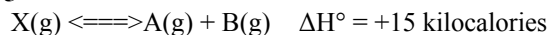


## Collected AP Exam Essay Answers for Chapter 12

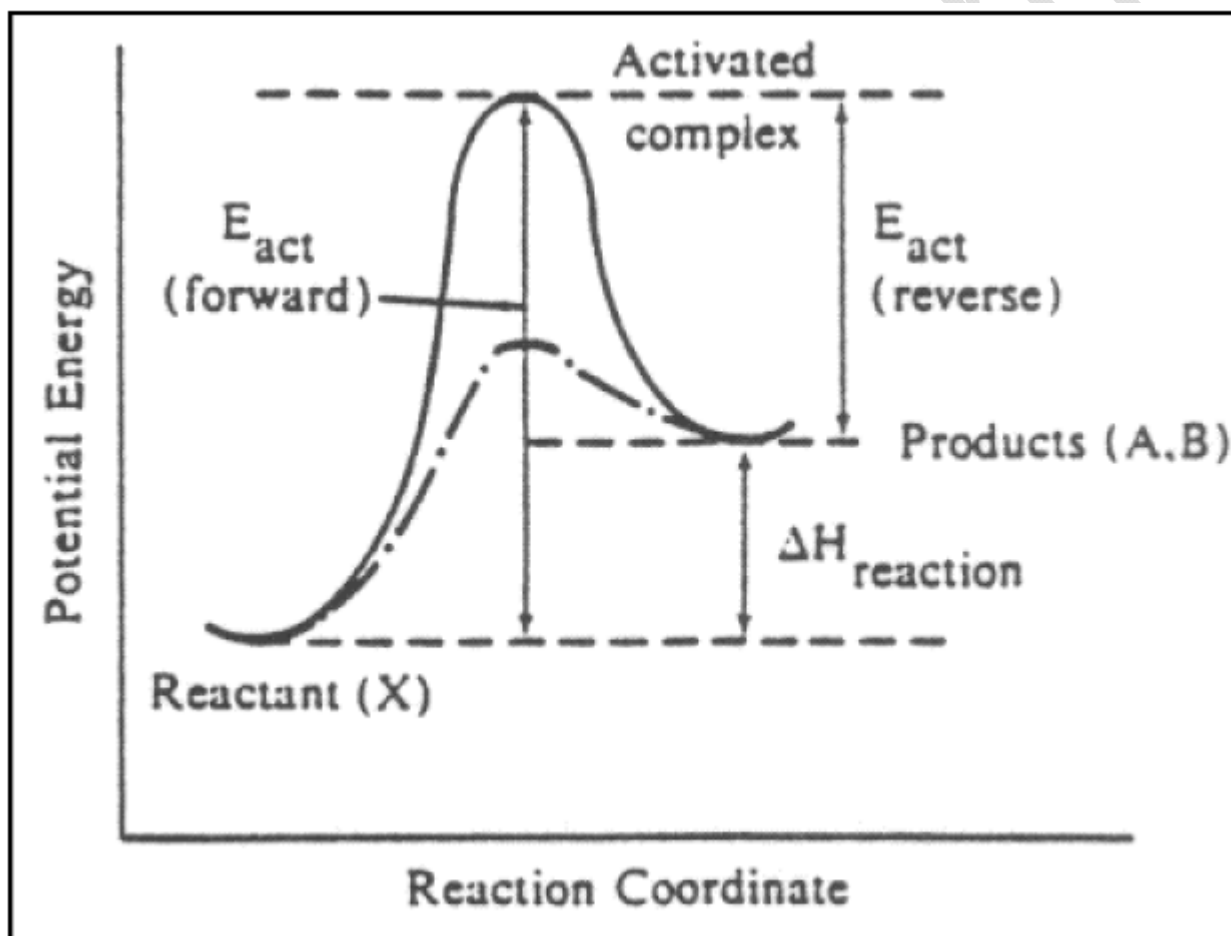
1980 - #5



The forward reaction is slow at room temperature but becomes rapid when a catalyst is added.

(a) Draw a diagram of potential energy versus reaction coordinate for the uncatalyzed reaction. On this diagram label

- (1) the axes
- (2) the energies of the reactants and the products
- (3) the energy of the activated complex
- (4) all significant energy differences



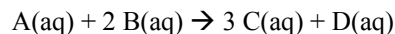
(b) On the same diagram indicate the change or changes that result from the addition of the catalyst. Explain the role of the catalyst in changing the rate of the reaction.

**Catalyzed path (dotted line on diagram)**

**Catalyst role: changes mechanism, or increases fraction of molecules with sufficient energy to react.**

(c) If the temperature is increased, will the ratio  $k_f / k_r$  increase, remain the same, or decrease? Justify your answer with a one- or two-sentence explanation. ( $k_f$  and  $k_r$  are the specific rate constants for the forward and the reverse reactions, respectively.) **The ratio,  $k_f / k_r$  increases with temperature, because  $k_f / k_r = K$  and LeChatelier shift**

## 1981 - #2



For the reaction above, carried out in solution at 30 °C, the following kinetic data were obtained:

Experiment	Initial concentration of Reactants mole liter <sup>-1</sup>		Initial Rate of Reaction mole liter <sup>-1</sup> hour <sup>-1</sup>
	A <sub>o</sub>	B <sub>o</sub>	
1	0.240	0.480	8.00
2	0.240	0.120	2.00
3	0.360	0.240	9.00
4	0.120	0.120	0.500
5	0.240	0.0600	1.00
6	0.140	1.35	?

(a) Write the rate-law expression for this reaction. **rate = k [A]<sup>2</sup>[B]<sup>1</sup>**

(b) Calculate the value of the specific rate constant k at 30°C and specify its units. **k = 289 L<sup>2</sup> mol<sup>-2</sup> hr<sup>-1</sup>**

(c) Calculate the value of the initial rate of this reaction at 30°C for the initial concentrations shown in experiment 6.  
**rate = 7.66 mol L<sup>-1</sup> hr<sup>-1</sup>**

(d) Assume that the reaction goes to completion. Under the conditions specified for experiment 2, what would be the final molar concentration of C?

$$[C] = (3C / 2B) \times 0.120 \text{ mol / L of B} = 0.18 \text{ M}$$

## 1984 - #2

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 L <sup>-1</sup> sec <sup>-1</sup> )	Initial [X] <sub>o</sub> , (mol L <sup>-1</sup> )	Initial [Y] <sub>o</sub> , (mol L <sup>-1</sup> )
7.0x10 <sup>-4</sup>	0.20	0.10
1.4x10 <sup>-3</sup>	0.40	0.20
2.8x10 <sup>-3</sup>	0.40	0.40
4.2x10 <sup>-3</sup>	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<sup>-1</sup>**

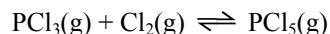
(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are [X]<sub>o</sub> = 0.80 molar, [Y]<sub>o</sub> = 0.60 molar and [Z]<sub>o</sub> = 0 molar? **57.9 seconds**

(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)  $X + Y \rightarrow M$  (slow)  
 $X + M \rightarrow Z$  (fast) **Rate = k[X][Y]**
- (2)  $X + X \rightarrow M$  (fast)  
 $Y + M \rightarrow Z$  (slow) **Rate = k[X]<sup>2</sup>[Y]**
- (3)  $Y \rightarrow M$  (slow)  
 $M + X \rightarrow N$  (fast)  
 $N + X \rightarrow Z$  (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.**

## 1985 - #8



In the equation above, the forward reaction is first order in both  $\text{PCl}_3$  and  $\text{Cl}_2$  and the reverse reaction is first order in  $\text{PCl}_5$ .

