

CHEMISTRY 202
 Hour Exam III
 November 30, 2023
 Dr. D. DeCoste

Name **KEY**
 Signature _____
 T.A. _____

This exam contains 23 questions on 12 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	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

$PV = nRT$

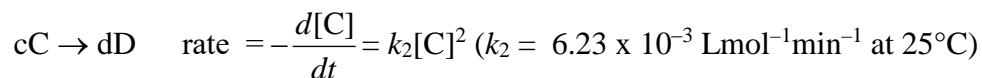
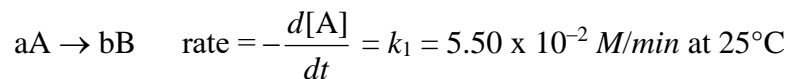
$R = 8.314 \text{ J/Kmol} = 0.08206 \text{ Latm/molK}$

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

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

7. How many of the following statements are **false**? Remember that not necessarily true means false!
- Any molecule exhibiting only London dispersion forces has a lower boiling point than any molecule exhibiting hydrogen-bonding.
 - Molecules with both a tetrahedral geometry and tetrahedral shape are nonpolar.
 - The molecules CF_4 and SF_4 have different geometries and different shapes.
 - For a given substance, the magnitude of the value of ΔH_{fusion} is generally greater than the magnitude of the value of $\Delta H_{\text{vaporization}}$.
- a) 0 b) 1 c) 2 **d) 3** e) 4
8. How many of the following polyatomic ions – carbonate, nitrate, sulfate, and phosphate – **must** be drawn with equivalent resonance structures?
- a) 0 b) 1 **c) 2** d) 3 e) 4
9. Which of the following has the **highest boiling point**?
- a) CH_3OCH_3 b) CH_3OH c) $\text{CH}_3\text{CH}_2\text{CH}_3$ d) HCl **e) $\text{CH}_3\text{CH}_2\text{OH}$**
10. Which of the following statements is **true** concerning the behavior of real gases?
- The observed pressure of a gas is lower than expected ideally, and the volume of the container is less than the volume available to the gas.
 - The observed pressure of a gas is lower than expected ideally, and the volume of the container is greater than the volume available to the gas.**
 - The observed pressure of a gas is greater than expected ideally, and the volume of the container is greater than the volume available to the gas.
 - The observed pressure of a gas is greater than expected ideally, and the volume of the container is less than the volume available to the gas.
11. Consider two reactions: Reaction I can be represented as $aA \rightarrow \text{Products}$ and is zero-order in A, and Reaction II can be represented as $bB \rightarrow \text{Products}$ and is second-order in B. Reaction II has a rate constant with a value two-times that of Reaction I. Consider beginning the separate reactions with concentrations of A and B both at $1.000M$ and letting them proceed until the concentration of each is $0.125M$. How do the times of the reactions compare?
- The time for [B] to equal $0.125M$ is four (4) times as great as the time for [A] to equal $0.125M$.**
 - The time for [B] to equal $0.125M$ is two (2) times as great as the time for [A] to equal $0.125M$.
 - The time for [A] and [B] to equal $0.125M$ is the same.
 - The time for [A] to equal $0.125M$ is two (2) times as great as the time for [B] to equal $0.125M$.
 - The time for [A] to equal $0.125M$ is four (4) times as great as the time for [B] to equal $0.125M$.

12-13. Consider the following two generic reactions:



In a particular experiment, A and C are placed in separate containers (at 25°C) under conditions such that $[A]_0 = [C]_0 = 3.14\text{M}$. You allow the reactions to progress until $[A] = [C]$.

12. Determine the time required such that $[A] = [C]$.

- a) 3 minutes b) 4 minutes c) 5 minutes **d) 6 minutes** e) $[A]$ will never equal $[C]$.

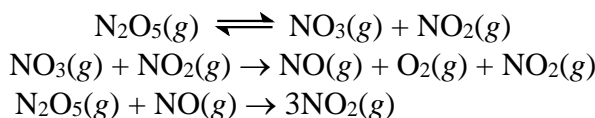
13. Determine the concentration of A and C when they are equal.

- a) 0.116M b) 2.77M **c) 2.81M** d) 2.87M e) $[A]$ will never equal $[C]$.

14. We want to study the kinetics of the decomposition of a compound into its elements in their standard states. We decide to do so by monitoring the total pressure of the system over time. For which of the following compounds will this approach **not** work?

- a) HF(g)**
 b) $\text{NH}_3(\text{g})$
 c) $\text{H}_2\text{O}(\text{g})$
 d) We can use total pressure to determine the kinetics of the decomposition for all of the compounds in a-c above.
 e) We cannot use total pressure to determine kinetic data because we need the partial pressure of the compound being studied.

