AP Chemistry Problem Set Chapter 12 Name____________________

Please indicate your multiple choice answers below.

1. __________ 2. __________ 3. __________ 4. __________ 5. __________

6. __________ 7. __________ 8. __________ 9. ___________ 10. ___________

Questions 1-2

$$H_3AsO_4 + 3I^- + 2\ H_3O^+ \rightarrow H_3AsO_3 + I_3^- + H_2O$$

The oxidation of iodide ions by arsenic acid in acidic aqueous solution occurs according to the stoichiometry shown above. The experimental rate law of the reaction is:

Rate = k $[H_3AsO_4]$ $[I^-]$ $[H_3O^+]$

1. What is the order of the reaction with respect to I^-?

(A) 1 (B) 2 (C) 3 (D) 5 (E) 6

2. According to the rate law for the reaction, an increase in the concentration of hydronium ion has what effect on this reaction?

(A) The rate of reaction increases.
(B) The rate of reaction decreases.
(C) The value of the equilibrium constant increases.
(D) The value of the equilibrium constant decreases.
(E) Neither the rate nor the value of the equilibrium constant is changed.

3. 2 A(g) + B(g) <===> 2 C(g)

When the concentration of substance B in the reaction above is doubled, all other factors being held constant, it is found that the rate of the reaction remains unchanged. The most probable explanation for this observation is that

(A) the order of the reaction with respect to substance B is 1
(B) substance B is not involved in any of the steps in the mechanism of the reaction
(C) substance B is not involved in the rate-determining step of the mechanism, but is involved in subsequent steps
(D) substance B is probably a catalyst, and as such, its effect on the rate of the reaction does not depend on its concentration
(E) the reactant with the smallest coefficient in the balanced equation generally has little or no effect on the rate of the reaction

4.

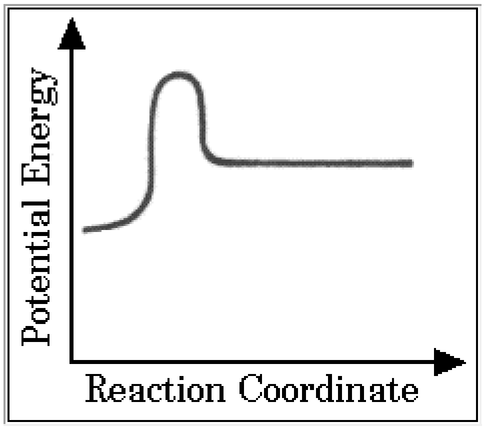
Step 1) $N_2H_2O_2 \rightleftharpoons N_2HO_2^- + H^+$	(fast equilibrium)
Step 2) $N_2HO_2^- \rightarrow N_2O + OH^-$	(slow)
Step 3) $H^+ + OH^- \rightarrow H_2O$	(fast)

Nitramide, $N_2H_2O_2$, decomposes slowly in aqueous solution. This decomposition is believed to occur according to the reaction mechanism above. The rate law for the decomposition of nitramide that is consistent with this mechanism is given by which of the following?

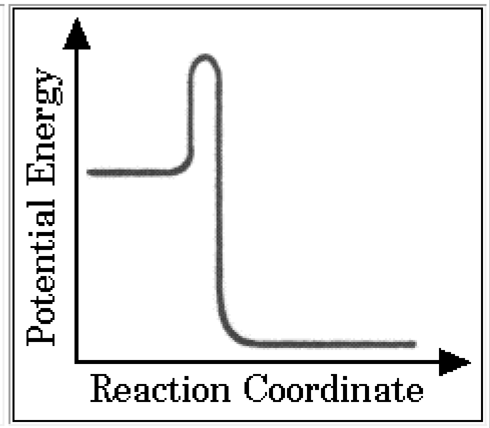
(A) Rate = k $[N_2H_2O_2]$
(B) Rate = k $[N_2H_2O_2]$ $[H^+]$
(C) Rate = (k $[N_2H_2O_2]$) / $[H^+]$
(D) Rate = (k $[N_2H_2O_2]$) / $[N_2HO_2^-]$
(E) Rate = k $[N_2H_2O_2]$ $[OH^-]$

5. Which of the following is a graph that describes the pathway of reaction that is endothermic and has high activation energy?

