Chemistry 3A - Spring 2000
Midterm 1

Professor Jean Fréchet

February 16, 2000

Your full signature_____

Print your full name_____
(Last name, First name, Middle)

Your SID_____

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

___161 Verdugo,Dawn
___171 Klopp,John
___181 Borths,Christopher
___191 Fujdala,Kyle
___111 Watkins,Gregory
___121 Blackwell,Bethany
___131 Fox,Daniel
___141 Werkema,Evan
___261 Peterka,Darcy
___271 Lee,Charles
___211 Tripp,Jennifer
___221 Padilla,Omayra
___361 Haman,Kristina
___371 Hecht,Stefan
___311 Saxon,Eliana
___321 Cook,Brian
___461 Purdy,Matthew
___471 Evans,John
___411 Holland,Andrew
___421 Duncan,Andrew
___431 Trimble,Alexander
___511 Marcaurelle,Lisa
_X_521 Jen,Wendy
___531 Ling,Frank

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.** 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 **one** answer to each problem; multiple answers will receive **no** credit, even if one of them is correct.

Note: 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 **no credit**.

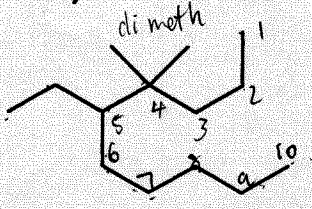
A partial periodic table and data needed for calculations can be found on page **10** of the exam.

Do Not Write in this Box.

1.	10	(13)
2.	16	(16)
3.	10	(11)
4.	7	(13)
5.	12	(12)
6.	7	(12)
7.	10	(12)
8.	7	(11)
Total	79	(100)

1. (13 points) Name or draw, as appropriate, the following molecules.

a.



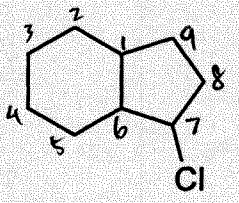
10C

(use IUPAC rules of nomenclature)

5-ethyl-4,4-dimethyldecane

3

b.

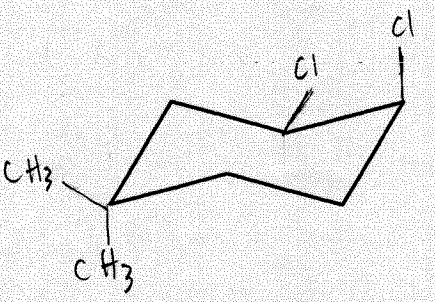


(use IUPAC rules of nomenclature)

7-chloro-bicyclo[4.3.0]nonane

2

c. cis-3,4-dichloro-1,1-dimethylcyclohexane
(chair form, use the template provided)



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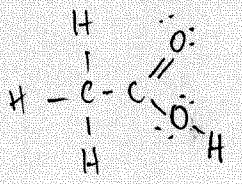
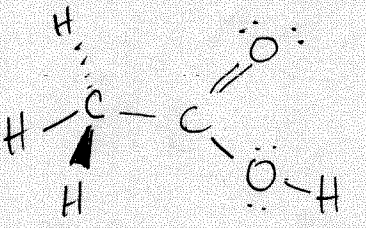
d. Acetic acid





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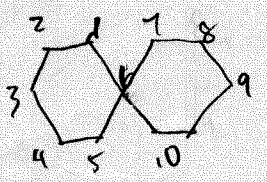
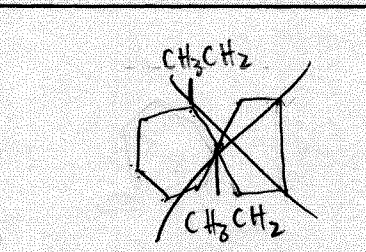
e. 1,6-dimethylspiro[4.5]decane



