Chem 314

Spring, 2006
Midterm Exam
Chem 314

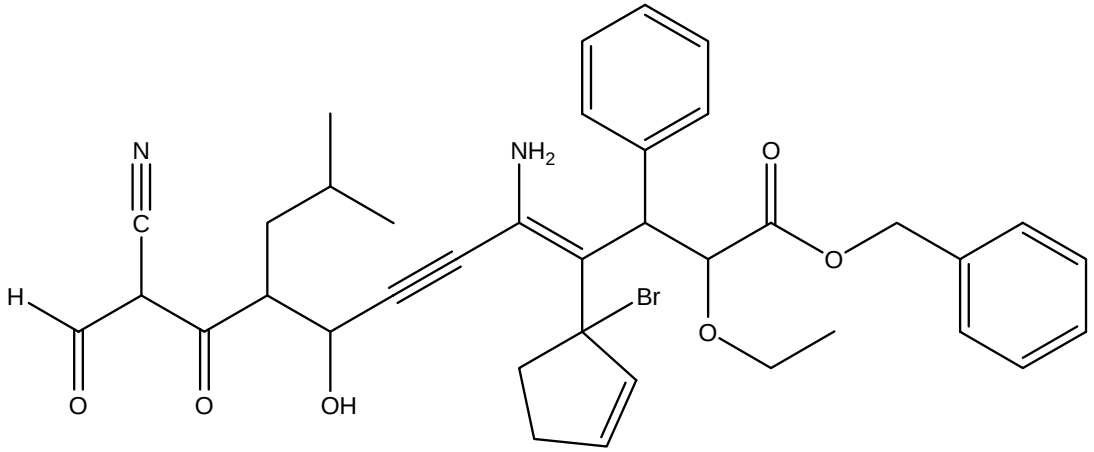
Name _____

Problem	Points	Credit
1. Nomenclature	25	
2. 2D Lewis structures	20	
3. 3D Structures, Formal Charge & Resonance	30	
4. Formulas, Functional Groups & Special Nomenclature Terms, Specific Bond Energies	20	
5. Thermodynamics, Bond Energies & Reactions	26	
6. Conformations, Energy (cylclohexanes & chains), Newman projections	32	
7. Physical Properties	12	
Total	165	

This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement wherever necessary. Also, consider the point values in your choice of questions. Do your best to show me what you know in the available time.

The immediate is often the enemy of the ultimate. Indira Gandhi

1. Provide an acceptable name for the following structure. (25 pts)

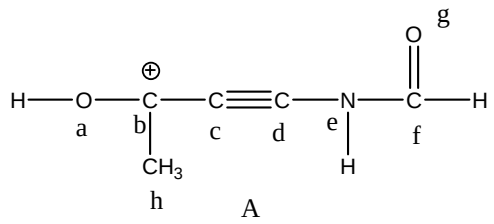


2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present, all lone pair electrons and completely draw out all atoms (e.g. do not write CH_3). (20 pts)

six carbon ring ↓ has formal charge ↓

$(CH_3)HNOCCHC(OCH_3)CHCNCOCHNH_2CHOHCH_2CCC_6H_4C(CH_3)_2CH(CHO)CO_2CH_2CH(NO_2)CO_2H$

3. First, draw three other reasonable 2D resonance structures that <u>delocalize the positive charge</u>. Include proper arrow conventions. Rank your structures from best (= 1) to poorest. Draw a three-dimensional Lewis structure for the given representation and the best resonance structure among B, C and D. Show σ bonds as lines, wedges and dashes and the p orbitals in π bonds, as well as any orbitals holding lone pairs. Draw two dots for lone pair and pi bond electrons. Indicate any formal charge present and give the hybridization, bond angles and shape of each nonhydrogen atom (below). <u>Assume that all non-hydrogen atoms have full octets, unless a carbocation is written</u>. (30 pts)



A

B

D

C

3D (A) 3D (best other)

Use structure A to fill in the following table.

