First Letter of Your
Last Name (Surname):

THE UNIVERSITY OF BRITISH COLUMBIA

CHEMISTRY 123 FINAL EXAMINATION 18 April 2012

This examination consists of 22 numbered pages. **TIME LIMIT:**

PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER **2.5 HOURS**

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

GIVEN NAME(S): ____ANSWER KEY________________ (FIRST NAME) (IN INK)
SURNAME: ________________________________ (LAST NAME) (IN INK)

STUDENT NUMBER: ________________________ (IN INK)
SIGNATURE: ________________________________ (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) Bizzotto/Sammis
___ 202 (MWF 2:00) Addison/Ryan
___ 203 (MWF 3:00) Addison/Ryan
___ 210 (MWF 10:00) Grant/Kunz
___ 211 (MWF 11:00) Grant/Sammis
___ 299 (T,Th 9:30) Lekhi
___ 222 (T,Th 2:00) Bizzotto/Kunz

ANSWER ALL QUESTIONS

*****Attached (last page) is an Equation Sheet and a Periodic Table. You may carefully remove the last page. *****

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 (Scantron)	45		
VI	9		
VII	10		
VIII	14		
IX	9		
X	9		
XI	10		
XII	4		
BONUS	1		
TOTAL	111		

SECTION 1

The first section of this exam consists of multiple choice questions.
Indicate your answer choice on BOTH the Scantron sheet AND in this exam booklet.
If there is a discrepancy between responses on the Scantron and this exam booklet, the Scantron will be marked.

I have read and understood these instructions. __________________ (please initial)

PART I [15 marks]:

Choose the best answer for the following questions. Indicate your choice on the SCANTRON sheet AND circle your answer on this page.

1. Deep within the Chemistry building lies an underground cellar from the Cold War era. This cellar is 150 meters below sea level (Pressure = 1.02 atm = 1.03 bar = 775 mmHg).

2 marks

In the cellar a CHEM 123 student is performing an experiment with a beaker containing hexane and another beaker containing 1-hexanol. Both beakers are heated and brought to a boil. What can be said about the vapour pressures of boiling hexane and boiling 1-hexanol?

A. Vapour pressure of 1-hexanol is higher
B. Vapour pressure of hexane is higher
[✓ C.] The vapour pressure is the same for hexane and 1-hexanol
D. Cannot be determined based on the information given

2. The CHEM 123 student is asked to measure the boiling point temperatures for the beakers containing hexane and 1-hexanol, as described in question (1). The student places a thermometer into each beaker to measure the boiling point temperature. What is the correct relationship between the measured boiling point temperatures for hexane and 1-hexanol?

2 marks

A. The temperature at which hexane boils is higher than 1-hexanol.
[✓ B.] The temperature at which 1-hexanol boils is higher than hexane.
C. The boiling point temperature is the same for 1-hexanol and hexane.
D. Cannot be determined based on the information given

3. 100 mL of ethanol is placed into a 500 mL vessel and the vessel is sealed (Vessel A). Similarly, 100 mL of ethanol is placed into a 1 L vessel and the vessel is sealed (Vessel B). Both vessels are held at 298 K and contain liquid.

2 marks

A CHEM 123 student measures the vapour pressure in each of the vessels. What best describes the vapour pressure relationship?

A. Vapour pressure in A is greater than the vapour pressure in B
B. Vapour pressure in A is less than the vapour pressure in B
[✓ C.] Vapour pressure in A is equal to the vapour pressure in B
D. Cannot be determined based on the information given

4. A 2 L flask contains 500 mL of liquid water at 70 °C. The flask is stoppered and connected to a vacuum pump. The vacuum pump is turned on, reducing the pressure inside the flask. The water starts to boil. What is the temperature of the boiling water?

