First Letter of Your Last Name (Surname):

THE UNIVERSITY OF BRITISH COLUMBIA

CHEMISTRY 123 FINAL EXAMINATION — SAMPLE

This examination consists of 20 numbered pages. **TIME LIMIT: 2.5 HOURS**

PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER

BONUS MARK! Fill out this page (name, student number AND section) correctly for 1 point on the exam.

GIVEN NAME(S): _____SOLUTIONS_____ SURNAME: _____
(FIRST NAME) (IN INK) (LAST NAME) (IN INK)

STUDENT NUMBER: _____ SIGNATURE: _____
(IN INK) (IN INK)

The only calculator allowed is the Sharp EL-510RB. All other calculators will be confiscated. Cell phones or other electronic communication devices are not permitted. Molecular models are allowed.

Lecture Section (check √ your section)

___ 201 (MWF 1:00) Li/Dake
___ 202 (MWF 2:00) Schafer
___ 203 (MWF 3:00) Johnson
___ 210 (MWF 10:00) Ryan
___ 211 (MWF 11:00) Sammis
___ 299 (T,Th 9:30) Lekhi/Bates
___ 222 (T,Th 2:00) Lekhi/Bates

ANSWER ALL QUESTIONS

*****An Equation Sheet and a Periodic Table is provided to you separately. *****

REGULATIONS FOR EXAMINATIONS

1. Each candidate must be prepared to produce upon request, a Library/AMS card for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidates shall be permitted to enter the examination room after the expiration of one half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates guilty of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:

(a) Having at the place of writing any books, papers or memoranda, calculators, audio or visual cassette players or other memory aid devices, other than those authorized by the examiners.
(b) Speaking or communicating with other candidates.
(c) Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.

5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.

PART(s)	Maximum	Obtained	Code
I, II, II,IV,V	58		
VI	9		
VII	10		
VIII	14		
IX	16		
X	9		
XI	10		
XII	4		
BONUS	1		
TOTAL	130		

PART I [30 marks]:

Choose the best answer for the following questions. Indicate your choice by bubbling in your choice on the "Chemistry 123 Final Exam Answer Sheet".

1. For a certain chemical reaction, progress in the forward direction absorbs heat and increases the entropy of the system.
   A. This reaction proceeds spontaneously at all temperatures.
   B. This reaction can proceed in the forward direction at low temperature, but is not spontaneous at high temperature.
   C. This reaction can proceed in the forward direction at high temperature, but is not spontaneous at low temperature.
   D. This reaction cannot proceed spontaneously at any temperature.

Answer: **C**

2. Given the following reaction:

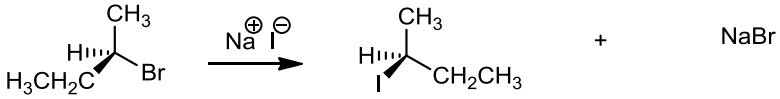
$$CO(g) \quad + \quad 2H_2(g) \rightarrow CH_3OH(l)$$

At 298 K, the ΔH° is −128 kJ for the reaction as written and K_{eq} is 1.21 x 10^5. Assuming ΔH° does not change with temperature, what would happen to the value of K_{eq} at 398 K:

   A. K_{eq} would increase
   B. K_{eq} would decrease
   C. K_{eq} would remain the same
   D. Insufficient data provided

Answer: **B**

3. Consider the following substitution reaction:



What is the rate law for this reaction?

   A. rate = $k[CH_3CHBrCH_2CH_3][NaI]$
   B. rate = $k[CH_3CHBrCH_2CH_3]$
   C. rate = $k[NaI]$
   D. rate = $k[CH_3CHBrCH_2CH_3][NaI] - k[CH_3CHICH_2CH_3][NaBr]$
   E. rate = $k[NaBr]$
   F. rate = $k[CH_3CHBrCH_2CH_3]^2$

Answer: **A**

4. Consider a change in state from a condition of P_1,V_1,T_1 to that of P_2,V_2,T_2. Which of the following statements is **not** a universally true characteristic of this process.

   A. The work depends only on ΔV.
   B. The temperature change is $\Delta T = T_2 - T_1$, regardless of path.
   C. The heat flow varies with the path.
   D. The pressure change for this change in state in the forward direction is exactly equal and opposite in sign to the pressure change for the reverse of this change in state, regardless of path.

Answer: **A**

5. Oxygen atoms (O) react with ethane (CH_3CH_3) in two ways.
In Reaction 1 the oxygen atom can insert into a C-H bond to form ethanol:

Reaction 1: $O + CH_3CH_3 \longrightarrow C_2H_5OH$

In Reaction 2 the oxygen atom can abstract a hydrogen atom from ethane to form a hydroxyl radical plus an ethyl radical:

Reaction 2: $O + CH_3CH_3 \longrightarrow \cdot OH + \cdot C_2H_5$

These two reactions proceed at about the same rate at room temperature. Reaction 2 has a much higher activation energy. How will these reactions compete at high temperature?

A. Reaction 1 has a lower activation energy. It will have a much higher rate than Reaction 2 at higher temperature.
B. Reaction 2 has a higher activation energy. It will have a much higher rate than Reaction 1 at higher temperature.
C. These reactions have the same rate at room temperature. They will have the same rate at high temperature.
D. Activation energies are positive, so increasing temperature will reduce reaction rate. Reaction 2 will slow down the most.