	Hybridization	Angles	Shape	#σ bonds	#π bonds	lone pairs
a						
b						
c						
d						
e						
f						
g						

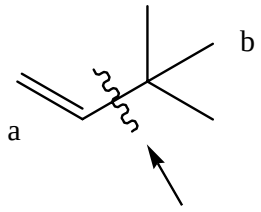
h

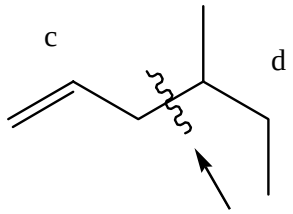
4. a. Use the given formula to provide an example that includes the listed functional groups. If you draw any other functional groups, identify them as well. Calculate the degree of unsaturation for your formula. (12 pts)

$C_{15}H_{20}ClNO_5$ degree of unsaturation calculation

alkyne, alkene, amine, ester,
ether, ketone, acid chloride

b. Indicate the bond energy between the two atoms indicated. Use the specific bond energy table provided on the last page. Write the common nomenclature term of each carbon group about the bond energy requested. Draw an arrow to any part of any structure to indicate where a methyl, methylene, methine, primary, secondary, tertiary and quaternary carbon is located. A table of bond energies is provided on the last page (8 pts)





indicate bond energy between a-b _____

common name of fragment "a" _____

common name of fragment "b" _____

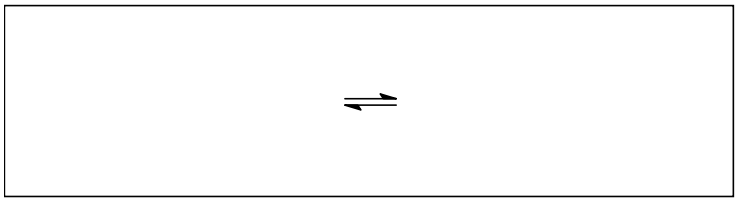
indicate bond energy between c-d _____

common name of fragment "c" _____

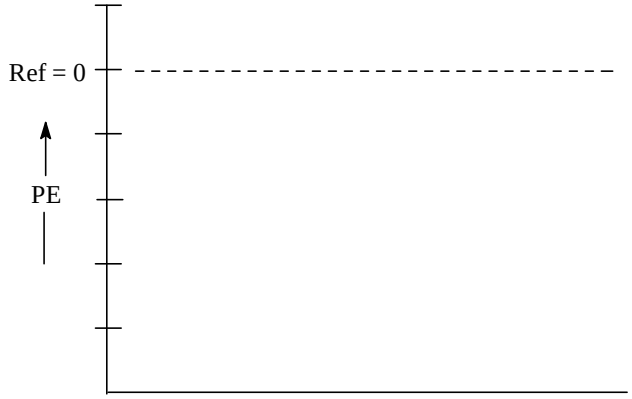
common name of fragment "d" _____

5. a The heat of combustion of **butanol** is –598.8 kcal/mole. Limited heats of formation are provided below. Write an equation for this reaction. Use this information to calculate a heat of formation for butanol. Draw an energy diagram that includes the zero energy reference point and the various other energy values. If you don't know the structure of butanol, it will be given provided for 2 points. (15 pts)

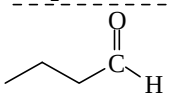
Combustion equation:



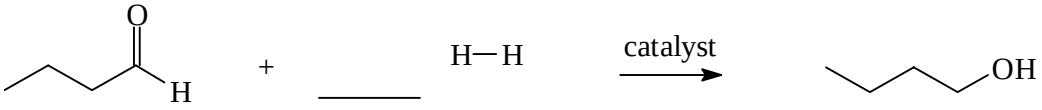
Show work.



Energy Diagram

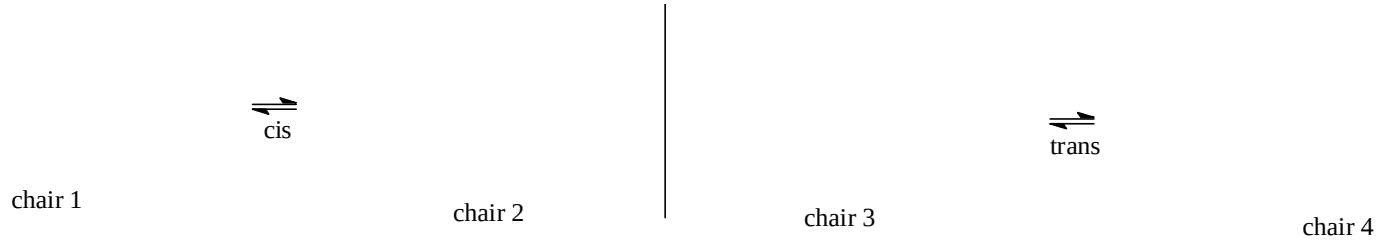
	ΔH_f^o (kcal/mole)
CO_2	-94.0
H_2O	-57.8
	-49.0

