Chemistry 3A - Spring 2001
Midterm 1

Professor Jean Fréchet

February 20, 2001

You chemistry 3A_Frechet_

Prin spring 2001_midterm 1

You

Please check the section number and name of your GSI/TA.

___161 Padilla-De Jesus,Omayra
___171 Fox,Daniel
___181 Furuta,Paul
___191 Ling,Frank
___111 Cordaro,Joseph
___121 Le,Scheherazade
___131 Thalji,Reema
___141 Catherine Seeley
___261 Peterka,Darcy
___271 Miljanic,Ognjen
___211 Dertz,Emily
___221 Simon,Matthew
___361 Barry,David
___371 Miljanic,Ognjen
___311 Sivamani,Raja
___321 Li, Ben
___461 Huang,Alan
X 471 Liang,Catherine
___411 Phillips,Scott
___421 Saxon,Eliana
___431 Osterhout,Robin
___561 Merolle,Mauro
___511 Klopp,John
___521 Wu,Sarah
___531 Rao,Vikas

If you are making up an I-grade, indicate the semester you took 3A_____ and the Professor_____.

This exam has **10** pages; **make sure that you have them all.**

Please be sure to use the <u>very</u> useful data given on page 10.

We will only grade answers that are in the designated spaces. Please do your scratch work on the backs of the exam pages. Write only **<u>one</u>** answer to each problem; multiple answers will receive **<u>no</u>** credit, even if one of them is correct.

<u>Note:</u> This examination runs for a total of 90 minutes. No questions will be answered by proctors after the exam begins. Please write legibly; ambiguous or messy answers will receive **<u>no credit</u>**.

Do

1 2 2 2 6 6 6 3

2 b, c

4 ii (Grau)

8 (David)

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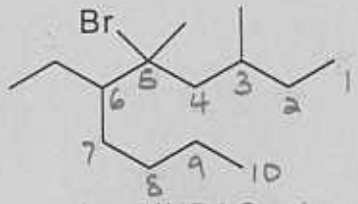
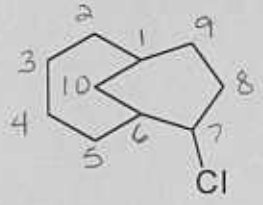
1. (10 points) Name or draw, as appropriate, the following molecules.

a. 

(use IUPAC rules of nomenclature)

5-bromo~~nyl~~- 6-ethyl-
3,5-dimethyl decane
+1

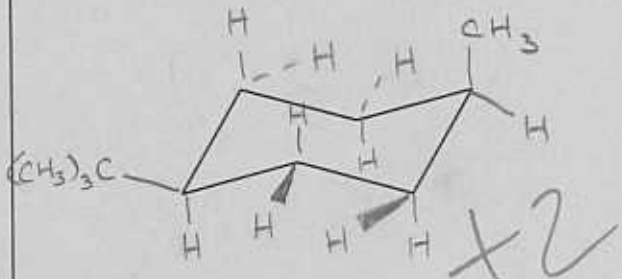
b. 

(use IUPAC rules of nomenclature)

