CHEMISTRY 202
Hour Exam III
December 5, 2024
Dr. D. DeCoste

Name **KEY**

Signature ______________________________

T.A. ___________________________________

This exam contains 23 questions on 11 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	(20 pts.)	_________
22	(20 pts.)	_________
23	(20 pts.)	_________
Total	(120 pts)	_________

Useful Information:

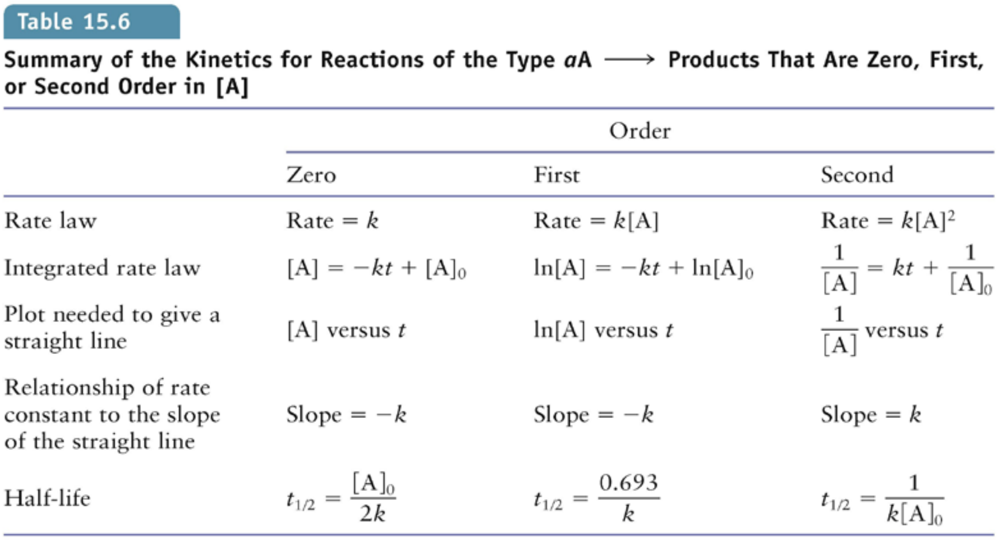


Table 15.6

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	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

$PV = nRT$ $\quad$ $K = {}^\circ C + 273$

$R = 8.314$ J/Kmol $= 0.08206$ Latm/molK

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

1. How many of the following statements are **true**?

   I. The ionization energy for the “X atom” has the same magnitude as the electron affinity for the “X^- ion”.
   II. In comparing phosphorus, oxygen, and nitrogen in forming a bond with hydrogen, the most polar bond is between the hydrogen and oxygen, and the least polar bond is between hydrogen and phosphorus.
   III. The first electron affinity for sodium is exothermic, while the second electron affinity for oxygen is endothermic.
   IV. Ionization energies for all neutral atoms are endothermic.

   a) 0 b) 1 c) 2 [✓ d) 3] e) 4

2. Which element is the **second most** electronegative?

   a) P b) S [✓ c) O] d) F e) Ne

3. Consider Lewis structures for the sulfate, carbonate, phosphate, and nitrate ions. How many of these polyatomic ions have **no** resonance Lewis structure for which the central atom has a formal charge of zero?

   a) 0 [✓ b) 1] c) 2 d) 3 e) 4

4. For how many of the following compounds are the names of the geometry and shape around the central atom of that compound the same?