b. Calculate the heat of reaction for the equation below. Clearly show your set up and the appropriate energy values. (4 pts)



c. Calculate the same heat of reaction, as in part b, using the **average** bond energies on the last page. How does this value compare to that of part b? Hint: You may need to solve for a pi bond energy. (7 pts)

6. a. Draw both chair conformations of cis-1-ethyl-3-methylcyclohexane and trans-1-ethyl-3-methylcyclohexane. Draw all axial and equatorial groups at substituted positions. Indicate which conformation is more stable in each pair. Which conformation, overall, is most and least stable? (12 pts)



most stable (1 or 2) = _____

most stable overall (1,2,3,4) = _____

most stable (3 or 4) = _____

least stable overall (1,2,3,4) = _____

b. Given that the heats of combustion of cis-1-ethyl-3-methylcyclohexane and trans-1-ethyl-3-methylcyclohexane are -1317.1 and -1319.0 respectively, which one is more stable and by how much? Propose a possible explanation for why one is more stable than the other (use structures, if it helps your explanation). Hint: Use the most stable conformation of each isomer. (3 pts)

c. Use the second most stable conformation from part a, and draw a Newman projection using bonds $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ for your structure (or…$C_6 \rightarrow C_1$ and $C_4 \rightarrow C_3$). Point out any gauche relationships in the branches and/or the ring. (5 pts)

d. Use a Newman projection of the C2→C3 bond of 2-methylbutane to show the most stable and least stable conformations. Using the energy values provided, calculate the energy difference between these two conformations. Calculate a $K_{equilibrium}$ and use it to estimate the ratio of each conformation at equilibrium. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection. Assume R = 2 cal/mol-K and T = 300 K. (12 pts)

Eclipsing Energy Values (kcal/mole)	
H/H	+1.0
H/CH_3	+1.3
CH_3/CH_3	+2.5
gauche	+0.8

most stable
(show work)

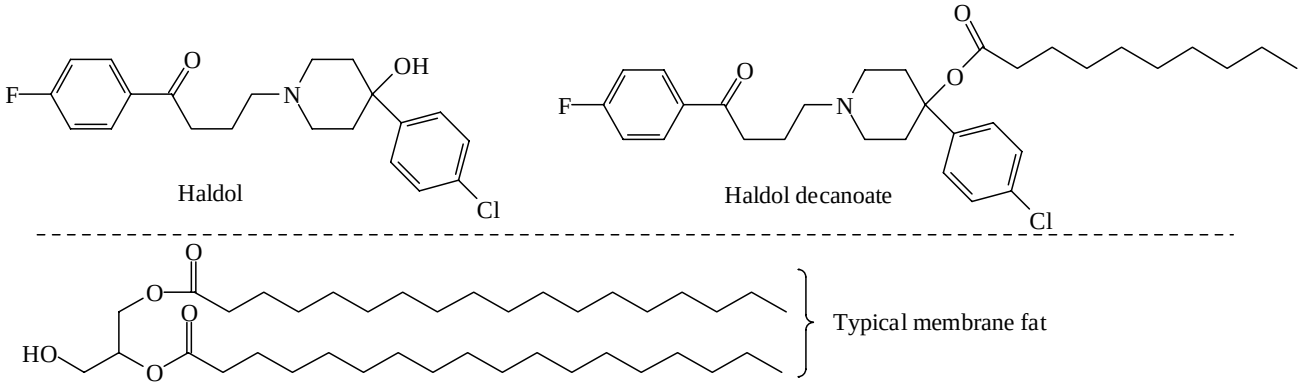
least stable
(show work)

$$\Delta G \approx \Delta H$$

$$K_{eq} = 10^{\frac{-\Delta G}{2.3RT}}$$

2D structure

7. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug was prepared to increase Haldol's lifetime in the body. When injected intramuscularly its anti-psychotic activity lasted about 1 month. Provide an explanation for its longer lifetime. (12 pts)



