

Name _____ **KEY** _____

Signature _____

T.A. _____

1-20	(60 pts.)	_____
21	(15 pts.)	_____
22	(17 pts.)	_____
23	(28 pts.)	_____
Total	(120 pts)	_____

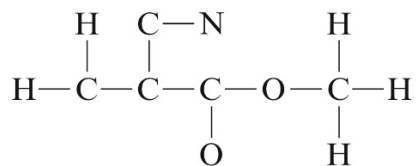
Table 15.6

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]}$
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	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

$$K = ^\circ C + 273$$

$$k = Ae^{-E_a/RT} \qquad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

1. How many of the following can we explain **without** using the concept of orbitals?
- The general trend of ionization energy vs. atomic number.
 - The demonstration of the effect of a magnet on liquid oxygen and liquid nitrogen.
 - The polarity of the water molecule.
 - The Lewis structure of ammonia (NH₃).
 - The demonstration of the effect of “black light” on club soda.
- a) 0 b) 1 c) 2 **d) 3** e) 4
2. Consider using data other than ΔH°_f values to determine the enthalpy of reaction of magnesium metal with hydrogen chloride gas to produce magnesium chloride and hydrogen gas. How many of the following values would **not** be needed to determine ΔH_{rxn} for this?
- The second ionization energy of magnesium.
 - The bond energy of hydrogen chloride.
 - The electron affinity of chlorine.
 - The ionization energy of hydrogen.
 - The enthalpy of hydration of magnesium chloride.
- a) 0 b) 1 **c) 2** d) 3 e) 4
3. Which of the following is the best estimate of ΔH°_f for the gaseous hydrogen atom?
- a) -432 kJ/mol b) -216 kJ/mol c) 0 kJ/mol **d) 216 kJ/mol** e) 432 kJ/mol
4. Complete the following Lewis structure and choose the correct statement below.



To complete the Lewis structure, there needs to be

- a) more lone pairs of electrons than additional bonds and not all atoms can have a formal charge of zero.
- b) more lone pairs of electrons than additional bonds and all atoms can have a formal charge of zero.**
- c) more additional bonds than lone pairs of electrons and not all atoms can have a formal charge of zero.
- d) more additional bonds than lone pairs of electrons and all atoms can have a formal charge of zero.
- e) the same number of additional bonds as lone pairs of electrons and not all atoms can have a formal charge of zero.

9. How many of the following statements is/are **false**?

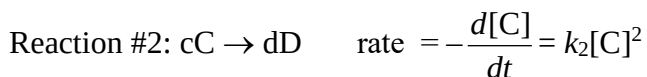
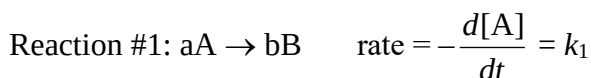
- Consider three different real gases. The gas that acts most ideally will have the highest boiling point.
- Consider the Noble gases He, Ne, Ar, Kr, and Xe. Of these, Xe is expected to have the largest correction factors in the van der Waals “real gas” equation.
- As the temperature of a real gas is increased, it is more likely that $PV/nRT = 1$ for that gas.
- Methane (CH_4) is a more ideal gas than propane (C_3H_8) at the same conditions of pressure and temperature.
- Consider that the pressure that we measure for a real gas is different from what we would predict using the ideal gas law. It is most likely the case that the measured pressure is smaller than the ideal pressure.

a) 1 b) 2 c) 3 d) 4 e) 5

10. How many different stable compounds exist that have the formula $\text{C}_3\text{H}_9\text{N}$, and how many of them exhibit hydrogen bonding?

- a) Two compounds exist and both of them exhibit hydrogen bonding.
- b) Three compounds exist and two of them exhibit hydrogen bonding.
- c) Three compounds exist and all of them exhibit hydrogen bonding.
- d) Four compounds exist and three of them exhibit hydrogen bonding.
- e) Four compounds exist and all of them exhibit hydrogen bonding.