(a) Suppose that 2 moles of  $\text{PCl}_3$  and 1 mole of  $\text{Cl}_2$  are mixed in a closed container at constant temperature. Draw a graph that shows how the concentrations of  $\text{PCl}_3$ ,  $\text{Cl}_2$ , and  $\text{PCl}_5$  change with time until after equilibrium has been firmly established.

**Points on ordinate take into account the initial amounts of the three substances, and  $\text{PCl}_5$  line rises while others fall. Lines curved at start and flat after equilibrium. Concentration changes should be consistent with the fact that all coefficients in the equation are unity.**

(b) Give the initial rate law for the forward reaction. **Rate =  $k [\text{PCl}_3] [\text{Cl}_2]$**

(c) Provide a molecular explanation for the dependence of the rate of the forward reaction on the concentrations of the reactants. **Reaction requires effective collisions between molecules of  $\text{PCl}_3$  and  $\text{Cl}_2$ . As concentrations of these molecules increase, the number of effective collisions must increase and the rate of action increases.**

(d) Provide a molecular explanation for the dependence of the rate of the forward reaction on temperature.

**The fraction of colliding molecules with the required activation energy increases as the temperature rises.**

## 1986 - #6

The overall order of a reaction may not be predictable from the stoichiometry of the reaction.

(a) Explain how this statement can be true. **order of reaction determined by the slowest step in the mechanism OR order of reaction determined by exponents in the rate law OR providing a counterexample where the coefficients in equation and exponents in rate law are different**

(b)  $2 \text{XY} \rightarrow \text{X}_2 + \text{Y}_2$

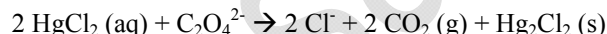
1. For the hypothetical reaction above, give a rate law that shows that the reaction is first order in the reactant XY. **Rate =  $k[\text{XY}]$**

2. Give the units for the specific rate constant for this rate law.  **$k = 1/\text{time}$  or units consistent with student's rate equation**

3. Propose a mechanism that is consistent with both the rate law and the stoichiometry.

**Mechanism proposed should show: steps adding up to the overall reaction; one step starting with XY; rate-determining step involving XY**

## 1987 - #2



The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table.

Experiment	Initial $[\text{HgCl}_2]$	Initial $[\text{C}_2\text{O}_4^{2-}]$	Initial Rate of formation of $\text{Cl}^-$ (mole/liter min)
(1)	0.0836 M	0.202 M	$0.52 \times 10^{-4}$
(2)	0.0836 M	0.404 M	$2.08 \times 10^{-4}$
(3)	0.0418 M	0.404 M	$1.06 \times 10^{-4}$
(4)	0.0316 M	?	$1.27 \times 10^{-4}$

(a) According to the data shown, what is the rate law for the reaction above? **Rate =  $k [\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2$**

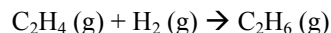
(b) On the basis of the rate law determined in part (a), calculate the specific rate constant. Specify the units.

**$k = 1.52 \times 10^{-2} \text{ M}^{-2} \text{ min}^{-1}$**

(c) What is the numerical value for the initial rate of disappearance of  $\text{C}_2\text{O}_4^{2-}$  for Experiment 1?  **$2.6 \times 10^{-5} \text{ M/min}$**

(d) Calculate the initial oxalate ion concentration for Experiment 4.  **$[\text{C}_2\text{O}_4^{2-}] = 0.514 \text{ M}$**

## 1989 - #8



For the above reaction,  $\Delta H^\circ = -137 \text{ kJ}$

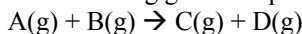
Account for the following observations regarding the exothermic reaction represented by the equation above.

(a) An increase in the pressure of the reactants causes an increase rate. **Effective concentration are increased So collision frequency is increased.**

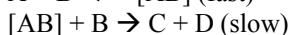
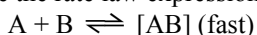
- (b) A small increase in temperature causes a large increase in the reaction rate. **Slight increase in collision frequency occurs. More molecules have enough energy that many more collisions have the necessary activation energy. Raises reaction rate a great deal.**
- (c) The presence of metallic nickel causes an increase in reaction rate. **Catalytic nickel lowers the activation energy needed for a reaction. More often molecules have the needed energy for a reaction.**
- (d) The presence of powdered nickel causes a larger increase in reaction rate than does the presence of a single piece of nickel of the same mass.  
**Greater surface area with powdered Ni. More catalytic sites means a greater rate.**

#### 1990 - #7

Consider the following general equation for a chemical reaction.



- (a) Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.
- 1. the kinetic energy of the molecules (A certain minimum energy is required for a reaction to occur (activation energy))**
  - 2. The orientation of the molecules relative to one another. Even very energetic collisions may not lead to a reaction if the molecules are not oriented properly.**
- (b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
- 1. A decrease in temperature would decrease the rate.**
  - 2. Fewer molecules would have the energy necessary to react. (Fewer effective collisions)**
- (c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.

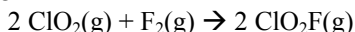


$$\text{Rate} = [A][B]^2$$

- (d) Explain why a catalyst increases the rate of a reaction but does not change the value of the equilibrium constant for that reaction.

**Catalyst increases the rate by providing an alternate pathway which has a lower activation**

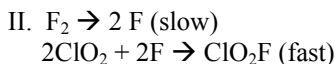
#### 1991 - #3



Experiment	Initial $[\text{ClO}_2]$ mol L <sup>-1</sup>	Initial $[\text{F}_2]$ mol L <sup>-1</sup>	Initial Rate of Increase of $[\text{ClO}_2\text{F}]$ mol L <sup>-1</sup> sec <sup>-1</sup>
1	0.010	0.10	$2.4 \times 10^{-3}$
2	0.010	0.40	$9.6 \times 10^{-3}$
3	0.020	0.20	$9.6 \times 10^{-3}$

The following results were obtained when the reaction represented above was studied at 25 °C.

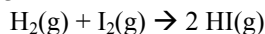
- (a) Write the rate law expression for the reaction above. **rate = k  $[\text{ClO}_2]$   $[\text{F}_2]$**
- (b) Calculate the numerical value of the rate constant and specify the units.  **$2.4 \text{ L mol}^{-1} \text{ sec}^{-1}$**
- (c) In experiment 2, what is the initial rate of decrease of  $[\text{F}_2]$ ?  **$4.8 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$**
- (d) Which of the following reaction mechanisms is consistent with the rate law developed in (a)? Justify your choice.