Typical Bond Energies for Common Substitution Patterns Found in Organic Chemistry (X-Y)

Y =	H-	Me-	Et- (1^o)	i-Pr- (2^o)	t-Bu- (3^o)	Ph- (phenyl)	F-	Cl-	Br-	I-	HO-	H_2N-	N≡C-
X =													
CH_3- methyl (Me-)	105	90	86	86	84	102	110	85	71	57	93	85	122
CH_3CH_2- primary (Et-)	98	86	82	81	79	98	108	80	68	53	92	82	118
$CH_3CH_2CH_2$- primary (Pr-)	98	86	82	80	79	98	107	81	68	53	92	82	117
$(CH_3)_2CH$- secondary (i-Pr-)	95	86	81	79	76	96	106	80	68	54	93	82	116
$(CH_3)_3C$- tertiary (t-Bu-)	93	84	79	76	71	93	110	80	67	52	93	82	-
C_6H_5- phenyl (Ph-)	111	102	97	96	93	115	126	96	80	65	111	102	131
$C_6H_5CH_2$- benzyl (Bn-)	88	76	72	71	70	90	-	72	58	48	81	71	-
CH_2=$CHCH_2$- allyl (al-)	86	74	70	70	67	-	-	68	54	41	78	-	-
CH_3CO- acyl (Ac-)	86	81	76	74	72	94	119	81	66	49	107	-	-
CH_3CH_2O- alkoxy	104	83	82	-	-	101	-	-	-	-	44	-	-
CH_2=CH- vinyl	110	100	96	95	90	103	-	90	78	-	-	-	130
H- hydrogen-	104	105	98	95	93	111	136	103	88	71	119	107	125

X—Y ⟶ X· ·Y (homolytic cleavage)

Average Bond Energies (kcal/mole)

	H	C	Si	N	O	S	F	Cl	Br	I
H	104	98	76	92	109	83	135	103	87	71
C		81	72	82	92	65	116	79	66	52
Si			-	-	108	-	135	91	74	56
N				39	39	-	65	46	-	-
O					34	-	45	52	48	56
S						60	-	61	52	-
F							37	-	-	-
Cl								58	-	-
Br									46	-
I										36

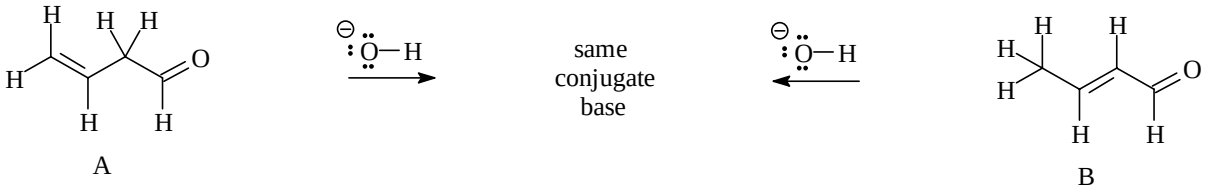
Bond Energy for multiple bonds

C═C	146
C═N	147
C═O	176
C≡C	200
C≡N	213

There is no shortcut to self-improvement. Alima Oyun

Not used on this exam, but consider as a possible question.

