

Chem 1105-Midterm Date: July 20, 2015 Instructor: Calvin Howley Time Period: 2 hours 1

Student:

Student #: _____

Instructions:

Please turn off all cell phones. Only scientific calculators are allowed in the exam room. Students found to be using any electronic organizer or other electronic device during the exam will be given a grade of zero and asked to leave the testing area.

All answers are to be done on test paper. If more room is needed use the back side of the paper and indicate.

Read all questions carefully.

Answer all questions for full point value. Partial marks may be awarded for incomplete questions.

Make sure you have all data sheets and test pages.

Complete as many questions as soon as possible and then go back to incomplete questions.

Test papers not turned in to the instructor at the end of the test period will <u>not</u> be accepted.

Part I: Short Answer

Instructions: Circle the correct answer or fill your answer in the space provided. 1. Circle the chiral carbons, if any, in the compound ephedrine.



2. Circle the correct answer to state if the pair of molecules below are:

b) the same



c) constitutional isomers

Rate = $k[NO_2]^2$

a) enantiomers

3. Circle the correct answer corresponding to the number of ¹³C and ¹H signals observed in the corresponding NMR spectrum for 2,3-dimethyl-2-butene.



a) ${}^{13}C: 0$ and ${}^{1}H: 0$ b) ${}^{13}C: 2$ and ${}^{1}H: 1$ c) ${}^{13}C: 6$ and ${}^{1}H: 4$ d) ${}^{13}C: 4$ and ${}^{1}H: 2$

4. For the reaction below, give the order for the following:

 $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

a) The order with respect to NO₂:

b) The order with respect to CO(g):

c) The Overall reaction order:

5. The half-life for a first-order reaction is 49 min. What is the rate constant(k) in s^{-1} .

k = ______ s⁻¹

6. For the reaction mechanism below, circle the intermediates, if any.

Step 1: $Cl_2 + H_2S \rightarrow HCl + Cl^+ + HS^-$ slow Step 2: $Cl^+ + HS^- \rightarrow HCl + S$ fast

a) Cl^+ b) Cl_2 c) HCl d) H_2S e) HS^- f) S

7. Circle the correct answer corresponding to the following radioactive process: ${}^{96}_{41}Nb \rightarrow {}^{96}_{42}Mo + {}^{0}_{-1}e$

a) alpha decay b) beta decay c) positron emission d) electron capture

8. Complete each equation:

a) $^{241}_{95}Am \rightarrow ^{237}_{93}Np + _$

b) $^{75}_{34}Se +$ \rightarrow $^{75}_{33}As$

Part II: Long Answer

Instructions: Fill your answer in the space provided. Show all work for full point value. A. Nomenclature, Isomers and Organic Reactions

Answer any 4 of the 5 questions for complete value.

1. Write five(5) structural formulas and name for any of the nine(9) structural isomers of heptane.



3. Give the structure or name for each of the following aromatic compounds:

a) p-chlorobenzoic acid



4. Give structural formulas for the following: a) cyclopentanol

b) 4-methyl-2-hexanone

c) heptanoic acid

d) ethyl pentanoate

5. Predict the most likely products for the following reactions.a) Addition:



b) Combustion:

$$2 \longrightarrow + 9O_2(g) \longrightarrow$$

c) Substitution:



B. Spectroscopy
Answer any 2 of the 3 questions for complete value.
6. What feature(s) in their IR spectra would be used to distinguish between phenol(hydroxybenzene) and benzoic acid?

7. For the following pair of molecules state which type of spectroscopic technique (IR, NMR, or UV-Vis) could be used to distinguish them? Justify your answer.a) ethylbenzene and toluene

b) 2-propanol and propanone

8. You must identify a **single** unknown compound which has been narrowed down to the following two(2) structures. The IR and 13 C spectrum for the single unknown compound are given below.



Identify the structure that corresponds to the spectra on the following page and be sure to justify your answer using all spectral data.

IR Spectrum:



¹³C-NMR Spectrum:



C. Kinetics Answer any 4 of the 5 questions for complete value.

9. For the reaction below the following data were obtained at constant temperature:

Experiment	[BrO ₃ ⁻] (M)	[Br ⁻] (M)	$[\mathbf{H}^{+}](\mathbf{M})$	Initial Rate (M/s)
1	0.10	0.10	0.10	8.0×10 ⁻⁴
2	0.20	0.10	0.10	1.6×10 ⁻³
3	0.20	0.20	0.10	3.2×10 -3
4	0.10	0.10	0.20	3.2×10 ⁻³

 $BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$

a) What is the order with respect to each reactant?

b) State the overall order.

c) Write the rate law.

d) Calculate k using data from experiment 1.

