AP Chem - Unit 8 Kinetics
Wkst: Review Packet - Key

ID: A

AP* Chemistry: Kinetics Practice MC REDESIGN
Answer Section

MULTIPLE CHOICE

1. ANS: C
Always keep in mind that chemical reactions occur because molecules collide with sufficient energy and orientation so as to break and make bonds. Heat 'em up and speed 'em up. The reactions are more energetic with an increase in temperature, more effectively oriented in the presence of a catalyst, more common if the container is crowded or the reactants have more surface area.

DIF: Easy OBJ: 4.1 TOP: Factors That Affect Reaction Rates
MSC: Whitten 7th edition

2. ANS: D
60 minutes is *six* 10-minute half-lives, so work backwards:

$$40 \xrightarrow{1} 80 \xrightarrow{2} 160 \xrightarrow{3} 320 \xrightarrow{4} 640 \xrightarrow{5} 1280 \xrightarrow{6} 2560$$

DIF: Hard OBJ: 4.3 TOP: Nuclear MSC: 1989 #68
NOT: 20% answered correctly

3. ANS: D
Adding a catalyst to any reaction increases the reaction rate by lowering the activation energy required. Adding a miscible liquid to a liquid reaction dilutes the concentration of the reactants thus decreasing the reaction rate.

Adding an inert gas to a gas phase reaction at constant volume has NO effect since, at constant volume, there is no dilution. Since the added gas is "inert", it takes no part in the reaction.

DIF: Hard OBJ: 4.9 TOP: Kinetics MSC: D&S 5th ed. Exam III #62

4. ANS: B
Sum all of the steps in the mechanism making sure to cross out the intermediates that cancel (N_2O_2 and N_2O).

The balanced reaction is : $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$

DIF: Easy OBJ: 4.7 TOP: Kinetics MSC: D&S 5th ed. Exam I #64

5. ANS: B
Cross off intermediates, then write the rate law for each step up to and including the rate determining or slow step. "Add" the steps together and the overall rate law that is consistent with the mechanism is:

$rate = k[NO]^2[H_2]$

DIF: Easy OBJ: 4.4 TOP: Kinetics MSC: D&S 5th ed. Exam I #63

6. ANS: C
Your first inclination is to say that the reaction is zero order in B, but that is not an answer choice.

Substance B is not involved in any step prior to the rate determining step nor in the rate determining step, but is involved in subsequent steps. It does have to be involved in the mechanism as a reactant in a step or the mechanism is invalid since all the steps of the mechanism must combine with the correct stoichiometry.

Substance B cannot be a catalyst. A catalyst is neither a reactant nor a product, substance B is clearly a reactant.

DIF: Easy OBJ: 4.7 TOP: Kinetics MSC: 1984 #28
NOT: 64% answered correctly

7. ANS: B
Resist the urge to use the kinetics math with this one. It's much faster to just think about how many half-lives are needed to get the job done and how much time that takes. It will also be faster if you round 19 minutes to 20 minutes.

$1.0 \xrightarrow{20\,\text{min}} 0.5 \xrightarrow{20\,\text{min}} 0.25 \xrightarrow{20\,\text{min}} 0.125$, so about 60 minutes.

DIF: Medium OBJ: 4.3 TOP: Kinetics MSC: 1994 #49
NOT: 49% answered correctly

8. ANS: C
As any reaction proceeds at constant temperature, the concentration of its reactants are decreasing thus the reaction rate is decreasing, so answer choices A and B cannot be correct. The rate of effective collisions at constant temperature with no catalyst remains the same, rather than decreases.

DIF: Medium OBJ: 4.1 TOP: Kinetics MSC: D&S 5th ed. Exam III #66

9. ANS: C
Trials 1 & 2 held [B] and [C] constant and cut the [A] in half, the rate was also cut in half, therefore the reaction is 1st order for reactant A.