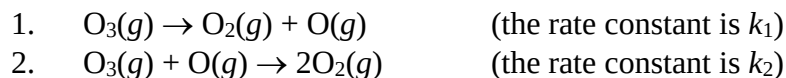
11. Consider the following two generic reactions:



The time required to reach the second half-life is the same for both Reaction #1 and Reaction #2. If the values of the rate constants (k_1 and k_2) for the reactions are equal and $[\text{A}]_0 = [\text{C}]_0$, can we determine the initial concentration of the reactants?

- a) Yes, and the value is 1.00M.
- b) Yes, and the value is 2.00M.
- c) Yes, and the value is 4.00M.
- d) Yes, but only in terms of ($k_1 \times k_2$) for the two reactions.
- e) No, we cannot.

12. Consider the conversion of ozone to oxygen gas, represented as $2\text{O}_3(g) \rightarrow 3\text{O}_2(g)$. You are told that the reaction follows the following mechanism:



You apply the steady-state approximation to this mechanism and use $\text{rate} = \frac{d[\text{O}_2]}{dt}$. Determine the rate law for the reaction.

- a) $\text{rate} = k_1[\text{O}_3]$
 b) $\text{rate} = 2k_1[\text{O}_3]$
 c) $\text{rate} = 3k_1[\text{O}_3]$
 d) $\text{rate} = k_1k_2[\text{O}_3]$
 e) $\text{rate} = 2k_1[\text{O}_2]$
13. Consider a reaction of the type $aA + bB \rightarrow \text{products}$. Because there are two reactants, you are going to run this in a “pseudo-order” fashion (as discussed in lecture, videos, and in the Ferroin Lab). You run two experiments in which $[\text{A}]_0$ is the same, but $[\text{B}]_0$ in experiment #1 is different from $[\text{B}]_0$ in experiment #2. And, of course, $[\text{B}]_0 \gg [\text{A}]_0$ in both experiments. After running the experiment and analyzing the data, you find that the apparent rate constant in experiment #1 is the same as the apparent rate constant in experiment #2, and this value results in different values for the rate constant, k . Which of the following best explains this?
- a) The reaction is zero order in both A and B.
 b) The reaction is first order in A and zero order in B.
 c) The reaction is zero order in A and first order in B.
 d) The reaction could be any order in A but it must be zero order in B.
 e) Something went wrong somewhere.

- 14, 15. Consider the reaction $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$. You run this reaction at a constant temperature of 25°C and obtain the following data:

time (minutes)	$[\text{N}_2\text{O}_5] \text{ (M)}$
0	1.00×10^{-2}
20.0	5.00×10^{-3}
40.0	3.33×10^{-3}
60.0	2.50×10^{-3}
80.0	2.00×10^{-3}

14. Calculate the value of the rate law, k , at 25°C.
- a) 1.00×10^{-4} b) 2.50×10^{-4} c) 3.47×10^{-2} d) 0.201 e) 5.00
15. The slow step of the mechanism is accomplished by the breaking of the N–O bond. Which of the following most closely estimates the first half-life if the same experiment (with $[\text{N}_2\text{O}_5]_0 = 1.00 \times 10^{-2} \text{ M}$) is carried out at 45°C?
- a) 7.30 seconds b) 58.2 seconds c) 4.95 minutes d) 10.0 minutes e) 19.9 minutes

- 16, 17. Consider the decomposition of ethanol at constant temperature as represented by the following reaction: $\text{C}_2\text{H}_5\text{OH}(g) \rightarrow \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g)$. Pure ethanol is added to a rigid container on an alumina surface and the reaction is monitored as it progresses. The following results are collected:

Time (sec)	Total Pressure (torr)
0	100.00
25.00	121.75
50.00	143.50
100.0	187.00

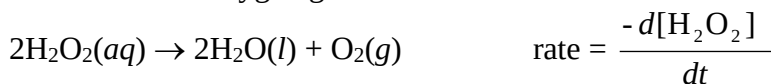
16. Determine the value of the rate constant, k .