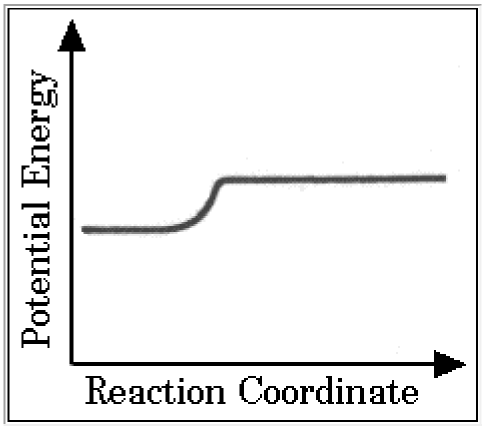
(A)



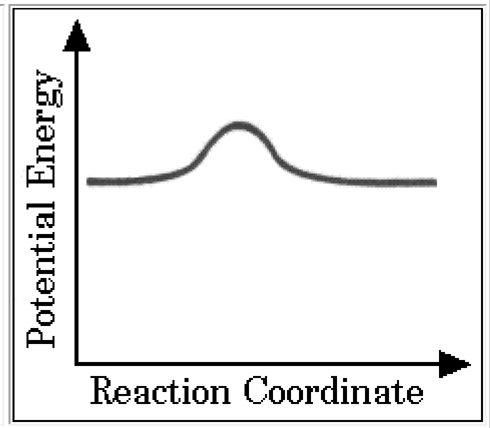
(B)



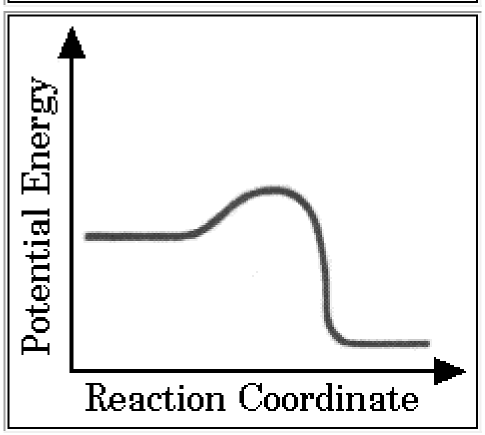
(C)



(D)



(E)



6. Relatively slow rates of chemical reaction are associated with which of the following?

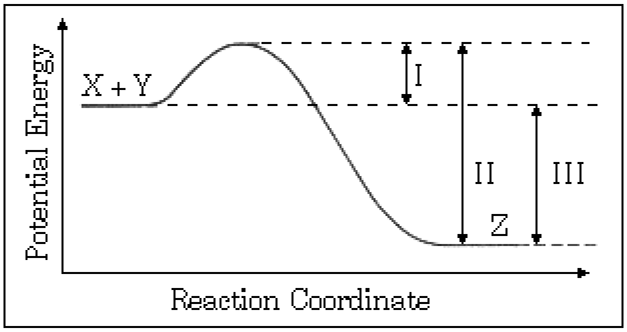
(A) The presence of a catalyst (B) High temperature (C) High concentration of reactants (D) Strong bonds in reactant molecules (E) Low activation energy

7.

Step 1: $Ce^{4+} + Mn^{2+}$ ---> $Ce^{3+} + Mn^{3+}$
Step 2: $Ce^{4+} + Mn^{3+}$ ---> $Ce^{3+} + Mn^{4+}$
Step 3: $Mn^{4+} + Tl^{+}$ ---> $Tl^{3+} + Mn^{2+}$

The proposed steps for a catalyzed reaction between Ce^{4+} and Tl^{+} are represented above. The products of the overall catalyzed reaction are

(A) Ce^{4+} and Tl^{+} (B) Ce^{3+} and Tl^{3+} (C) Ce^{3+} and Mn^{3+}
(D) Ce^{3+} and Mn^{4+} (E) Tl^{3+} and Mn^{2+}



8. The energy diagram for the reaction X + Y ---> Z is shown above. The addition of a catalyst to this reaction would cause a change in which of the indicated energy differences?

