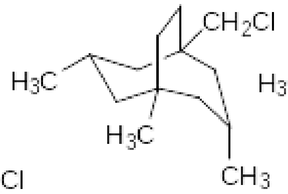


1



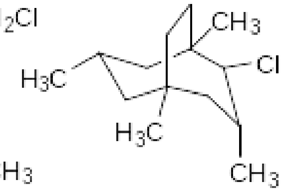
A

Chiral
[✓ Achiral]
Optically active



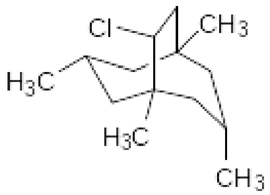
B

Chiral
[✓ Achiral]
Optically active



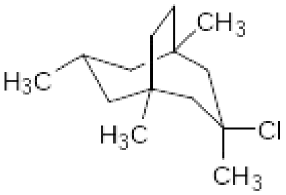
C

[✓ Chiral]
Achiral
Optically active



D

[✓ Chiral]
Achiral
Optically active



E

Chiral
[✓ Achiral]
Optically active

b. The selectivity for the respective hydrogens in this chlorination is tert : sec : prim = 5 : 4 : 1. In the box below, give the expected product ratio in whole numbers (in other words, no need to normalize the ratios).

Ratio of **A** : **B** : **C** : **D : E** = 6 : 6 : 32 : 16 : 10

VIII. [18 Points]

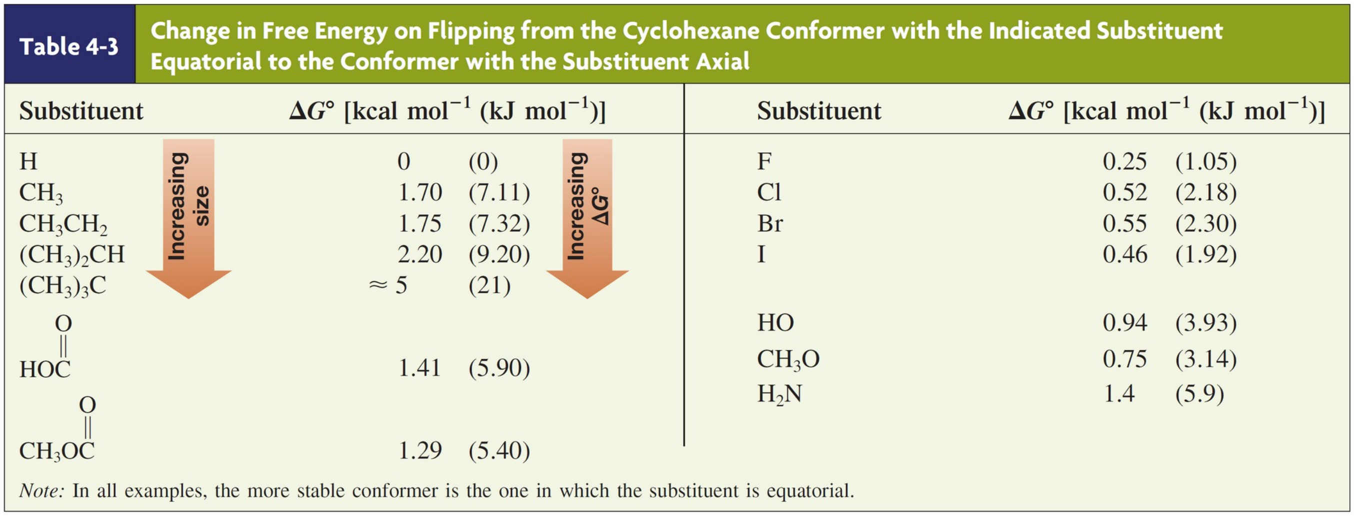


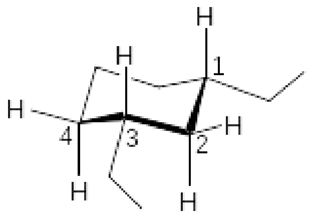
Table 4-3 **Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial**

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	0.94 (3.93)
$HO\overset{O}{\overset{\|}{C}}$	1.41 (5.90)	CH_3O	0.75 (3.14)
		H_2N	1.4 (5.9)
$CH_3O\overset{O}{\overset{\|}{C}}$	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, 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 and H atoms.

A: *cis*-1,3-Diethylcyclohexane



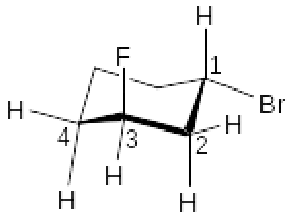
ΔG° ring flip (kcal mol^{-1})

☐ 0

☒ +3.50

☐ -3.50

B: *trans*-1-Bromo-3-fluorocyclohexane



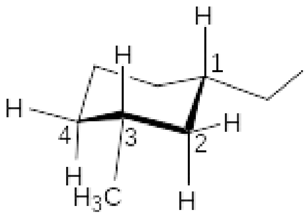
ΔG° ring flip

☐ +0.55

☒ +0.30

☐ +0.80

C: *cis*-1-Ethyl-3-methylcyclohexane



ΔG° ring flip

☐ +1.70

☐ -1.70

☒ +3.45

IX. [27 Points]

a. Mark the boxes next to your choice of a correct statement. Leave blank the boxes next to incorrect statements.