#### Mechanism I

**Defense: slow step is first order three equations add to proper stoichiometry**

1992 - #5



For the exothermic reaction represented above, carried out at 298 K, the rate law is as follows.

$$\text{Rate} = k [\text{H}_2] [\text{I}_2]$$

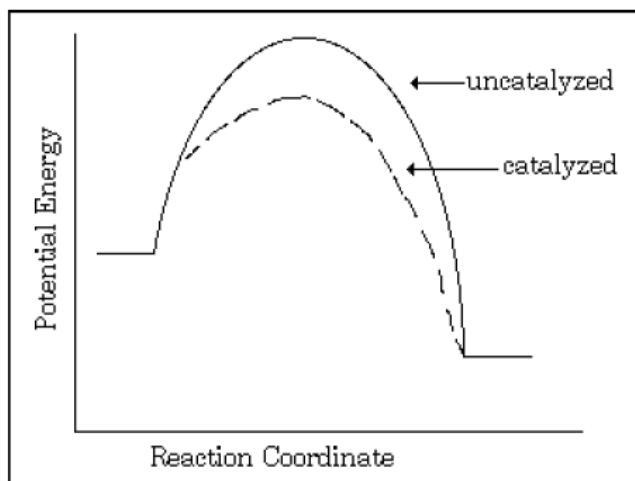
Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume. **EFFECT: addition of  $\text{H}_2$  would increase the rate. EXPLANATION: Since the reaction is first-order in  $\text{H}_2$ , doubling the concentration would double the rate. The inclusion of  $\text{H}_2$  in the rate law indicates it participates in the rate-determining step.**

(b) Increase in volume of the reaction vessel at constant temperature. **EFFECT: The initial rate would decrease. EXPLANATION: Increasing the volume would decrease the concentration of both  $\text{H}_2$  and  $\text{I}_2$ . At the lower concentration there would be a lesser number of overall collisions (due to greater distance between individual molecules), leading to a lesser number of effective collisions.**

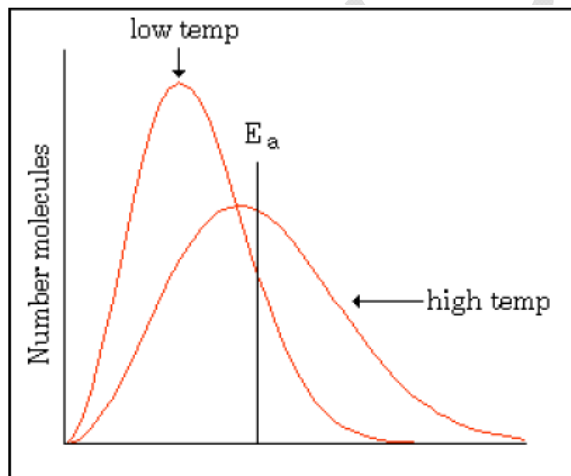
(c) Addition of a catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate. **EFFECT: addition of a catalyst will increase the rate of both forward and reverse reactions.**

**EXPLANATION:**

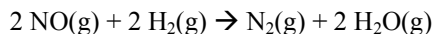


(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy. **EFFECT: The initial rate of reaction will increase.**

**EXPLANATION:**



## 1994 - #2



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 <sub>2</sub> (mol/L min)
	[NO]	[H <sub>2</sub> ]	
1	0.0060	0.0010	$1.8 \times 10^{-4}$
2	0.0060	0.0020	$3.6 \times 10^{-4}$
3	0.0010	0.0060	$0.30 \times 10^{-4}$
4	0.0020	0.0060	$1.2 \times 10^{-4}$

(a)

(i) Determine the order for each of the reactants, NO and H<sub>2</sub>, 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<sub>2</sub>] is first order. In experiments 1 and 2 the concentration doubles and the rate doubles.**

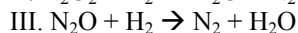
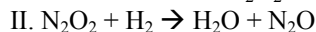
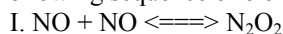
(ii) Write the overall rate law for the reaction.

$$\text{Rate} = k[\text{H}^+][\text{NO}]^2$$

(b) Calculate the value of the rate constant, k, for the reaction. Include units. **K = 5000 L<sup>2</sup>mol<sup>-2</sup>min<sup>-1</sup>**

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H<sub>2</sub> has been consumed. **0.0050 M**

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



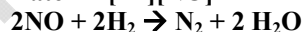
Based on the data present, which of the above is the rate-determining step? Show that the mechanism is consistent with:

**The second step is the rate determining step.**

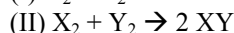
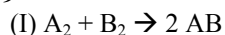
(i) the observed rate law for the reaction, and

$$\text{Rate} = k[\text{H}^+][\text{NO}]^2$$

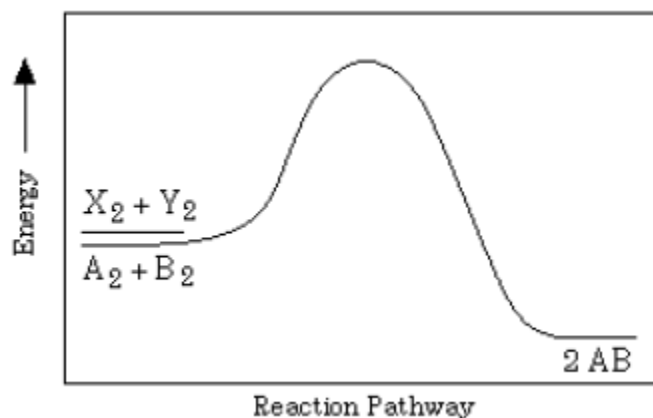
(ii) the overall stoichiometry of the reaction.



## 1995 - #9



Two reactions are represented above. The potential-energy diagram for reaction I is shown below. The potential energy of the reactants in reaction II is also indicated on the diagram. Reaction II is endothermic, and the activation energy of reaction I is greater than that of reaction II.



(a) Complete the potential-energy diagram for reaction II on the graph above.

**Sketch must show start at X<sub>2</sub> + Y<sub>2</sub>, rise to E<sub>a</sub> that is less than that for reaction I, then drop to 2 XY, which must be at a higher PE than X<sub>2</sub> + Y<sub>2</sub> to show an endothermic process.**

(b) For reaction I, predict how each of the following is affected as the temperature is increased by 20°C. Explain the basis for each prediction.

- (i) Rate of reaction **The rate increases because more molecules have energy greater than  $E_a$  at higher temperature and/or the higher speed of the molecules generates a greater collision frequency.**
- (ii) Heat of reaction  **$\Delta H$  for the reaction is changed only slightly, or not at all with small changes in temperature.**

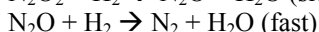
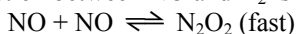
(c) For reaction II, the form of the rate law is  $\text{rate} = k[X_2]^m[Y_2]^n$ . Briefly describe an experiment that can be conducted in order to determine the values of  $m$  and  $n$  in the rate law for the reaction.