(A) I only (B) II only (C) III only (D) I and II only (E) I, II, and III

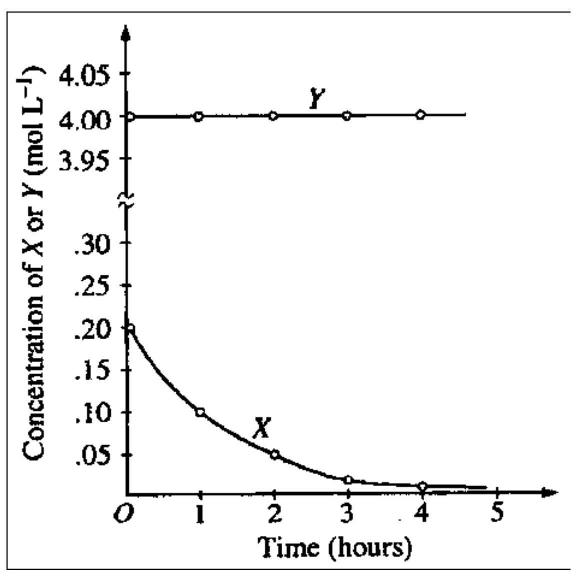
Experiment	Initial [NO] (mol L^{-1})	Initial [O_2] (mol L^{-1})	Initial Rate of Formation of NO_2 (mol $L^{-1}s^{-1}$)
1	0.10	0.10	2.5×10^{-4}
2	0.20	0.10	5.0×10^{-4}
3	0.20	0.40	8.0×10^{-3}

9. The initial-rate data in the table above were obtained for the reaction represented below. What is the experimental rate la for the reaction?

(A) rate = k[NO] [O_2]
(B) rate = k[NO] $[O_2]^2$
(C) rate = $k[NO]^2$ [O_2]
(D) rate = $k[NO]^2$ $[O_2]^2$
(E) rate = k[NO] / [O_2]

10. The graph to the right shows the results of a study of the reaction of X with a large excess of Y to yield Z. The concentrations of X and Y were measured over a period of time. According to the results, which of the following can be concluded about the rate of law for the reaction under the conditions studied?

(A) It is zero order in [X].
(B) It is first order in [X].
(C) It is second order in [X].
(D) It is the first order in [Y].
(E) The overall order of the reaction is 2.



Essays

$$5\ Br^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ Br_2O(l) + 3\ H_2O(l)$$

1. In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

Experiment	Initial $[Br^-]$ ($mol\ L^{-1}$)	Initial $[BrO_3^-]$ ($mol\ L^{-1}$)	Initial $[H^+]$ ($mol\ L^{-1}$)	Rate of Disappearance of BrO_3^- ($mol\ L^{-1}\ s^{-1}$)
1	0.00100	0.00500	0.100	2.50×10^{-4}
2	0.00200	0.00500	0.100	5.00×10^{-4}
3	0.00100	0.00750	0.100	3.75×10^{-4}
4	0.00100	0.01500	0.200	3.00×10^{-3}

(a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br^-
(ii) BrO_3^-
(iii) H^+

(b) Write the rate law for the overall reaction.
(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

2. $$2\ NO(g) + Br_2(g) \rightarrow 2\ NOBr(g)$$

A rate study of the reaction represented above was conducted at 25°C. The data that were obtained are shown in the table below.

Experiment	Initial [NO] ($mol\ L^{-1}$)	Initial $[Br_2]$ ($mol\ L^{-1}$)	Initial Rate of Appearance of NOBr ($mol\ L^{-1}\ s^{-1}$)
1	0.0160	0.0120	3.24×10^{-4}
2	0.0160	0.0240	6.38×10^{-4}
3	0.0320	0.0060	6.42×10^{-4}

(a) Calculate the initial rate of disappearance of $Br_2(g)$ in experiment 1.
(b) Determine the order of the reaction with respect to each reactant, $Br_2(g)$ and $NO(g)$. In each case, explain your reasoning.
(c) For the reaction, write the rate law that is consistent with the data, and calculate the value of the specific rate constant, *k*, and specify units.
(d) The following mechanism was proposed for the reaction:

$Br_2(g) + NO(g) \longrightarrow NOBr_2(g)$ *slow*
$NOBr_2(g) + NO(g) \longrightarrow 2\ NOBr(g)$ *fast*

Is this mechanism consistent with the given experimental observations? Justify your answer.

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.