1 mark

A. Greater than 100 °C
B. 100 °C
[✓ C.] 70 °C
D. Less than 70 °C
E. Cannot be determined based on the information given.

5. Given the following reaction:

1 mark

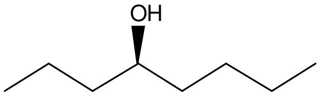
$$CO(g) \quad + \quad 2H_2(g) \; \rightarrow \; CH_3OH(l)$$

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

6. Name the following compound according to IUPAC nomenclature:

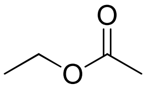
2 marks



[✓ 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

7. Name the following compound according to IUPAC nomenclature:

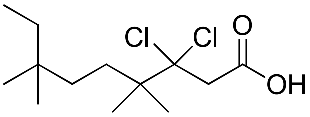
1 mark



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

8. Name the following compound according to IUPAC nomenclature:

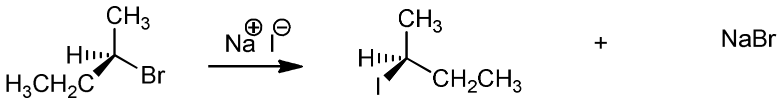
2 marks



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

9. Consider the following substitution reaction:

1 mark

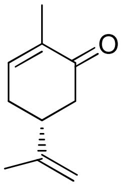


What is the rate law for this reaction?

[✓ 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 = $k[CH_3CHBrCH_2CH_3]^2$

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

1 mark

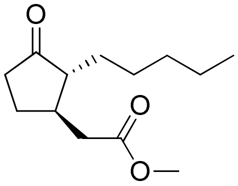


[✓ A.] R
B. S

PART II [10 marks] (Question 11-17):

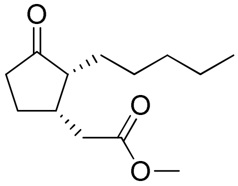
Choose the best answer for the following questions. Indicate your choice on the SCANTRON sheet AND circle your answer on this page.

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).

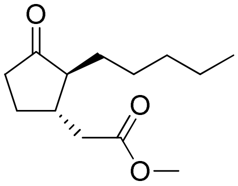


A

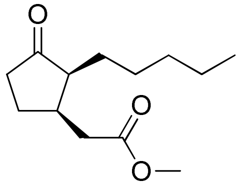
odor threshold: 240 ppb
boiling point: 307.8 °C at 1 atm
density: 0.984 g cm^{-3}
optical rotation: 33.8 °



B



C



D

11. What is the number of asymmetric centres in dihydrojasmonate A?

1 mark

A. 1
[✓ B.] 2
C. 3
D. 4
E. 5
F. 6
G. 7
H. 8
I. 9

12. What is the relationship between compound A and compound B shown on the previous page?

1 mark

A. Identical
B. Conformers
C. Constitutional isomers
D. Enantiomers
[✓ E.] Diastereomers
F. No relationship

13. 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?

2 marks

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.

14. Identify the normal boiling point (°C) of dihydrojasmonate **C.**

1 mark

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

15. Identify the odor threshold (ppb) of dihydrojasmonate **C**:

2 marks

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

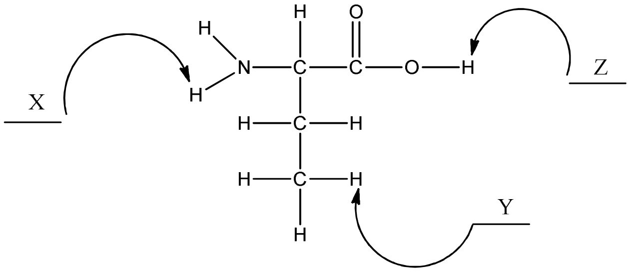
16. Identify the optical rotation (°) of dihydrojasmonate **C**:

1 mark

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

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

2 marks



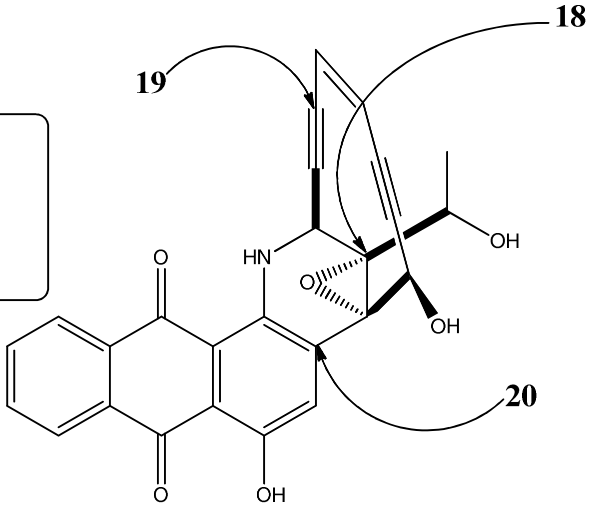
A. (Most acidic) X > Y > Z (Least Acidic)
B. (Most acidic) X > Z > Y (Least Acidic)
C. (Most acidic) Z > Y > X (Least Acidic)
[✓ D.] (Most acidic) Z > X > Y (Least Acidic)
E. (Most acidic) Y > Z > X (Least Acidic)
F. (Most acidic) Y > X > Z (Least Acidic)

PART III [3 marks] (Questions 18-20):

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 on the SCANTRON sheet AND on this page. NOTE: Each term may be used more than once and not all terms need to be used.

