CHEMISTRY 202
Hour Exam III
December 1, 2022
Dr. D. DeCoste

Name ____________**KEY**____________

Signature ______________________________

T.A. ______________________________

This exam contains 23 questions on 13 numbered pages. Check now to make sure you have a complete exam. You have two hours to complete the exam. Determine the best answer to the first 20 questions and enter these on the special answer sheet. Also, circle your responses in this exam booklet. **Show all of your work and provide complete answers to questions 21, 22, and 23.**

1-20	(60 pts.)	________
21	(15 pts.)	________
22	(15 pts.)	________
23	(30 pts.)	________
Total	(120 pts)	________

Useful Information:

Table 15.6

Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of the straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

PV = nRT

R = 8.314 J/Kmol = 0.08206 Latm/molK

$k = Ae^{-Ea/RT}$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

1. The first four successive ionization energies for elements X and Y (both in the same Group on the periodic table) are given in the table below (the units are not kJ/mol):

	X	**Y**
First	170	200
Second	350	400
Third	1800	3500
Fourth	2500	5000

Which of the following **cannot** be element Y?

a) Be b) Mg c) Ca d) Sr e) Y could be any of these (a-d).

2. Which of the following bonds is the **most** polar?

a) N—O
b) P—O
c) S—O
d) Cl—O
e) F—O

3. Hydrocarbons, as the name implies, consist only of carbon and hydrogen. For so-called *saturated* hydrocarbons (with the maximum number of hydrogen atoms per molecule), the general formula is C_nH_{2n+2}. When hydrocarbons combust with oxygen gas, the products are carbon dioxide and water vapor. Estimate the **magnitude** of the difference between $\Delta H°$ values for these reactions for two hydrocarbons, one with x carbon atoms per molecule and the other with (x + 1) carbon atoms per molecule, in units of kJ/mol of hydrocarbon.

a) 400 kJ/mol b) 600 kJ/mol c) 800 kJ/mol d) 1000 kJ/mol e) 1200 kJ/mol

4. For ozone gas (O_3), the value of $\Delta H°_f$ is 143 kJ/mol. Which of the following is the best estimate for the average bond energy in the ozone molecule?

a) 72.0 kJ/mol b) 150 kJ/mol c) 300 kJ/mol d) 400 kJ/mol e) 500 kJ/mol

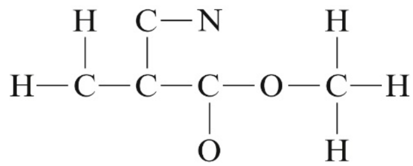
5. Consider the most stable species of an element as an isolated atom/ion and the most stable species of this element in an ionic compound. For which of the following are these the same?

a) sodium
b) magnesium
c) oxygen
d) All of the above (a-c).
e) None of the above (a-c).

6. Consider the following gases, all at 500K: Ne, C_3H_8, H_2O, He, C_2H_6. Arrange them from most ideal to least ideal behavior as gases. Which gas is in the middle of the order?

a) Ne b) C_3H_8 c) H_2O d) He e) C_2H_6

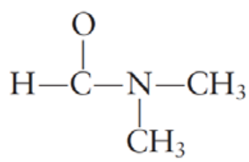
7. The skeletal structure of methyl cyanoacrylate (the main ingredient of Super Glue) is



Draw the complete Lewis structure for methyl cyanoacrylate by minimizing formal charge and determine the C—C—N bond angle.

a) 90° b) 109° c) 120° d) 180°

8. The skeletal structure for N,N-dimethylformamide (a common organic solvent, commonly abbreviated as DMF) is



How many possible resonance structures exist for DMF?

a) 0 b) 1 c) 2 d) 3 e) 4

9. You are your friends are playing this really cool game where you have found small molecules with the general formula XY_2 and written their formulas on separate pieces of paper. You make enough so that there is one example of every geometry-shape combination for a molecule with the formula XY_2. You then randomly take a piece of paper and determine the shape. What are the odds that the shape will be *bent*?

a) 10% b) 20% c) 33% d) 40% e) 60%

10. Each of the four groups below has two molecules with the same general formula:

- CO_2 and SO_2
- BF_3 and NF_3
- CF_4 and SF_4
- PF_5 and IF_5

How many groups include one nonpolar and one polar molecule?