Step I $O_3 + Cl \rightarrow O_2 + ClO$
Step II $ClO + O \rightarrow Cl + O_2$

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above.
(b) Clearly identify the catalyst in the mechanism above. Justify your answer.
(c) Clearly identify the intermediate in the mechanism above. Justify your answer.
(d) 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

4. $2\ NO(g) + 2\ H_2(g) \dashrightarrow N_2(g) + 2\ H_2O(g)$

Experiments conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L)		Initial Rate of Formation of N_2 (mol/L min)
	[NO]	[H_2]	
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a)
(i) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 has been consumed.

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. $NO + NO \Longleftrightarrow N_2O_2$
II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$
III. $N_2O + H_2 \rightarrow N_2 + H_2O$

Based on the data present, which of the above is the rate-determining step? Show that the mechanism is consistent with:
(i) the observed rate law for the reaction, and
(ii) the overall stoichiometry of the reaction.

5. For a hypothetical chemical reaction that has the stoichiometry $2\ X + Y \rightarrow Z$, the following initial rate data were obtained. All measurements were made at the same temperature.

Initial Rate of Formation of Z, ($mol \cdot L^{-1} \cdot sec^{-1}$)	Initial $[X]_o$, ($mol \cdot L^{-1}$)	Initial $[Y]_o$, ($mol \cdot L^{-1}$)
7.0×10^{-4}	0.20	0.10
1.4×10^{-3}	0.40	0.20
2.8×10^{-3}	0.40	0.40
4.2×10^{-3}	0.60	0.60

(a) Give the rate law for this reaction from the data above.

(b) Calculate the specific rate constant for this reaction and specify its units.

(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are $[X]_o = 0.80$ molar, $[Y]_o = 0.60$ molar and $[Z]_0 = 0$ molar?

(d) Select from the mechanisms below the one most consistent with the observed data, and explain your choice. In these mechanisms M and N are reaction intermediates. Write a rate equation for each slow step.

(1)	$X + Y \rightarrow M$	(slow)
	$X + M \rightarrow Z$	(fast)
(2)	$X + X \rightarrow M$	(fast)
	$Y + M \rightarrow Z$	(slow)
(3)	$Y \rightarrow M$	(slow)
	$M + X \rightarrow N$	(fast)
	$N + X \rightarrow Z$	(fast)

AP Chemistry Problem Set Chapter 12 Name___________________

Please indicate your multiple choice answers below.

1. A - 61% **2. A - 75%** **3. C - 64%** **4. C - 11%** **5. A - 65%**

6. D - 82% **7. B - 71%** **8. D - 55%** **9. B - 52%** **10. B – 34%**

Essays

1. **(2003)**

$$5\ Br^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ Br_2O(l) + 3\ H_2O(l)$$

In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

Experiment	Initial $[Br^-]$ (mol L^{-1})	Initial $[BrO_3^-]$ (mol L^{-1})	Initial $[H^+]$ (mol L^{-1})	Rate of Disappearance of BrO_3^- (mol L^{-1} s^{-1})
1	0.00100	0.00500	0.100	2.50×10^{-4}
2	0.00200	0.00500	0.100	5.00×10^{-4}
3	0.00100	0.00750	0.100	3.75×10^{-4}
4	0.00100	0.01500	0.200	3.00×10^{-3}

(a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br^- = **1st order**

(ii) BrO_3^- = **1st order**

(iii) H^+ = **2nd order**

(b) Write the rate law for the overall reaction. **rate = $k[Br^-]^1[BrO_3^-]^1[H^+]^2$**

(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

$k = 5.00 \times 10^3$ L^3 mol^{-3} s^{-1}

2. **(1999)**

$$2\ NO(g) + Br_2(g) \rightarrow 2\ NOBr(g)$$

A rate study of the reaction represented above was conducted at 25°C. The data that were obtained are shown in the table below.