1 mark each

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

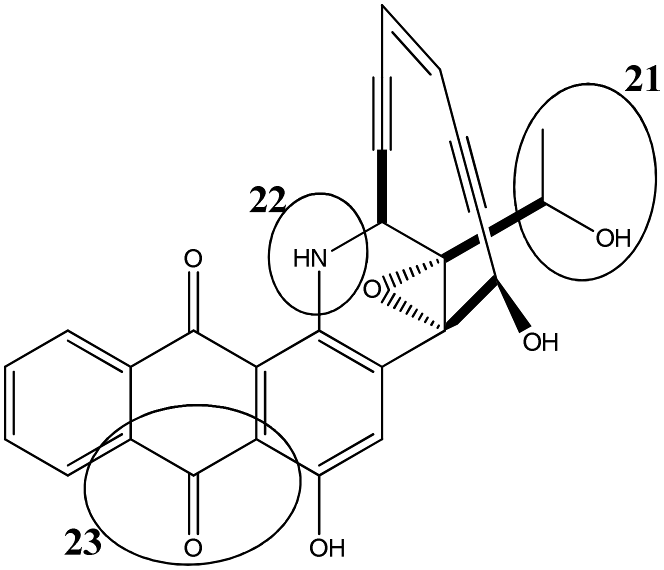


18. _C__________
19. _A_________
20. _B__________

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 the SCANTRON sheet AND on this page. NOTE: Each term may be used more than once and not all terms need to be used.

1 mark each



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

21. __A____________
22. __C____________
23. __B____________

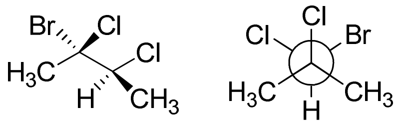
PART V [14 marks] (Questions 24-30):

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 on the SCANTRON sheet AND on this page. NOTE: Each term may be used more than once and not all terms need to be used.

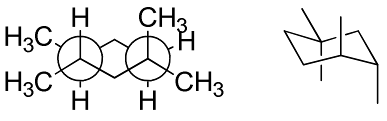
2 marks each

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

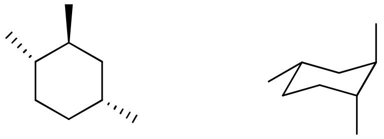
24. B



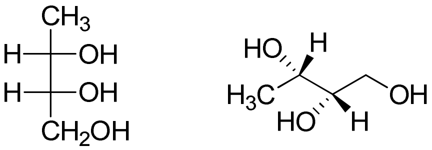
25. A



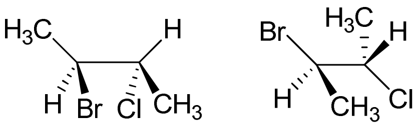
26. C



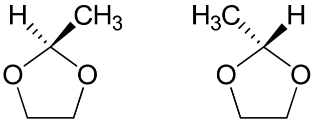
27. D



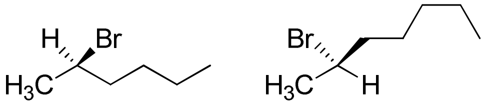
28. C



29. A



30. E



SECTION 2

The second section of this exam consists of open-ended questions.

DO NOT USE YOUR SCANTRON SHEET FOR SECTION 2.

Write your responses in this exam booklet.