1. Basicity increases from left to right of a row in the periodic table, because atoms become more electronegative. ☐

2. Hybridization of atomic orbitals occurs to maximize bonding and minimize electron repulsion.

☒

3. Acidity increases down a column of the periodic table. ☒

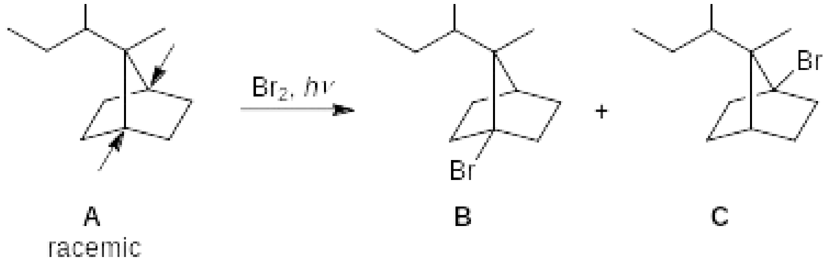
4. Water is less basic than ammonia, because oxygen is more electronegative than nitrogen.

☒

5. *cis*-1,2-Dimethylcyclooctane is meso. ☒

6. In radical chlorination, the second propagation step is rate determining. ☐

b. Consider the bromination of **A** at the indicated (arrows) “bridgehead” positions to give **B** and **C**.



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

In equal amounts [✓ In unequal amounts]

2. The products have the following properties (circle the correct answer):

All are optically active One is optically active and the other is not

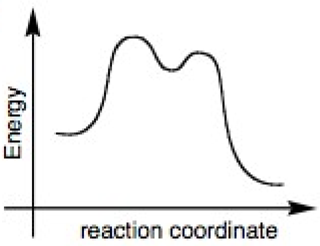
[✓ None are optically active]

c. Which one of the following potential-energy diagrams describes the radical chlorination of methane?

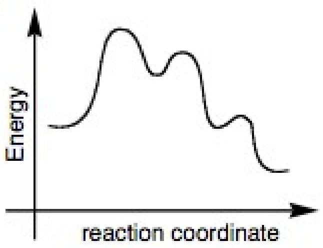
○

Circle the correct answer: **(A)** **(B)** **(C)** **(D)**

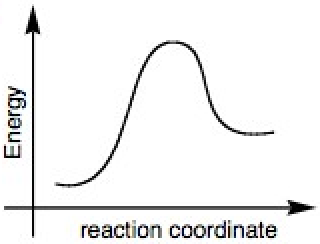
(A)



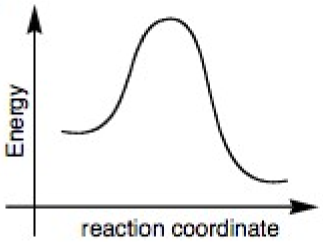
(B)



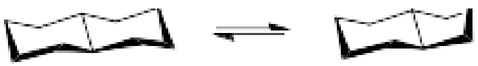
(C)



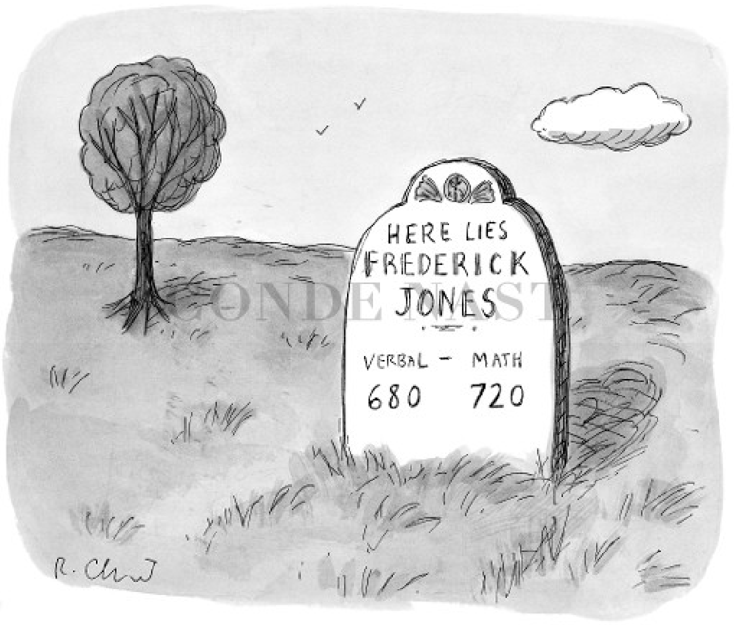
(D)



d. Which one of the above potential-energy diagrams describes the equilibrium shown below?



Circle the correct answer: **(A)** **(B)** [✓ **(C)**] **(D)**



♬ The End ♬