Trials 2 & 3 held [A] and [C] constant and doubled [B], the rate doubled, therefore the reaction is 1st order for reactant B.

Trials 3 & 4 held [A] and [B] constant and increased [C] by a factor of 1.5 with NO CHANGE in the rate, therefore the reaction is zero order for reactant C.

Therefore, the overall rate law is: Rate = k [A][B][C]^0 OR Rate = k [A][B]

DIF: Hard OBJ: 4.1 TOP: Kinetics MSC: D&S 5th ed. Exam III #65

10. ANS: B
Cross out intermediates and add the steps together as a system of equations.

The overall equation is: $CHCl_3(g) + Cl_2(g) \rightarrow HCl(g) + CCl_4(g)$

DIF: Medium OBJ: 4.7 TOP: Kinetics MSC: D&S 5th ed. Exam II #63

11. ANS: D
When a catalyst is added to a reaction system, a new mechanism with a new and lower energy of activation take over. Why? Remember what catalysts do...they provide an alternate surface or pathway for reactions to occur. Thus, (A) is incorrect. The enthalpy and free energy stay the same since all thermodynamics is concerned with is the beginning and ending energy of reactants and products, respectively.

DIF: Easy OBJ: 4.9 TOP: Thermodynamics & Kinetics
MSC: D&S 5th ed. Exam II #61

12. ANS: D
In general, reactions are slow when the reactant's chemical bonds are strong. It takes a lot of energy during a collision to break a strong bond. Enthalpy change does not tell the whole story. The remaining answers all contribute to a faster reaction rate.

DIF: Medium OBJ: 4.1 TOP: Kinetics MSC: D&S 5th ed. Exam I #67

13. ANS: A
The rate constant is a constant at constant temperature. The only time its value ever changes is IF the temperature of the reaction changes, therefore only answers A-C are possible. As the reaction proceeds, collisions occur and reactants are converted to products so...mathematically if Rate = k[A][B]..., then the concentration of the reactants decrease and so does the rate of the reaction.

DIF: Medium OBJ: 4.1 TOP: Kinetics MSC: D&S 5th ed. Exam I #62

14. ANS: D
In trial I & II, pressure of NO was held constant, while the pressure of H_2 was doubled, the rate doubled, therefore 1st order in H_2.

In trials IV & V, pressure of H_2 was held constant, while the pressure of NO was doubled, the rate quadrupled, therefore 2nd order in NO.

So, the overall rate law is: RATE = $k\,(P_{NO})^2\,(P_{H2})^1$

DIF: Easy OBJ: 4.1 TOP: Kinetics MSC: D&S 5th ed. Exam II #67

We don't have a mean for this question, so we'll assume 4pts.

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Question 1
(8 points)

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

The table below gives data for a reaction rate study of the reaction represented above.

Experiment	Initial $[H_2]$ (mol L^{-1})	Initial $[Cl_2]$ (mol L^{-1})	Initial Rate of Formation of HCl (mol L^{-1} s^{-1})
1	0.00100	0.000500	1.82×10^{-12}
2	0.00200	0.000500	3.64×10^{-12}
3	0.00200	0.000250	1.82×10^{-12}

(a) Determine the order of the reaction with respect to H_2 and justify your answer.

The order of the reaction with respect to H_2 is 1. Comparing experiments 1 and 2, doubling the initial concentration of H_2 while keeping the initial concentration of Cl_2 constant results in a doubling of the reaction rate.	One point is earned for the correct order with justification.

(b) Determine the order of the reaction with respect to Cl_2 and justify your answer.

The order of the reaction with respect to Cl_2 is 1. Comparing experiments 2 and 3, halving the initial concentration of Cl_2 while keeping the initial concentration of H_2 constant results in a halving of the reaction rate.	One point is earned for the correct order with justification.

(c) Write the overall rate law for the reaction.

rate $= k[H_2][Cl_2]$	One point is earned for a rate law consistent with part (a) and part (b).