I have read and understood these instructions. ____________________ (please initial)

PART VI [9 marks]

31. The amount of work done by an electrochemical reaction can be calculated using $w_{el} = -nF\Delta\varepsilon_{cell.}$ Consider a concentration cell at 298 K composed of:

$$\text{Pt (s)} \mid \text{H}_2\text{ (g,1atm)} \mid \text{HCl (aq, 1mM)} \parallel \text{HCl (aq, 10mM)} \mid \text{H}_2\text{(g, 1atm)} \mid \text{Pt (s)}$$

The following are reduction potentials that you may or may not need to answer questions a-e:

Half cell reduction reactions:

$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 V
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.229 V
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	1.188 V
$PtCl_4^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4Cl^-(aq)$	0.755 V
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.358 V

a. The standard cell potential, $\Delta\varepsilon^0$ is:

$$\begin{array}{lll} 2H^+(aq) + 2e^- \rightarrow H_2(g) & \Delta\varepsilon_{1/2}{}^0 = 0.00V & (right) \\ H_2(g) \rightarrow 2H^+(aq) + 2e^- & \Delta\varepsilon_{1/2}{}^o = 0.00V & (left) \\ \hline \end{array}$$

$$H_2^{left}(g) + 2H_{right}^+(aq) \rightarrow H_2^{right}(g) + 2H_{left}^+(aq)$$

Answer:

$\Delta\varepsilon_{cell}{}^0 = 0.00$ V

b. Calculate the cell potential ($\Delta\varepsilon_{cell}$) for the conditions given.

$$\Delta\varepsilon_{cell} = \Delta\varepsilon_{cell}^o - \frac{RT}{nF}\ln\frac{[H^+]_{left}^2}{[H^+]_{right}^2}$$

$$\Delta\varepsilon_{cell} = 0 - \frac{RT}{2F}\ln\frac{1^2}{10^2}$$

$$\Delta\varepsilon_{cell} = 0.059V$$

Answer:

$\Delta\varepsilon_{cell} = 0.059$ V

c. Calculate the amount of electrical work done by the system if 1 mol of electrons is allowed to flow through this cell under reversible conditions.

$$\begin{aligned} w_{elec} &= -nF\Delta\varepsilon_{cell} \\ &= -1mol(96500\,Cmol^{-1})(0.059V) \\ &= -5705\,J \end{aligned}$$

Answer:

w_{elec} = -5.71 kJ

d. Assuming that the system is isolated (therefore $\Delta U=0$ or $\Delta E=0$) calculate the ΔS for this process, recognizing that you do not have to consider $P\Delta V$ work in your calculations and that the temperature of the system does not change.

$$\Delta U = q + w = 0$$

$$\therefore q = -w$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{-w_{el}}{T} = \frac{5.71\times10^{3}\,J}{298\,K}$$

$$\Delta S = 19.1\,J\,K^{-1}$$

Answer:

$\Delta S = 19.1\ J\ K^{-1}$

e. Why was $P\Delta V$ not considered in the calculation in (d)? Circle the best answer.

i. System is at equilibrium
ii. System is open
iii. System is closed
iv. System is isolated
[✓ v.] System has no net change in the number of moles of gas
vi. H_2 gas is supplied at 1 atm on both sides
vii. No net reaction occurs

PART VII [10 marks]

32. The following overall reaction was demonstrated by Dr. Tamara Kunz and is called the “Frozen Flask” demonstration:

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

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

$$\Delta H^o_{rxn} = \sum \Delta H^0_{f,prod} - \sum \Delta H^0_{f,react}$$
$$\Delta H^0_{rxn} = [2(-46\,kJ\ mol^{-1}) + 10(-286\,kJ\ mol^{-1}) + (-988\,kJ\ mol^{-1})] - [2(-3342kJ\ mol^{-1}) + 2(-366kJ\ mol^{-1})]$$
$$\Delta H^0_{rxn} = 134\,kJ$$

Answer:

$\Delta H^0 = 134$ kJ

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

$$\Delta S^o{}_{rxn} = \sum S^o_{prod} - \sum S^o_{react}$$
$$= [2(193J\ K^{-1}mol^{-1}) + 10(70J\ K^{-1}mol^{-1}) + (214J\ K^{-1}mol^{-1})] - [(427JK^{-1}mol^{-1}) + 2(151J\ K^{-1}mol^{-1})]$$
$$= 571\,J\ K^{-1}$$

$$\Delta G^o_{rxn} = \Delta H^0 - T\Delta S^0$$
$$\Delta G^0_{rxn} = 134000J - (298K)(571J\ K^{-1})$$
$$\Delta G^0_{rxn} = -36158J = -36.2kJ$$

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

c. Determine the temperature at which the reaction changes from non-spontaneous to spontaneous.