10. For the reaction $2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g)$, the rate law is rate = $k[\text{NOCl}]^2$ and $k = 5.9 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$ at 400 K. If the initial concentration of NOCl is 0.025 M, what [NOCl] will remain after 5.00 hours?

11. For the decomposition reaction below:



 $E_a = 262 \text{ kJ/mol}$ and $k = 6.1 \times 10^{-8} \text{ s}^{-1}$ at 600 K. At what temperature is $k = 1.00 \times 10^{-4} \text{ s}^{-1}$. **BONUS:** Name the reactant and product in the reaction equation. 12.a) State the two(2) factors that determine whether or not a collision leads to reaction?

b) Explain why increasing the temperature increases the rate of most reactions very rapidly.

13. For the reaction $CO(g) + N_2O(g) \rightarrow CO_2(g) + N_2(g)$, $\Delta H_{rxn}^{\circ} = -365 \text{ kJ/mol}$ and $E_a(\text{fwd}) = 96 \text{ kJ/mol}$. Assuming a one-step reaction a) draw a reaction energy diagram.

Energy

Reaction coordinate

b) Calculate E_a(reverse reaction).

D. Nuclear Chemistry

Answer any 2 of the 4 questions for complete value. 14.a) The nuclide $^{212}_{84}Po$ decays to $^{208}_{82}Pb$. What kind of decay does polonium-212 undergo? Write the equation.

b) Write the equation for the reaction when the nuclide ${}^{30}_{15}P$ undergoes positron emission.

15. Arrange the following isotopes of magnesium in order of decreasing stability. Justify your answer.

12Ma	^{24}Ma	28Ma
12 ¹⁴ 9	$12^{101}9$	$12^{M}g$

16. A 3.50 μg sample of calcium-47 has an activity of 7.92×10¹⁰ Bq.
a) What is the half-life of Ca-47 in days?
b) How many days will it take for the activity to decrease to 8.02×10⁸ Bq?

17. The carbon in a sample of charcoal from the remains of an ancient campfire found in a cave has an activity of four disintegrations per minute per gram of carbon. Carbon has a half-life of 5715 years. If the carbon C-12/14 ratio has a specific activity of 15.3 disintegrations per minute per gram of carbon.

a) How old is the charcoal?

b) Explain how the decay of carbon-14 can be used to date the ancient charcoal.

Grade Sheet

The points awarded for this exam are outlined below. Please review. If there are any questions or possible corrections please consult the instructor.

Question	Points Awarded	
Part I		
1-8		
Part II		
Α		
1-5		
В		
6-8		
С		
9-13		
D		
14-17		
Total		

Comments:

Some Useful Data or Not!

Constants:	
1 mole = 6.022×10^{23} elementary particles	$1 \ \mu m = 1 \times 10^{-6} \ m$
$N_a = 6.0223 \times 10^{23}$	1 L = 1000 mL
1000 g = 1 kg	$R = 0.0821 L \cdot atm/K \cdot mole$
1 g = 1000 mg = 0.001 kg	$R = 8.314 \text{ J/K} \cdot \text{mole}$
1 lb = 453.6 g	$R = 8.314 \text{ kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{K} \cdot \text{mole}$
$1 \text{ pg} = 1 \times 10^{-12} \text{ g}$	1 kJ =1000 J
$1 \ \mu g = 1 \times 10^{-6} g$	1 cal = 4.184 J
1 km = 1000 m	1 Bq = 1 disintegration per second(d/s)
1 cm = 0.01 m	$1 \text{ Ci} = 3.70 \times 10^{10} \text{ d/s}$
$1 \text{ nm} = 1 \times 10^{-9} \text{m}$	$mCi = 1 \times 10^{-3} Ci$
$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$	$\mu Ci = 1 \times 10^{-6} Ci$

Equations:

$$T^{\circ}C = (5^{\circ}C/9^{\circ}F) \times (T^{\circ}F - 32^{\circ}F) \qquad T(K) = T(^{\circ}C) + 273.15^{\circ}C$$

$$t_{1/2} = \frac{In2}{k} = \frac{0.693}{k} \qquad In\frac{[A]_{t}}{[A]_{o}} = -kt \qquad \frac{1}{[A]_{t}} = kt + \frac{1}{[A]_{o}}$$

$$t_{1/2} = \frac{1}{k[A]_{o}} \qquad In\frac{k_{2}}{k_{1}} = \frac{E_{A}}{R}(\frac{1}{T_{1}} - \frac{1}{T_{2}}) \qquad Ink = \frac{-E_{A}}{RT} + InA$$

$$In\frac{N_{t}}{N_{o}} = In\frac{A_{t}}{A_{o}} = -kt \qquad A = kN \qquad A = \epsilon bc$$

Typical Wavenumber Absorption Ranges for Bond Stretching in the IR spectrum:

Bond type	Wavenumber range ${\rm cm}^{-1}$
C–H alkane	2960-2850
C–H alkene	3080-3020
C–H alkyne	3300
C–H aldehyde	2950-3200
$C{\equiv}C$ alkyne	2260-2100
$C{=}C$ alkene	1680-1620
$C{=}O \text{ ketone }$	1725-1705
$C{=}O$ aldehyde	1740-1720
$C{=}O$ ester	1750-1735
$C{=}O$ acid	1725-1700
O–H alcohol	3650-3600
O–H acid	3650-3600
N–H	3500-3300

<u>SCRAP PAPER(</u>Do not pass in!!)