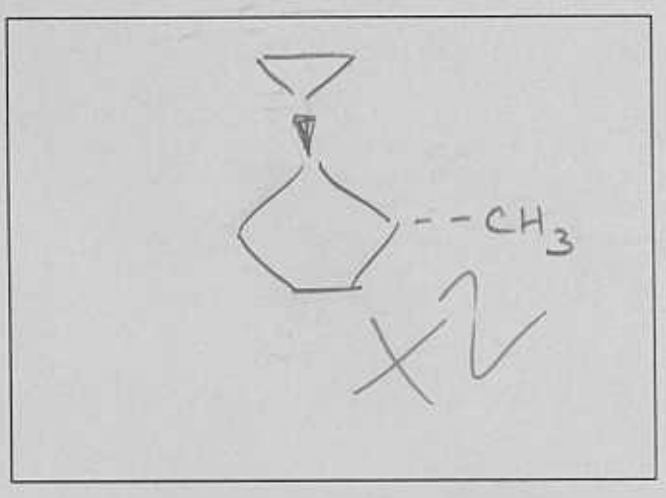
7-chlorobicyclo[4.3.1]decane
+2

c. *Cis*-t-butyl-4-methylcyclohexane

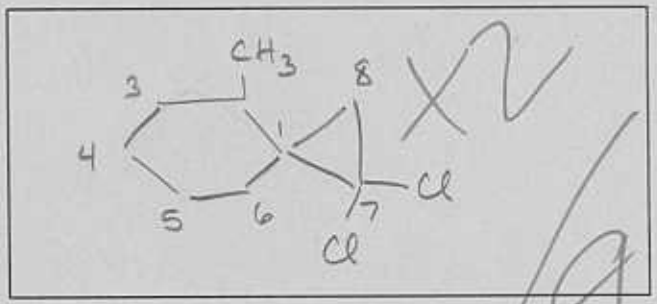
(Most stable conformation use the template provided)



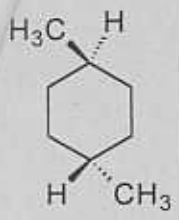
d. *Trans*-1-cyclopropyl-2-methylcyclopentane

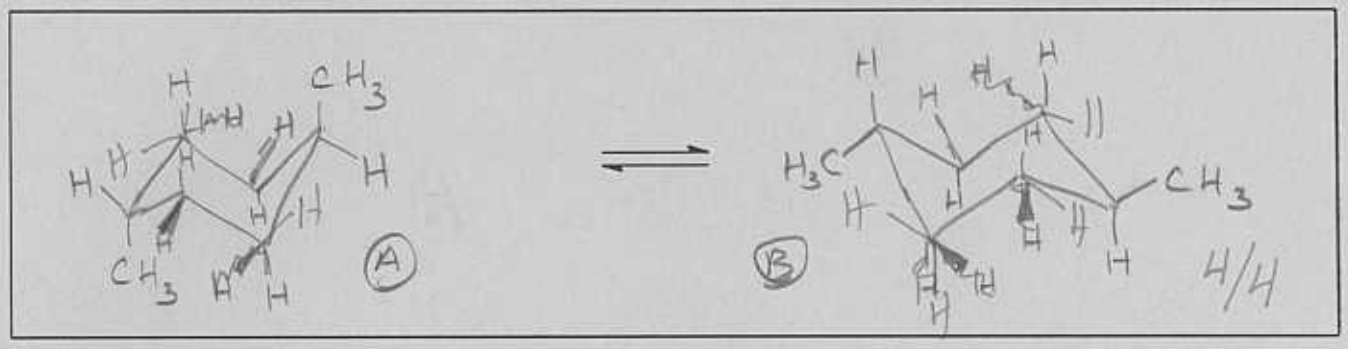


e. 7,7-dichloro-2-methylspiro[5.2]octane



2. (16 points) (a)Draw the two chair conformations of trans-1,4-dimethylcyclohexane.





4/4

Calculate ΔG°, explaining the origin of the energy difference.

In (A), there are 4 (1) $CH_3 \cdots H$ 1,3-diaxial interactions. 4×0.9 kcal/mol = 3.6 kcal/mol.

$\Delta G^\circ = -3.6$ (1) kcal/mol from (A) to (B)

3/3

Calculate the ratio of the two conformers at **100°C**, show all work.

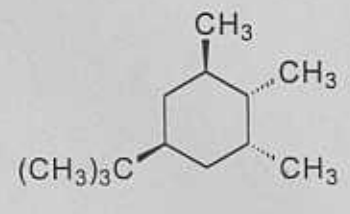
$$K_{eq} = \frac{[B]}{[A]} = e^{-\Delta G^\circ/RT} \quad (1)$$