Answer:
A

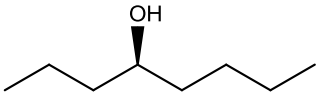
6. A gas expands reversibly at a constant temperature of 25 °C. In the course of the process, 298 J of heat is transferred to the system. What is the ΔS for the surroundings?
A. 1 J K^{-1}
B. 2 J K^{-1}
C. −1 J K^{-1}
D. −2 J K^{-1}
E. 12 J K^{-1}
F. −12 J K^{-1}
G. none of the above

Answer:
C

7. An engine absorbs 23 kJ of heat from its surroundings and undergoes an irreversible change in state. During this state change, the temperature of the system increases by 50 K and its energy increases by 7 kJ. What is the work done <u>on</u> the system?
A. 0 kJ, because an irreversible change in state produces no work.
B. −23 kJ, because heat flow into and work done on the system must balance for any change in state.
C. −16 kJ, because the sum of heat flow into and work done on the system must be the same, regardless of path.
D. 14 kJ, because the heat capacity of the system is 2 kJ K^{-1}.

Answer:
C

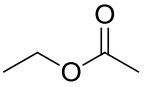
8. Name the following compound according to IUPAC nomenclature:



A. (*R*)-4-octanol
B. (*S*)-4-octanol
C. (*R*)-5-octanol
D. (*S*)-5-octanol
E. (*R*)-4-hydroxyoctane
F. (*S*)-4-hydroxyoctane
G. (*R*)-5-hydroxyoctane
H. (*S*)-5-hydroxyoctane
I. (*S*)-1-propylpentanol
J. (*R*)-1-propylpentanol

Answer:
A

9. Name the following compound according to IUPAC nomenclature:

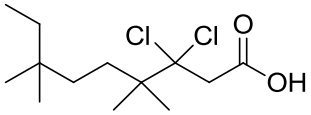


A. ethyl methyl ether
B. ethyl butanoate
C. 2-oxybutanone
D. ethyl methanoate
E. ethyl ethanoate
F. 2-ethoxyethanone
G. ethyl acetic acid
H. ethyl ethanoic acid

Answer:

E

10. Name the following compound according to IUPAC nomenclature:

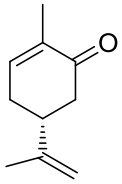


A. 6,6-dichloro-2-ethyl-2,5,5-trimethylnonanoic acid
B. 3,3-dichloro-4,4,7,7-tetramethyloctanoic acid
C. 3,3-dichloro-4,4,7-trimethyl-7-ethyloctanoic acid
D. 1-hydroxy-3,3-dichloro-4,4,7,7-tetramethylnonanone
E. 3,3-dichloro-4,4,7,7-tetramethyl-9-oxy-nonanol
F. 3,3-dichloro-4,4,7,7-tetramethylnonanoic acid
G. 3,3-dichloro-4,4-dimethyl-7,7-dimethylnonanoic acid

Answer:

F

11. Assign absolute stereochemistry (R,S) to the asymmetric centre in the following molecule:

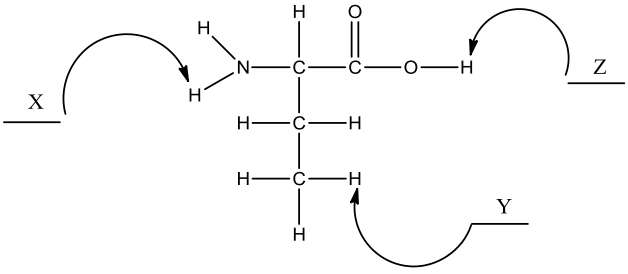


A. R
B. S
C. E
D. Z
E. There are no asymmetric centres in this molecule

Answer:

A

12. Three protons are labeled as X, Y, Z in the following molecule. Rank these protons in order of most acidic to the least.

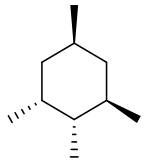


A. (Most acidic) X > Y > Z (Least Acidic)
B. (Most acidic) X > Z > Y (Least Acidic)
C. (Most acidic) Z > Y > X (Least Acidic)
D. (Most acidic) Z > X > Y (Least Acidic)
E. (Most acidic) Y > Z > X (Least Acidic)
F. (Most acidic) Y > X > Z (Least Acidic)

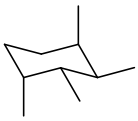
Answer:

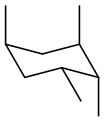
D

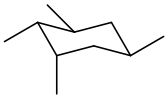
13. Which drawings correctly represent the two chair conformations of the following molecule **A**?

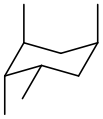


A

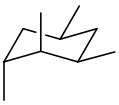
I. 

IV. 

II. 

V. 

III. 

VI. 

A. I and II
B. II and V
C. IV and VI
D. III and VI
E. III and IV
F. IV and I

Answer:

E

14. In question 13, which drawing represented the lowest energy conformation of molecule **A**?

A. I
B. II
C. III
D. IV
E. V
F. VI

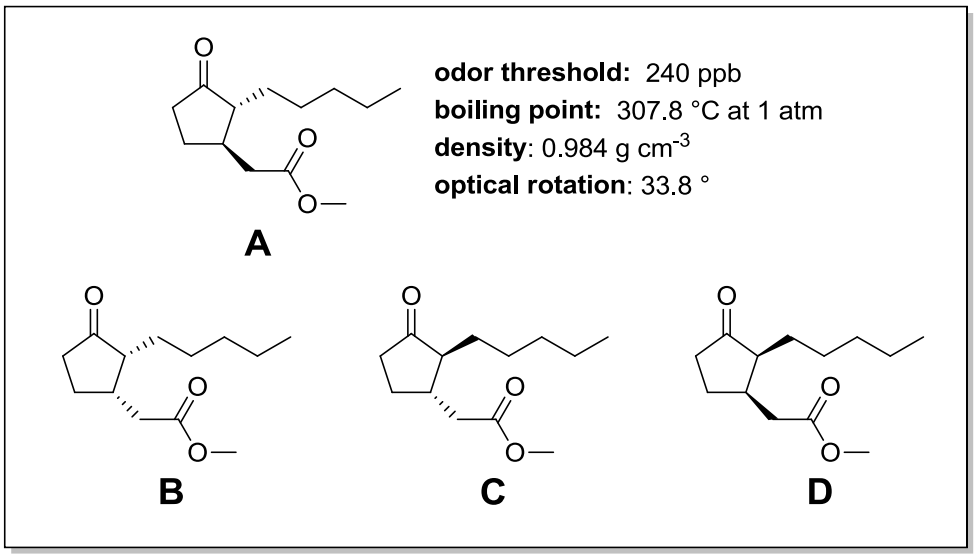
Answer:

C

PART II [10 marks]:

Choose the best answer for the following questions. Indicate your choice by bubbling in your choice on the "Chemistry 123 Final Exam Answer Sheet".

The dihydrojasmonates and epididihydrojasmonate, pictured below, are isolated from plants and flowers. These compounds are common components of perfumes and colognes. Dihydrojasmonate A has a sweet floral jasmine-like smell. The minimum concentration of dihydrojasmonate A that can be detected by the chiral receptors in the human nose (*i.e.*, its odor threshold) is 240 parts per billion (ppb).



1. What is the number of asymmetric centres in dihydrojasmonate A?
   A. 1
   B. 2
   C. 3
   D. 4
   E. 5
   F. 6
   G. 7
   H. 8
   I. 9

Answer:

B

2. What is the relationship between compound A and compound B shown on the previous page?
   A. Identical
   B. Conformers
   C. Constitutional isomers
   D. Enantiomers
   E. Diastereomers
   F. No relationship

Answer:

E

3. Dihydrojasmonate **A** has a sweet floral smell while dihydrojasmonate **C** has a much weaker floral odor and is more tea-like with a hint of lemon-peel. Why do the two compounds have a different odor?
   A. Dihydrojasmonate **A** and dihydrojasmonate **C** are diastereomers and diastereomers interact differently with chiral molecules such as the receptors responsible for human smell. They also have different physical properties.
   B. Dihydrojasmonate **A** and dihydrojasmonate **C** are diastereomers and diastereomers interact differently with chiral molecules such as the receptors responsible for human smell. They also have identical physical properties.
   C. Dihydrojasmonate **A** and dihydrojasmonate **C** are enantiomers and enantiomers interact differently with chiral molecules such as the receptors responsible for human smell. They also have different physical properties.
   D. Dihydrojasmonate **A** and dihydrojasmonate **C** are enantiomers and enantiomers interact differently with chiral molecules such as the receptors responsible for human smell. They also have identical physical properties.
   E. There is no relationship between dihydrojasmonate **A** and dihydrojasmonate **C** so they interact differently with chiral molecules such as the receptors responsible for human smell. They also have different physical properties.

Answer:

D

4. Identify the normal boiling point (°C) of dihydrojasmonate **C.**
   A. 240
   B. 307.8
   C. 0.984
   D. 159.9
   E. 120
   F. 33.8
   G. 1
   H. −33.8
   I. −307.8
   J. Not enough information provided

Answer:

B

5. Identify the odor threshold (ppb) of dihydrojasmonate **C**:
   A. 240
   B. 307.8
   C. 0.984
   D. 159.9
   E. 120
   F. 33.8
   G. 1
   H. −33.8
   I. −307.8
   J. Not enough information provided

Answer:

J

6. Identify the optical rotation (°) of dihydrojasmonate **C**:
   A. 240
   B. 307.8
   C. 0.984
   D. 159.9
   E. 120
   F. 33.8
   G. 1
   H. −33.8
   I. −307.8
   J. Not enough information provided

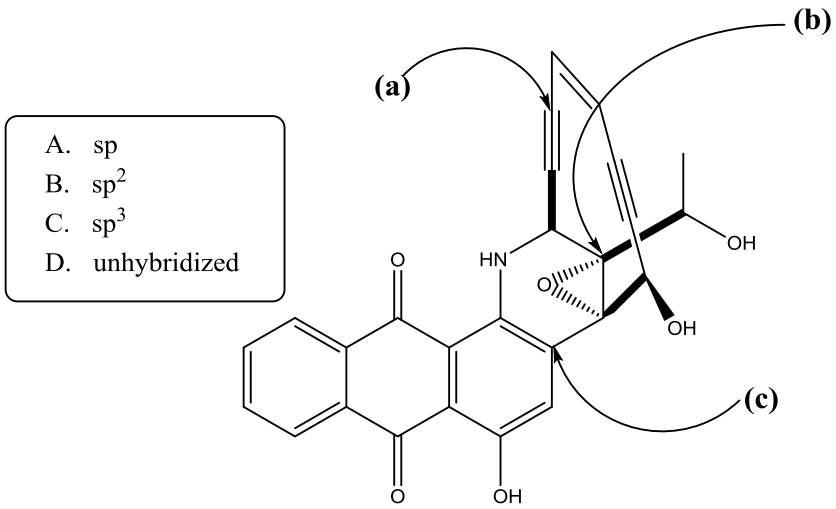
Answer:

H

PART III [3 marks]

Uncialamycin is an antibiotic that was isolated in British Columbia. Identify the hybridization of the indicated atoms from the list provided in the box. Indicate your choice by bubbling in your choice on the "Chemistry 123 Final Exam Answer Sheet".

NOTE: Each term may be used more than once and not all terms need to be used.