Answer Set For Chem 1105-Midterm:

Part I A.



2.a)

3.b)

4.a) 2nd order; b) zero; c) 2nd order overall

5. 2.4×10⁻⁴ s⁻¹

6.a) Cl⁺, e) HS⁻

7. b)

8.a) $^{241}_{95}Am \rightarrow ^{237}_{93}Np + ^{4}_{2}He$

b) ${}^{75}_{34}Se + {}^{0}_{-1}e \rightarrow {}^{75}_{33}As$

Part II

A. 1. Any 5 of the following 9. n-heptane

2-methylhexane



2,3-dimethylpentane



3,3-dimethylpentane

2,2-dimethylpentne

2,4-dimethylpentane

2,2,3-trimethylbutane



3-ethylpentane



2.a) 1-ethyl-3,5-dimethylcyclohexaneb) 2,2,3-trimethylpentanec) 3,3-dimethyl-1-butyned) cis-3-octene

3.a)









В.

6. While both contain the –OH stretch at \sim 3600 cm⁻¹, benzoic acid would contain the C=O stretch at \sim 1700 cm⁻¹ while phenol does not.

7.a) Since both contain an aromatic ring and a linear alkyl group, both contain the same type of functional groups thus could not be distinguished by IR. NMR would contain an extra ¹H and ¹³C signal for the $-CH_2$ - group in ethylbenzene in comparison to toluene.

b) Both IR and NMR could be used to distinguish 2-propanol from propanone. In IR 2-propanol would contain the –OH stretch at \sim 3600 cm⁻¹, absent in propanone. Propanone would contain the C=O stretch at \sim 1700 cm⁻¹ which would be absent for 2-propanol.

¹H-NMR would contain 3 signals for 2-propanol while propanone would contain a single signal. ¹³C-NMR would be less useful as both compounds would contain 2 signals.

8. The correct structure is



due to to the fact that the IR spectrum contains the –OH stretch at \sim 3600 cm⁻¹ while the C=O stretch at \sim 1700 cm⁻¹ is absent. The ¹³C-NMR spectrum has 7 signals which is consistent with the alcohol while the ketone would only contain 5 signals.

C.

9.a) First order with respect to BrO_3^- , first order with respect to Br^- , second order with respect to H^+ .

b) Fourth order overall.

c) rate = $k[BrO_3^{-}][Br^{-}][H^{+}]^2$

d) $k = 8.0 \text{ M}^{-3} \cdot \text{s}^{-1}$

10. 0.020 M

11. 698 K BONUS: cyclobutane, ethene

12.a) The collision must have the necessary kinetic energy(E_a) and orientation.

b) Typically increasing the temperature increases the rate of reaction because a higher temperature results in more molecules having the necessary kinetic energy(E_a) to convert reactants into products.





Reaction coordinate

b) 461 kJ/mole

D.

14.a) Alpha decay. $^{212}_{84}Po \rightarrow ^{208}_{82}Pb + ^{4}_{2}He$

b) ${}^{30}_{15}P \rightarrow {}^{30}_{14}Si + {}^{0}_{+1}e$

15. Most stable: Mg-24 > Mg-28 > Mg-12 Least stable.

The average atomic mass of Mg is 24.31 amu. The closer the atomic mass of the isotope is to the average atomic mass, the more stable the nuclei.

If you calculate the ratio of neutrons to protons(N/Z) you get 1 for Mg-24, 0 for Mg-12, and 1.33 for Mg-28. The most stable nuclei with Z = 12 has a N/Z ratio of 1.0.

16.a) 4.53 days b) 30. days.

17.a) 11,000 years.

b) In the atmosphere cosmic rays generate C-14. With the natural decay of C-14 these competing processes result in a constant ratio of C-12/C-14 in the environment. When C-14 is converted into ¹⁴CO₂ and taken into living organisms (plants and animals) this constant ratio is also found in living organisms. When an organism dies it stops incorporating C-14 and the natural decay of C-14 results in a gradual decrease in the amount and thus activity that can be measured and used to determine the age of the object.