1.

Directions: Write your answers to the following questions in the space provided. For problem solving, show all of your work. Make sure that your answers show proper units, notation, and significant digits. Do not use a calculator on the multiple-choice questions.

Three major methods used to increase the rate of a reaction are adding a catalyst, increasing the temperature, and

	g the concentration of a reactant. From the perspective of collision theory, explain how each of these methods the reaction rate.
a.	adding a catalyst
b.	increasing the temperature
c.	increasing the concentration of the reactants
Why do	large crystals of sugar burn more slowly than finely ground sugar?
How do	homogeneous catalysts and heterogeneous catalyst differ?
Express a.	the rate of reaction in terms of the rate of change of each reactant and each product in the following. $3ClO(aq) \rightarrow ClO_3(aq) + 2Cl(aq)$
b.	$3SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
c.	$C_2H_4(g) + Br_2(g) \rightarrow C_2H_4Br_2(g)$
In the Ha	the process for the production of ammonia, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
What	is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?
6. A. B. C. D. E.	The rate constant always shows an exponential increase with the Kelvin or absolute temperature. increases with increasing concentration. usually increases with increased pressure for gases. never changes (it is a constant). is the same for a given reaction at the same Kelvin or absolute temperature.
	the units for each of the following if the concentrations are expressed in moles per liter and the time in seconds
	of a chemical reaction
	constant for a zero-order rate law
	constant for a first-order rate law
	a. b. c. Why do I How do I Express t a. b. c. In the Ha What  6. A. B. C. D. E. What are a. rate b. rate c. rate

8. The reaction,  $2\Gamma(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ , was studied at 25°C. The following results were obtained where

Rate = 
$$\frac{-\Delta[S_2O_8^{2^-}]}{\Delta t}$$

[I <sup>-</sup> ] <sub>0</sub> (mol/L)	$[S_2O_8^{2-}]_0 \text{ (mol/L)}$	Initial Rate (mol/L • s)
0.080	0.040	12.5×10 <sup>-6</sup>
0.040	0.040	6.25×10 <sup>-6</sup>
0.080	0.020	6.25×10 <sup>-6</sup>
0.032	0.040	5.00×10 <sup>-6</sup>
0.060	0.030	7.00×10 <sup>-6</sup>

- a. Determine the rate law.
- b. Calculate a value for the rate constant for each experiment and an average value for the rate constant.
- 9. The following rate data were obtained at 25°C for the following reaction. What is the rate law expression? What is the overall order of the reaction?

$$2A + B \rightarrow 3C$$

Experiment	[A] <sub>0</sub> (mol/L)	[B] <sub>0</sub> (mol/L)	Initial Rate (mol/L • s)
1	0.10	0.10	$2.0 \times 10^{-4}$
2	0.30	0.30	$6.0 \times 10^{-4}$
3	0.10	0.30	$2.0 \times 10^{-4}$
4	0.20	0.40	$6.0 \times 10^{-4}$

10. What is the rate law expression for the following reaction, given the data below? What is the overall order of the reaction?

$$2A + B + 2C \rightarrow 3D + 2E$$

Experiment	[A] <sub>0</sub> (mol/L)	[B] <sub>0</sub> (mol/L)	[C] <sub>0</sub> (mol/L)	Initial Rate (mol/L • min)
1	0.20	0.10	0.10	$2.0 \times 10^{-4}$
2	0.20	0.30	0.20	$18.0 \times 10^{-4}$
3	0.20	0.10	0.30	$2.0 \times 10^{-4}$
4	0.10	0.60	0.40	$3.6 \times 10^{-4}$

11. Use the rate law determined in question 9 to answer the following question. What would happen to the rate of the reaction if the concentration of A was halved and the concentration of B was tripled during a reaction?

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12. Rate data were collected for the following reaction at a particular temperature.

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

Experiment	[ClO <sub>2</sub> ] <sub>0</sub> (mol/L)	[OH <sup>-</sup> ] <sub>0</sub> (mol/L)	Initial Rate (M/s)
1	0.012	0.012	$2.07 \times 10^{-4}$
2	0.024	0.012	$8.28 \times 10^{-4}$
3	0.012	0.024	$4.14 \times 10^{-4}$
4	0.024	0.024	$1.66 \times 10^{-3}$

- What is the rate-law expression for this reaction? What method did you use to find this?
- b. Calculate a value for k.
- Describe the order of the reaction with respect to each reactant and to the overall order. c.
- 13. Consider a chemical reaction between compounds A and B that is first order in A and first order in B. From the information shown here, fill in the blanks.