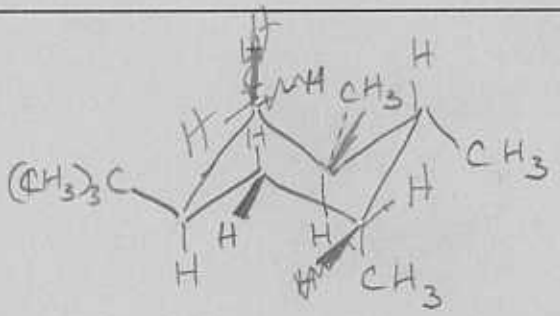
$$-\frac{\Delta G^\circ}{RT} = -\frac{(-3.6\ \text{kcal/mol})}{(2.0\ \frac{\text{cal}}{\text{deg mol}})(373\ \text{deg})} \times \frac{1000\ \text{cal}}{1\ \text{kcal}} = 4.83 \quad (1)$$

$K_{eq} = e^{4.83} = 125$ (2)

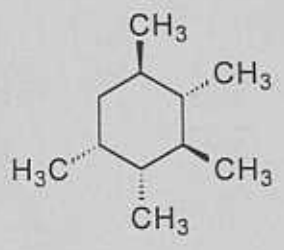
ratio = 125 to 1 B to A 3/3

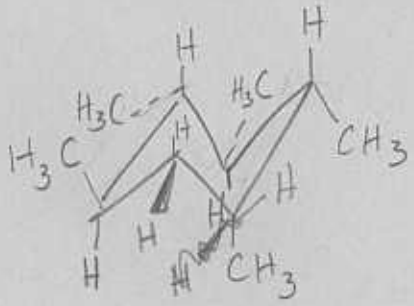
(b) Draw a structure for each of the following molecules in the more stable chair conformation.





2/3



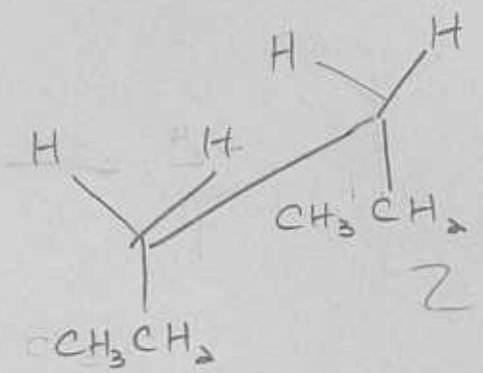


2/3

14/16

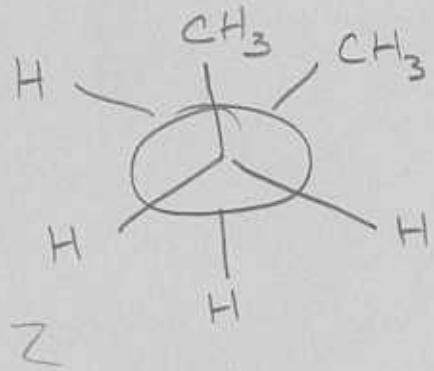
3. (12 points) 12

3a. Draw a **sawhorse** projection of the **least stable** conformation of hexane $CH_3(CH_2)_4CH_3$ as seen along the C_3-C_4 bond .



2

3b Draw a **Newman** projection of the GAUCHE conformation of butane C_4H_{10} seen along the C_2-C_3 bond.



2

3b. Write a balanced chemical equation for the combustion of propane C_3H_8 and calculate how much carbon dioxide is produced by the combustion of 44grams of propane (use C = 12, H = 1, O = 16).

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$ 2

balanced chemical equation

$$44g\ C_3H_8 \times \frac{1\ mol\ C_3H_8}{44g\ C_3H_8} \times \frac{3\ mol\ CO_2}{1\ mol\ C_3H_8} \times \frac{44g\ CO_2}{1\ mol\ CO_2} =$$ 2

Weight of carbon dioxide produced = 132g CO_2 2

3c. Match the name of a famous chemist with the following (choose amongst: Grignard, Lewis, Kekule, Bohr, Planck, Einstein, Pasteur, van der Waals, Pauling, Newman, Pauli, Shrödinger).

