If you encounter any technical problems during the entire exam period, Zoom Jack Hayward Cooke at https://berkeley.zoom.us/j/93271902365
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:_____   **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 26, 2022

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 **15** 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 the "Tools" tab in the top left, then scroll down and open the "Comments" tool, then 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.
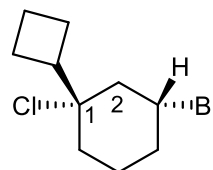
a.
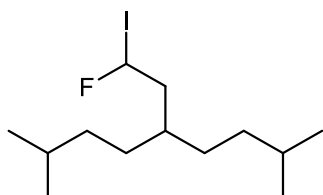
(No stereochemistry)
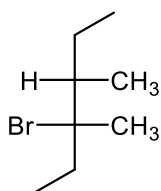
5-(2-Fluoro-2-iodoethyl)-2,8-dimethylnonane

b.

(1*S*,3*R*)-3-Bromo-1-chloro-1-cyclobutylcyclohexane

(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 "cyclobutyl", use the letters "Cyc"**)
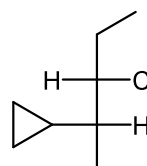
c.

H——CH₃
Br——CH₃

(Name this enantiomer)

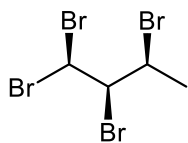(3*S*,4*S*)-3-Bromo-3,4-dimethylhexane

d.

(1*R*,2*S*-2-Chloro-1-methylbutyl)cyclopropane

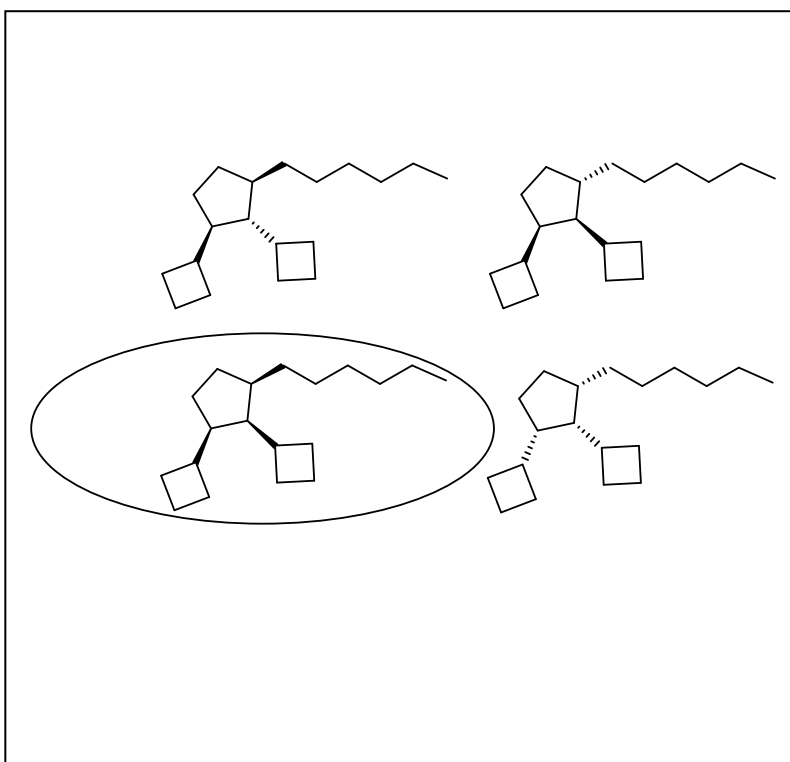(Complete the Fischer stencil in the box)

H——Cl
——H

e.

(2*R*,3*S*)-1,1,2,3-Tetrabromobutane

f.