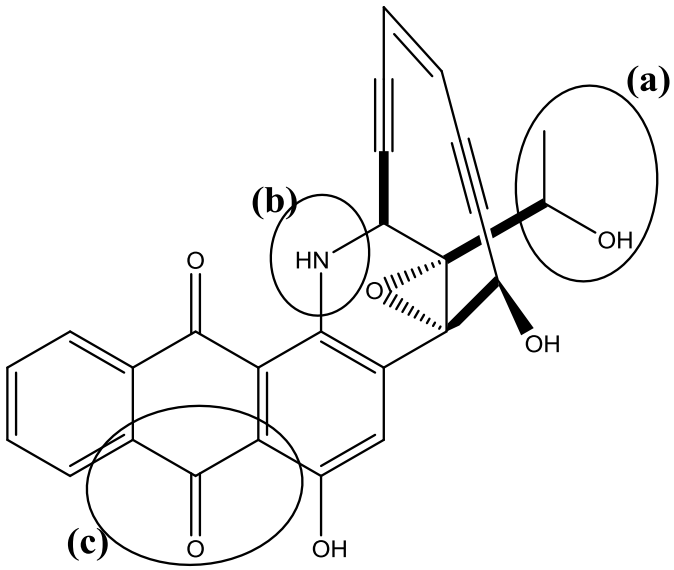


A. sp
B. sp^2
C. sp^3
D. unhybridized

a) ____**A**_____
b) ____**C**_____
c) ____**B**_____

PART IV [3 marks] (Questions 21-23):

Uncialamycin is an antibiotic that was isolated in British Columbia. Identify the functional groups that are circled from the list provided in the box. Indicate your choice on this page. NOTE: Each term may be used more than once and not all terms need to be used.



A. Alcohol
B. Ketone
C. Amine
D. Amide
E. Ester
F. Ether
G. Carboxylic acid
H. Nitrile
I. Aldehyde
J. Thiol

a) _____**A**_____
b) _____**C**_____
c) _____**B**_____

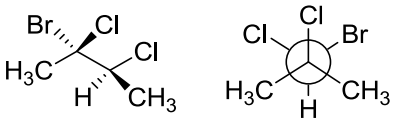
PART V [14 marks]

Below are 7 pairs of structural formulas. Identify the letter that corresponds to the term describing the relationship between the two structures. Indicate your choice by bubbling in your choice on the "Chemistry 123 Final Exam Answer Sheet".

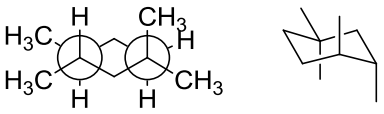
NOTE: Each term may be used more than once and not all terms need to be used.

A. Identical
B. Constitutional Isomers
C. Enantiomers
D. Diastereomers
E. None of the above

1. **B**

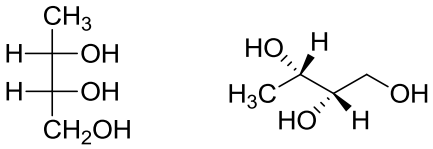


2. **A**

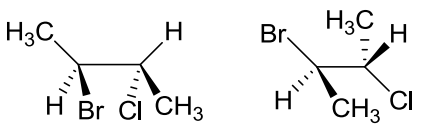


3. **C**

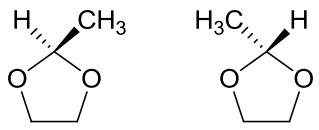
4. **D**



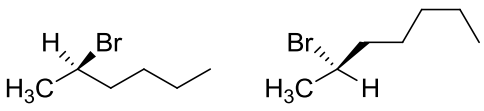
5. **C**



6. **A**



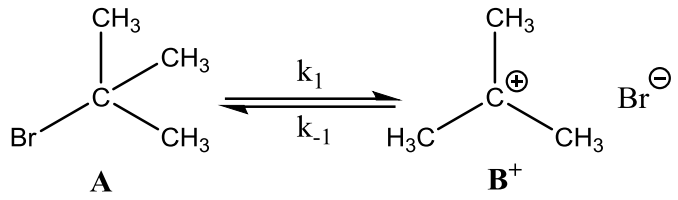
7. **E**



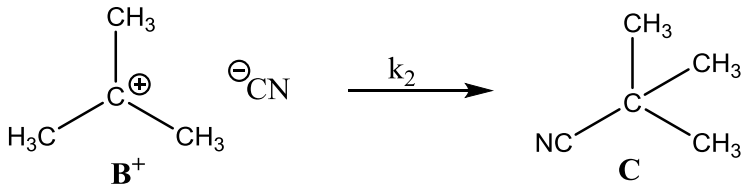
PART VI [9 marks]

1. The reaction between *tert*-butyl bromide and cyanide proceeds via the two step mechanism shown below:

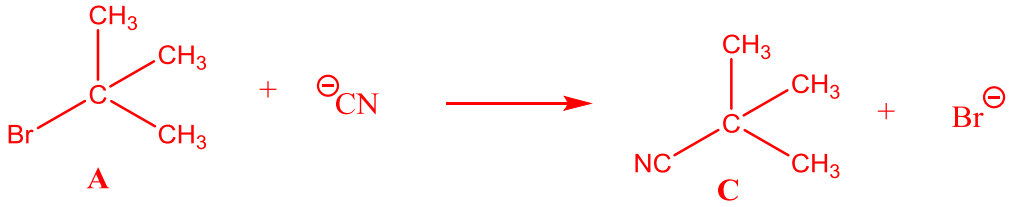
Step 1:



Step 2:



a) What is the overall (or net) reaction?



b) Use the steady-state approximation to derive an expression for the concentration of the carbocation ($\mathbf{B}^+$) in terms of reactants (**A** and CN^-) and/or products (**C**) only.