Experiment	[A]	[B]	Rate (M•s <sup>-1</sup> )
1	0.20 M	0.050 M	0.24
2		0.030 M	0.20
3	0.40 M		0.80

- \_14. The rate of a chemical reaction
  - is always dependent of the concentration of all reactants.
  - is always increased with increasing temperatures.
  - C. is directly proportional to the value of  $\Delta E$ .
  - is greater with higher activation energies.
  - is independent of surface area.
- For the first-order reactions of different substances A and X \_\_15.

$$A \rightarrow B$$
  $t_{1/2} = 30.0$  mir

$$\begin{array}{ll} A & \rightarrow B & t_{1/2}\!=30.0 \text{ min} \\ X & \rightarrow Y & t_{1/2}\!=60.0 \text{ min} \end{array}$$

This means that

- doubling the concentration of A will have ½ the effect on half-life that doubling the concentration of B will have on its half-life.
- B. a certain number of grams of A will react twice as fast as the same number of grams of X.
- C. a certain number of grams of X will react twice as fast as the same number of grams of A.
- D. the rate constant for  $A \to B$  is lower than the rate constant of  $X \to Y$ .
- 3 moles of A will react more rapidly than 3 moles of X.
- A reaction is first order with respect to [X] and second order with respect to [Y]. When [X] is 0.20 M and [Y] = 0.20 M the rate is  $8.00 \times 10^{-3}$  M/min. The value of the rate constant, including correct units, is:
  - 1.00 M min<sup>-1</sup> A.
  - 1.00 M<sup>-2</sup> min<sup>-1</sup> B.
  - 2.00 M<sup>-1</sup> min<sup>-1</sup> C.
  - 2.00 M<sup>-2</sup> min<sup>-1</sup> D.
  - $8.00 \times 10^{-3} \text{ min}^{-3}$

17. The rate constant for the decomposition of nitrogen dioxide

$$2NO_2 \rightarrow 2NO + O_2$$

with a laser beam is 1.70 M<sup>-1</sup>· min<sup>-1</sup>. Find the time, in seconds, needed to decrease 2.00 mol/L of NO<sub>2</sub> to 1.25 mol/L.

- 18. What is meant by the half-life of a reactant?
- 19. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120.	0.91

$$Rate = \frac{-\Delta[H_2O_2]}{\Delta t}$$

300.	0.78
600.	0.59
1200.	0.37
1800.	0.22
2400.	0.13
3000.	0.082
3600.	0.050

- a. Determine the rate law
- b. Determine the integrated rate law
- c. Determine the value of the rate constant
- d. Calculate the  $[H_2O_2]$  at 4000. s after the start of the reaction.
- 20. It took 143 s for 50.0% of a particular substance to decompose. If the initial concentration was 0.060 M and the decomposition reaction follows second-order kinetics, what is the value of the rate constant?

21. The dimerization of butadiene,  $2C_4H_6(g) \rightarrow C_8H_{12}(g)$ , was studied at 500. K, and the following data were obtained:

$$Rate = \frac{-\Delta[H_2O_2]}{\Delta t}$$

Time (s)	[C <sub>4</sub> H <sub>6</sub> ] (mol/L)
195	$1.6 \times 10^{-2}$
604	$1.5 \times 10^{-2}$
1246	$1.3 \times 10^{-2}$
2180	$1.1 \times 10^{-2}$
6210	$0.68 \times 10^{-2}$

- a. Determine the form of the rate law.
- b. Determine the integrated rate law.
- c. Determine the rate constant.
- 22. A certain first-order reaction is 45.0% complete in 65 s. What are the rate constant and the half-life for this process?

23. The rate law for the decomposition of phosphine  $(PH_3)$  is

Rate = 
$$\frac{-\Delta[PH_3]}{\Delta t} = k[PH_3]$$

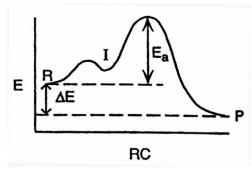
It takes 120. s for  $1.00 \text{ M PH}_3$  to decrease to 0.250 M. How much time is required for  $2.00 \text{ M PH}_3$  to decrease to a concentration of 0.350 M?