(1*R*,2*R*,3*R)*-1,2-Dicyclobutyl-3-hexylcyclopentane

(Circle the correct answer in the box)

II. [30 Points]

TABLE 1-1 Partial Periodic Table

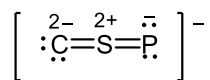| Period								Halogens	Noble gases
First	H^1								He^2
Second	$Li^{2,1}$	$Be^{2,2}$	$B^{2,3}$	$C^{2,4}$	$N^{2,5}$	$O^{2,6}$		$F^{2,7}$	$Ne^{2,8}$
Third	$Na^{2,8,1}$	$Mg^{2,8,2}$	$Al^{2,8,3}$	$Si^{2,8,4}$	$P^{2,8,5}$	$S^{2,8,6}$		$Cl^{2,8,7}$	$Ar^{2,8,8}$
Fourth	$K^{2,8,8,1}$							$Br^{2,8,18,7}$	$Kr^{2,8,18,8}$
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.
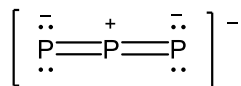
Pauling Electronegativities

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.

$$\left[\;:\overset{2-}{\underset{..}{C}}=\overset{2+}{S}=\overset{..}{\underset{..}{P}}: \;\right]^{-}$$

b.

$$\left[\;\overset{..}{\underset{..}{P}}=\overset{+}{P}=\overset{..}{\underset{..}{P}}: \;\right]^{-}$$
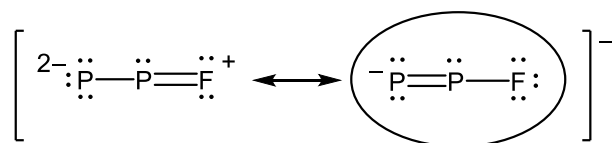
The central P in P_3^- is *sp* hybridized. What is the geometry of P_3^-? Place an "x" mark into the box next to your answer.

Linear ☒

Bent ☐

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

$$\left[{}^{2-} \ddot{:}\!P\!—\!P\!\!=\!\!\overset{..}{\underset{..}{F}}\!{}^{+} \quad \longleftrightarrow \quad \left(\!{}^{-}P\!\!=\!\!P\!—\!\ddot{F}\!:\!\right) \right]^{-}$$

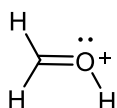d. Why is resonance in molecules energetically advantageous? Answer in your own words in the box (one sentence suffices). Reminder: Do not copy and paste from anywhere, as my program will immediately flag it.

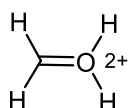Spreading out electron density minimizes electron repulsion.

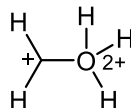e. In the boxes provided, enter the hybridization at oxygen in the following four species.
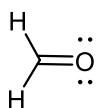
| sp^2 | sp^2 | sp^2 | sp^3 |

III.   [20 Points]

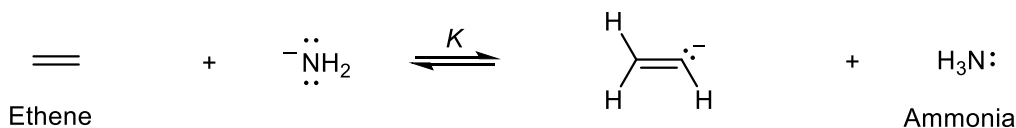## Table 2.2 Relative Acidities of Common Compounds (25°C)

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, $HC{\equiv}CH$ or $RC{\equiv}CH$	~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 and your chemical intuition, indicate the direction of the equilibria shown below in the respective boxes provided.

a.

$$\text{Ethene} \quad = \quad + \quad {}^-\ddot{N}H_2 \quad \underset{}{\overset{K}{\rightleftharpoons}} \quad \begin{matrix} H \\ \diagdown \\ H \end{matrix} {=} \begin{matrix} \ddot{}{}^- \\ \diagup \\ H \end{matrix} \quad + \quad H_3N{:} \quad \text{Ammonia}$$

Ethene   Ammonia

Equilibrium lies to the

left   [X]

right   [ ]

$K \approx 1$ [ ]

b.

$$H_3C(CH_2)_5\!-\!\overset{..}{\underset{..}{O}}\!:^- \quad + \quad H_3C(CH_2)_4\!-\!\overset{..}{\underset{..}{O}}\!-\!H \quad \overset{K}{\rightleftharpoons} \quad H_3C(CH_2)_5\!-\!\overset{..}{\underset{..}{O}}\!-\!H \quad + \quad H_3C(CH_2)_4\!-\!\overset{..}{\underset{..}{O}}\!:^-$$

Pentanol   Hexanol

Equilibrium lies to the

left   ☐

right   ☐

$K \approx 1$ ☐ X

c. BH_3 is a stronger Lewis acid than CH_3OBH_2. Why? Explain in the box.

CH_3OBH_2 has an octet structure that features donation of a lone pair to boron.