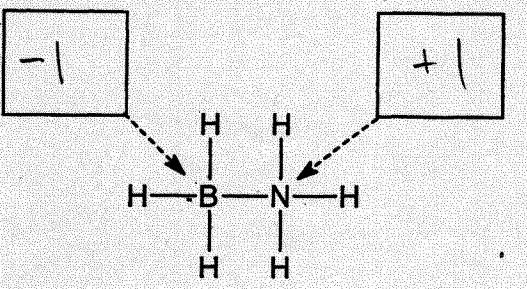


0

10

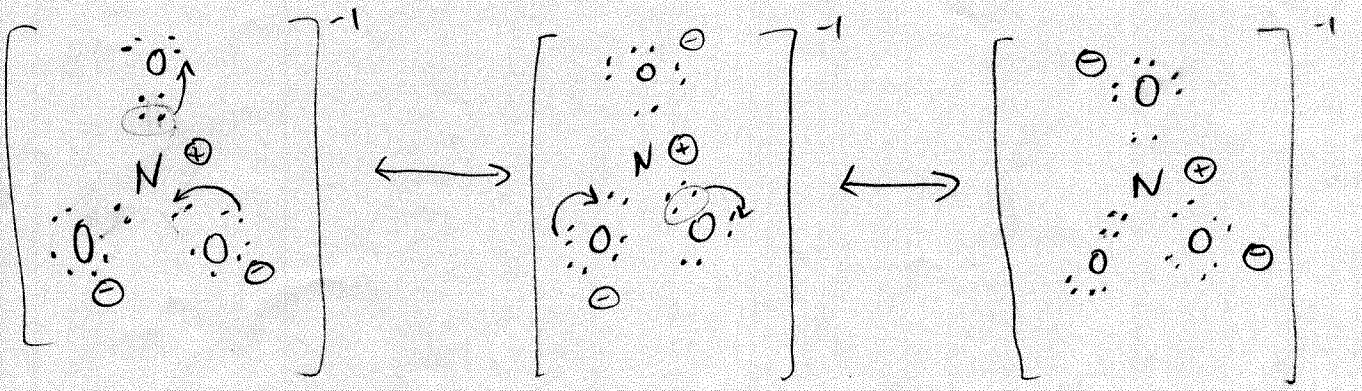
2. (16 points)

2a. Calculate the formal charge on each of the atoms indicated by an arrow in the structure below. Write the answer in the appropriate box (do not forget the sign!)



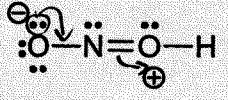
4

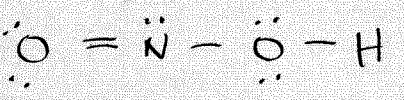
2b. Use Lewis-dot and all appropriate arrow notations to write all the major resonance forms for the NITRATE anion $[NO_3]^{-1}$ (**Hint:** *in at least one of the structures, the nitrogen atom is surrounded by three oxygen atoms and the sum of all formal charges in this ion is -1. Do not forget to use curved arrows to show the movement of electrons.)*



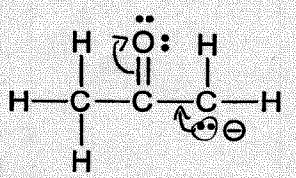
8

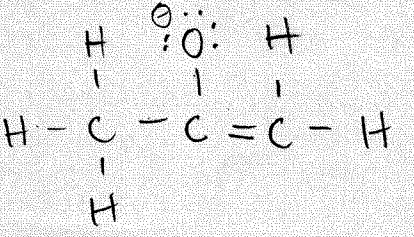
2c. For each of the structures below write **one** plausible resonance form. Use curved arrows to show the movement of electrons.





4

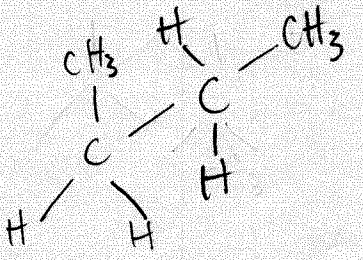




16

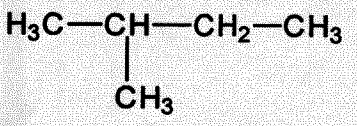
3. (11 points)

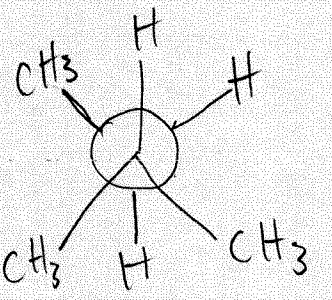
3a. Draw a sawhorse projection of the gauche conformation of butane $CH_3CH_2CH_2CH_3$ (As seen along the central C_2-C_3 bond)