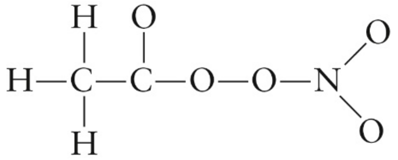
   CH_4, PCl_5, SO_2, BF_3, SF_4, CO_2, NH_3, $XeCl_2$, OCl_2

   [✓ a) 4] b) 5 c) 6 d) 7 e) 8

5. In studying VSEPR we have discussed eleven different names for shapes of small molecules (bent, linear, octahedral, see-saw, square planar, square pyramidal, tetrahedral, trigonal planar, trigonal bipyramidal, trigonal pyramidal, and T-shape). Consider a molecule with the general formula XZ_n (X is the central atom). For how many of the shapes is the molecule symmetrical around the central atom?

   a) 2 b) 4 c) 5 [✓ d) 6] e) 9

6. Consider the following skeletal Lewis structure. For the resonance structure that **minimizes** formal charge, how many of the atoms do **not** have a formal charge of zero?



   a) 0 b) 1 [✓ c) 2] d) 3 e) 4

7. For similarly sized molecules, how many of the following are **directly** related?

- Strength of intermolecular force and boiling point.
- Strength of intermolecular force and vapor pressure.
- Vapor pressure and boiling point.
- Vapor pressure and deviation from ideal gas law.

a) 0 [✓ b) 1] c) 2 d) 3 e) 4

8. Of H_2CO, CH_3OCH_3, CH_2F_2, and $(CH_3)_3N$, how many are **polar molecules** that do **not** exhibit hydrogen bonding?

a) 0 b) 1 c) 2 d) 3 [✓ e) 4]

9. Which of the following correctly ranks the given diatomic halogens from **highest to lowes**t melting point?

a) $I_2 > Cl_2 > Br_2$
[✓ b) $I_2 > Br_2 > Cl_2$]
c) $Cl_2 > Br_2 > I_2$
d) $Cl_2 > I_2 > Br_2$
e) $Br_2 > Cl_2 > I_2$

10. Which of the following is the correct rate law if the reaction $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$ is assumed to proceed by the following mechanism?

$$\begin{array}{ll} Cl_2(g) \rightleftharpoons 2Cl(g) & \text{(fast equilibrium)} \\ CO(g) + Cl(g) \rightleftharpoons COCl(g) & \text{(fast equilibrium)} \\ COCl(g) + Cl_2(g) \rightarrow COCl_2(g) + Cl(g) & \text{(slow)} \\ 2Cl(g) \rightarrow Cl_2(g) & \text{(fast)} \end{array}$$

a) $k[COCl][Cl_2]$
b) $k[CO][Cl_2]$
c) $k[CO][Cl_2]^2$
d) $k[CO][Cl_2]^{1/2}$
[✓ e) $k[CO][Cl_2]^{3/2}$]

11. Which of the following is **true** about the effect of adding a catalyst to a reaction system?

[✓ a) The catalyst does not change the value of ΔH_{rxn} or the value of the equilibrium constant.]
b) The catalyst does not change the value of ΔH_{rxn} but it does change the value of the equilibrium constant.
c) The catalyst changes the value of ΔH_{rxn} but it does not change the value of the equilibrium constant.
d) The catalyst changes the value of ΔH_{rxn} and the value of the equilibrium constant.

12. Consider two reactions: Reaction I can be represented as $aA \rightarrow Products$ and is first-order in A, and Reaction II can be represented as $bB \rightarrow Products$ and is second-order in B. Both reactions have the same first half-life. If 93.75% of A has reacted after 100.0 seconds, how much time is required for 87.5% of B to react?

a) 75.0 s   b) 100.0 s   c) 153.4 s   [✓ d) 175.0 s]   e) 275.0 s

13. Suppose the breaking of a N-H bond is the slow step in a mechanism. At what temperature is the initial rate expected to double compared to the initial rate at 25.0°C?

[✓ a) 26.3°C]   b) 50.0°C   c) 87.9°C   d) 323°C   e) 361°C

14. We discussed how a catalyst lowers the activation energy of a reaction. Suppose an uncatalyzed reaction has an activation energy of 314 kJ/mol at 25°C. The catalyzed reaction happens about a million (1,000,000) times faster than the uncatalyzed reaction. Which of the following is the best estimate of the activation energy (kJ/mol) of the catalyzed reaction at 25°C? Assume the pre-exponential factor, *A*, is the same for each reaction.

a) 22.7   b) 150.   [✓ c) 280.]   d) 310.   e) 350.