15. Consider the following proposed mechanism for the decomposition of dinitrogen pentoxide (N_2O_5) to produce nitrogen dioxide and oxygen gases:

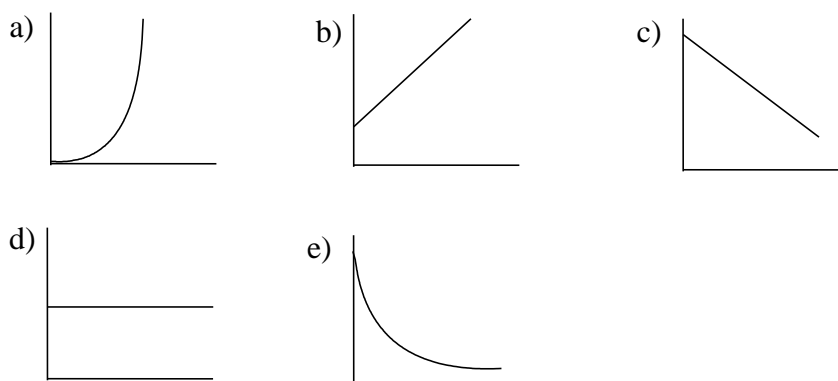


To apply the steady-state approximation which of the following equations should be used? Note, the subscripts for the rate constants represent what we discussed in lecture and videos.

- a) $k_1[\text{N}_2\text{O}_5] = k_2[\text{NO}_3][\text{NO}_2]$
 b) $k_2[\text{NO}_3][\text{NO}_2] = k_{-2}[\text{NO}][\text{O}_2][\text{NO}_2]$
 c) $k_1[\text{N}_2\text{O}_5] + k_2[\text{NO}_3][\text{NO}_2] = k_3[\text{N}_2\text{O}_5][\text{NO}] + k_{-1}[\text{NO}_3][\text{NO}_2]$
d) $k_1[\text{N}_2\text{O}_5] = k_{-1}[\text{NO}_3][\text{NO}_2] + k_2[\text{NO}_3][\text{NO}_2]$
 e) Two of the above (a-d) should be used.

16. Catalysts can be specific for a certain reaction. Suppose you invent a catalyst to target a reaction you've been studying. The catalyzed reaction (which has an activation energy of 49 kJ/mol) occurred after about 10 seconds at 25°C. When uncatalyzed, the reaction has an activation energy of 75 kJ/mol. About how long does the uncatalyzed reaction take at 25°C? Assume the catalyzed and uncatalyzed reactions have the same form and orders, and the pre-exponential factor, A , is the same for both.
- a) About 15-20 seconds.
b) About 45 minutes.
c) About 12 hours.
 d) About 4 days.
e) About 2 weeks.
17. How many of the following will change both the value of the equilibrium constant, K , and the value of the rate constant, k , for a given reaction?
- Adding a catalyst.
 - Changing the concentrations of the reactants and/or products.
 - Changing the temperature.
 - Carrying out the reaction in a closed container.
- a) 0 b) 1 c) 2 d) 3 e) 4

18-20. Choose the best graph for the plots described below. A graph may be used once, more than once, or not at all.



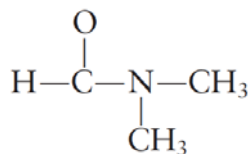
18. Length of half-life (y) vs. time (x) for reaction type $aA \rightarrow \text{Products}$ which is second-order in A . b
19. Rate of reaction (y) vs. $[A]$ (x) for reaction type $aA \rightarrow \text{Products}$ which is zero-order in A . d
20. $1/[A]$ (y) vs. time (x) for reaction type $aA \rightarrow \text{Products}$ which is second-order in A . b

21. We discussed how we can often use bond energies to estimate enthalpies of reactions instead of using ΔH°_f values. In this problem you will consider two examples.
- a. The standard state of bromine at 1 atm and 25°C is a liquid. Use bond energies (Table 13.6) and the fact that ΔH°_f for $\text{HBr}(g)$ is -36 kJ/mol to **estimate ΔH°_f for $\text{Br}_2(g)$** . **Full credit is reserved for showing all work in a coherent fashion** so that we can follow what you are doing. **[6 pts.]**
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ΔH°_f for $\text{Br}_2(g) = 29 \text{ kJ/mol}$

[Note: actual value is 31 kJ/mol]

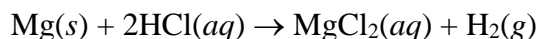
21. b. The molecule N,N-dimethylformamide (which is used as an organic solvent and is commonly abbreviated as DMF) has the following skeletal structure:



We can synthesize DMF by reacting the gases carbon monoxide and dimethylamine, which has the formula $\text{HN}(\text{CH}_3)_2$. Considering **all possible resonance structures** for DMF and **formal charge arguments**, use bond energies (Table 13.6) to **estimate ΔH° for the synthesis of DMF** from carbon monoxide and dimethylamine and **justify your answer. Full credit is reserved for showing all work in a coherent fashion** so that we can follow what you are doing. [9 pts.]