3

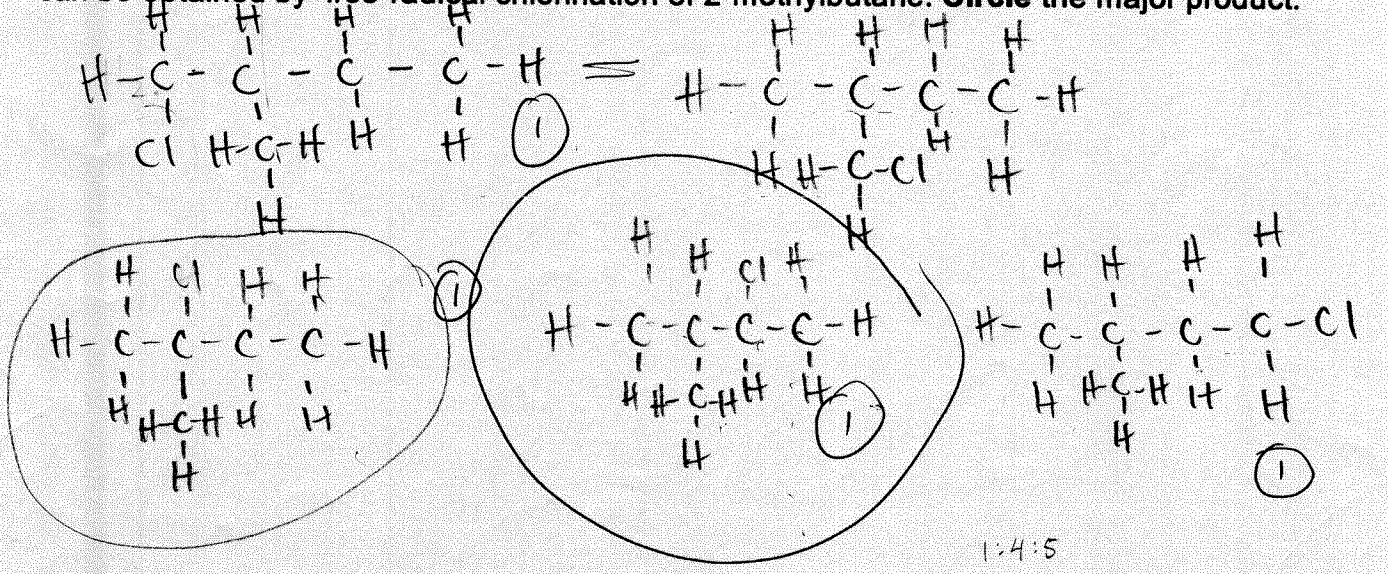
3b. Draw a Newman projection of the most stable conformation of 2-methylbutane as seen along the C2-C3 bond





3

3c. Write clear structures for all of the monochlorinated products (containing 5 C atoms) that can be obtained by free-radical chlorination of 2-methylbutane. Circle the major product.



1 : 4 : 5

1 2 1

10

4. (13 points) 7/13

(4a) Calculate $\Delta H°$ for the following reaction that takes place under strong exposure to light. (see data on page 10) Show your calculations

$$CH_3I + HI \xrightarrow{h\nu} CH_4 + I_2$$

Break bonds: $+\Delta H°$: H-I, CH_3-I | +71 +57
Create bonds: $-\Delta H°$: CH_3-H, I-I | -105 -36
} $\Delta H°$ = -3

Answer: $\Delta H°$ = $-13 \frac{kcal}{mol}$

(4b) Write an equation for the initiation step for the radical chain reaction above

$I_2 \xrightarrow{h\nu} 2I\cdot$

$CH_3-I \xrightarrow{h\nu} CH_3\cdot + I\cdot$

$CH_3\cdot + HI \rightarrow CH_4 + I\cdot$

$I\cdot + CH_3-I \rightarrow I_2 + CH_3\cdot$

(4c) Write the propagations steps for the radical chain reaction of part 4a above

$I\cdot + CH_3-H \rightarrow CH_3\cdot + HI$

$CH_3\cdot + I_2 \rightarrow CH_3I + I\cdot$

(4d) Consider the equilibrium below for which the equilibrium constant is 0.4. Write an equation for the equilibrium constant and calculate the percentage of butane gauche conformer at equilibrium. Show the details of your calculation.