15-17. Consider the reaction of nitrogen dioxide and fluorine as represented by the following equation:$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$.

You run this reaction at the same (constant) temperature in two experiments and obtain the following data (note: $[P(F_2)]_0$ denotes the initial pressure of $F_2(g)$):

Expt #1; $[P(F_2)]_0 = 20.0$ atm

Time (min)	$P(NO_2)$ atm
0	0.0100
10.0	0.00802
20.0	0.00643
30.0	0.00516
40.0	0.00414
50.0	0.00332
60.0	0.00266

Expt #2; $[P(F_2)]_0 = 40.0$ atm

Time (min)	$P(NO_2)$ atm
0	0.0100
10.0	0.00414
20.0	0.00171
30.0	7.08×10^{-4}
40.0	2.93×10^{-4}
50.0	1.21×10^{-4}
60.0	5.01×10^{-5}

15. Determine the value of the rate constant, *k* (units of atm and min).

[✓ a) 5.52×10^{-5}]   b) 2.21×10^{-3} c) 1.10×10^{-3} d) 0.0221   e) 0.0883

16. Determine the total time required for the pressure of NO_2 in experiment #1 to be 0.00100 atm.

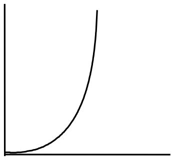
a) 41.7 min   b) 86.1 min   [✓ c) 104 min]   d) 128 min   e) 314 min

17. Determine the pressure of NO_2F in experiment #2 at 20.0 min.

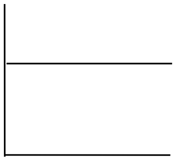
a) 0.00171 atm   b) 0.00342 atm   c) 0.00415 atm   d) 0.00684 atm   [✓ e) 0.00829 atm]

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

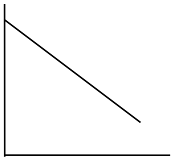
a)



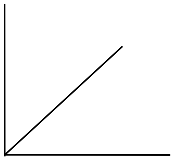
b)



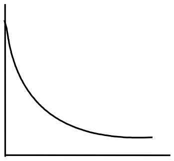
c)



d)



e)



18. Length of half-life (y) vs. time (x) for reaction type $aA \rightarrow Products$ which is first-order in A. $\boxed{\text{B}}$

19. A plot of [A] vs. time for reaction type $aA \rightarrow Products$ which is first-order in A. $\boxed{\text{E}}$

20. Rate of reaction (y) vs. [A] for reaction type $aA \rightarrow Products$ which is first-order in A. $\boxed{\text{D}}$

21. We discussed in lecture (and the videos) that we can estimate ΔH_{rxn} using the bond energies for the bonds in the reactants and products. In this question, we will examine that further.

    a. For the following reactions (balanced in standard form; lowest whole numbers), estimate the change in enthalpy using the bond energies (Table 13.6). Take **resonance structures** into consideration where appropriate. **Full credit is reserved for showing all work** in a **neat, coherent fashion** so that we can follow what you are doing. **[14 points]**

        i. Propene gas (C_3H_6) reacts with ammonia gas (NH_3) and oxygen gas to produce acrylonitrile gas (C_3H_3N) and water vapor. The nitrogen atom in acrylonitrile is at the end of the carbon chain and is not bonded to any hydrogen atoms.

Overall, ΔH = **–1077 kJ**

        ii. Nitrous oxide gas (N_2O, for which one of the nitrogen atoms is the central atom) reacts with water vapor to produce ammonia gas (NH_3) and oxygen gas.