a) 0 b) 1 c) 2 d) 3 e) 4

11. Consider the reaction $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$. You find that by doubling the partial pressures of both of the reactants, you increase the initial rate by a factor of 4. Assuming that the orders of reaction with respect to each reactant is limited to 0, 1, or 2, how many possible rate laws match this observation?

a) 0 b) 1 c) 2 d) 3 e) 4

12. The reaction aA → Products in which $[A]_0 = 8.00$ *M* is 31.4% complete after 14.0 minutes and 52.9% complete after 28.0 minutes. What is the rate law for this reaction?

a) rate = k
b) rate = $k[A]$
c) rate = $k[A]^2$
d) rate = $k[A]^3$
e) The rate law cannot be determined from these data.

13. We saw the decomposition of hydrogen peroxide, $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$, in lecture in a couple of different demonstrations. Suppose the following mechanism is proposed:

1. $H_2O_2(aq) \rightarrow 2HO(aq)$
2. $H_2O_2(aq) + OH(aq) \rightarrow H_2O(l) + HO_2(aq)$
3. $HO_2(aq) + OH(aq) \rightarrow H_2O(l) + O_2(g)$

Which of the following best follows from this mechanism?

a) The first step is most likely rate determining and the rate law = $k[H_2O_2]^2$.
b) The first step is most likely a fast equilibrium step and the rate law = $k[H_2O_2]^{3/2}$.
c) The steady state approximation is required because the rates of the steps have not been listed.
d) The first step is most likely rate determining and the rate law = $k[H_2O_2]$.
e) The first step is most likely a fast equilibrium step and the rate law = $k[H_2O_2]$.

14. How many of the following are true concerning the steady-state approximation?

I. We use this approximation when the rate determining step is known.
II. The concentration of an intermediate is assumed to be 0 *M*.
III. The rate of production of a reactant = the rate of consumption of a reactant.
IV. The rate law should include the intermediate given in the mechanism.

a) 0 b) 1 c) 2 d) 3 e) 4

15. You carry out three reactions at the same temperatures (as measured in Kelvin) and measure their rates. You then carry out these reactions at double the Kelvin temperature and find that the rate of reaction I increases by a factor of two, the rate of reaction II increases by a factor of three, and the rate of reaction III increases by a factor of four. Which reaction has the **lowest** activation energy? Assume the pre-exponential factors are constant with temperature.

a) Reaction I
b) Reaction II
c) Reaction III
d) The reactions have the same activation energy.
e) We cannot determine this without knowing the temperatures.

16. Consider a reaction as represented by the general equation aA + bB → Products.

You run this reaction with $[A]_0 = 1.0 \times 10^{-4}$ *M*, and $[B]_0 = 2.5$ *M* and obtain the following data:

Time (sec)	**[A] (M)**
0	1.0×10^{-4}
20.	6.3×10^{-5}
40.	4.0×10^{-5}
60.	2.5×10^{-5}
80.	1.6×10^{-5}

Assuming that the order of B limited to 0, 1, or 2, which of the following **cannot** be the value of the rate constant, *k* (with units of *M* and sec) at this temperature?

a) 6.8×10^{-4} b) 3.7×10^{-3} c) 9.2×10^{-3} d) 2.3×10^{-2} e) All of these could be the value of *k*.

17. Which of the following statements concerning the kinetics demonstrations in lecture is **true**?

a) We could not use the times for the reactions to determine relative initial rates for the "Iodine Clock Reaction" because the reactions happened rather quickly.
b) The catalyst in the "Activated Complex" demonstration took part in the reaction but was re-produced at the end.
c) Adding the $MnO_2(s)$ catalyst in the "Magic Genie" demonstration produced more oxygen than otherwise could have been produced by the reaction over time.
d) Because the concentrations of both HCl and acetic acid were 3.0 *M*, they reacted with baking soda with the same rates.
e) None of these are true.