$$K_1[A] - K_{-1}[B^+][Br^-] - K_2[B^+][CN^-] = 0$$

$$K_1[A] = K_{-1}[B^+][Br^-] + K_2[B^+][CN^-]$$

$$K_1[A] = [B^+](K_{-1}[Br^-] + K_2[CN^-])$$

$$[B^+] = \frac{K_1[A]}{K_{-1}[Br^-] + K_2[CN^-]}$$

c) Derive the rate late for the formation of *tert*-butyl cyanide (**C**).

$$\frac{d[C]}{dt} = \text{rate} = K_2[B^+][CN^-] = \frac{K_2K_1[A][CN^-]}{K_{-1}[Br^-] + K_2[CN^-]}$$

*Since this is an S_N1 mechanism, the following simplifications can also be made: For S_N1 we know $K_1, K_{-1} \ll K_2$ So... $K_{-1}[Br^-] \approx 0$

$$\text{rate} = \frac{K_2K_1[A][CN^-]}{K_{-1}[Br^-] + K_2[CN^-]} = K_1[A]$$

PART VII [10 marks]

1. The following overall reaction was demonstrated by Dr. Crane and is called the "Frozen Flask" demonstration:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \rightarrow 2NH_3(g) + 10H_2O(l) + Ba(NO_3)_2(s)$$

a. With the information given in the table below, calculate the standard enthalpy for reaction.

Substance	$\Delta H°_{f,\ 298\ K}$ (kJ mol^{-1})	$S°_{298\ K}$ (J K^{-1} mol^{-1})
$Ba(OH)_2 \cdot 8H_2O(s)$	-3342	427
$Ba(NO_3)_2(s)$	-988	214
$NH_4NO_3(s)$	-366	151
$NH_3(g)$	-46	193
$H_2O(l)$	-286	70

$$\Delta H^o_{rxn} = \sum \Delta H^0_{f,prod} - \sum \Delta H^0_{f,react}$$

$$\Delta H^0_{rxn} = [2(-46\,kJ\,mol^{-1}) + 10(-286\,kJ\,mol^{-1}) + (-988\,kJ\,mol^{-1})] - [2(-3342 kJ\,mol^{-1}) + 2(-366 kJ\,mol^{-1})]$$

$$\Delta H^0_{rxn} = 134\,kJ$$

Answer:

ΔH^0 = 134 kJ

b. Using calculations, show that this reaction is spontaneous at 298 K.

$$\Delta S^o{}_{rxn} = \sum S^o_{prod} - \sum S^o_{react}$$

$$= [2(193 J\,K^{-1}mol^{-1}) + 10(70 J\,K^{-1}mol^{-1}) + (214 J\,K^{-1}mol^{-1})] - [(427 JK^{-1}mol^{-1}) + 2(151 J\,K^{-1}mol^{-1})]$$

$$= 571\,J\,K^{-1}$$

$$\Delta G^o_{rxn} = \Delta H^0 - T\Delta S^0$$

$$\Delta G^0_{rxn} = 134000 J - (298 K)(571 J\,K^{-1})$$

$$\Delta G^0_{rxn} = -36158 J = -36.2 kJ$$

Answer:
Since ΔG^0 is negative, the reaction is spontaneous.

2. In another demonstration, Dr. Crane showed you a glass tube containing a mixture of brown nitrogen dioxide gas (NO_2) in equilibrium with colourless dinitrogen tetraoxide gas (N_2O_4) as shown below:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \qquad \Delta H° = +\ 14.8\ kJ$$

colouress *brown*

At room temperature, 298 K, the tube exhibits a light brown colour.

(b) What colour change, if any, would you expect to see if Angela placed the tube into an ice-water bath at 273 K? **Circle the correct answer below.**

become colourless **remain the same** **become darker brown**

(b) Provide a brief rationale for the correct answer in (a).

As the reaction is endothermic, therefore heat is added to the system. If you lower the temperature, you are removing heat so Le Chatlier's Principle will shift the equilibrium to the side of the reaction where the heat is being taken in/let off – the colourless reactant side.

(c) Imagine the same mixture of gas was placed in a sealed syringe with a moveable plunger at 298 K. What colour change, if any, would you expect to see if Angela pushed the plunger further into the syringe?
Circle the correct answer below.

become colourless **remain the same** **become darker brown**

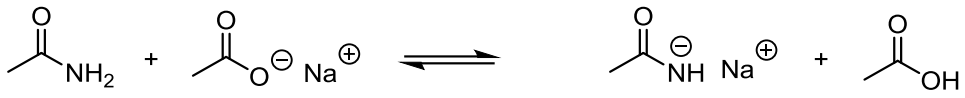
(d) Provide a brief rationale for the correct answer in (c).

There are more moles of gas on the product side. Squeezing the tube results in an increase in pressure (or decrease in volume) favouring the side with less moles of gas, which is the colourless reactant side.

PART VIII [14 marks]

2. Acetic acid, CH_3COOH is found in vinegar. It has a distinctive sour taste and pungent smell. The pK_a of acetic acid is 4.792 at 298 K.

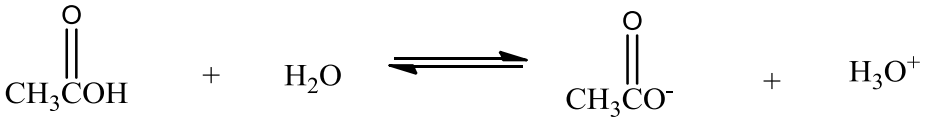
   a. In the following acid/base reaction between ethanamide acid and sodium acetate,



   what can you say about the magnitude of the equilibrium constant, K? Circle the correct answer.

   i. K < 1
   ii. K = 1
   iii. K > 1
   iv. Not enough information.

   b. Household vinegar is a mixture of acetic acid and water. Here is the balanced reaction of acetic acid with water:



   For a solution of 0.12 M acetic acid in 100 mL water, calculate the pH of the resultant solution.

$$K_a = 10^{-4.792} = 1.614 \times 10^{-5}$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.614 \times 10^{-5}$$

$$K_a = \frac{x^2}{0.12} = 1.614 \times 10^{-5}$$

Solving for x:

$$x = [H_3O^+] = 1.39 \times 10^{-3}$$

$$pH = 2.86$$

Answer:

pH = 2.86

c. Determine the ratio of acetic acid to acetate ion in water at pH 3.82 and 298 K.