**Hold one reactant concentration constant, vary the other, and measure initial rate of reactant disappearance or product formation. Take ratios of rates equal to  $([1]/[2])^n$ ; repeat for the other reactant.**

(d) From the information given, determine which reaction initially proceeds at the faster rate under the same conditions of concentration and temperature. Justify your answer. **Reaction II proceeds faster. The reaction with the lower  $E_a$ , under the same conditions of concentration and temperature, will have a faster rate.**

#### 1996 - #8

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



(a) Write a balanced equation for the overall reaction.  **$2 NO + 2 H_2 \rightarrow N_2 + 2 H_2O$**

(b) Identify the intermediates in the reaction. Explain your reasoning.  **$N_2O_2$  and  $N_2O$  are intermediates because they appear in the mechanism but not in the overall products (or reactants)**

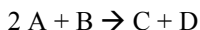
(c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is  $\text{rate} = k[NO]^2[H_2]$ . The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an  $H_2$  molecule. Are conclusions (1) and (2) correct? Explain.

**Student indicates conclusion (1) is correct, because the sum of the exponents in rate law is  $2 + 1 = 3$**

**Student indicates conclusion (2) is incorrect, because no step involves two NO molecules and a  $H_2$  molecule**

(d) Explain why an increase in temperature increases the rate constant,  $k$ , given the rate law in (c). **T goes up therefore  $k$  goes up: because increasing number of collisions between reactants are occurring with sufficient energy to form an activated complex**

#### 1997 - #4



The following results were obtained when the reaction represented above was studied at 25°C

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C ( $\text{mol L}^{-1}\text{min}^{-1}$ )
1	0.25	0.75	$4.3 \times 10^{-4}$
2	0.75	0.75	$1.3 \times 10^{-3}$
3	1.50	1.50	$5.3 \times 10^{-3}$
4	1.75	??	$8.0 \times 10^{-3}$

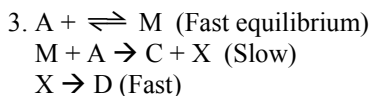
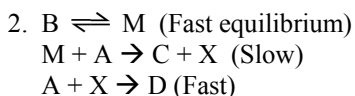
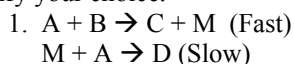
(a) Determine the order of the reaction with respect to A and B. Justify your answer. **first order in A; first order in B**

(b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.  **$\text{rate} = k[A][B]$   
 $K = 2.3 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}$**

(c) Determine the initial rate of change of [A] in Experiment 3.  **$1.06 \times 10^{-2} \text{ M}^{-1} \text{ min}^{-1}$**

(d) Determine the initial value of [B] in Experiment 4.  **$[B] = 2.0 \text{ M}$**

(e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.



**Mechanism 2 is consistent rate proportional to  $[M][A]$  and  $[M]$  proportional to  $[B] \Rightarrow$  rate proportional to  $[A][B]$**

### 1998 - #6

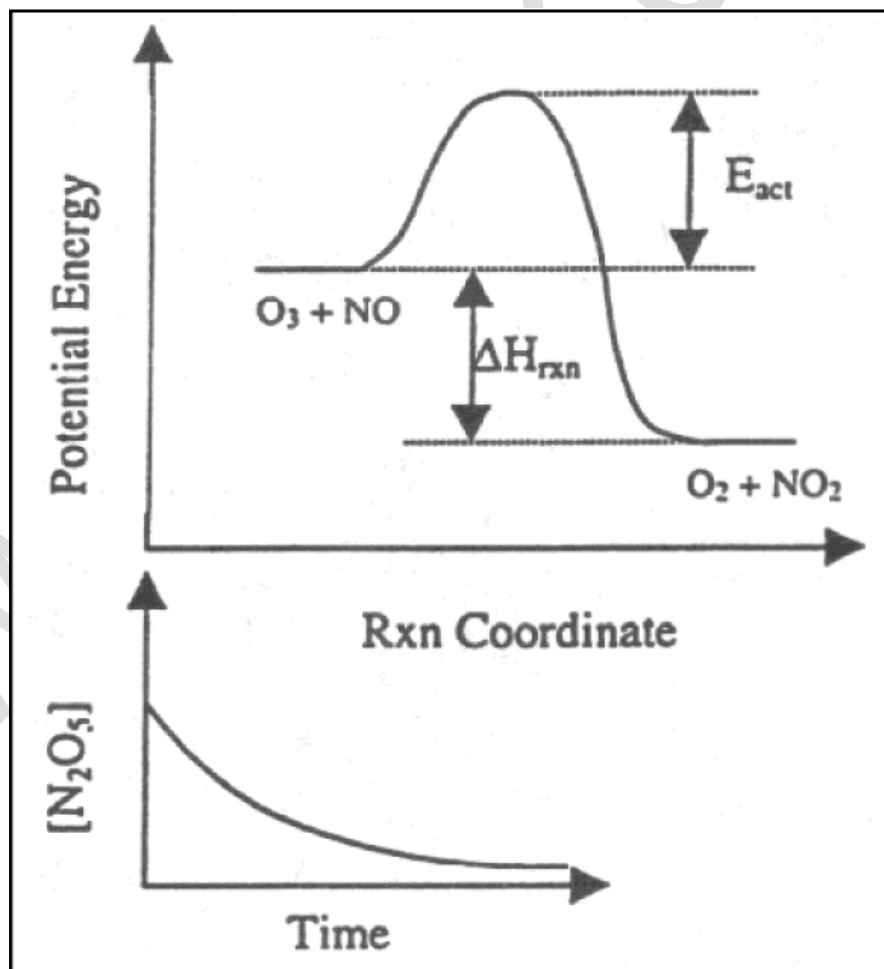
Answer the following questions regarding the kinetics of chemical reactions.

(a) The diagram below at right shows the energy pathway for the reaction  $O_3 + NO \rightarrow NO_2 + O_2$ . Clearly label the following directly on the diagram above.

- (i) The activation energy ( $E_a$ ) for the forward reaction
- (ii) The enthalpy change ( $\Delta H$ ) for the reaction