(i) "No orbital may be occupied by more than two electrons" — Pauli 2

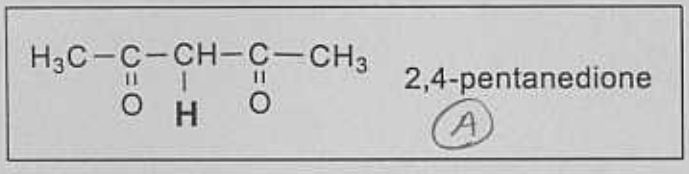
(ii) The concept of intermolecular attractive forces — van der Waals 2

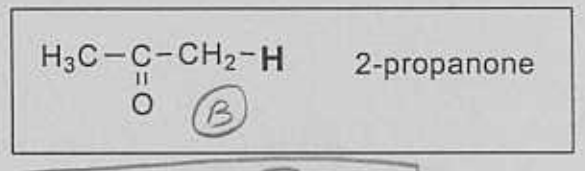
4. (13 points)

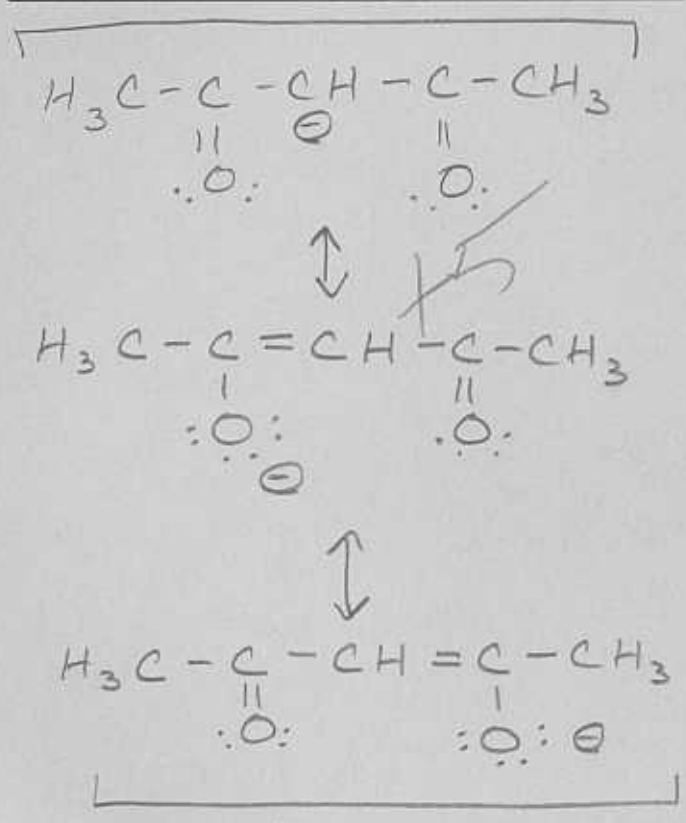
(i) Which of the following is the stronger acid, **(a)** water or **(b)** ammonia?

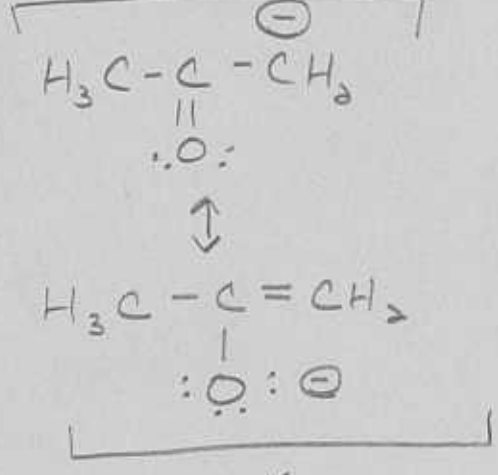
Answer: A +1

(ii) 2,4-pentanedione (pKa = 9) is a stronger acid than 2-propanone (pKa = 22). Note that in each structure below the proton involved in acid base chemistry is highlighted. Write the structure for the conjugate base of each acid and consider possible resonance forms, then explain why 2,4-pentanedione is more acidic than 2 propanone.