a) 7.146×10^{-5} b) 1.112×10^{-4} c) 7.872×10^{-3} d) 9.810×10^{-3} **e) 0.8700**

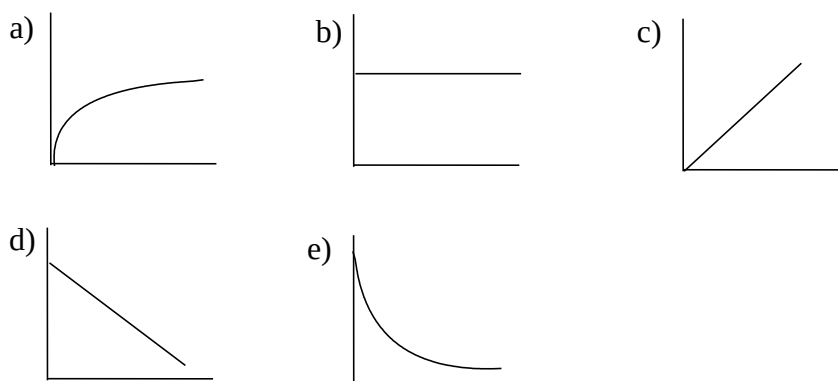
17. Determine the total pressure at $t = 150.0$ seconds.

a) 191.5 torr **b) 200.0 torr** c) 230.5 torr d) 250.0 e) 268.5 torr

- 18-20. These questions consider the decomposition of an aqueous solution of hydrogen peroxide in which we collect oxygen gas at constant volume:



Choose the **best** graph for the plots described below. A graph may be used once, more than once, or not at all. All reactions described are at constant temperature.



18. Pressure of $\text{O}_2(g)$ (y) vs. time (x) if the reaction is first order in $\text{H}_2\text{O}_2(aq)$. **A**
19. Pressure of $\text{O}_2(g)$ (y) vs. time (x) if the reaction is second order in $\text{H}_2\text{O}_2(aq)$. **A**
20. Rate of reaction (y) vs. $[\text{H}_2\text{O}_2]$. The reaction has an activation energy of around 150 kJ/mol and the following mechanism applies: **C**
- $\text{H}_2\text{O}_2 \rightarrow 2 \text{OH}$
 - $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$
 - $\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$

21. Recall from the first two exams that a saturated hydrocarbon has the general formula C_xH_{2x+2} (surely you saw this coming!). A saturated hydrocarbon reacts with oxygen gas, and the products are carbon dioxide and water. Please answer the following questions:
- Using appropriate bond energies, **derive an equation** to determine the enthalpy of reaction in terms of x . **Show all work. Define bond energy** as part of your answer.
 - For an “unknown” hydrocarbon, there are two values of ΔH_{rxn} for the hydrocarbon with oxygen gas: -2044.5 kJ/mol and -2220.5 kJ/mol , depending on the state of water.
 - Use your derived equation and the given values of ΔH_{rxn} to **determine the formula** for the unknown hydrocarbon.
 - **Match the values** of ΔH_{rxn} with the state of water (vapor or liquid) and **justify** your answer in **two ways**.
 - Consider if your derived equation will **predict ΔH_{rxn} more or less accurately** as the **value of x increases**. Provide one piece of support for each answer. That is, what is one reason why it might predict ΔH_{rxn} more accurately? What is one reason why it might predict ΔH_{rxn} less accurately?