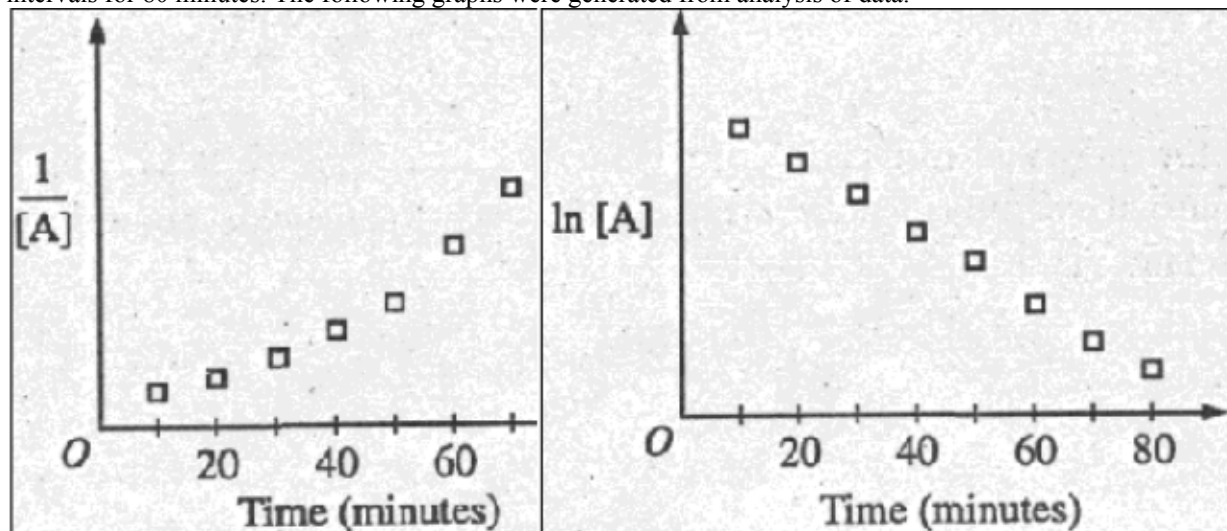
(b) The reaction  $2 N_2O_5 \rightarrow 4 NO_2 + O_2$  is first order with respect to  $N_2O_5$ .

- (i) Using the axes at right, complete the graph that represents the change in  $[N_2O_5]$  over time as the reaction proceeds.
- (ii) Describe how the graph in (i) could be used to find the reaction rate at a given time,  $t$ . **Reaction rate is the slope of the line tangent to any point on the curve.**
- (iii) Considering the rate law and the graph in (i), describe how the value of the rate constant,  $k$ , could be determined. **Since "rate = slope =  $k[N_2O_5]$ ", the value of  $k$  can be determined algebraically from the slope at a known value of  $[N_2O_5]$ .**
- (iv) If more  $N_2O_5$  were added to the reaction mixture at constant temperature, what would be the effect on the rate constant,  $k$ ? Explain. **The value of the rate constant is independent of the reactant concentrations, so adding more reactant will not affect the value of  $k$ .**





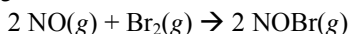
(c) Data for the chemical reaction  $2A \rightarrow B + C$  were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of data.



Use the information in the graphs above to answer the following.

- Write the rate-law expression for the reaction. Justify your answer. **Rate =  $k[A]$  or  $\ln([A]/[A]_0) = kt$ . Since graph of  $\ln[A]$  vs. time is linear, it must be a first-order reaction.**
- Describe how to determine the value of the rate constant for the reaction. **Determine the slope of the second graph and set " $k = -\text{slope}$ ."**

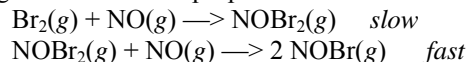
1999 - #3



A rate study of the reaction represented above was conducted at  $25^\circ\text{C}$ . The data that were obtained are shown in the table below.

Experiment	Initial $[\text{NO}]$ ( $\text{mol L}^{-1}$ )	Initial $[\text{Br}_2]$ ( $\text{mol L}^{-1}$ )	Initial Rate of Appearance of NOBr ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	0.0160	0.0120	$3.24 \times 10^{-4}$
2	0.0160	0.0240	$6.38 \times 10^{-4}$
3	0.0320	0.0060	$6.42 \times 10^{-4}$

- Calculate the initial rate of disappearance of  $\text{Br}_2(g)$  in experiment 1.  **$1.62 \times 10^{-4} \text{ M sec}^{-1}$**
- Determine the order of the reaction with respect to each reactant,  $\text{Br}_2(g)$  and  $\text{NO}(g)$ . In each case, explain your reasoning. **Comparing experiments 1 and 2,  $[\text{NO}]$  remains constant,  $[\text{Br}_2]$  doubles, and rate doubles; therefore, reaction is first-order with respect to  $[\text{Br}_2]$ . The reaction is second order with respect to  $[\text{NO}]$ . A mathematical calculation must be shown to earn credit.**
- 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 =  $k[\text{NO}]^2[\text{Br}_2]$ ;  $105 \text{ M}^{-2} \text{ sec}^{-1}$**
- The following mechanism was proposed for the reaction:



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  $[\text{NO}]$ , and first-order in  $[\text{Br}_2]$ , as those are the two reactants in the rate-determining step. Kinetic data show the reaction is second-order in  $[\text{NO}]$  (and first-order in  $[\text{Br}_2]$ ), so this cannot be the mechanism.**

## 2000 - #6



Consider the reaction represented above.

(a) Referring to the data in the table below, calculate the standard enthalpy change,  $\Delta H^\circ$ , for the reaction at 25°C. Be sure to show your work.

	$\text{O}_3(\text{g})$	$\text{NO}(\text{g})$	$\text{NO}_2(\text{g})$
Standard enthalpy of formation, $\Delta H_f^\circ$ , at 25°C (kJ mol <sup>-1</sup> )	143	90.	33

$$\Delta H^\circ = 33 - (90. + 143) \text{ kJ} = -200 \text{ kJ}$$

(b) Make a qualitative prediction about the magnitude of the standard entropy change,  $\Delta S^\circ$ , for the reaction at 25°C. Justify your answer.  **$\Delta S^\circ$  for this reaction should be small or negligible (near zero or zero) because the number of moles (of gas) is the same on each side of the equation.**

(c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change,  $\Delta G^\circ$ , for the reaction at 25°C. Explain your reasoning.  **$\Delta G^\circ$  is negative (-) at 298 K  $\Delta G^\circ = \Delta H^\circ - T(\Delta S^\circ)$ ,  $\Delta H^\circ$  is negative, and  $\Delta S^\circ$  is near zero, thus it follows that  $\Delta G^\circ$  will be negative.**

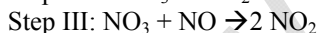
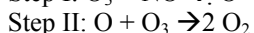
(d) Use the information in the table below to write the rate-law expression for the reaction, and explain how you obtained your answer.

Experiment Number	Initial $[\text{O}_3]$ (mol L <sup>-1</sup> )	Initial $[\text{NO}]$ (mol L <sup>-1</sup> )	Initial Rate of Formation of $\text{NO}_2$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.0010	0.0010	$x$
2	0.0010	0.0020	$2x$
3	0.0020	0.0010	$2x$
4	0.0020	0.0020	$4x$

When  $[\text{O}_3]$  is held constant and  $[\text{NO}]$  is doubled (as in Experiments 1 and 2), the rate also doubles so the reaction is first-order in  $[\text{NO}]$ . When  $[\text{NO}]$  is held constant and  $[\text{O}_3]$  is doubled (as in Experiments 1 and 3), the rate also doubles so the reaction is first-order in  $[\text{O}_3]$ .

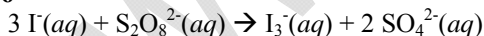
**Rate =  $k [\text{O}_3] [\text{NO}]$  (or Rate =  $k [\text{O}_3]^1 [\text{NO}]^1$ , or Rate =  $106 (x) [\text{O}_3] [\text{NO}]$ )**

(e) The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.