ΔH° for DMF should be closer to 0 kJ/mol than +77 kJ/mol

22. In lecture we discussed how to determine the enthalpy change for the reaction between magnesium metal and hydrogen chloride gas (to produce magnesium chloride solid and hydrogen gas). Somebody asked during lecture (thank you, by the way!) about the reaction between magnesium metal and an aqueous solution of hydrochloric acid, which produces an aqueous solution of magnesium chloride and hydrogen gas:



Use the following data (some of which you may not need to use, depending on how you carry out the calculations) and Table 13.6 to **determine the enthalpy of hydration of the Mg^{2+} ion.**

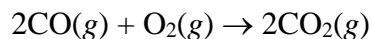
Enthalpy of sublimation of $\text{Mg}(s)$ (kJ/mol): 150.
Enthalpy of formation of $\text{Mg}^{2+}(aq)$ (kJ/mol): -462
Enthalpy of formation of $\text{H}^+(aq)$ (kJ/mol): 0
Enthalpy of hydration of $\text{H}^+(g)$ (kJ/mol): -1091
Enthalpy of hydration of $\text{Cl}^-(g)$ (kJ/mol): -378
Ionization energy for $\text{H}(g)$ (kJ/mol): 1312
Successive ionization energies of $\text{Mg}(g)$ (kJ/mol): 735, 1445
Electron affinity of $\text{Cl}(g)$ (kJ/mol): -349
Lattice energy for MgCl_2 (kJ/mol): -2493

Full credit is reserved for showing all work in a coherent fashion in a coherent fashion so that we can follow it. Make sure to show the reactants and products of each step, along with **phases**. Use the next page if needed. [15 pts.]

$$\Delta H_{\text{hydration of Mg}^{2+}(g)} = -1918 \text{ kJ.} \quad [\text{NOTE: ACTUAL VALUE} = -1926 \text{ kJ}]$$

22. Continue work on this problem below, if needed.

23. A friend from another university who is studying kinetics asks you for help. Specifically, this friend does not understand how different mechanisms can result in different rate laws and does not understand how to use “pseudo-order” data to determine a rate law. You decide to help this friend using the following reaction:



- a. You first show this friend how different mechanisms can result in different rate laws.
- i. **Develop** a “simple” **mechanism** (that is, no steps reaching equilibrium, no use of the steady-state approximation) that results in the rate law: $\text{rate} = k[\text{CO}][\text{O}_2]$. **Draw Lewis structures** for all reactants and products in the elementary steps to show how this reaction proceeds. **Label** the steps as slow or fast and **justify**. **Justify your mechanism.** [7 pts.]
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See lectures, textbook, and videos.

23. a. ii. Your friend asks, "So they are all simple like this?" **Develop a mechanism** that results in a rate law of: $\text{rate} = k[\text{CO}]^2$, which has a step that quickly reaches **equilibrium**. **Label** the steps as slow or fast and **justify**. **Justify your mechanism.** [7 pts.]
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See lectures, textbook, and videos.

23. a. iii. Your friend says, "I would think the rate law should be: $\text{rate} = k[\text{CO}]^2[\text{O}_2]$ for this reaction because of the balanced equation." You, of course, tell your friend that it *could* be. Develop a mechanism that results in a rate law of $\text{rate} = k[\text{CO}]^2[\text{O}_2]$. It could be a "simple mechanism" or include a step that reaches equilibrium, but please **don't** introduce the steady-state approximation. **Label** the steps as slow or fast and **justify**. **Justify your mechanism. [7 pts.]**
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See lectures, textbook, and videos.

23. b. You then help your friend with using data to determine a rate law. Specifically pseudo-order rate law data (let's hear it for the Ferroin lab report!).

You run two experiments: in Experiment #1 you begin with 1.00000 atm CO(g) and 1.00×10^{-3} atm O₂(g), and in Experiment #2 you begin with 2.00000 atm CO(g) and 2.00×10^{-3} atm O₂(g)

Your data are as follows:

Experiment #1

P_{total}	Time
1.00100 atm	0 seconds
1.00050 atm	8.0000 seconds
1.00025 atm	12.0000 seconds

Experiment #2

P_{total}	Time
2.00200 atm	0 seconds
2.00100 atm	2.0000 seconds
2.00050 atm	3.0000 seconds

Which of the mechanisms you developed in part a do these data support? **Show all work and justify your answer. [9 pts.]**

Supports the mechanism in part ii of part a.