Answer **around 550 (a bit higher)**

21. b. In part a, you were asked to **estimate** the change in enthalpy using bond energies. **Why** must this be an estimate? Discuss why using bond energies is **not a completely accurate** method to determine ΔH_{rxn}. Of the two examples in part a, which is predicted to **less accurate** and why? **Explain** in a **coherent, logical** fashion. **[6 points]**

- See lectures, videos, Discussion.

22. We discussed in lecture (and the videos) how the phrase “wants to be like a Noble gas” is not a causal reason for the charges we see on metal ions in ionic compounds. Consider the following data:

	Sodium (Na)	**Magnesium (Mg)**	**Aluminum (Al)**
1st Ionization Energy	495	735	580
2nd Ionization Energy	4560	1445	1815
3rd Ionization Energy	6910	7730	2740
4th Ionization Energy	9540	10,540	11,600
5th Ionization Energy	13,355	13,630	14,840

- Enthalpy of solution of NaCl(*s*) = 4 kJ/mol
- Enthalpy of hydration of ions in sodium chloride = –783 kJ/mol

Given the above data, **verify that the charges** for Na, Mg, and Al in ionic compounds match the phrase about Noble gases. In your answer, make sure to **discuss the factors involved** in deciding the magnitude of the charges in an ionic compound. **Discuss** how you used **the given data** to make these determinations and **quantitatively support** your answers. Also **explain the trends** in **successive ionizations energies** for each ion, and how they result in the phrase about “wanting to be like Noble gases” to hold true (even if it is not a cause). **Full credit is reserved for a neat, logical, coherent explanation**, so please **consider** what you are going to write **before** you write it. Use the next page, if needed. **[20 points]**

- See lectures, videos, Discussion.

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

23. We discussed in lecture (and the videos) how to evaluate a mechanism for a reaction. Consider that you and a lab partner are studying the kinetics of the decomposition of water vapor as represented by the following balanced equation:

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$$

Your lab partner proposes the following mechanism:

1. $H_2O(g) \rightarrow \cdot OH(g) + H\cdot(g)$
2. $H_2O(g) + H\cdot(g) \rightarrow \cdot OH(g) + H_2(g)$
3. $\cdot OH(g) + \cdot OH(g) \rightarrow H_2(g) + O_2(g)$

a. Because none of the steps is labeled as rate determining, you develop a rate law using the **steady-state approximation**. Derive the rate law in **two ways**: first, by defining the rate as the **change in water vapor pressure over time**, and second by defining the rate as the **change in oxygen gas pressure over time**. **Show** how these rate laws are **consistent** with each other. **Show all work** and briefly **explain your process**. **[8 points]**

- $-d[H_2O]/dt = 2k_1[H_2O]$
- $d[O_2]/dt = k_1[H_2O]$
- Because of the 2:1 ratio of H_2O and O_2 in the balanced equation, we expect that the rate we consume water will be twice the rate we produce oxygen.

23. b. Your lab partner says, “It would be easier to develop a rate law if we could label one of the steps as significantly slower than the others.”

Given what happens in the proposed first step of the mechanism, you realize that there is a way to test if this first step is the rate-determining step. “If we carry out the reaction at two temperatures,” you say, “we can test the relative initial rates and see if this matches our choice of the first step as the slow one.”

If you run the reaction at 900.0 K and 916.8 K and the first step is rate determining, provide a **reasonable estimate** for **how much faster** the initial rate will be at the higher temperature. **Show all work** and **briefly explain** your process. **[5 points]**

- The rate at the higher temperature will be about 3.14 times as fast.

23. c. You monitor the progress of the reaction by carrying out the reaction in a closed, rigid container and measuring the total pressure. You collect the following data:

Time (minutes)	Total Pressure (atm)
0	10.00
2.50	11.00
6.67	12.00
15.0	13.00
40.0	14.00

Do these data match the rate law that you determined in part a? **Why or why not**? **Show all work** and **briefly explain** your process. **[7 points]**

- Rate law in part a is first order with respect to water vapor.
- These do not match (data point to second-order).