Full credit is reserved for a **logical approach** and **legible presentation** to the problem that **we can follow**. Use the front of the next page if needed. [15 points]

C₃H₈

21. Please continue any work on this page, if needed.

22. In the simplest model of aqueous acids, a proton (H^+) is donated to water in the solution, and the reaction can be represented as $\text{HA}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$. When “A” is a halogen (F, Cl, Br, or I), these are known as hydrohalic acids. Of the hydrohalic acids, only HF is “weak”, meaning that the equilibrium constant for the acid, designated as K_a , is less than 1. Why? Thermodynamics, of course! Part of the reason is that the H–F bond is so strong (resulting in a less favorable enthalpy of reaction for HF compared to the others), and part of the reason is the strong attraction of the fluoride ion to water (resulting in a less favorable entropy of reaction for HF compared to the others).
- Use the following data to **determine the value of K_a for hydrofluoric acid** at 25.0°C ; that is, for the equation: $\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$. **Show all work.**
 - It is often useful to compare weak acids by their $\text{p}K_a$ values, in which $\text{p}K_a = -\log_{10}(K_a)$. **Determine the $\text{p}K_a$ of hydrofluoric acid** at 25.0°C .

Enthalpy of hydration of $\text{HF}(\text{g})$	-78.0 kJ/mol
Enthalpy of hydration of $\text{H}^+(\text{g})$	-1130.0 kJ/mol
Enthalpy of hydration of $\text{F}^-(\text{g})$	-510.0 kJ/mol
Ionization energy of $\text{H}(\text{g})$	1312.2 kJ/mol
Electron affinity of $\text{F}(\text{g})$	-327.8 kJ/mol
Bond energy of $\text{HF}(\text{g})$	565 kJ/mol
S° for $\text{HF}(\text{aq})$	88.6 J/Kmol
S° for $\text{F}^-(\text{aq})$	-13.8 J/Kmol

Notes: S° for $\text{H}^+(\text{aq}) = 0 \text{ J/K}$; recall that $\Delta G = \Delta G^\circ + RT\ln(Q)$ and $G = H - TS$

Full credit is reserved for a **logical approach** and **legible presentation** to the problem that **we can follow**. Use the front of the next page if needed. **Remember:** What are you looking for? What does this mean? What are you given? etc. It would be good to plan your solution on scratch paper before beginning below. [17 points]

- $K_a = 7.28 \times 10^{-4}$
- $\text{p}K_a = 3.14$

22. Please continue any work on this page, if needed.

23. You study the kinetics of the reaction of the conversion of ozone to oxygen gas, represented as $2\text{O}_3(g) \rightarrow 3\text{O}_2(g)$, at a constant temperature of 25°C . You begin by adding pure ozone to a container fitted with a massless, frictionless piston until the volume is 100.0 L. You then allow the reaction to progress, collecting the following data:

Time (minutes)	Volume (L)
0	100.0
2.224	105.0
4.595	110.0
7.163	115.0
10.000	120.0
13.222	125.0
17.008	130.0
21.704	135.0
28.079	140.0
38.587	145.0

NOTES

- Define the rate as $-\frac{d[\text{O}_3]}{dt}$
 - You may be thinking, "But wait! This is a closed container so the reaction will reach equilibrium." But fear not! A quick check of ΔG_f° values shows us that not only is the reaction spontaneous, but the value of the equilibrium constant is so great that we can essentially treat this reaction as going to completion.
 - Full credit is reserved for a **logical approach** and **legible presentation** to the problem that **we can follow**.
- a. **Determine the rate law** for the reaction, along with **the value, with unit(s), of the rate constant. Show all work and justify your answer.** Use the front of the next page if needed. **[18 points]**
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- **rate = $k[\text{O}_3]$**
- **$k = 0.0693 \text{ min}^{-1}$**

23. a. Please continue any work on this page, if needed.

23. b. Determine the **volume of the container** after the reaction has progressed at 25°C for 50.000 minutes. **Show all work.** [4 points]

- $V = 147.7 \text{ L}$

- c. Given that the activation energy for the reaction is 45.0 kJ/mol, determine the **volume of the container** after 3.014 minutes if the reaction is carried out at 35°C instead of 25°C. **Show all work** and **explain why** your relative **answer makes sense.** [6 points]

- $V = 111.7 \text{ L}$

- Reaction is faster, so volume at ~3 seconds at 35°C is greater than at ~3 seconds at 25°C.