Chemistry 3A - Spring 2000
Midterm 1

Professor Jean Fréchet
February 16, 2000

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
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.

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

a. \[ \text{5-ethyl-4,4-dimethyldecane} \]
   (use IUPAC rules of nomenclature)

b. \[ \text{7-chloro bicyclo[4.3.0]nonane} \]
   (use IUPAC rules of nomenclature)

c. \[ \text{cis-3,4-dichloro-1,1-dimethylcyclohexane} \]
   (chair form, use the template provided)

d. \[ \text{Acetic acid} \]

e. \[ \text{1,6-dimethylspiro[4.5]decane} \]
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!)

\[ \text{Formal charges: } \]

2b. Use Lewis-dot and all appropriate arrow notations to write all the major resonance forms for the NITRATE anion \([\text{NO}_3]^\text{-1}\) (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.)

\[ \text{Resonance forms: } \]

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

\[ \text{Resonance structures: } \]
3. (11 points)

3a. Draw a sawhorse projection of the gauche conformation of butane CH₃CH₂CH₂CH₃
(As seen along the central C₂-C₃ bond)

3b. Draw a Newman projection of the most stable conformation of 2-methylbutane as seen along the C2-C3 bond
H₃C—CH—CH₂—CH₃

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.
4. (13 points)

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

$$\text{CH}_3\text{I} + \text{HI} \xrightleftharpoons[\text{hv}]{\text{hv}} \text{CH}_4 + \text{I}_2$$

Break bonds: $+ \Delta H^\circ$: $\text{H-I, CH}_3\text{I}$
Create bonds: $- \Delta H^\circ$: $\text{H}_2\text{H, I-I}$

$$+71 + 57 \quad \Delta H^\circ: -105 - 36$$

Answer: $\Delta H^\circ = -13 \text{ kcal/mol}$

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

$$\text{I}_2 \xrightarrow[\text{hv}]{\text{hv}} 2\text{I}^\cdot$$

$$\text{CH}_3\cdot + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}^\cdot$$

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

$$\text{I}^\cdot + \text{CH}_3\cdot \rightarrow \text{CH}_3\text{I}^\cdot$$

(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

$$\text{Keq} = 0.4 \quad \Delta G^\circ = -6.9 \text{ kcal/mol} - 0 = -0.9 \text{ kcal/mol}$$

$$\Delta G^\circ = -RT \ln \text{Keq}$$

$$0.9 = -\frac{20 \text{ kcal/mol}}{T} \ln 0.4$$

$$0.4 \text{ gauche: } 1.0 \text{ anti}$$

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

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.

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 di axial interactions with it because the oxygens aren't bonded to any H's. At the equatorial position the methyl group has 2 di axial interactions.

\[
\Delta G^\circ = \Delta G^\circ_{\text{equat}} - \Delta G^\circ_{\text{axial}} = \frac{(0.9 \text{ kcal/mol}) \times 2}{\text{mol}} - 0 = 1.8 \text{ kcal/mol}
\]

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.

less dipole moment means trans arrangement with axial Cl
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)

(b) Singlet methylene :CH₂ is an unusual 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)

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

Answer:

\(1s^2 2s^2 2p^6 3s^2 3p^2\)
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.

\[
\text{H}_3\text{C}-\text{C}-\text{O}-\text{CH}_3
\]

\[
2\text{C}_8\text{H}_{12}\text{O} + 15\text{O}_2 \rightarrow 10\text{CO}_2 + 12\text{H}_2\text{O} + 2
\]

\[
8.8 \text{ g} \times \frac{1\text{ mole C}_8\text{H}_{12}\text{O}}{88\text{ g}} \times \frac{15\text{ mol O}_2}{2\text{ mol C}_8\text{H}_{12}\text{O}} = 0.75 \text{ g O}_2
\]

\[
\text{Answer: Weight of oxygen} \quad 0.75 \text{ g O}_2
\]

(b) calculate the equilibrium constant for the reaction of \( \text{CH}_4 \) with \( \text{Cl}_2 \) to give \( \text{CH}_3\text{Cl} \) and \( \text{HCl} \) at 127°C. For this reaction \( \Delta S = +0.004 \text{ kcal mole}^{-1} \text{ K}^{-1} \). Show the details of your calculations. Note that other useful data is given on the last page of the exam.

\[
\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} + 2
\]

\[
\Delta H^{\circ} = (105 + 58) - (85 + 103)
\]

\[
\Delta G^{\circ} = -RT \ln K_a + 2 = -25 \text{ kcal mol}^{-1}
\]

\[
\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}
\]

\[
\Delta G^{\circ} = -25 \text{ kcal mol}^{-1} - (400K)(0.004 \text{ kcal mol}^{-1})
\]

\[
= -26.6 \text{ kcal mol}^{-1} + 2
\]

\[
-26.6 = -(2.0 \text{ kcal mol}^{-1})(400K) \ln K_a
\]

\[
33.25 = \ln K_{eq} + 2
\]

\[
\text{Answer: } K_{eq} = 2.8 \times 10^{14}
\]
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.

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

<table>
<thead>
<tr>
<th>Nitric acid</th>
<th>Picric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td></td>
</tr>
<tr>
<td>pKₐ = -1.3</td>
<td>pKₐ = 0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H₂O</th>
<th>HC≡CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKₐ = 15.7</td>
<td>pKₐ = 25</td>
</tr>
</tbody>
</table>

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

5d. In a competition reaction, equimolar amounts of the four alkanes listed below were allowed to react with a limited amount of Cl₂ 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: [Diagram]

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) C₇H₁₈O  (b) C₆H₁₂  (c) C₁₄H₃₂  (d) C₂H₄  (e) C₁₄H₂₂

Answer: [Diagram]
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: \( R = 2.0 \text{ cal deg}^{-1} \text{ mol}^{-1} \)

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**

<table>
<thead>
<tr>
<th>GROUP</th>
<th>IA</th>
<th>II A</th>
<th>III B</th>
<th>IV B</th>
<th>VB</th>
<th>VI B</th>
<th>VII B</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>VALENCES</td>
<td>+1</td>
<td>+2</td>
<td>+3</td>
<td>-4</td>
<td>-3</td>
<td>-2</td>
<td>-1</td>
<td>0</td>
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<tr>
<td>PERIOD</td>
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<td>Rb</td>
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<td>In</td>
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<td>I</td>
<td>Xe</td>
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<td>118.7</td>
<td>121.8</td>
<td>127.6</td>
<td>126.9</td>
<td>131.3</td>
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