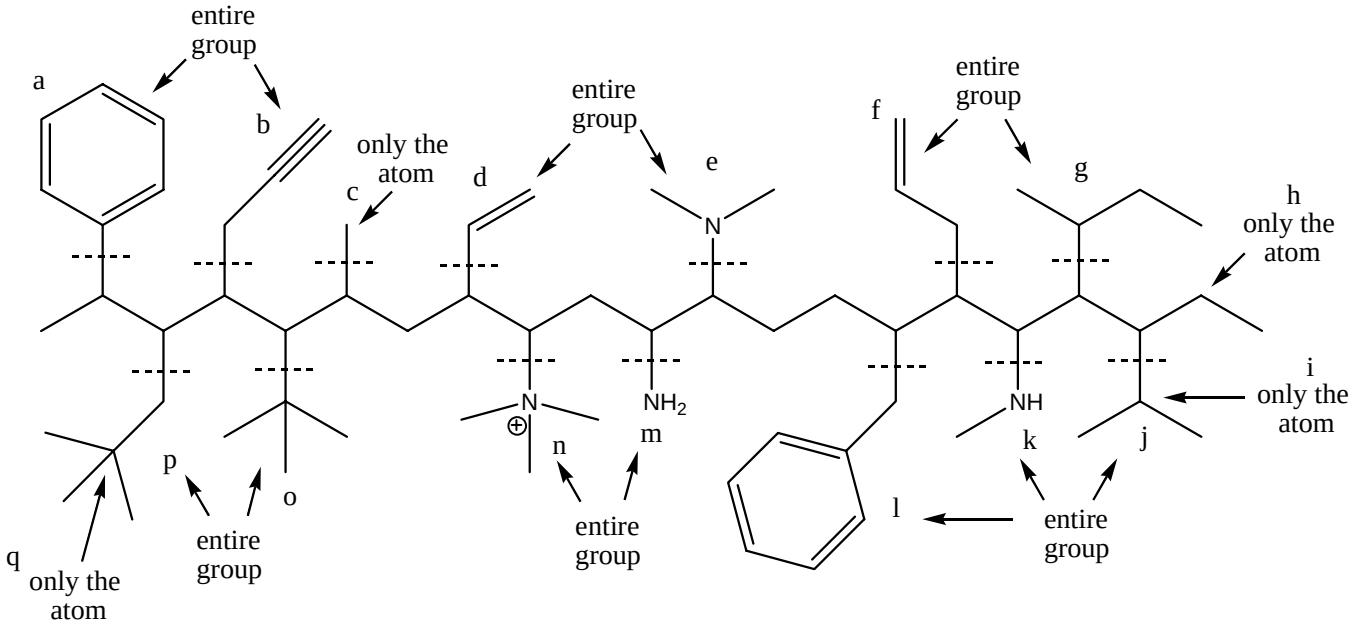
d. Acids A and B have different structures, but share a common conjugate base. Draw the curved arrows to show how the proton transfer occurs in each case and explain why the conjugate base is the same for each acid. (10 pts)



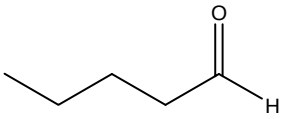
A B

Match the arrows with the terms. Some arrows may be associated with more than one term. (14 pts)

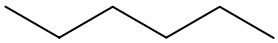
1. methyl _____
2. methylene _____
3. methine _____
4. primary _____
5. secondary _____
6. tertiary _____
7. quarternary _____
8. isopropyl _____
9. isobutyl _____
10. sec-butyl _____
11. t-butyl _____
12. neopentyl _____
13. vinyl _____
14. allyl _____
15. propargyl _____
16. phenyl _____
17. benzyl _____
18. primary amine _____
19. secondary amine _____
20. tertiary amine _____
21. quaternary ammonium ion _____



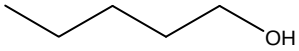
8. Match the given boiling points with the structures below and give a short reason for your answers. (+69°C, +103 °C, +139 °C, +157°C, 1265°C) (10 pts)



pentanal
MW = 86 g/mol

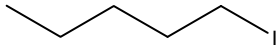


hexane
MW = 86 g/mol



1-pentanol
MW = 88 g/mol

KCl
lithium bromide
MW = 87 g/mol



1-iodopentane
MW = 198 g/mol

Which compound above would you expect to be the most soluble in water? Which compound would you expect to be the most soluble in octane? Briefly, explain you choices. (5 pts)

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1. high priority group plus lots of lower priority groups, alkene (E/Z), alkyne, complex branches
2. long 2D structure with lots of functional groups and a little bit of formal charge
3. just like in the example exams, need to know resonance, formal charge, arrow pushing, hybridization details, how to draw 3D shapes
4. need to know functional groups, calculate degree of unsaturation, common nomenclature, specific bond energies
5. work with heat of formation, heat of reaction, use bond energy table, sketch energy diagram
6. need to know how to put substituents on a cyclohexane ring, draw all possible chair conformations, evaluate their energy, do the same for an open chain compound (staggered / eclipsed), use ΔH to calculate an equilibrium ratio, draw Newman projections for rings and open chains

7. biological explanation using physical properties