Butane anti conformer $\rightleftharpoons$ Butane gauche conformer

$K_{eq} = 0.4$ $\quad \Delta G° = -(0.9 \frac{kcal}{mol}) - 0 = 0.9 \frac{kcal}{mol}$ 4

$\Delta G° = -RT \ln K_{eq}$

$0.9 = -(2 \frac{cal}{K\,mol})(T) \ln K_{eq}$

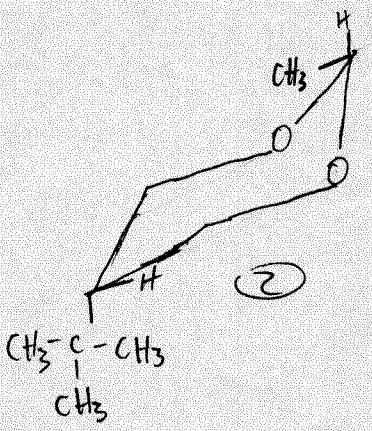
$K_{eq} = 0.4 = \frac{[gauche]}{[anti]}$

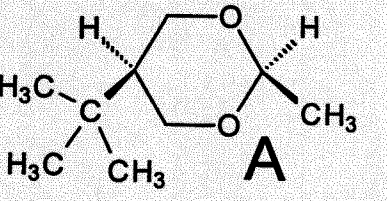
0.4 gauche : 1.0 anti

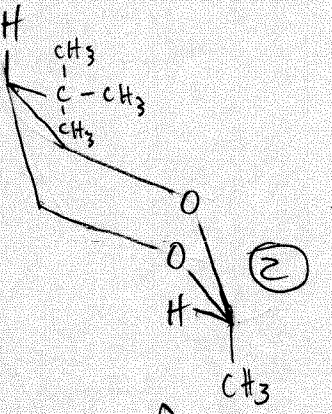
$\frac{0.4}{1.0+0.4} \times 100\% = 28.6\% \sim 29\%$

Answer: 29% or 30% (with sig figs)

5. (12 points) (a) Draw the two chair conformations for compound **A**. Surprisingly, the equilibrium between these conformations favors that with the t-butyl group *axial.* Compare the two structures and explain clearly (with words and energy values) the reasons for this unexpected finding.







for t-butyl

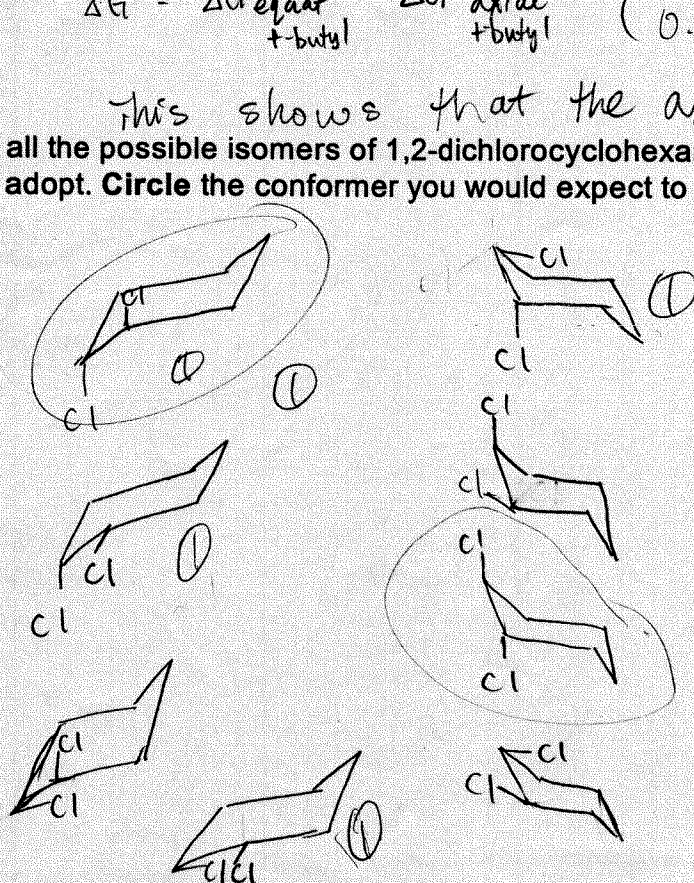
Due to the fact that instead of a 6 carbon ring we have a 4C, 2O ring, the axial t-butyl group won't have any diaxial interactions with H because the oxygens aren't bonded to any H's ① At the equatorial position the methyl group has 2 diaxial ① interactions

$\Delta G^\circ = \Delta G^\circ_{\text{equat t-butyl}} - \Delta G^\circ_{\text{axial t-butyl}} = \left(0.9 \frac{\text{kcal}}{\text{mol}}\right) \times 2 - 0 = 1.8 \frac{\text{kcal}}{\text{mol}}$ ①

This shows that the axial t-butyl position is more stable.

(b) Draw all the possible isomers of 1,2-dichlorocyclohexane showing all the chair conformations they may adopt. Circle the conformer you would expect to have the smallest dipole moment.