(d) Write the units of the rate constant.

$k = \frac{rate}{[H_2][Cl_2]} = \frac{\text{mol L}^{-1}\text{ s}^{-1}}{\text{mol L}^{-1}\ \text{mol L}^{-1}} = \frac{\text{s}^{-1}}{\text{mol L}^{-1}} = \text{L mol}^{-1}\text{ s}^{-1}$	One point is earned for units consistent with part (c).

Question 1 (continued)

(e) Predict the initial rate of the reaction if the initial concentration of H_2 is 0.00300 mol L^{-1} and the initial concentration of Cl_2 is 0.000500 mol L^{-1}.

For this reaction, the initial concentration of Cl_2 is the same as in Experiment 1 but the initial concentration of H_2 is three times as large. And because the reaction is first order with respect to each reactant, the initial rate of the reaction would be 5.46×10^{-12} mol L^{-1} s^{-1}, which is three times the rate of the initial rate of the reaction in Experiment 1.	One point is earned for the correct numerical answer or correct multiplier consistent with the rate law from part (c).

The gas-phase decomposition of nitrous oxide has the following two-step mechanism.

Step 1: $N_2O \rightarrow N_2 + O$

Step 2: $O + N_2O \rightarrow N_2 + O_2$

(f) Write the balanced equation for the overall reaction.

$2\,N_2O \rightarrow 2\,N_2 + O_2$	One point is earned for the correct balanced equation.

(g) Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain.

The O atom is an intermediate because it is formed and then consumed during the course of the reaction. (Had it been a catalyst, it would have been present both at the beginning and the end of the reaction.)	One point is earned for the correct choice with explanation.

(h) Identify the slower step in the mechanism if the rate law for the reaction was determined to be $rate = k\,[N_2O]$. Justify your answer.

Step 1 is slower because N_2O appears in Step 1 as the single reactant, which is consistent with the given rate law.	One point is earned for the correct choice with justification.

We don't have a mean for this question, so we'll assume 4.5 pts.

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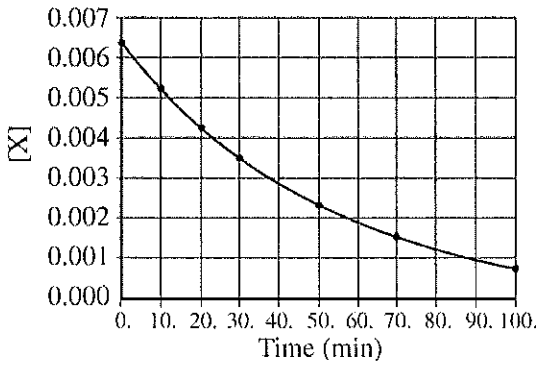
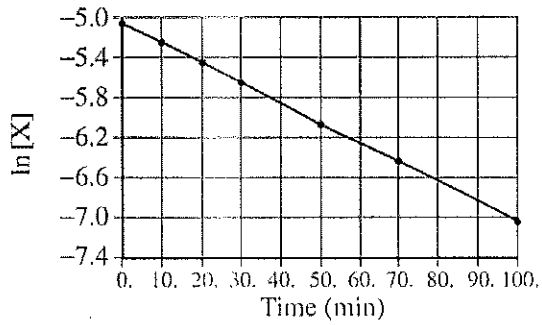
Question 2
(9 points)

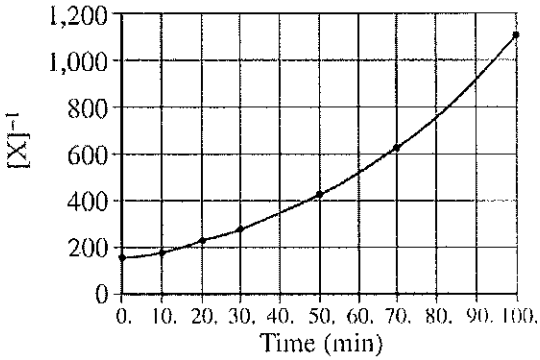
$$X \rightarrow 2Y + Z$$

The decomposition of gas X to produce gases Y and Z is represented by the equation above. In a certain experiment, the reaction took place in a 5.00 L flask at 428 K. Data from this experiment were used to produce the information in the table below, which is plotted in the graphs that follow.