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

$$\therefore T = \frac{\Delta H^0}{\Delta S^0} = \frac{134\times 10^3 J}{571 J\ K^{-1}} = 235K$$

Answer:

T = 235 K

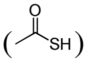
d. This reaction is spontaneous despite the large amount of heat that has to be added to this reaction. What is the driving force behind the spontaneous nature? You may use point form or an equation to explain.

Entropy is the driving force behind this reaction. ΔS^o for the reaction is a large positive quantity.

$$\Delta G^o = \Delta H^o - \underbrace{T\Delta S^o}_{\substack{\text{This term dominates, leading} \\ \text{to a spontaneous reaction} \\ \text{above 235 K}}}$$

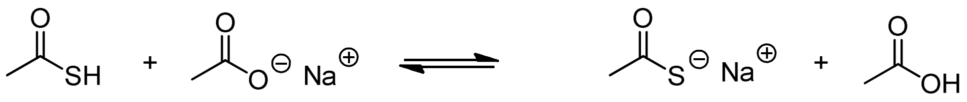
PART VIII [14 marks]

33. 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. Acetic acid is a weaker acid than thioacetic acid (). Which of the following statements best explains this observation? Circle the correct answer.

i. There is more resonance in acetic acid compared to thioacetic acid.
ii. Acetate ion is a weaker base compared to the thioacetate ion.
iii. Oxygen is more electronegative than sulfur.
iv. There is a stronger inductive effect in thioacetic acid compared to acetic acid.
[✓ v.] Sulfur is more polarizable than oxygen.
vi. The carbon attached to the acidic proton in acetic acid is sp^2 hybridized while the sulfur attached to the acidic proton is not hybridized at all.

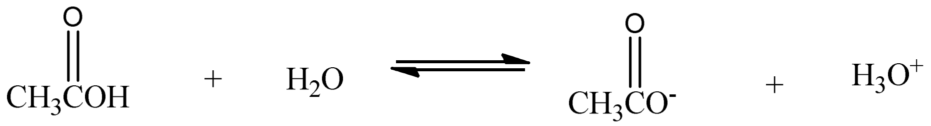
b. In the following acid/base reaction between thioacetic acid and sodium acetate,



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.

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



$$CH_3\overset{\overset{O}{\|}}{C}OH + H_2O \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}O^- + H_3O^+$$

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

$$K_a = 10^{-4.792} = 1.614\times10^{-5}$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.614\times10^{-5}$$

$$K_a = \frac{x^2}{0.12} = 1.614\times10^{-5}$$

Solving for x:

$$x = [H_3O^+] = 1.39\times10^{-3}$$

$$pH = 2.86$$

Answer:

pH = 2.86

d. 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.

e. 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

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

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

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

$$pOH = 5.15$$

$$pH = 8.85$$

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

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

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

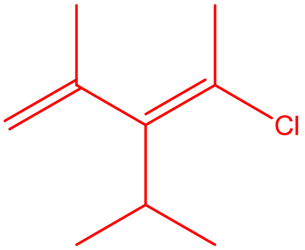
iii. No, because there is a conjugate acid/base pair present.

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

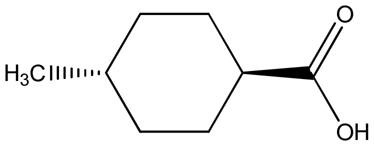
v. No because there are not enough OH^- present.

PART IX [9 marks]

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

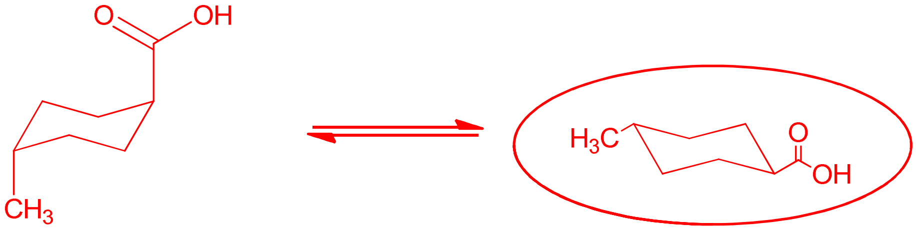


35. Consider the following disubstituted cyclohexane:



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



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

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

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

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

$$170 - 170x = x$$

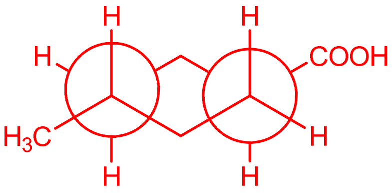
$$x = 0.994$$

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

Answer:

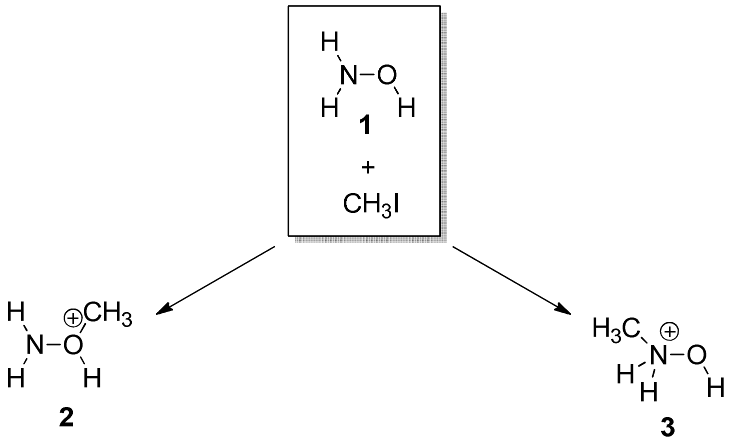
99.4 % equatorial conformer.

c. Complete the following Newman projection of the disubstituted cyclohexane:

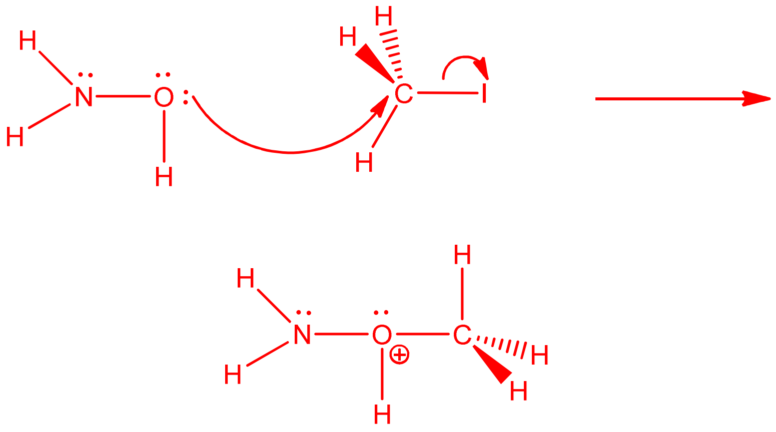


PART X [9 marks]

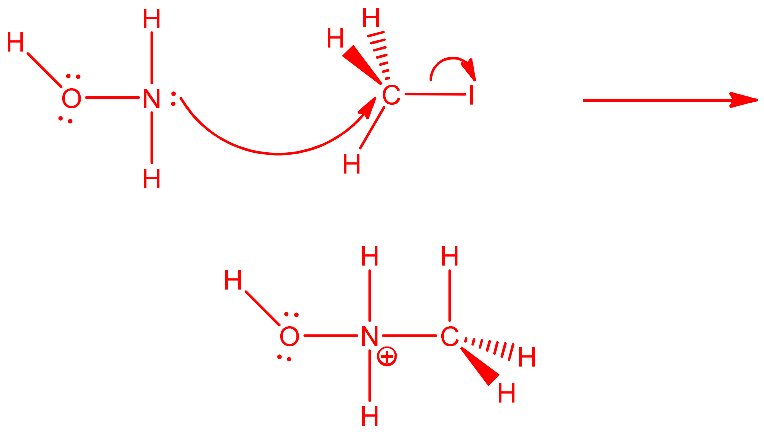
36. Hydroxylamine (H_2NOH, compound **1**) has two sites of potential nucleophilicity. Treatment of hydroxylamine with 1 equivalent of iodomethane has the potential to provide either oxygen alkylated product **2** or nitrogen alkylated product **3**, but only one is observed.



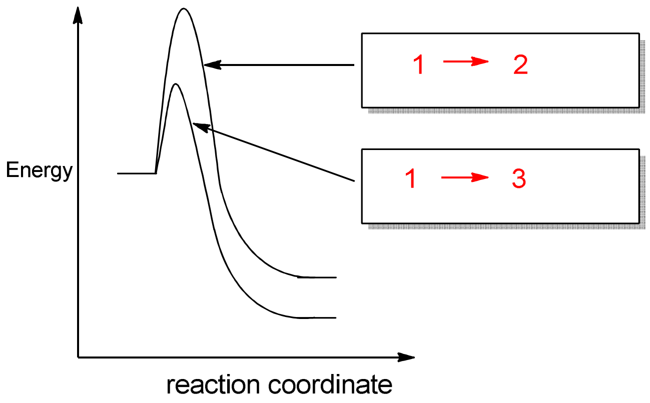
a. Draw a mechanism for the formation of compound **2.**



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**).