7/7



less dipole moment means trans arrangement with axial Cl

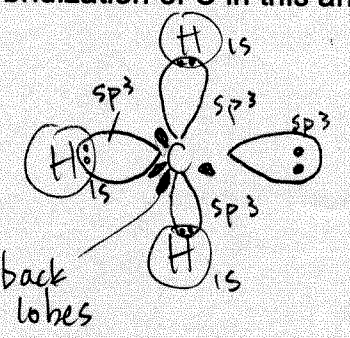
5/5

12/12

6. (12 points) (a) Draw a clear structure showing all orbitals of the methyl anion. What is the shape of the anion? what is the hybridization of C in this anion? What is the value of the H-C-H bond angle? (Hint: Use VSEPR)

$^{\ominus}CH_3$

3

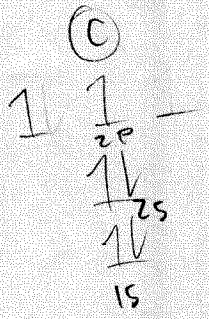


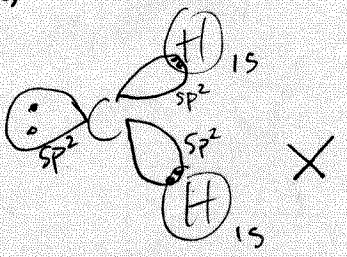
tetrahedral, sp^3 hybridized

Shape: tetrahedral ✗ Hybridization: sp^3 ✓ H-C-H bond angle: a little less than 109.5° ✓ due to the e^- pair

(b) Singlet methylene :CH_2 is an ususual moiety in which the two non-bonding electrons are paired in a single orbital. Draw a clear structure of singlet methylene showing all orbitals. What is the shape of the molecule? What is the hybridization of C? What is the value of the H-C-H bond angle? (Hint: Use VSEPR)

1





✗

2

Shape: trigonal planar ✗ Hybridization: sp^2 ✓ H-C-H bond angle: a little less than 120° due to e^- lone pair ✓

(c). Write the electronic configuration for Silicon (Si, Z = 14)

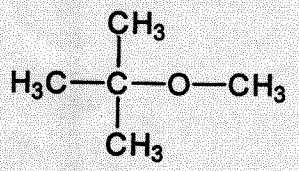
Answer: $1s^2 2s^2 2p^6 3s^2 3p^2$ ✓

2

17

(2)

7. (12 Points) (a) The fuel additive MTBE has the formula given below. Calculate how many grams of oxygen would be required for the complete combustion of 8.8 grams of MTBE. (C = 12.0; H = 1.00; O = 16.0). Show a balanced equation and the details of your calculation.



$$2C_5H_{12}O + 15O_2 \xrightarrow{\Delta} 10CO_2 + 12H_2O \quad +2$$

$$8.8\,g \times \frac{1\,mol\,C_5H_{12}O}{88\,g} \times \frac{15\,O_2}{2\,mol\,C_5H_{12}O} = 0.75\,g\,O_2$$

$$15\,mol\,O_2 \times \frac{32\,g\,O_2}{1\,mol\,O_2}$$

Answer: Weight of oxygen $0.75\,g\,O_2$

(b) calculate the equilibrium constant for the reaction of CH_4 with Cl_2 to give CH_3Cl and HCl at 127°C.

For this reaction ΔS = +0.004 kcal mole^{-1} K^{-1} Show the details of your calculations.

Note that other useful data is given on the last page of the exam.

(8)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad +2 \qquad \Delta H^\circ = (105+58) - (85+103)$$

$$\Delta G^\circ = -RT\ln K_{eq} \quad +2 \qquad = -25\ \frac{kcal}{mol}$$

$$CH_4 + Cl_2 \xrightarrow{127^\circ} CH_3Cl + HCl$$

$$\Delta G^\circ = -25\ \frac{kcal}{mol} - (400K)\left(0.004\ \frac{kcal}{mol\,K}\right)$$