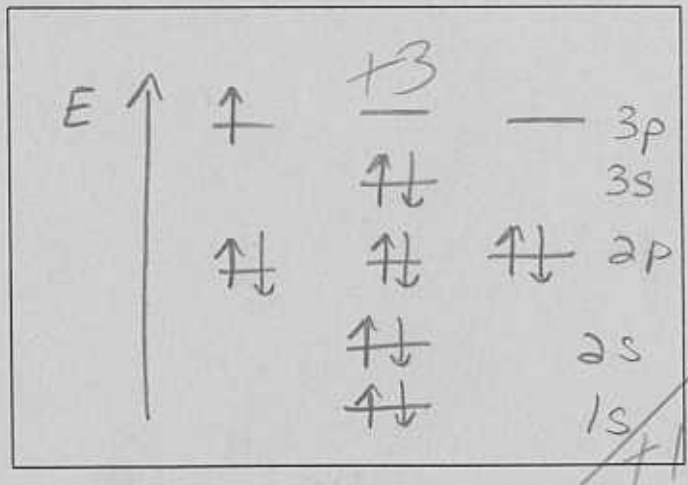




1. $pK_a = -\log K_a$
For (A) $K_a = 10^{-9}$
For (B) $K_a = 10^{-22}$
(A) is more acidic than (B) because its K_a is larger (meaning it is more likely to donate its proton) and its conjugate base has more resonance forms.

iii) Write the electronic configuration and show the orbital energy diagram for Al^{13+}.

$1s^2 2s^2 2p^6 3s^2 3p^1$ +2



+1

5. (12 points).

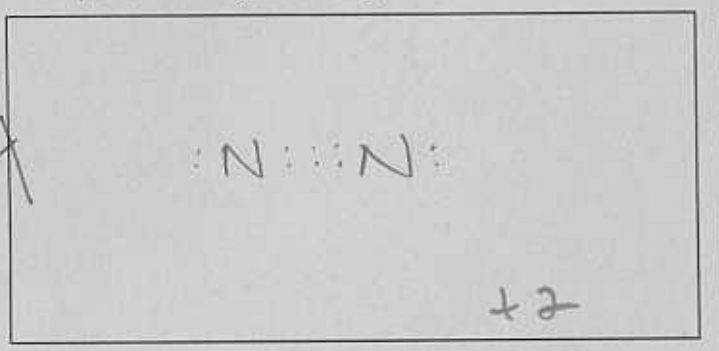
(a) Name the scientist who introduced the following concept: *"Bonds are made by the in-phase overlap of atomic orbitals".*

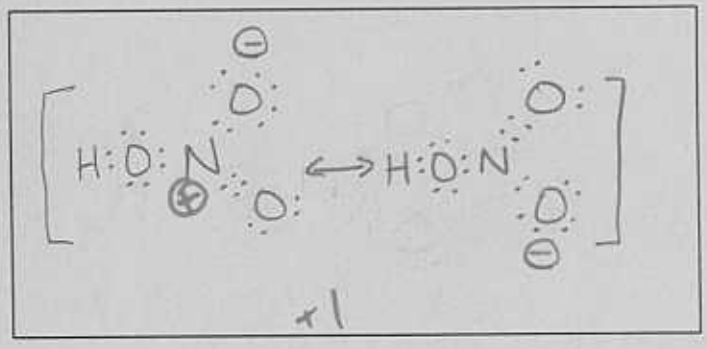
2

Answer : Pauling

(b) Write the Lewis-dot structure for nitrogen N_2 and for nitric acid HNO_3 ($HONO_2$). *(Show charges if any).*

3/4





(c) What is the shape and approximate H-C-C bond angle for the molecule of ethyne C_2H_2? Draw it in Kekule form and explain your answer using VSEPR.

3/3

$$H-\ddot{C}=\ddot{C}-H$$

The middle carbon in a H-C-C bond is attached to 3 things: a hydrogen, a carbon and a lone pair. In VSEPR, the shape would be trigonal ~~pyramidal~~, which has an angle of 120°. Since one of these things is a lone pair, which will compress the angle, the bond is bent with an angle of less than 120° (but more than 109.5° of a tetrahedral).