24. The rate of the reaction,  $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ , depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected:

Time (s)	[NO <sub>2</sub> ] (mol/L)
0	0.500
$1.20 \times 10^{3}$	0.444
$3.00 \times 10^{3}$	0.381
$4.50 \times 10^{3}$	0.340
$9.00 \times 10^{3}$	0.250
$1.80 \times 10^{4}$	0.174

- a. Determine the rate law.
- b. Determine the integrated rate law.
- c. Determine the value of the rate constant.
- d. Calculate the  $[NO_2]$  at  $2.70 \times 10^4$  s after the start of the reaction.
- \_\_\_\_\_25. A reaction mechanism
  - A. is the sum of all steps in a reaction except the rate determining step.
  - B. has a  $\Delta H$  equal to the  $\Delta H$  for the most demanding step.
  - C. always has a rate determining step.
  - D. may be absolutely proven from the rate law.
  - E. is determined from the balanced expression only.
- 26. Write the rate laws for the following elementary reactions.
  - a.  $CH_3NC(g) \rightarrow CH_3CN(g)$
  - $b. \quad \ O_{3}(g) \ + \ NO(g) \ \to \ O_{2}(g) \ + \ NO_{2}(g)$

27. Most reactions occur by a series of steps. The energy profile for a certain reaction that proceeds by a two-step mechanism is



On the energy profile, indicate:

- a. The positions of reactants (R) and products (P).
- b. The activation energy for the overall reaction (E<sub>a</sub>).
- c.  $\Delta E$  for the reaction.
- d. Which point on the plot represents the energy of the intermediate in the two-step reaction?
- e. Which step in the mechanism for this reaction is rate determining, the first or the second step? Explain.
- 28. A proposed mechanism for a reaction is

$$C_4H_9Br \rightarrow C_4H_9^+ + Br^-$$
 Slow  $C_4H_9 + H_2O \rightarrow C_4H_9OH_2^+$  Fast  $C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$  Fast

- a. What is the overall balanced equation for the reaction?
- b. What are the intermediates in the proposed mechanism? \_\_\_\_
- c. Write the rate law expected for this mechanism.
- 29. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

$$NO_2 + NO_2 \rightarrow NO_3 + NO$$
 Slow  
 $NO_3 + CO \rightarrow NO_2 + CO_2$  Fast

- a. What is the overall balanced equation for the reaction?
- b. What is the intermediate in the proposed mechanism?
- c. Write the rate law expected for this mechanism.
- 30. The ozone, O<sub>3</sub>, of the stratosphere can be decomposed by reaction with nitrogen oxide (commonly called nitric oxide), NO from high-flying jet aircraft.

$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$

The rate expression is rate =  $k[O_3][NO]$ . Which of the following mechanisms are consistent with the observed rate expression?

a. 
$$NO + O_3 \rightarrow NO_3 + O$$
 slow  $NO_3 + O \rightarrow NO_2 + O_2$  fast  $O_3 + NO \rightarrow NO_2 + O_2$  overall

$$\begin{array}{c|ccccc} + O_2 & fast & O + O_3 \rightarrow 2O_2 & fast \\ + O_2 & overall & O_2 + N \rightarrow NO_2 & fast \\ \hline O_3 + NO \rightarrow NO_2 + O_2 & overall \end{array}$$

d.  $NO \rightarrow N + O$ 

b. 
$$NO + O_3 \rightarrow NO_2 + O_2$$
 slow

c. 
$$O_3 \rightarrow O_2 + O$$
 slow  
 $O + NO \rightarrow NO_2$  fast  
 $O_3 + NO \rightarrow NO_2 + O_2$  overall

e. 
$$NO \leftrightarrows N + O$$
 fast  
 $O + O_3 \rightarrow 2O_2$  slow  
 $O_2 + N \rightarrow NO_2$  fast  
 $O_3 + NO \rightarrow NO_2 + O_2$  overall

slow

31. A proposed mechanism for the following reaction,  $H_2 + I_2 \rightarrow 2HI$  is

$I_2 \leftrightarrows 2I$	fast, equilibrium
$I + H_2 \leftrightarrows H_2I$	fast, equilibrium
$H_2I + I \rightarrow 2HI$	slow

- a. Identify any reaction intermediates in this proposed mechanism.
- b. Show that this mechanism predicts the correct rate law, rate =  $k[H_2][I_2]$ .