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$\frac{K_a}{[H_3O^+]} = \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\frac{1.614\times10^{-5}}{10^{-3.82}} = \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\frac{0.11}{1} = \frac{[CH_3COO^-]}{[CH_3COOH]}$$

Therefore, the ratio of acetic acid:acetate ion is 9.37 : 1.

d. Calculate the resultant pH of the solution when 100 mL of 0.12 M acetic acid is combined with 50 mL of 0.24 M NaOH at 298 K.

This is a neutralization reaction, since the number of mols of base = number of mols of initial amount of acid = 0.012 mols.

All of the original amount of acid is used up to to form a 0.08 M solution of CH_3COO^-.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

At equilibrium, [acetic acid] = $[OH^-]$ = x

and [acetate ion] = 0.08-x ≈ 0.08 M

$$K_b = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.614\times10^{-5}} = 6.196\times10^{-10} = \frac{[acetic\ acid][OH^-]}{[acetate\ ion]}$$

$$6.196\times10^{-10} = \frac{x^2}{0.08M}$$

$$x = [OH^-] = 7.04\times10^{-6}$$

$$pOH = 5.15$$

$$pH = 8.85$$

e. Is the resultant mixture described in part (d) a buffer? Circle the best answer.

i. No, because the pH of the mixture in part (d) is larger than the pK_a of acetic acid by > 1 unit

ii. Yes, because the pH of the mixture in part (d) is larger than the pK_a of acetic acid by >1 unit

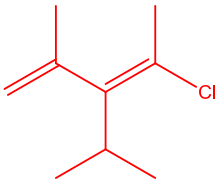
iii. No, because there is a conjugate acid/base pair present.

iv. Yes, because there is a conjugate acid/base pair present.

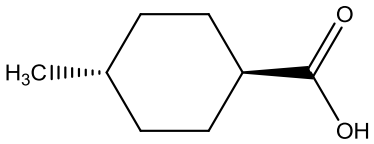
v. No because there are not enough OH^- present.

PART IX [16 marks]

1. Draw the structure of (*E*)-4-chloro-2-methyl-3-isopropyl-1,3-pentadiene.



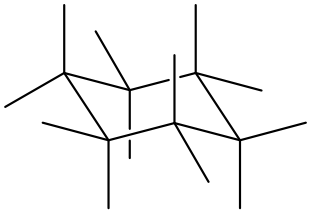
2. Consider the following disubstituted cyclohexane:



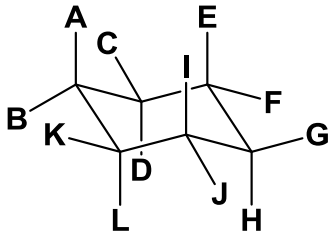
At 298 K, the ΔG° between the two chair conformers of this disubstituted cyclohexane is −3.05 kcal mol^{-1} (or −12.73 kJ mol^{-1}).

a. Convert the 2D line-bond structure of the disubstituted cyclohexane shown above into the **LOWEST ENERGY CHAIR CONFORMATION** by bubbling in the position of the substituents based on the answer input template provided. ***An empty chair template is provided for rough work below.*** **More than one solution is possible; All correct solutions will be accepted.**

Template for rough work

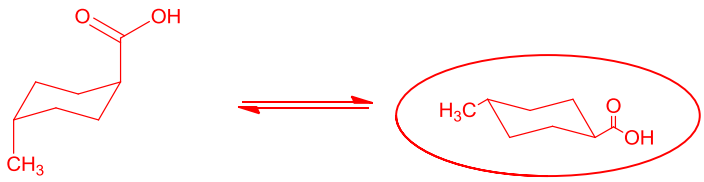


Template for answer input



methyl	carboxylic acid
B	**G**
F	**K**
J	**C**
C	**J**
K	**F**
G	**B**

b. Draw both chair conformations of this disubstituted cyclohexane and circle the more stable conformer.



c. What percentage of the substituted cyclohexane exists as the equatorial isomer?

$$\Delta G^{o} = -RT \ln K_{eq}$$

$$-12730 J = -(8.314 J\, mol^{-1})(298 K) \ln K_{eq}$$

$$K_{eq} = 170 = \frac{[equatorial\ conformer]}{[axial\ conformer]} = \frac{x}{1-x}$$

$$170 - 170x = x$$

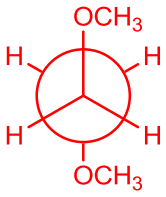
$$x = 0.994$$

$$\therefore 99.4\%\ is\ equatorial\ conformer$$

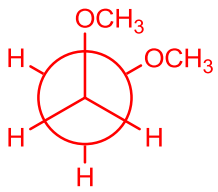
Answer:

99.4 % equatorial conformer.

3. For 1,2-dimethoxyethane ($CH_3OCH_2CH_2OCH_3$), the anti conformer is preferred. Draw Newman projections for the anti and one gauche conformer for 1,2-dimethoxyethane along the C-C axis.