IV. **[25 Points]** Consider the two structural renditions of (1-bromo-2-methylpropyl)-cyclohexane, **1** and **2**, shown below.

1   **2**

a. What is the relationship between **1** and **2**? Place an X mark next to the correct answer.

☐ Constitutional isomers

☐ Enantiomers

☐ Diastereomers

☒ Rotamers

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 CH3 (no subscript) for the methyl group and Cy for the cyclohexyl substituent.

Newman projection of **1**:

A

c. Draw the Newman projections **B** and **C** of **1** 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**

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.
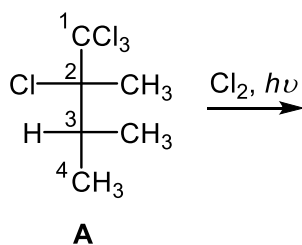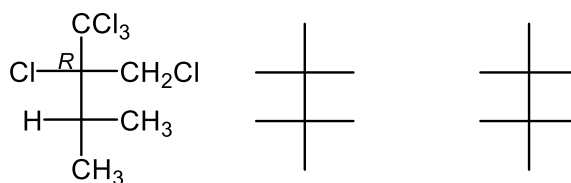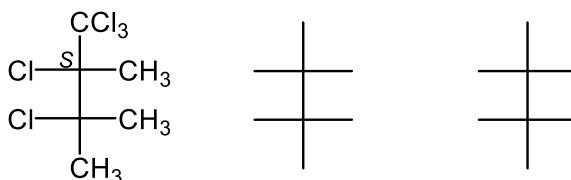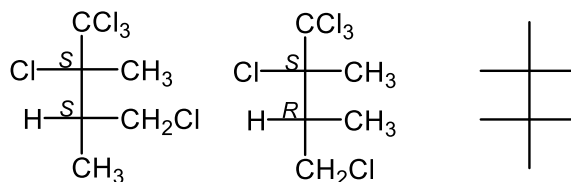

(S)-1,1,1,2-tetrachloro-2,3-dimethylbutane

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

c. How many optically **active** products are generated in the preceding radical chlorination of **A**? Circle your answer.

~~All of them~~   None of them   One   Two   Three

d. Does the preceding radical chlorination of **A** result in any diastereomeric products? Circle your answer.
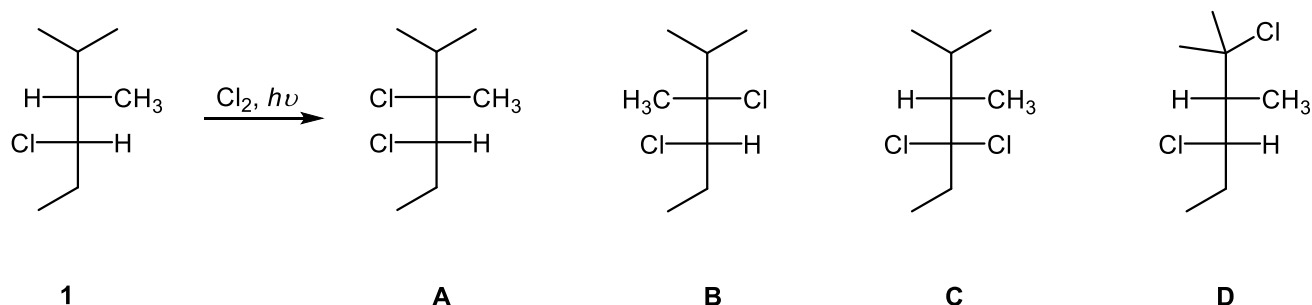
~~Yes~~   No

e. If your answer to d. is yes, circle the position of attack (below) that results in such a products.

At C_2 methyl   At C_3 ~~At C_3 methyl~~

VI.   [15 Points]
The monochlorination of pure enantiomer **1** gives the dichloro isomers **A**–**D**.
a. Circle the applicable properties written below each product.

	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 ratio of all-tertiary to all-secondary to all primary C–H activation products in whole numbers (in other words, no need to normalize the ratio).

Ratio of tert : sec : prim C–H activation products = 15 : 8 : 12

c. Products **A** and **B** are formed in unequal amounts. Why? Explain in one sentence in the box.