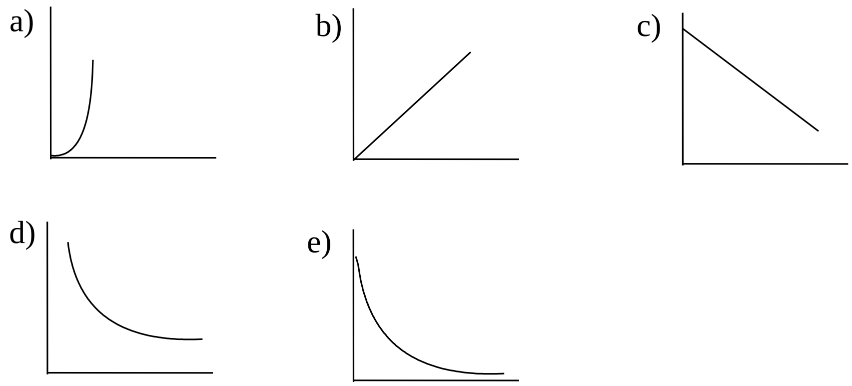
18. Consider the decomposition of ethanol, $C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g)$, at 125°C. You run the reaction and collect the following data:

Time (sec)	**$P[C_2H_5OH]$ (atm)**
0	3.200
30.00	1.684
60.00	1.143
90.00	0.8649
120.0	0.6957

What is the order of the reaction with respect to ethanol?

a) Zero order
b) First order
c) Second order
d) It cannot be determined with these data.

19, 20. Choose the best graph for the plots described below.



19. ln(*k*) vs. 1/T (K) for a typical chemical reaction. C

20. A plot of [A] vs. time for reaction type *aA* $\rightarrow$ *Products* which is not zero-order in A. E

21. We discussed Lewis structures as models – their significance and limitations. In this question we will examine these.

a. When drawing a Lewis structure of ozone (O_3), we need to include resonance structures. When drawing a Lewis structure of carbon dioxide, we do not need to use resonance structures. **Explain** why this is true, discussing **why we use resonance structures** and **why they show there is a flaw** in the Lewis structure model. **[5 pts.]**

See lectures, videos, and the textbook.

b. Consider the reaction of ozone to oxygen gas [$2O_3(g) \rightarrow 3O_2(g)$]. Use Lewis structures, bond energies (Table 13.6), and your understanding of thermodynamics, to decide if the reaction as written is: always spontaneous, never spontaneous, or spontaneous only at a certain temperature range (if you choose this one, specify if it spontaneous at relatively high or relatively low temperatures). If you believe that more information is needed to answer this, explain why, what is needed, and how it would help you to decide. Whichever you chose, make sure to **defend your answer**. **[5 pts.]**

See lectures, videos, and the textbook.

21. c. Use bond energies to estimate $\Delta H°_f$ for ozone, $O_3(g)$, and $\Delta H°_f$ for atomic oxygen, $O(g)$. **Show all work**. Which value, if either, is expected to be more accurate? **Defend your answer** by addressing in general why bond energies can be used to accurately determine $\Delta H°_f$ values, and why sometimes using bond energies is not as accurate. **[5 pts.]**

$3O_2(g) \rightarrow 2O_3(g)$:
= **101.5 kJ/mol**

$O_2(g) \rightarrow 2O(g)$: = **247.5 kJ/mol**

- The $\Delta H°_f$ for atomic oxygen is more accurate.

See lectures, videos, and the textbook.

22. In class we reacted sodium metal with water (and with chlorine gas!). It turns out sodium can react with ozone as well:

$$2Na(s) + O_3(g) \rightarrow Na_2O(s) + O_2(g)$$

Use the bond energies table (Table 13.6 from the textbook) and the given data to answer these questions.

a. Knowing ΔH°_f for sodium oxide is –416 kJ/mol, and given the table of bond energies (Table 13.6) and the following data, **determine the lattice energy** of sodium oxide. **Show all work. [8 pts.]**

$\Delta H_{sublimation}$ for Na(*s*) = 109 kJ/mol
1st ionization energy for Na(*g*) = 495 kJ/mol
Successive electron affinity values for O(*g*) = –149 kJ/mol, 886 kJ/mol

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LATTICE ENERGY = –2608.5 kJ

22. b. Using your answer to part a, Table 13.6, and the data below, **determine $\Delta H°$** for the reaction between sodium metal and ozone as written below (if you were not able to get a value for the lattice energy of sodium oxide, use –3014 kJ/mol). **Show all work. [7 pts.]**

$$2Na(s) + O_3(g) \rightarrow Na_2O(s) + O_2(g)$$

$\Delta H_{sublimation}$ for Na(*s*) = 109 kJ/mol
1st ionization energy for Na(*g*) = 495 kJ/mol
Successive electron affinity values for O(*g*) = –149 kJ/mol, 886 kJ/mol