(d) What does the abbreviation VSEPR stand for?

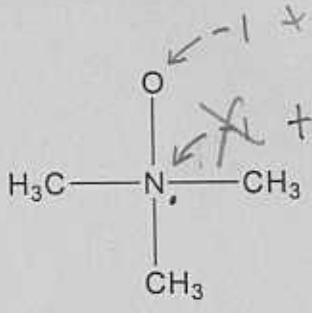
1/1

~~Visualization~~ of Spatial . . . ?

Valence Shell Electron Pair Repulsion

(e) Using arrows, show which atoms of the molecule of trimethylamine oxide have a formal charge. Specify the formal charge by writing it clearly (e.g.: +3) next to the arrow.

1/2



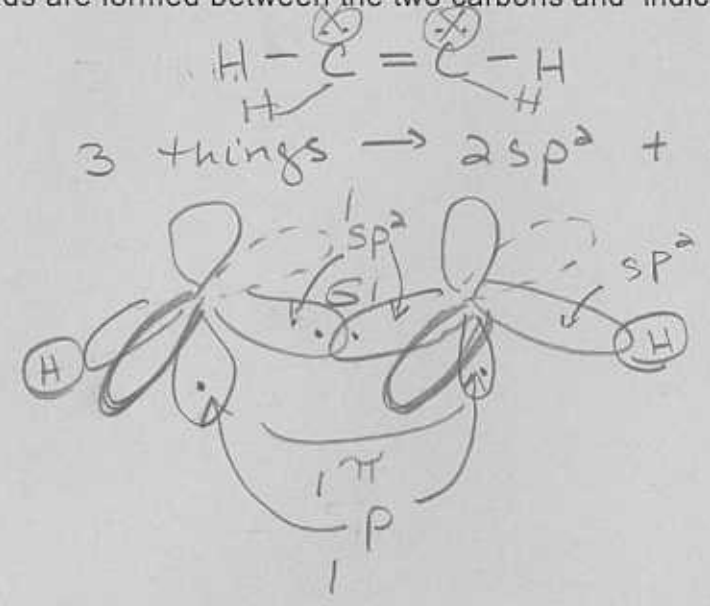
~~3 - 5 - ½(8)~~

$5 - \frac{1}{2}(8) = 1$

6

6. (14 points)

(a) What is the hybridization of C in ethene C_2H_4. Draw the orbitals involved **in bonding the two C atoms to each other**. Label these orbitals showing their type (e.g. s or sp, etc..), Explain what types of bonds are formed between the two carbons and indicate their type with a Greek letter.



4 16

overlap of π bonds
attraction of
p orbitals

(b) What is the approximate bond angle in the following triatomic molecules?

4

BeH_2	H_2S 2
Answer: 180° 2	Answer: 109.5°

(c) Name the process used to convert alkanes into aromatic compounds.

Answer: transformation ½ reforming

(d) Arrange the following alkanes in order of increasing boiling points.

(1) 2-methylbutane **(2)** propane **(3)** pentane **(4)** 2,2-dimethylpropane

0

2	3	1	4
lowest			*highest*

8

7. (11 Points) 5

(a) In 1,2-dichloroethane at room temperature, the ratio of molecules in the ANTI to GAUCHE conformation is 7.6 to 1. Calculate the difference in energy between these two conformations. Show equations and detailed calculations.

gauche ⟷ anti (1)

$K_{eq} = \frac{[anti]}{[gauche]} = \frac{7.6}{1} = e^{-\Delta G°/RT}$ (1)

(1) $-\frac{\Delta G°}{RT} = \ln K_{eq}$

$\Delta G° = -RT \ln K_{eq} = -\left(\frac{2.0 cal}{deg\ mol}\right)(298 deg) \ln 7.6 \times \frac{1\ kcal}{1000\ cal}$

$= (-)1.3$ kcal/mol

ok

Answer: −1.3 kcal/mol (2)

(b) Calculate the equilibrium constant for the reaction below.