$$= -26.6\ \frac{kcal}{mol} \quad +2$$

$$-26.6 = -\left(2.0\ \frac{cal}{K\,mol}\right)(400K)\ln K_{eq}$$

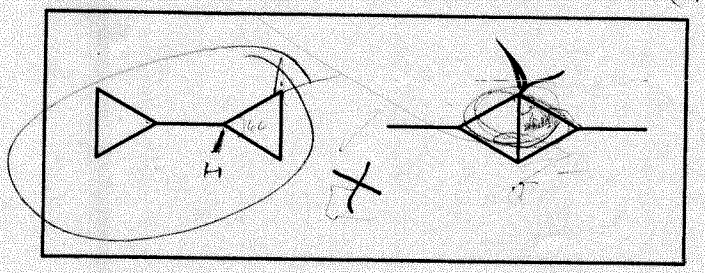
$$33.25 = \ln K_{eq} \qquad +2$$

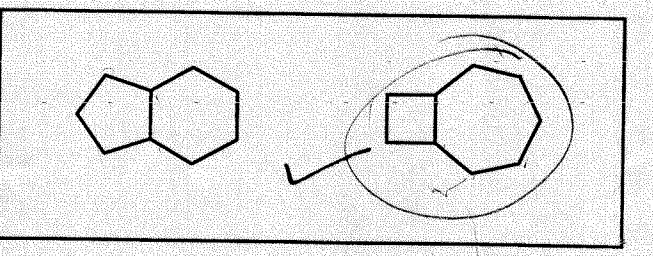
Answer: $K_{eq} = 2.8 \times 10^{14}$

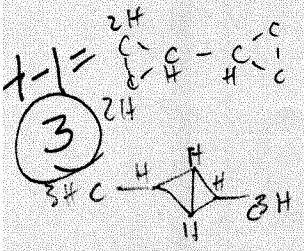
10/12

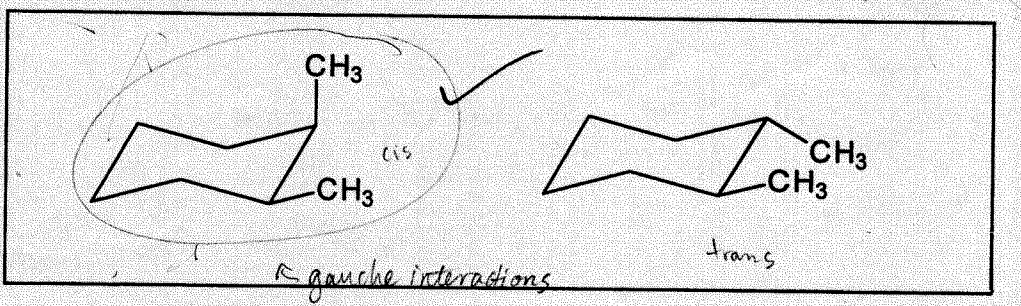
8. (11 points) *For multiple choice questions 5a-c, credit will be given for each correct answer, and 1 point will be deducted for each incorrect answer (no credit if no answer is given). For questions 5d and 5e, credit will only be given for correct answers (incorrect answers will not be penalized).*

5a. Consider the following pairs of isomeric compounds. Within each pair circle the compound that has the higher heat of combustion. → (more strain E)









5b. For each pair of compounds, circle the stronger acid

Nitric acid HNO_3 pKa = -1.3	Picric acid pKa = 0.4
H_2O pKa = 15.7	$HC\equiv CH$ pKa = 25

pKa = -log Ka

5c. Circle the strongest base (hint: consider the pKa values given in 5b)

$NO_3^{\ominus}$ $HO^{\ominus}$ $HC\equiv C^{\ominus}$

$10^{-25} = Ka$

$Kw = KaKb$ $Kb = 10^{11}$

5d. In a competition reaction, equimolar amounts of the four alkanes listed below were allowed to react with a limited amount of Cl_2 at 300°C. Which one of these alkanes would be depleted most from the mixture? (a) Propane, (b) 2-Methylpropane, (c) Pentane, (d) Butane

Answer: B

A) 1:4:5 B) 6:8:0 C) 9:0:5 D) 6:24:0 6:16 or

5e. A certain organic compound was found on combustion analysis to contain 84% carbon and 16% hydrogen (C = 12.0 and H = 1.00). A molecular formula for the compound could be:

(a) $C_7H_{16}O$ (b) C_6H_{12} (c) $C_{14}H_{32}$ (d) C_2H_4 (e) $C_{14}H_{22}$

7C 16H

Answer: C

17

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

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

Bond dissociation energies (in kcal $mole^{-1}$): Cl-Cl 58; CH_3-H 105; CH_3-Cl 85; H-Cl 103

CH_3-I 57; H-I 71; I-I 36

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

GROUP	I A	II A	III B	IV B	V B	VI B	VII B	0
VALENCES	+1	+2	+3	−4 +4	−3 +5	−2 +6	−1 +7	0
PERIOD 1	1 H 1.008							2 He 4.003
2	3 Li 6.941	4 Be 9.012	5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3