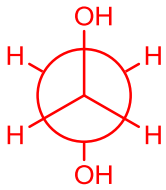


Anti

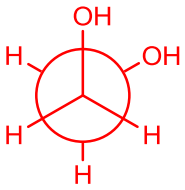


Gauche

4. Studies of 1,2-ethandiol ($HOCH_2CH_2OH$) show that the conformer in which the hydroxyl groups are gauche to each other is more stable than when the hydroxyl groups are anti to each other. Draw Newman projections for the anti and one gauche conformer for 1,2-ethandiol, along the C-C axis.



Anti



Gauche

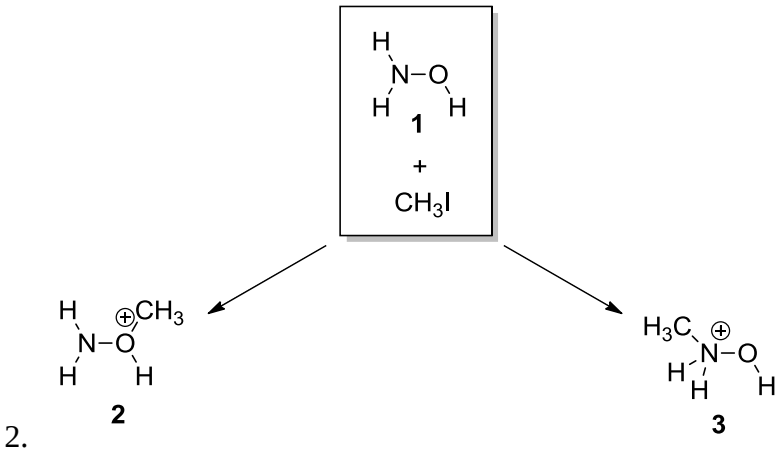
Provide a rationale for why the gauche form of 1,2-ethandiol is more stable than the anti.

H-bonding between the hydroxyl groups is possible in the gauche form. The hydrogen bonding stabilizes this conformation.

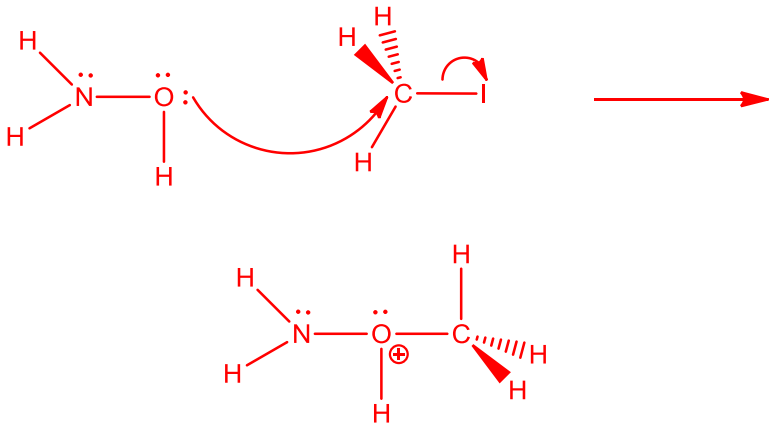
PART X [9 marks]

1. Hydroxylamine (H_2NOH, compound **1**) has two sites of potential nucleophilicity. Treatment of hydroxylamine with 1 equivalent of iodomethane has the potential to provide either oxygen alkylated product **2** or nitrogen alkylated product **3**, but only one is observed.

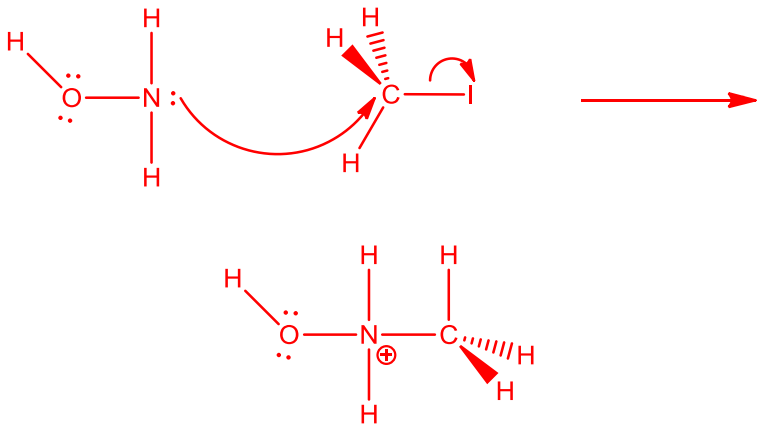
2.



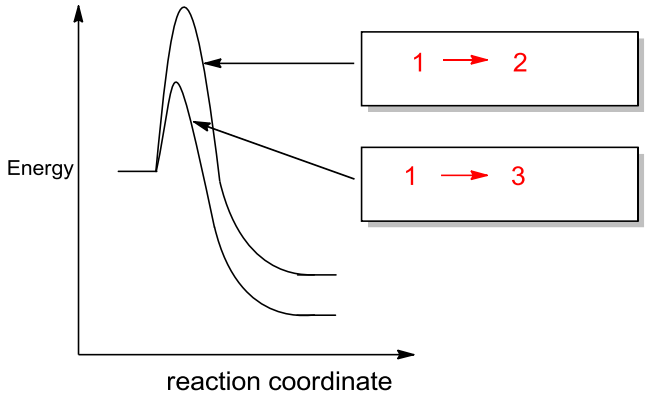
a. Draw a mechanism for the formation of compound **2.**



b. Draw a mechanism for the formation of compound **3**.



c. Below are the reaction coordinate diagrams for the conversion of **1** to **2** and for the conversion of **1** to **3**. In the boxes provided, label each reaction coordinate diagram (i.e. **1** → **2** or **1** → **3**).