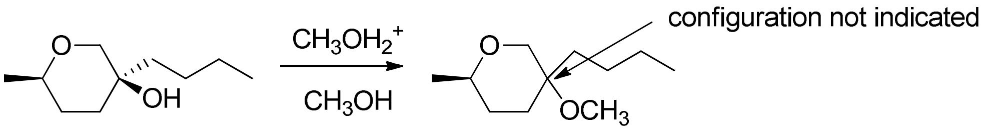
d. Only one product is formed. Predict whether compound 2 or 3 is formed in this reaction. Using your answer in part (c), provide a brief explanation.

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.

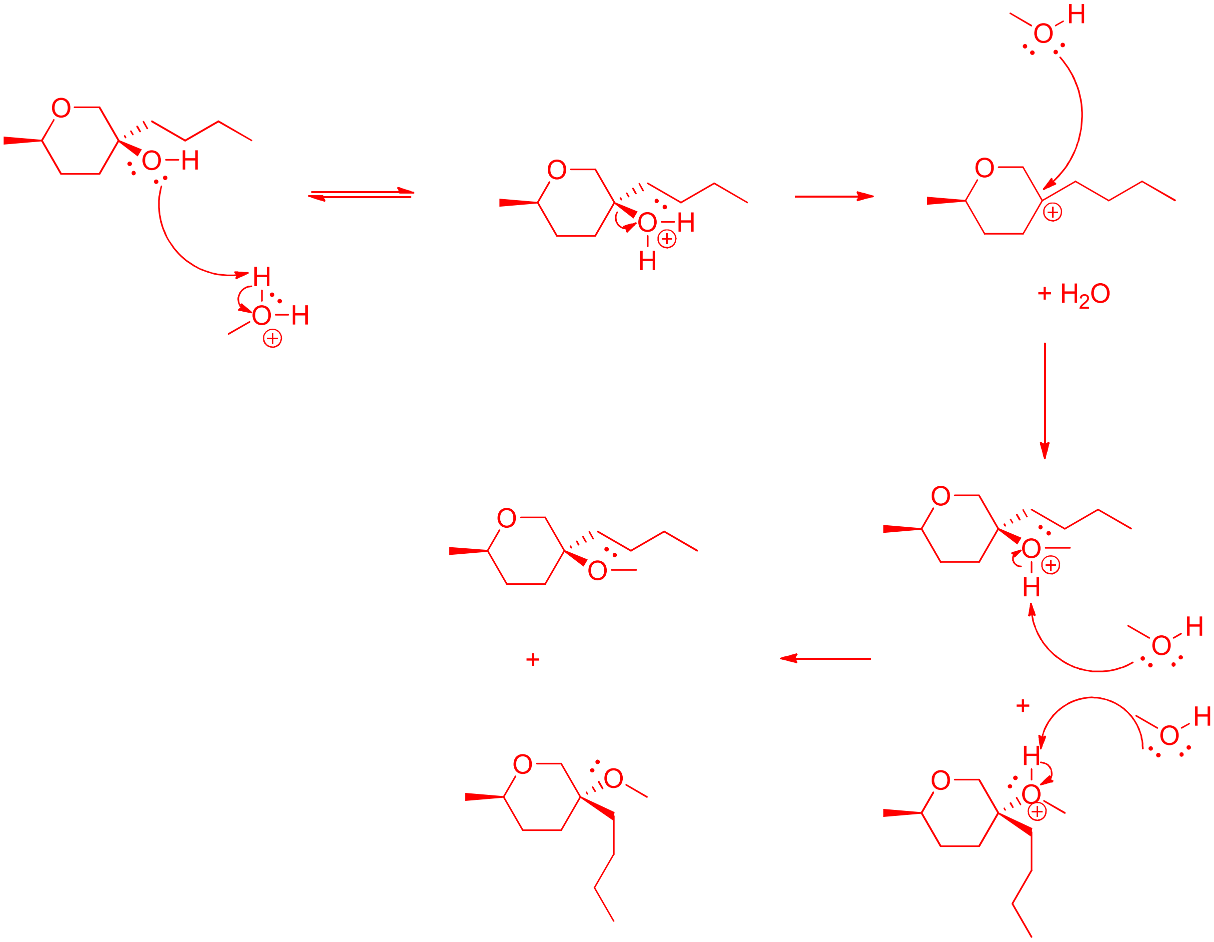
PART XI [10 marks]

37. 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.