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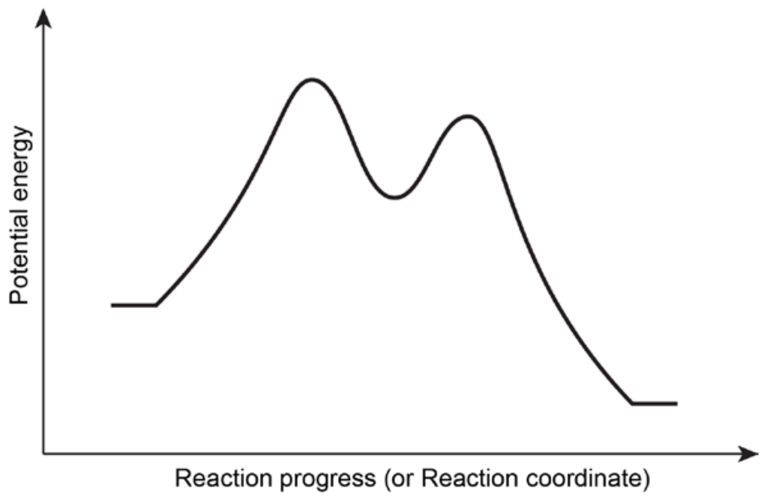
$\Delta H°$ = –517.5 kJ

23. Let's again consider the reaction in which ozone becomes oxygen gas [$2O_3(g) \rightarrow 3O_2(g)$]. Consider you are doing a kinetics experiment with this reaction and you have the following information:

- In monitoring the reaction, you find the successive half-lives to be constant.
- The activation energy of the reaction is about 300 kJ.
- The reaction coordinate looks like the following:



In this problem you will be developing a mechanism, evaluating experimental data, and applying the steady-state approximation.

Please **show all work** and **provide concise, yet complete, explanatory answers**. Think about what you want to do/say before writing.

PLEASE DO NOT INCLUDE ANY ANSWERS ON THIS PAGE

23. a. **Develop a mechanism** for the reaction and **determine the rate law**. **Defend your answer** by explaining how you used each of the three pieces of information given on the previous page. In your discussion, use the bond energies on Table 13.6 (you can also use your estimates of $\Delta H^\circ_\mathbf{f}$ for ozone and atomic oxygen from problem #21 if you wish) to **justify the shape of the reaction coordinate**. Also, **discuss** how your mechanism and rate law **make sense chemically**. **[10 pts.]**

Potential mechanism to match this:

1. $O_3(g) \rightarrow O_2(g) + O(g)$ slow
2. $O_3(g) + O(g) \rightarrow 2O_2(g)$ fast

Rate law: **rate = k[O_3(g)]**

See lectures, videos, and the textbook.

23. b. You are going to run the experiment starting with 5.000 atm O_3 in an otherwise evacuated 10.0-L rigid container at 298K. The first two readings are given. Please **fill in the rest of the expected data** in the table below and **defend your answers** with calculations. Note: you are to estimate as closely as possible the time when maximum pressure is reached and include it in the table below. **Show/explain all work. [10 pts.]**

Time (seconds)	P_{total} (atm)
0	5.000
15.00	5.732
30.00	(6.250)
45.00	(6.616)
60.00	(6.875)
75.00	(7.058)
(2400)	Max. = 7.500

23. c. You should know which step is the rate-determining-step both from the reaction coordinate and from your mechanism (and you should have discussed this in part a). But just to make sure, you decide to **apply the steady-state approximation** (SSA) to your mechanism. **Define the rate** of the reaction in **two ways**, and show how the SSA in both cases **gives consistent answers** to each other. (use different symbols for the rate constants as we did in lecture, text, and videos, such as k_1, etc. to distinguish the different steps of the mechanism as appropriate). **[10 pts.]**

- rate = $-\frac{d[O_3]}{dt} = 2k_1[O_3]$

- rate = $\frac{d[O_2]}{dt} = 3k_1[O_3]$

See lectures, videos, and the textbook.