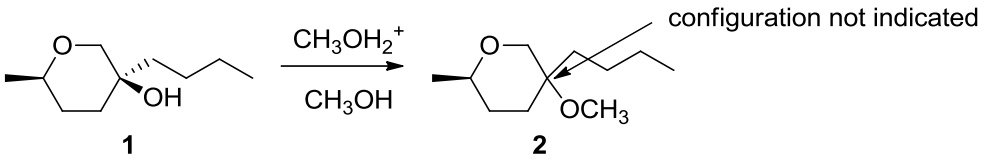
d. Only one product is formed. Predict whether compound 2 or 3 is formed in this reaction. Using your answer in part (c), provide a brief explanation.

Compound 3 is formed.

The nitrogen is a stronger base and better nucleophile than oxygen because it is less electronegative than oxygen and so is more willing to donate its electrons. Since it is a better nucleophile, the reaction will be faster for 1 → 3 and the reaction profile will have a lower transition state or activation barrier.

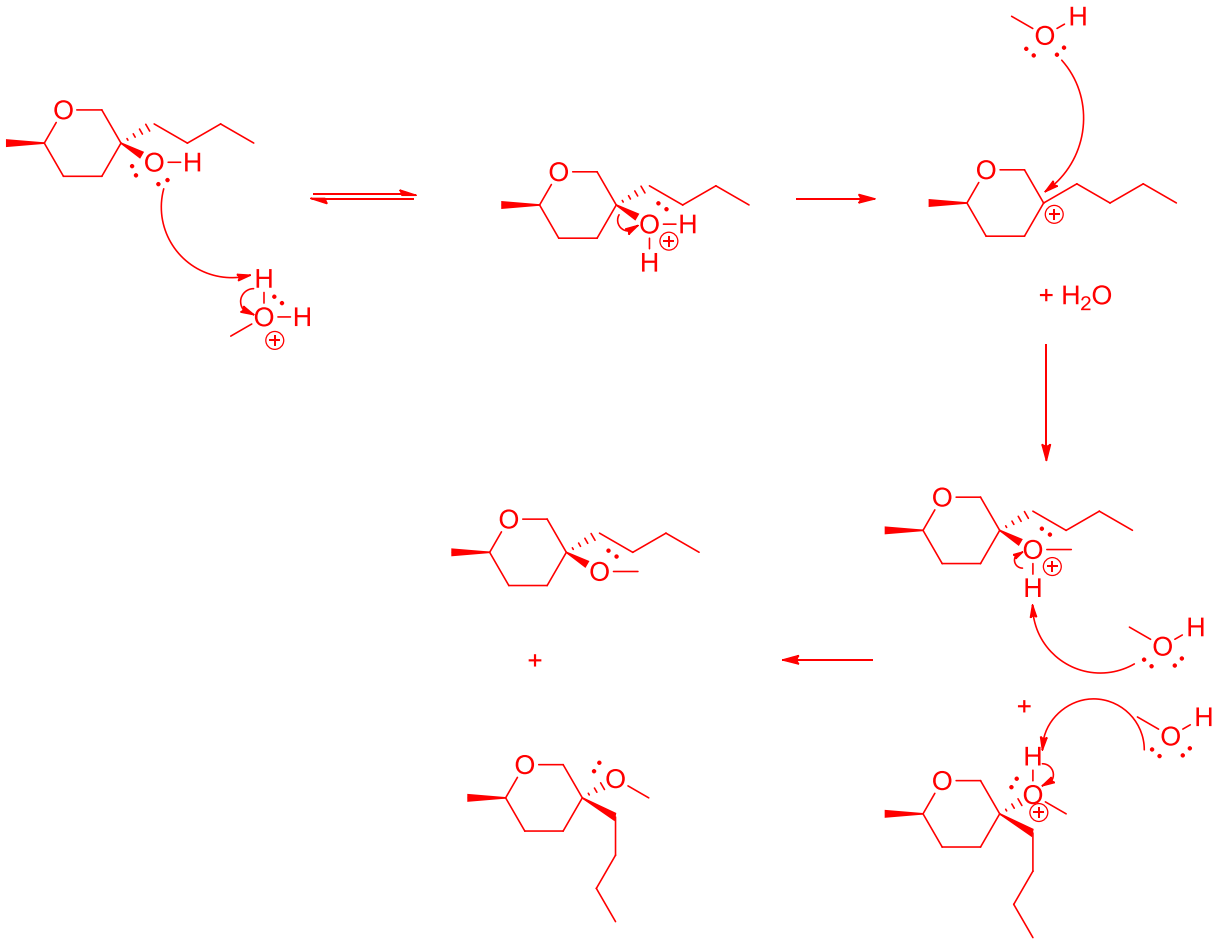
PART XI [10 marks]

1. Holly, a first year graduate student, is following a published procedure to convert optically pure compound **1** to product **2** using a catalytic amount of acid. However, the procedure she is following does not provide the configuration at the indicated carbon.



1 **2**

a. Draw a mechanism for the transformation from **1** to **2**. Please clearly indicate the product(s) of the reaction.



b. Briefly explain why only a catalytic amount of acid is required in this transformation.

For every molecule of acid that is required to initiate the reaction, a molecule of acid is regenerated in the last step.

c. What can Holly do to the reaction to double the rate? Briefly explain your answer.

Rate = k[electrophile]
Doubling the concentration of the starting material (compound 1) will double the reaction rate.

d. After Holly runs the reaction, she examines the product(s) using polarimetry. Would you expect the solution to rotate plane polarized light? Briefly explain your answer.

Yes, the solution should rotate plane polarized light. The product mixture contains two diastereomers, both of which will rotate plane polarized light.

PART XII [4 marks]

1. This reaction below gives rise to two different products. The molecular formula of the **major** product is $C_8S_2H_8$.

   Draw the mechanism that leads to the major product.