**Step 1 must be rate-determining, as the rate law for this elementary step is the only one that agrees with the rate law determined experimentally in part (d) above.**

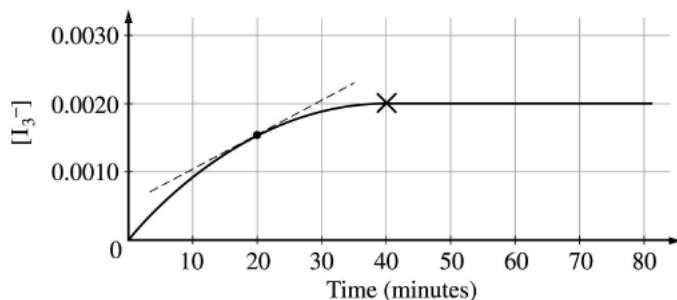
## 2001 - #6



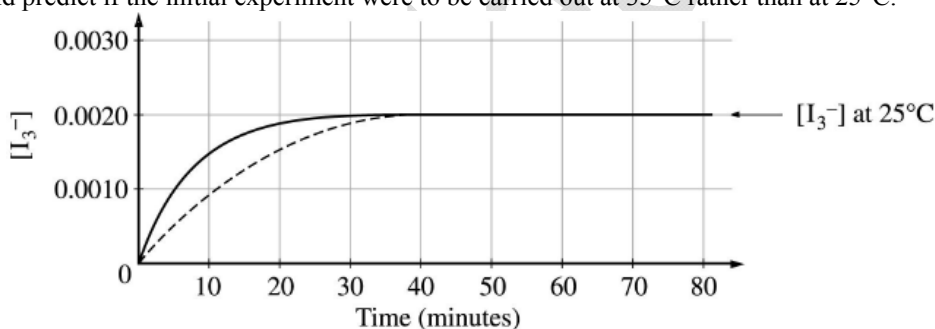
Iodide ion,  $\text{I}^-(\text{aq})$ , reacts with peroxydisulfate ion,  $\text{S}_2\text{O}_8^{2-}(\text{aq})$ , according to the equation above. Assume that the reaction goes to completion.

(a) Identify the type of reaction (combustion, disproportionation, neutralization, oxidation-reduction, precipitation, etc.) represented by the equation above. Also, give the formula of another substance that could convert  $\text{I}^-(\text{aq})$  to  $\text{I}_3^-(\text{aq})$ . **The reaction is an oxidation-reduction (redox) reaction. To go from  $\text{I}^-$  to  $\text{I}_3^-$ , the iodine has to be oxidized, so credit is earned for the formula of any reasonable oxidizing agent (e.g.,  $\text{F}_2$ ,  $\text{Co}^{3+}$ ,  $\text{O}_2$ ,  $\text{MnO}_4^-$ )**

(b) In an experiment, equal volumes of 0.0120 M  $\text{I}^-(\text{aq})$  and 0.0040 M  $\text{S}_2\text{O}_8^{2-}(\text{aq})$  are mixed at 25°C. The concentration of  $\text{I}_3^-(\text{aq})$  over the following 80 minutes is shown in the graph below.

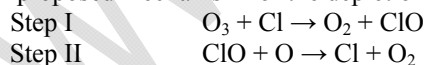


- (i) Indicate the time at which the reaction first reaches completion by marking an "X" on the curve above at the point that corresponds to this time. Explain your reasoning. **This is where the curve levels off.**
- (ii) Explain how to determine the instantaneous rate of formation of  $I_3^-(aq)$  at exactly 20 minutes. Draw on the graph above as part of your explanation. **The instantaneous rate of the reaction at 20 minutes is the slope of the line tangent to the curve at 20 minutes.**
- (c) Describe how to change the conditions of the experiment in part (b) to determine the order of the reaction with respect to  $I^-(aq)$  and with respect to  $S_2O_8^{2-}(aq)$ . **Keep the initial concentration of  $S_2O_8^{2-}$  constant, change the initial concentration of  $I^-$  by a known amount, and see what effect this change has on the measured rate of the reaction. This procedure should be repeated, but this time keeping the concentration of  $I^-$  constant and changing the concentration of  $S_2O_8^{2-}$ .**
- (d) State clearly how to use the information from the results of the experiments in part (c) to determine the value of the rate constant,  $k$ , for the reaction. **The general rate law expression is:  $rate = k [I^-]^x [S_2O_8^{2-}]^y$**
- (e) On the graph below (which shows the results of the initial experiment as a dashed curve), draw in a curve for the results you would predict if the initial experiment were to be carried out at  $35^\circ C$  rather than at  $25^\circ C$ .



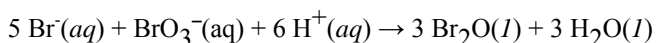
#### 2002 - #7

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.



- (a) Write a balanced equation for the overall reaction represented by Step I and Step II above.  **$O_3 + O \rightarrow 2O_2$**
- (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.
- The overall order of the reaction. **Second order.**
  - Appropriate units for the rate constant,  $k$ .  **$L \cdot mol^{-1} \cdot sec^{-1}$**
  - 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.**

## 2003 - #3



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

Experiment	Initial $[\text{Br}^-]$ (mol L <sup>-1</sup> )	Initial $[\text{BrO}_3^-]$ (mol L <sup>-1</sup> )	Initial $[\text{H}^+]$ (mol L <sup>-1</sup> )	Rate of Disappearance of $\text{BrO}_3^-$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.00100	0.00500	0.100	$2.50 \times 10^{-4}$
2	0.00200	0.00500	0.100	$5.00 \times 10^{-4}$
3	0.00100	0.00750	0.100	$3.75 \times 10^{-4}$
4	0.00100	0.01500	0.200	$3.00 \times 10^{-3}$

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

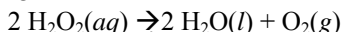
- (i)  $\text{Br}^-$  = **1<sup>st</sup> order**
- (ii)  $\text{BrO}_3^-$  = **1<sup>st</sup> order**
- (iii)  $\text{H}^+$  = **2<sup>nd</sup> order**

(b) Write the rate law for the overall reaction. **rate =  $k[\text{Br}^-]^1[\text{BrO}_3^-]^1[\text{H}^+]^2$**

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

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

## 2004B - #3

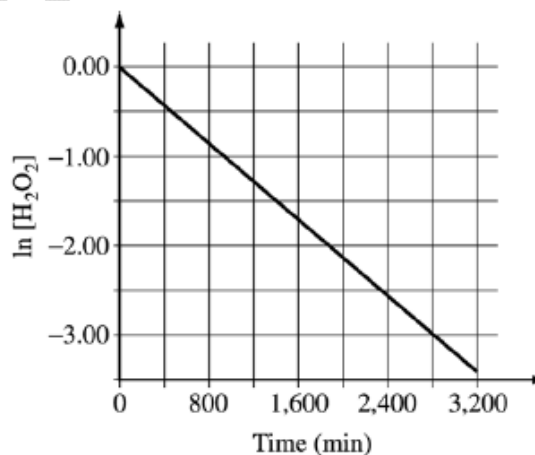
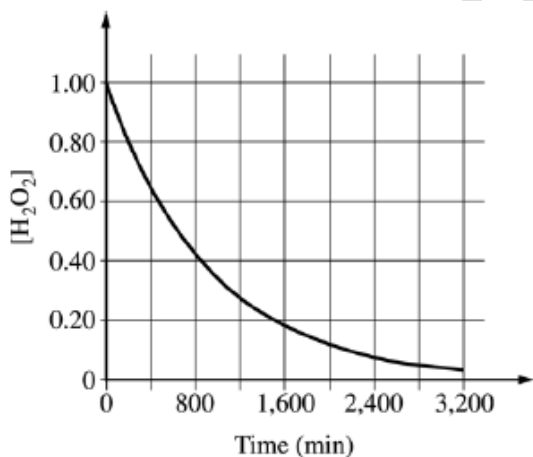


Hydrogen peroxide decomposes according to the equation above.