The stereocenter next to the intermediate radical renders the two faces of the latter unequal

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	$\Delta G°$ [kcal mol^{-1} (kJ mol^{-1})]		Substituent	$\Delta G°$ [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$_3$CH$_2$	1.75	(7.32)	Br	0.55	(2.30)
(CH$_3$)$_2$CH	2.20	(9.20)	I	0.46	(1.92)
(CH$_3$)$_3$C	5	(21)			
			HO	0.94	(3.93)
HOC(=O)	1.41	(5.90)	CH$_3$O	0.75	(3.14)
			H$_2$N	1.4	(5.9)
CH$_3$OC(=O)	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**, respectively. For each, place an "X" in the box next to the correct energy of the "ring flip" to the other conformer. Make sure to "cap off" all axial and equatorial bonds that are explicitly shown with substituents or H atoms.
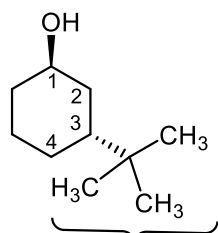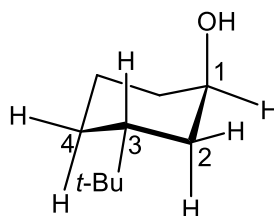
A: *cis*-1,2-Dibromocyclohexane
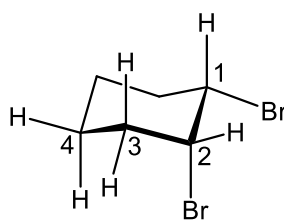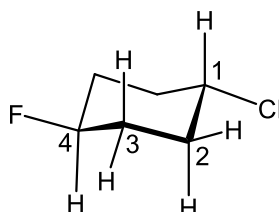

or conformer

$\Delta G°$ ring flip (kcal mol^{-1})

X	0
	+0.80
	−0.55

B:

Use t-Bu for this substituent

$\Delta G°$ ring flip

	−1.26
X	+4.06
	+2.20

C: *trans*-1-Chloro-4-fluorocyclohexane

$\Delta G°$ ring flip

	+0.25
	+0.52
X	+0.77

VIII.   [25 Points]

a. Answer the questions in one sentence in the respective boxes.

1. Why is the C–H bond in ethane weaker than that in methane?

> The ethyl radical is stabilized by hyperconjugation

2. Why is twist-boat cyclohexane more stable than the boat form?
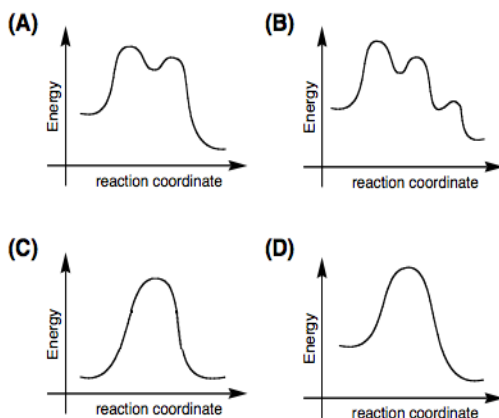
> It has less eclipsing interactions

3. Why is the F–F bond so weak, compared to the other X–X bonds?

> The two sets of three lone pairs are comparatively close

4. Why are radical fluorinations unselective?

> The abstraction of H by F˙ features an early transition state with little radical character on carbon

b. Which one of the following potential-energy diagrams describes the 120° rotation of ethane?
Circle the correct answer: **(A)   (B) (C)   (D)**

(A)

Energy
reaction coordinate

(B)

Energy
reaction coordinate

(C)

Energy
reaction coordinate

(D)

Energy
reaction coordinate

IX.   [47 Points]

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

A in A–B	B 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$_3$CH$_2$—	101 (423)	111 (464)	84 (352)	70 (293)	56 (234)	94 (393)	85 (356)
CH$_3$CH$_2$CH$_2$—	101 (423)	110 (460)	85 (356)	70 (293)	56 (234)	92 (385)	84 (352)
(CH$_3$)$_2$CH—	98.5 (412)	111 (464)	84 (352)	71 (297)	56 (234)	96 (402)	86 (360)
(CH$_3$)$_3$C—	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 → A· + ·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