Time (minutes)	[X] (mol L^{-1})	ln [X]	$[X]^{-1}$ (L mol^{-1})
0	0.00633	−5.062	158
10.	0.00520	−5.259	192
20.	0.00427	−5.456	234
30.	0.00349	−5.658	287
50.	0.00236	−6.049	424
70.	0.00160	−6.438	625
100.	0.000900	−7.013	1,110







(a) How many moles of X were initially in the flask?

[X] at 0 minutes = 0.00633, so $5.00\ L \times 0.00633\ \frac{mol\ X}{L} = 3.17 \times 10^{-2}\ mol\ X$	One point is earned for correct number of moles of X.

(b) How many molecules of Y were produced in the first 20. minutes of the reaction?

After 20. minutes of reaction, the number of moles of X remaining in the flask is $(5.00\ \text{L}) \times (0.00427\ \frac{\text{mol X}}{\text{L}}) = 2.14 \times 10^{-2}$ mol X. Then the number of moles of X that reacted in the first 20 minutes is $(3.17 \times 10^{-2}\ \text{mol X}) - (2.14 \times 10^{-2}\ \text{mol X}) = 1.03 \times 10^{-2}$ mol X.	One point is earned for the number of moles of X that react or for the correct stoichiometry between X and Y.
Thus the number of molecules of Y produced in the first 20. minutes is $(1.03 \times 10^{-2}\ \text{mol X}) \times \left(\frac{2\ \text{mol Y produced}}{1\ \text{mol X reacted}}\right) \times \left(\frac{6.02 \times 10^{23}\ \text{molecules Y}}{1\ \text{mol Y}}\right)$ $= 1.24 \times 10^{22}$ molecules Y produced	One point is earned for the number of molecules of Y produced.

(c) What is the order of this reaction with respect to X ? Justify your answer.

The reaction is first order with respect to X because a plot of ln [X] versus time produces a straight line with a negative slope.	One point is earned for the correct order and an explanation.

(d) Write the rate law for this reaction.

rate $= k[\text{X}]^1$	One point is earned for the rate law consistent with part (c).

(e) Calculate the specific rate constant for this reaction. Specify units.

$\ln \frac{[\text{X}]_t}{[\text{X}]_0} = -kt$ From the first two data points, $\ln\left(\frac{0.00520}{0.00633}\right) = -k\ (10\ \text{min})$ $k = -\left(\frac{\ln 0.821}{10\ \text{min}}\right) = 0.0197\ \text{min}^{-1}$	One point is earned for the magnitude of the rate constant. One point is earned for the units.

(f) Calculate the concentration of X in the flask after a total of 150. minutes of reaction.

$\ln \frac{[X]_t}{[X]_0} = -kt$ means the same thing as $\ln [X]_t - \ln[X]_0 = -kt$ $\ln [X]_{150} - \ln (0.00633) = -(0.0197 \text{ min}^{-1})(150 \text{ minutes})$ $\ln [X]_{150} = -(0.0197 \text{ min}^{-1})(150 \text{ minutes}) + \ln (0.00633)$ $\ln [X]_{150} = -(0.0197 \text{ min}^{-1})(150 \text{ minutes}) + (-5.062)$ $\ln [X]_{150} = -2.955 + (-5.062) = -8.017$	One point is earned for substituting into the integrated rate law.
$e^{\ln[X]_{150}} = e^{-8.017} = 3.30 \times 10^{-4}$ [X] at 150. minutes $= 3.30 \times 10^{-4}\ M$	One point is earned for the correct concentration of X.