(a) An aqueous solution of  $\text{H}_2\text{O}_2$  that is 6.00 percent  $\text{H}_2\text{O}_2$  by mass has a density of 1.03 g mL<sup>-1</sup>. Calculate each of the following.

- (i) The original number of moles of  $\text{H}_2\text{O}_2$  in a 125 mL sample of the 6.00 percent  $\text{H}_2\text{O}_2$  solution  
**0.227 mol  $\text{H}_2\text{O}_2$**
- (ii) The number of moles of  $\text{O}_2(g)$  that are produced when all of the  $\text{H}_2\text{O}_2$  in the 125 mL sample decomposes  
**0.114 mol  $\text{O}_2(g)$**

(b) The graphs below show results from a study of the decomposition of  $\text{H}_2\text{O}_2$ .



(i) Write the rate law for the reaction. Justify your answer. **rate =  $k[\text{H}_2\text{O}_2]^1$  A plot of  $\ln[\text{H}_2\text{O}_2]$  versus time is a straight line, so the reaction follows simple first-order kinetics.**

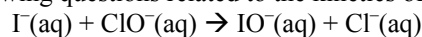
(ii) Determine the half-life of the reaction. **650 minutes; Any value between 600 - 700 minutes**

(iii) Calculate the value of the rate constant,  $k$ . Include appropriate units in your answer.  **$1.1 \times 10^{-3} \text{ min}^{-1}$**

(iv) Determine  $[\text{H}_2\text{O}_2]$  after 2,000 minutes elapse from the time the reaction began. **0.12 M; Any value between 0.009 and 0.013**

2005 - #3

Answer the following questions related to the kinetics of chemical reactions.



Iodide ion,  $\text{I}^-$ , is oxidized to hypoiodite ion,  $\text{IO}^-$ , by hypochlorite,  $\text{ClO}^-$ , in basic solution according to the equation above. Three initial-rate experiments were conducted; the results are shown in the following table.

Experiment	$[\text{I}^-]$ (mol L <sup>-1</sup> )	$[\text{ClO}^-]$ (mol L <sup>-1</sup> )	Initial Rate of Formation of $\text{IO}^-$ (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.017	0.015	0.156
2	0.052	0.015	0.476
3	0.016	0.061	0.596

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.

(i)  $\text{I}^-(\text{aq})$  – **1<sup>st</sup> order**

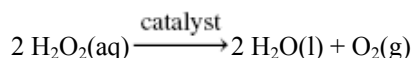
(ii)  $\text{ClO}^-(\text{aq})$  – **1<sup>st</sup> order**

(b) For the reaction,

(i) write the rate law that is consistent with the calculations in part (a); **Rate =  $k[\text{I}^-][\text{ClO}^-]$**

(ii) calculate the value of the specific rate constant,  $k$ , and specify units.  **$K = 612 \text{ L mol}^{-1} \text{ sec}^{-1}$**

The catalyzed decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2(\text{aq})$ , is represented by the following equation.



The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below.

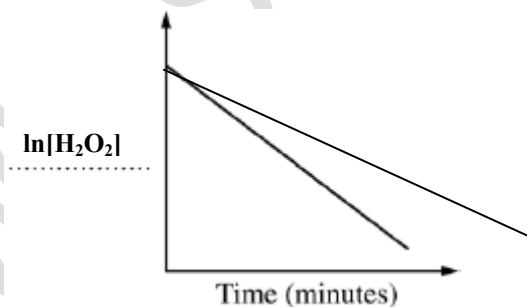
$[\text{H}_2\text{O}_2]$ (mol L <sup>-1</sup> )	Time (minutes)
1.00	0.0
0.78	5.0
0.61	10.0

(c) During the analysis of the data, the graph below was produced.

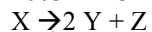
(i) Label the vertical axis of the graph.

(ii) What are the units of the rate constant,  $k$ , for the decomposition of  $\text{H}_2\text{O}_2(\text{aq})$ ? **min<sup>-1</sup>**

(iii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M  $\text{H}_2\text{O}_2(\text{aq})$ .

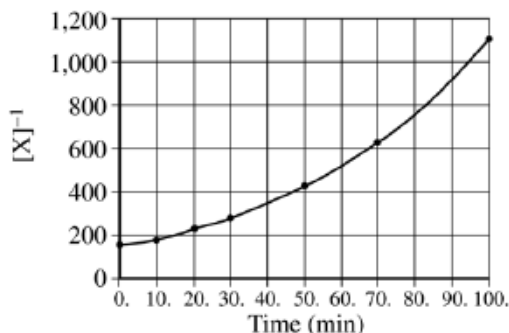
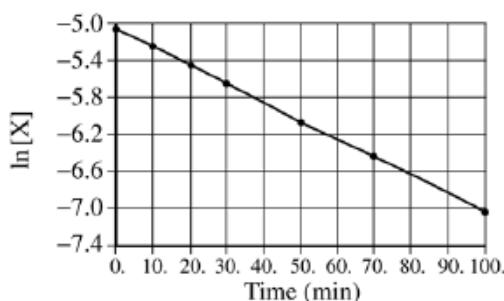
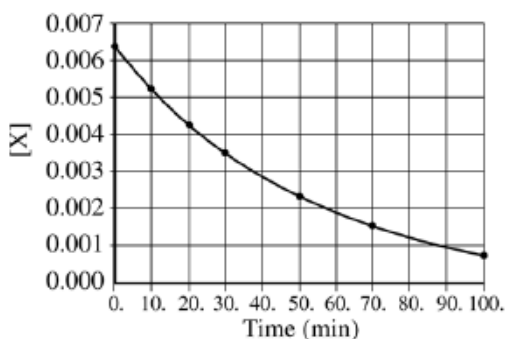


## 2005B - #3



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 <sup>-1</sup> )	ln [X]	[X] <sup>-1</sup> (L mol <sup>-1</sup> )
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?  $3.17 \times 10^{-2}$  mol X  
 (b) How many molecules of Y were produced in the first 20. minutes of the reaction?  $1.24 \times 10^{22}$  molecules  
 (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.**  
 (d) Write the rate law for this reaction. **rate = k[X]<sup>1</sup>**  
 (e) Calculate the specific rate constant for this reaction. Specify units. **0.0197 min<sup>-1</sup>**  
 (f) Calculate the concentration of X in the flask after a total of 150. minutes of reaction.  **$3.30 \times 10^{-4}$  M**

## 2006 - #6d

- (d) Consider the four reaction-energy profile diagrams shown below.