$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$ Show detailed equations & calculations.

a₁) $CH_3COOH + H_2O \longleftrightarrow CH_3COO^- + H_3O^+$ $pK_{a_1} = 9.24$

$K_{a_1} = 10^{-9.24}$

a₂) $NH_4^+ + H_2O \longleftrightarrow NH_3 + H_3O^+$ $pK_{a_2} = 4.76$

$K_{a_2} = 10^{-4.76}$

$NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$ $K = \frac{1}{K_{a_2}} = \frac{1}{10^{-4.76}} = 10^{4.76}$

$K_{eq} = K_a \cdot K = 10^{-9.24} \cdot 10^{4.76} = 3.31 \cdot 10^{-5}$

$K_{a_1} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$ $K_{a_2} = \frac{[NH_3][H_3O^+]}{[NH_4^+][H_2O]}$

$K_{eq} = \frac{K_{a_1}}{K_{a_2}} =$

Answer: $K_{eq} = 3.31 \cdot 10^{-5}$

8. (12 points) (a) The monobromination of propane affords one major product . Write the propagation steps for the preparation of the major product and calculate ΔH° for the overall reaction.

$CH_3CH_2CH_3 + Br_2 \rightarrow CH_3CH_2CH_2Br + HBr$

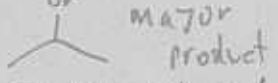
Propogation #1: $CH_3CH_2CH_3 + :\dot{B}r\cdot \rightarrow CH_3CH_2CH_2\cdot + HBr$ (+2)

Bonds broken: $CH_3CH_2CH_2-H$ 95 kcal/mol

Bonds made: $H-Br$ 88 kcal/mol

ΔH° = bonds broken - bonds made

= 95 kcal/mol - 88 kcal/mol = 7 kcal/mol



Propogation #2: $CH_3CH_2CH_2\cdot + Br_2 \rightarrow CH_3CH_2CH_2Br + :\dot{B}r\cdot$

Bonds broken: $Br-Br$ 46 kcal/mol

Bonds made: $CH_3CH_2CH_2-Br$ 68 kcal/mol

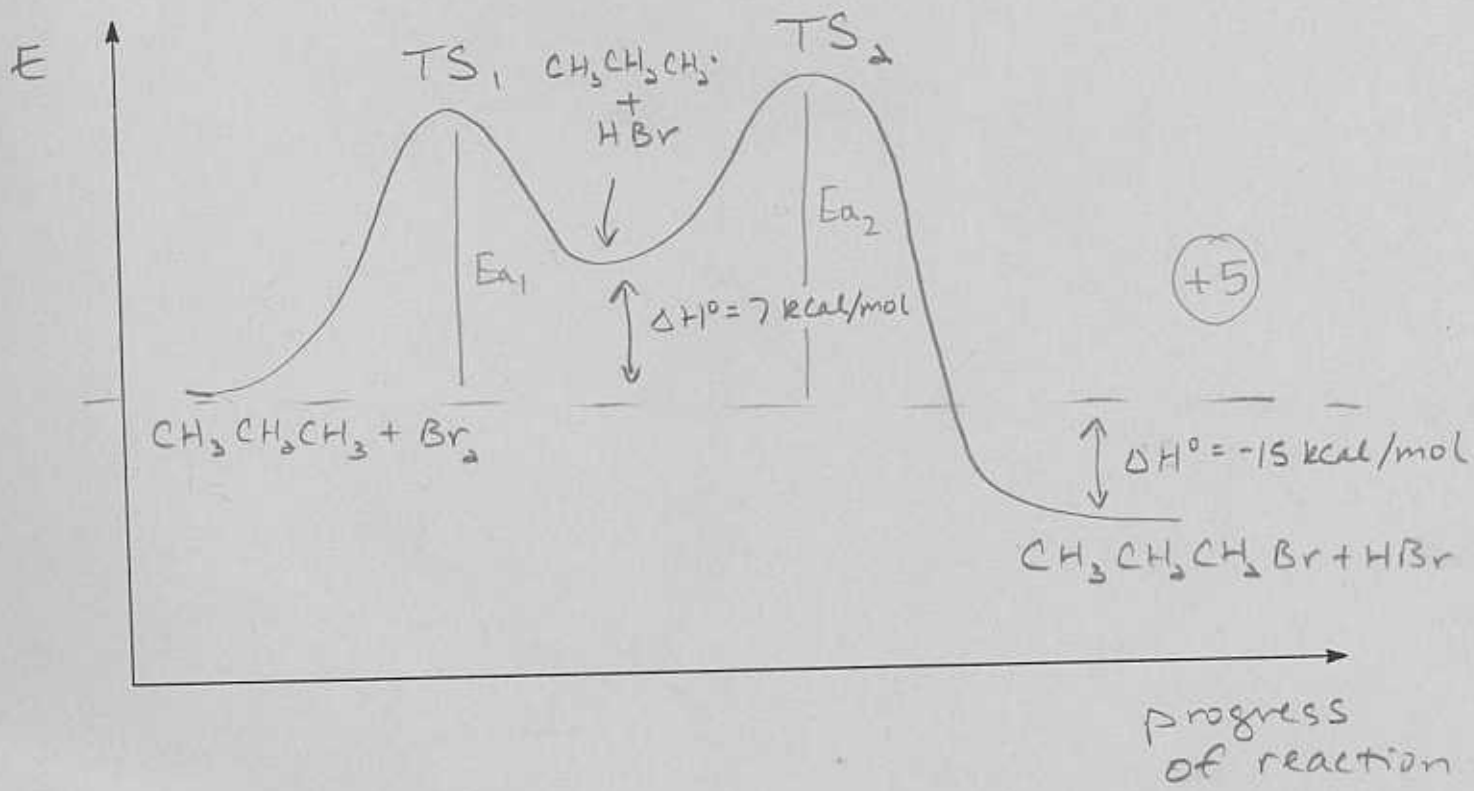
ΔH° = 46 kcal/mol - 68 kcal/mol = -22 kcal/mol