We don't have a mean for this question, so we'll assume 2.0 pts.

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Question 3
(4 points)

3. An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below.

$$\text{Step I} \quad O_3 + Cl \rightarrow O_2 + ClO$$
$$\text{Step II} \quad ClO + O \rightarrow Cl + O_2$$

(a) Clearly identify the intermediate in the mechanism above. Justify your answer.

ClO is the intermediate in the reaction. It is a product in Step I and reappears as a reactant in Step II.	1 point earned for identifying ClO as intermediate with justification

(b) If the rate law for the overall reaction is found to be $rate = k[O_3][Cl]$, determine the following.

(i) The overall order of the reaction

(ii) Appropriate units for the rate constant, k

(iii) The rate-determining step of the reaction, along with justification for your answer

(i) overall order is $1 + 1 = 2$	1 point earned for overall order
(ii) $k = \frac{rate}{[O_3][Cl]} = \frac{M \text{ time}^{-1}}{M^2} = M^{1} \text{ time}^{-1}$	1 point earned for correct units
(iii) Step I is the rate-determining step in the mechanism. The coefficients of the reactants in Step I correspond to the exponents of the species concentrations in the rate law equation. **OR** The reaction rate is affected by the concentrations of $[O_3]$ and [Cl], both appearing only in Step I.	1 point earned for the correct step <u>and</u> justification

We don't have a mean for this question, so we'll assume 2.0 pts.

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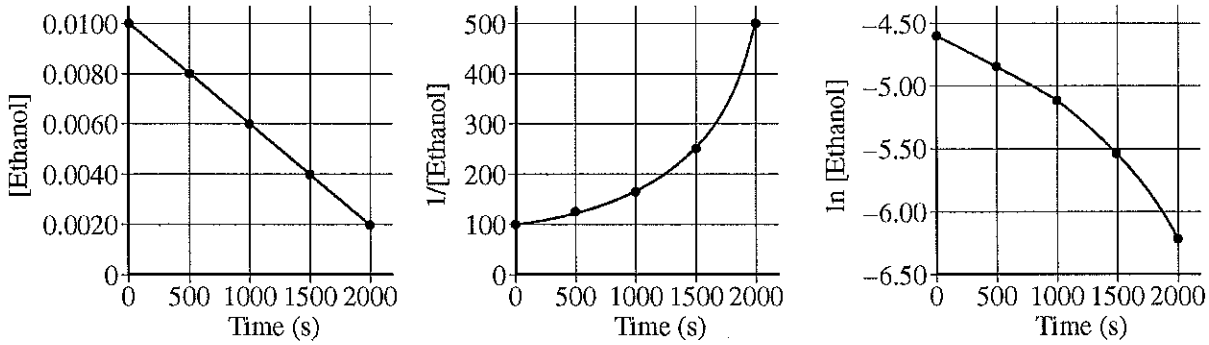
Question 4
(4 points)

In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 *M*. The ethanol begins to decompose according to the chemical reaction represented below.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

The concentration of ethanol gas over time is used to create the three graphs below.



(a) Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

(i) Determine the order of the reaction with respect to ethanol. Justify your answer.

The order of the reaction is zero. The plot on the left is a straight line, indicating that the rate of decrease in [ethanol] is constant as [ethanol] changes. Therefore the rate of reaction does not depend on [ethanol].	1 point is earned for the correct choice with a valid justification.

(ii) Write the rate law for the reaction.

rate = k	1 point is earned for the correct rate law.

(iii) Determine the rate constant for the reaction, including units.

rate = $k = -\dfrac{\Delta[\text{ethanol}]}{\Delta t} = -\dfrac{(0.0020 - 0.0100)\ \text{mol/L}}{2000\ \text{s}}$ $= 4.0 \times 10^{-6}\ M\ \text{s}^{-1}$	1 point is earned for the correct setup. 1 point is earned for the correct units.