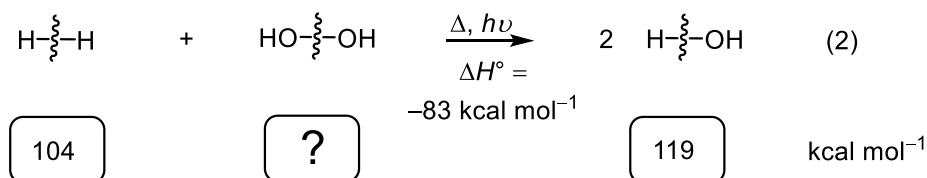| Halogen	$DH°$ [kcal mol^{-1} (kJ mol^{-1})]
F$_2$	38 (159)
Cl$_2$	58 (243)
Br$_2$	46 (192)
I$_2$	36 (151)

a. Hydrogen, H$_2$, reacts with fluorine explosively to generate HF [equation (1)]. Give the bond dissociation energies (kcal mol^{-1}) in the three boxes provided, using the relevant data in the Tables above.

H–⧸–H   +   F–⧸–F $\xrightarrow{\text{Room temperature}}$ 2 H–⧸–F   (1)

| 104 | | 38 | | | 136 | kcal mol^{-1} |
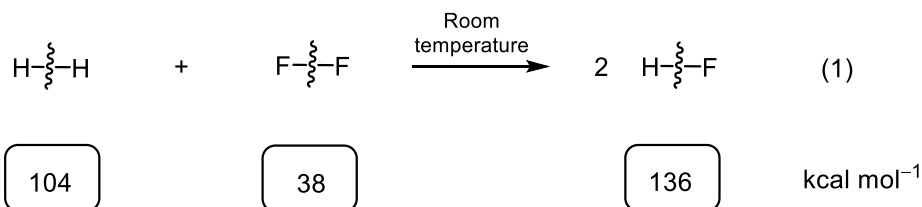
b. Calculate the $\Delta H°$ value (kcal mol^{-1}) for reaction (1). Show your work.

$\Delta H°$ (1) : 104 + 38 − (2x136) = −130 kcal/mol

c. Compare equation (1) with that for the reaction of hydrogen peroxide with hydrogen to give water, equation (2). The $\Delta H°$ for this process is measured to be −83 kcal mol^{-1}.

$$H-\overset{\xi}{\underset{\xi}{}}-H \quad + \quad HO-\overset{\xi}{\underset{\xi}{}}-OH \quad \xrightarrow[\Delta H° = \\ -83 \text{ kcal mol}^{-1}]{\Delta, h\upsilon} \quad 2 \quad H-\overset{\xi}{\underset{\xi}{}}-OH \quad (2)$$

| 104 | ? | 119 | kcal mol^{-1} |

Fill in the first and last box above with the relevant data, and calculate the strength of the HO–OH bond (kcal mol^{-1}) in the following box. Show your work.

$$HO-\overset{\xi}{\underset{\xi}{}}-OH \qquad 104 + a - (2 \times 119) = -83$$
$$a = +51 \text{ kcal mol}^{-1}$$

The following three problems should be answered on two consecutive separate pages of hard copy white paper using a dark (at least #2) pencil. Label these pages "IX.d" and "IX.e+f", respectively. 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, followed by IX.e+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.
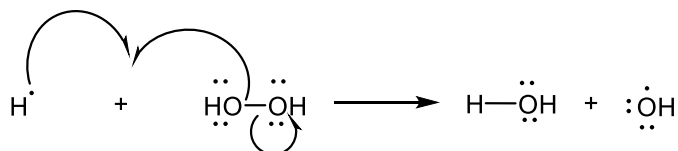**Label the final pdf file with your name and the words "3AExam1" (namely: Last Name, First Name, 3AExam1) and upload it to Gradescope.**

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

Propagation step 1
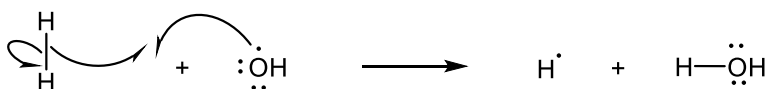
Propagation step 2

e. Calculate the respective $\Delta H°$ values (kcal mol^{-1}) for the two propagation steps. Show your work.

<div align="center">

Propagation step 1

$\Delta H° = 119 - 104 = -15$ kcal mol^{-1}

Propagation step 2

$\Delta H° = 51 - 119 = -68$ kcal mol^{-1}

</div>

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

Reaction (1) is likely faster because the rate-determining step forms the relatively strong H-F bond, compared to H-OH in (2).

"They become aggressive when you recline them."

♫ The End ♫