Experiment	Initial [NO] (mol L^{-1})	Initial $[Br_2]$ (mol L^{-1})	Initial Rate of Appearance of NOBr (mol L^{-1} s^{-1})
1	0.0160	0.0120	3.24×10^{-4}
2	0.0160	0.0240	6.38×10^{-4}
3	0.0320	0.0060	6.42×10^{-4}

(a) Calculate the initial rate of disappearance of $Br_2(g)$ in experiment 1. **1.62×10^{-4} *M* sec^{-1}**

(b) Determine the order of the reaction with respect to each reactant, $Br_2(g)$ and $NO(g)$. In each case, explain your reasoning. **Comparing experiments 1 and 2, [NO] remains constant, $[Br_2]$ doubles, and rate doubles; therefore, reaction is first-order with respect to $[Br_2]$. The reaction is second order with respect to [NO]. A mathematical calculation must be shown to earn credit.**

(c) For the reaction, write the rate law that is consistent with the data, and calculate the value of the specific rate constant, *k*, and specify units. **Rate = $k[NO]^2[Br_2]$; 105 M^{-2} sec^{-1}**

(d) The following mechanism was proposed for the reaction:

$Br_2(g) + NO(g) \longrightarrow NOBr_2(g)$ *slow*

$NOBr_2(g) + NO(g) \longrightarrow 2\ NOBr(g)$ *fast*

Is this mechanism consistent with the given experimental observations? Justify your answer.

No, it is not consistent with the given experimental observations. This mechanism gives a reaction that is first-order in [NO], and first-order in $[Br_2]$, as those are the two reactants in the rate-determining step. Kinetic data show the reaction is second-order in [NO] (and first-order in $[Br_2]$), so this cannot be the mechanism.

3. **(2002)**
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.

Step I $O_3 + Cl \rightarrow O_2 + ClO$
Step II $ClO + O \rightarrow Cl + O_2$

(a) Write a balanced equation for the overall reaction represented by Step I and Step II above. $\mathbf{O_3 + O \rightarrow 2O_2}$
(b) Clearly identify the catalyst in the mechanism above. Justify your answer. **Cl; It is a reactant in Step I and reappears as a product in Step II.**
(c) Clearly identify the intermediate in the mechanism above. Justify your answer. **ClO; It is a product in Step I and reappears as a reactant in Step II.**
(d) 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. **Second order.**
(ii) Appropriate units for the rate constant, k. **L mol^{-1} sec^{-1}**
(iii) The rate-determining step of the reaction, along with justification for your answer 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.**

4. **(1994)**
$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$
Experiments conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L)		Initial Rate of Formation of N_2 (mol/L min)
	[NO]	$[H_2]$	
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a)
(i) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
[NO] is second order. In experiments 3 and 4 the concentration doubles and the rate increases 4 times.
$[H^+]$ is first order. In experiments 1 and 2 the concentration doubles and the rate doubles.
(ii) Write the overall rate law for the reaction. **Rate = $k[H^+][NO]^2$**
(b) Calculate the value of the rate constant, k, for the reaction. Include units. **K = 5000 L^{2}mol^{-2}min^{-1}**
(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 has been consumed. **0.0050 M**
(d) The following sequence of elementary steps is a proposed mechanism for the reaction.
I. $NO + NO \Longleftrightarrow N_2O_2$
II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$
III. $N_2O + H_2 \rightarrow N_2 + H_2O$

Based on the data present, which of the above is the rate-determining step? Show that the mechanism is consistent with:
The second step is the rate determining step.
(i) the observed rate law for the reaction, and **Rate = $k[H^+][NO]^2$**
(ii) the overall stoichiometry of the reaction. $\mathbf{2NO + 2H_2 \rightarrow N_2 + 2\ H_2O}$

5. **(1984)**
For a hypothetical chemical reaction that has the stoichiometry 2 X + Y → Z, the following initial rate data were obtained. All measurements were made at the same temperature.

Initial Rate of Formation of Z, ($mol\cdot L^{-1}\cdot sec^{-1}$)	Initial $[X]_o$, ($mol\cdot L^{-1}$)	Initial $[Y]_o$, ($mol\cdot L^{-1}$)
$7.0x10^{-4}$	0.20	0.10
$1.4x10^{-3}$	0.40	0.20
$2.8x10^{-3}$	0.40	0.40
$4.2x10^{-3}$	0.60	0.60

(a) Give the rate law for this reaction from the data above. **Rate = k[Y]**
(b) Calculate the specific rate constant for this reaction and specify its units. **K = 0.0070 sec^{-1}**
(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are $[X]_o$ = 0.80 molar, $[Y]_o$ = 0.60 molar and $[Z]_0$ = 0 molar? **57.9 seconds**
(d) Select from the mechanisms below the one most consistent with the observed data, and explain your choice. In these mechanisms M and N are reaction intermediates. Write a rate equation for each slow step.