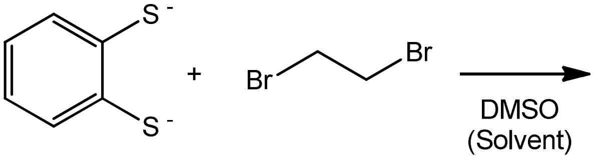
d. After Holly runs the reaction, she examines the product(s) using polarimetry. Would you expect the solution to rotate plane polarized light? Briefly explain your answer.

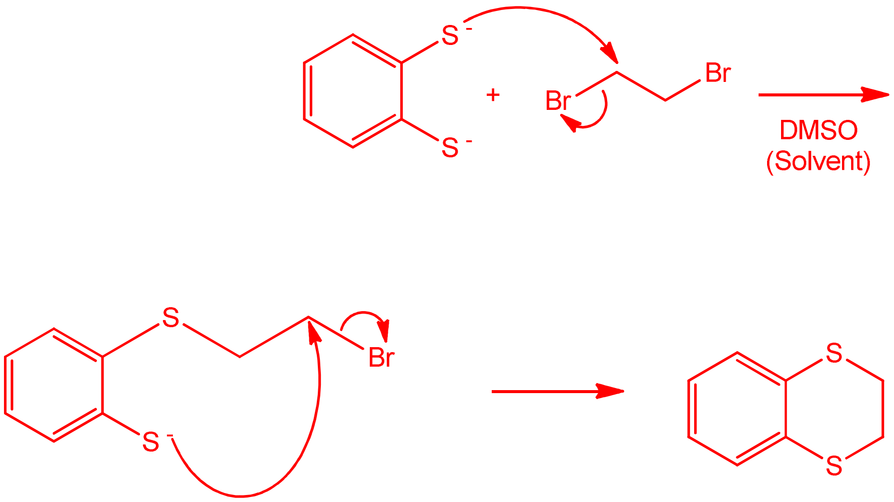
Yes, the solution should rotate plane polarized light. The product mixture contains two diastereomers, both of which will rotate plane polarized light.

PART XII [4 marks]

38. 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.





Equation Sheet

1. $\Delta E = q + w$ or $\Delta U = q + w$
2. $H = E + PV$ or $H = U + PV$
3. $\Delta S = \frac{q_{rev}}{T}$
4. $G = H - TS$
5. $\Delta G_{reaction} = \Delta G^{o}_{reaction} + RT \ln Q$
6. $\Delta G^{o}_{reaction} = -RT \ln K$
7. $\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^{o}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
8. $\Delta G = w_{el} = -nF\, \Delta\mathcal{E}$
9. $\Delta\mathcal{E} = \Delta\mathcal{E}^{\circ} - \frac{RT}{nF} \ln Q$
10. $\Delta\mathcal{E}^{\circ} = \frac{RT}{nF} \ln K$
11. R = 8.314 J K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1}
    = 0.0821 L atm K^{-1} mol^{-1}
12. 1 L atm = 101.3 J
13. F = 96,500 coulombs mol^{-1}
14. 1 J = 1 volt coulomb
15. $K_w = 1.00 \times 10^{-14}$ at 25°C (298.15 K)
16. Kelvins = degrees Celsius + 273.15
17. 1 atm = 760 mmHg
18. $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
19. $rate = k[A]^m[B]^n$
20. $k = Ae^{\frac{-E_a}{RT}}$

PERIODIC TABLE OF THE ELEMENTS

Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																1 H 1.008	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.99	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.9	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.7	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.8
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc "(98)"	44 Ru 101.07	45 Rh 102.9	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.33	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po "(209)"	85 At "(210)'	86 Rn "(222)"
87 Fr 223	88 Ra 226.03	89 Ac# 227.03	104 Rf	105 Db {261}	106 Sg	107 Bh	108 Hs	109 Mt									
		*	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 145	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	
		#	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	