ΔH° overall = 7 kcal/mol - 22 kcal/mol

(+2)

Answer ΔH° = - 15 kcal/mol

(b) Draw and label the energy diagram for the formaton of the major monobromination product of propane.



(+5)

Note: **There are no questions to be answered on this page**, it only contains data that may be of use in solving the questions contained in this exam. Not all of the data given is needed.

Value of gas constant: R = 2.0 cal deg^{-1} mol^{-1}

Value of e (base for natural logarithms) e = 2.718

pK_a of CH_3COOH = 4.76

pK_a of NH_4^+ = 9.24

Value of absolute zero (kelvin) = -273°C

Bond dissociation energies (in kcal $mole^{-1}$): RCH_2-H 98 R_2CH-H 95 R_3C-H 91; Cl—Cl 58; Br—Br 46; H—Br 88; H—Cl 103 RCH_2-Cl 81 RCH_2-Br 68 R_2CH-Cl 80 R_2CH-Br 68 R_3C-Cl 79; R_3C-Br 65;

Values of strain energies:

Each CH_3 - H eclipsing interaction: 1.5 kcal mol^{-1}

Each H - H eclipsing interaction: 1.0 kcal mol^{-1}

Each CH_3 - CH_3 eclipsing interaction: 2.5 kcal mol^{-1}

Each CH_3 - CH_3 butane-gauche interaction: 0.9 kcal mol^{-1}

Each t-Butyl - CH_3 gauche interaction: 2.0 kcal mol^{-1}

Each CH_3 - H 1,3-diaxial interaction: 0.9 kcal mol^{-1}

Each Cl - H 1,3-diaxial interaction: 0.25 kcal mol^{-1}

Each CH_3 - CH_3 1,3-diaxial interaction: 1.6 kcal mol^{-1}

Each H - CN 1,3-diaxial interaction : 0.1 kcal mol^{-1}

Each H - $C(CH_3)_3$ 1,3-diaxial interaction: 2.5 kcal mol^{-1}

Partial periodic table of the elements

IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1 H 1.00794									2 He 4.00260
3 Li 6.941	4 Be 9.01218			5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050			13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80