(1)	X + Y → M	(slow)	
	X + M → Z	(fast)	**Rate = k[X][Y]**
(2)	X + X → M	(fast)	
	Y + M → Z	(slow)	**Rate = k$[X]^2$[Y]**
(3)	Y → M	(slow)	
	M + X → N	(fast)	
	N + X → Z	(fast)	**Rate = k[Y] Choice three is the best mechanisms**

because it shows that the reaction is first order in Y and 0 order for X.

7. The reaction between NO and H_2 is believed to occur in the following three-step process.

$NO + NO \leftrightarrow N_2O_2$ (fast)

$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

(a) Write a balanced equation for the overall reaction.
(b) Identify the intermediates in the reaction. Explain your reasoning.
(c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is rate = $k[NO]^2[H_2]$. The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an H_2 molecule. Are conclusions (1) and (2) correct? Explain.
(d) Explain why an increase in temperature increases the rate constant, k, given the rate law in (c).

1989 - #57
rate = k[X] For the reaction whose rate law is given above, a plot of which of the following is a straight line?
(a) [X] versus time
(b) log [X] versus time
(c) 1/[X] versus time
(d) [X] versus 1/time
(e) log [X] versus 1/time

1989 - #58.

$$(CH_3)_3CCl(aq) + OH^- \rightarrow (CH_3)_3COH(aq) + Cl^-$$

For the reaction represented above, the experimental rate law is given as follows.

$$\text{Rate} = k\,[(CH_3)_3CCl]$$

If some solid sodium solid hydroxide is added to a solution that is 0.010-molar in (CH3)3CCl and 0.10-molar in NaOH, which of the following is true? (Assume the temperature and volume remain constant.)
(a) Both the reaction rate and k increase.
(b) Both the reaction rate and k decrease.
(c) Both the reaction rate and k remain the same.
(d) The reaction rate increases but k remains the same.
(e) The reaction rate decreases but k remains the same.

68. The specific rate constant k for radioactive element X is 0.023 min -1. What weight of X wsa originally present in a sample if 40. grams is left after 60. minutes?

(A) 10. grams
(B) 20. grams
(C) 80. grams
(D) 120 grams
(E) 160 grams

1977 B

$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$

For the reaction above, the rate constant at 380˚C for the forward reaction is 2.6x10^3 liter^2/mole^2-sec and this reaction is first order in O_2 and second order in NO. The rate constant for the reverse reaction at 380˚C is 4.1 liter/mole-sec and this reaction is second order in NO_2.

(a) Write the equilibrium expression for the reaction as indicated by the equation above and calculate the numerical value for the equilibrium constant at 380˚C.

(b) What is the rate of the production of NO2 at 380˚C if the concentration of NO is 0.0060 mole/liter and the concentration of O2 is 0.29 mole/liter?

(c) The system above is studied at another temperature. A 0.20 mole sample of NO2 is placed in a 5.0 liter container and allowed to come to equilibrium. When equilibrium is reached, 15% of the original NO2 has decomposed to NO and O2. Calculate the value for the equilibrium constant at the second temperature.

1983 C

Graphical methods are frequently used to analyze data and obtain desired quantities.

(a) 2 HI(g) -> H2(g) + I2(g)

The following data give the value of the rate constant at various temperatures for the gas phase reaction above.....
Describe, without doing any calculations, how a graphical method can be used to obtain the activation energy for this reaction.

(b) A(g) -> B(g) + C(g)

The following data give the partial pressure of A as a function of time and were obtained at 100˚C for the reaction above....

Describe, without doing any calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.

1991

2 ClO2(g) + F2(g) ---> 2 ClO2F(g)
The following results were obtained when the reaction represented above was studied at 25 °C.
(a) Write the rate law expression for the reaction above.
(b) Calculate the numerical value of the rate constant and specify the units.
(c) In experiment 2, what is the initial rate of decrease of [F2]?
(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a)? Justify your choice.
I.
ClO2 + F2 <---> ClO2F2 (fast)
ClO2F2 ---> ClO2F + F (slow)
ClO2 + F ---> ClO2F (fast)
II.
F2 ---> 2 F (slow)
2 (ClO2 + F ---> ClO2F) (fast)