32. The rearrangement of cyclopropane to propene has been studied at various temperatures. The following values for the specific rate constant have been determined experimentally.

T(K)	k (s <sup>-1</sup> )
600.	3.30×10 <sup>-9</sup>
650.	2.19×10 <sup>-7</sup>
700.	7.96×10 <sup>-6</sup>
750.	1.80×10 <sup>-4</sup>
800.	2.74×10 <sup>-3</sup>
850.	3.04×10 <sup>-2</sup>
900.	2.58×10 <sup>-1</sup>

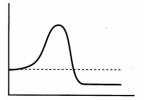
- a. From the appropriate plot of these data, determine the value of the activation energy for this reaction.
- b. Use the graph to estimate the value of k at 500. K.
- c. Use the graph to estimate the temperature at which the value of k would be equal to  $5.00 \times 10^{-5}$  s<sup>-1</sup>.
- 33. The activation energy for the reaction,  $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ , is 125 kJ/mol, and  $\Delta E$  for the reaction is 216 kJ/mol. What is the activation energy for the reverse reaction  $[NO(g) + CO_2(g) \rightarrow NO_2(g) + CO(g)]$ ?
- 34. The reaction  $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$  in a certain solvent is first order with respect to  $(CH_3)_3CBr$  and zero order with respect to  $OH^-$ . In several

experiments the rate constant k was determined at different temperatures. A plot of  $\ln k$  versus 1/T was constructed resulting in a straight line with a slope value of  $-1.10 \times 10^4$  K and y-intercept of 33.5. Assume k has units of s<sup>-1</sup>.

- a. Determine the activation energy for this reaction.
- b. Determine the value of the frequency factor A.
- c. Calculate the value of k at 25°C.
- 35. One mechanism for the destruction of ozone in the upper atmosphere is

$$\begin{array}{lll} O_3(g) \,+\, NO(g) \,\rightarrow\, NO_2(g) \,+\, O_2(g) & Slow \\ \underline{NO_2(g)} \,+\, O(g) \rightarrow NO(g) \,+\, O_2(g) & Fast \end{array}$$

- a. What is the overall reaction?
- b. Which species is a catalyst?
- c. Which species is an intermediate?
- d.  $E_a$  for the uncatalyzed reaction is 14.0 kJ.  $E_a$  for the same reaction when catalyzed is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor A is the same for each reaction.
- \_\_\_\_\_36. The activation energy for this reaction,  $X + 2Y \rightarrow 3Z$ , shown in the potential energy diagram, could be
  - A. increased by increasing [X].
  - B. increased by increasing [X] and [Y].
  - C. increased by increasing the temperature.
  - D. decreased by removing Z from the system as it forms.
  - E. decreased by adding a suitable catalyst.



- \_\_\_\_37. For all zero-order reactions
  - A. a plot of time vs. concentration squared is linear.
  - B.  $E_a$  is very low.
  - C. the rate is independent of time.
  - D. the rate constant is zero.
- \_\_\_\_\_38. If both  $\Delta H$  and  $E_a$  for the forward reaction are known, the reverse reaction would have an  $E_a$ 
  - A. of  $(-\Delta H \rightarrow) + E_{a\rightarrow}$
  - B. of  $\Delta H \rightarrow + E_{a\rightarrow}$

			C. D. E.	equal $E_a$ for the forward reaction equal (- $E_a$ ) for the forward reaction. but none of the above describes the value of $E_a$ .	
		_39.	value A. B. C.	values for the change in enthalpy, $\Delta H$ , and the activation energy, $E_a$ , for a given reaction are known. The of $E_a$ for the reverse reaction equals $E_a$ for the forward reaction $-(E_a)$ for the forward reaction. The sum of $-\Delta H$ and $E_a$ . The sum of $\Delta H$ and $E_a$ the difference of $\Delta H$ and $E_a$	The
40.	. Write balanced net ionic equations for each of the following.				
a. Solid calcium carbonate is strongly heated.			d calc	ium carbonate is strongly heated.	
	b.	o. Solid barium oxide is added to distilled water.			
	c.	Solu	ıtions	of manganese(II) sulfate and ammonium sulfide are mixed.	
	d.	Cart	oon di	sulfide vapor is burned in excess oxygen.	
	e.	A so	olution	n of potassium dichromate is added to an acidified solution of iron(II) chloride	