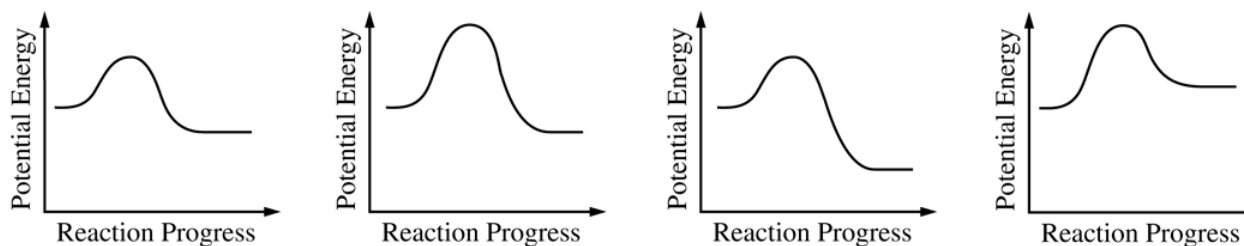


Diagram 1

Diagram 2

Diagram 3

Diagram 4

(i) Identify the two diagrams that could represent a catalyzed and an uncatalyzed reaction pathway for the same reaction. Indicate which of the two diagrams represents the catalyzed reaction pathway for the reaction. **Diagram 1 represents a catalyzed pathway and diagram 2 represents an uncatalyzed pathway for the same reaction.**

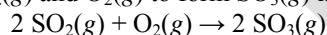
(ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

Adding a catalyst to a reaction mixture adds energy that causes the reaction to proceed more quickly.

**I disagree with the statement. A catalyst does not add energy, but provides an alternate reaction pathway with a lower activation energy.**

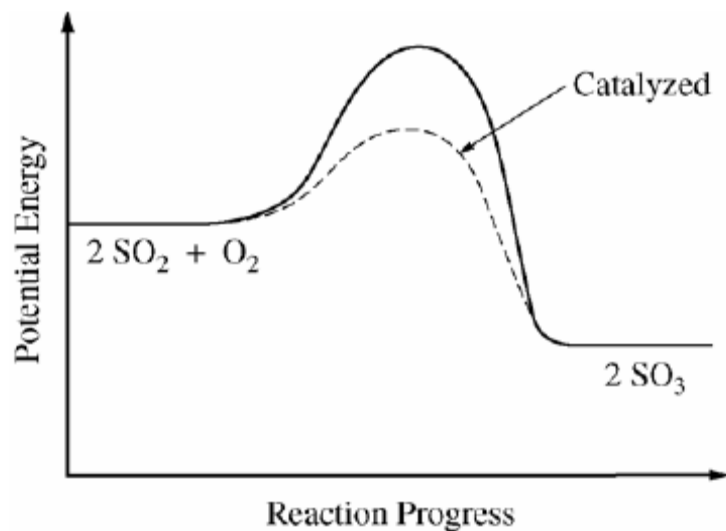
#### 2007 - #6e

The reaction between  $\text{SO}_2(g)$  and  $\text{O}_2(g)$  to form  $\text{SO}_3(g)$  is represented below.



The reaction is exothermic. The reaction is slow at  $25^\circ\text{C}$ ; however, a catalyst will cause the reaction to proceed faster.

(e) Using the axes provided on the next page, draw the complete potential-energy diagram for both the catalyzed and uncatalyzed reactions. Clearly label the curve that represents the catalyzed reaction.



#### 2008 - #3d-f

Nitrogen monoxide gas, a product of the reaction above, can react with oxygen to produce nitrogen dioxide gas, as represented below.  $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$

(d) Determine the order of the reaction with respect to each of the following reactants. Give details of your reasoning, clearly explaining or showing how you arrived at your answers.

Experiment	Initial Concentration of NO (mol L <sup>-1</sup> )	Initial Concentration of O <sub>2</sub> (mol L <sup>-1</sup> )	Initial Rate of Formation of NO <sub>2</sub> (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.0200	0.0300	$8.52 \times 10^{-2}$
2	0.0200	0.0900	$2.56 \times 10^{-1}$
3	0.0600	0.0300	$7.67 \times 10^{-1}$

(i) NO - Comparing experiments 1 and 3, the tripling of the initial concentration of NO while the initial concentration of oxygen remained constant at 0.0300 mol L<sup>-1</sup> resulted in a nine-fold increase in the initial rate of formation of NO<sub>2</sub>. Since  $9 = 3^2$ , the reaction is second order with respect to NO.

(ii) O<sub>2</sub> - Comparing experiments 1 and 2, the tripling of the initial concentration of O<sub>2</sub> while the initial concentration of NO remained constant at 0.0200 mol L<sup>-1</sup> resulted in a tripling in the initial rate of formation of NO<sub>2</sub>. Since  $3 = 3^1$ , the reaction is first order with respect to O<sub>2</sub>.

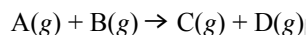
(e) Write the expression for the rate law for the reaction as determined from the experimental data.

**rate =  $k$  [NO]<sup>2</sup>[O<sub>2</sub>]**

(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

**$3.55 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$**

#### 2008B - #2



For the gas-phase reaction represented above, the following experimental data were obtained.

Experiment	Initial [A] (mol L <sup>-1</sup> )	Initial [B] (mol L <sup>-1</sup> )	Initial Reaction Rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.033	0.034	$6.67 \times 10^{-4}$
2	0.034	0.137	$1.08 \times 10^{-2}$
3	0.136	0.136	$1.07 \times 10^{-2}$
4	0.202	0.233	?

(a) Determine the order of the reaction with respect to reactant A. Justify your answer.

**Between experiments 2 and 3, [B] stays the same and [A] is quadrupled, but the initial reaction rate stays the same. This means that the initial reaction rate is not dependent on [A], so the reaction is zero order with respect to A.**

(b) Determine the order of the reaction with respect to reactant B. Justify your answer.

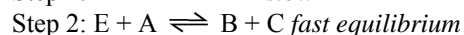
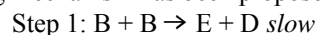
**The reaction is second order with respect to B**

(c) Write the rate law for the overall reaction. **rate =  $k$  [B]<sup>2</sup>**

(d) Determine the value of the rate constant,  $k$ , for the reaction. Include units with your answer.  **$0.577 \text{ M}^{-1} \text{ sec}^{-1}$**

(e) Calculate the initial reaction rate for experiment 4.  **$3.13 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$**

(f) The following mechanism has been proposed for the reaction.



Provide two reasons why the mechanism is acceptable.

**(1) When steps 1 and 2 are added together, the overall reaction is  $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ . This is the stoichiometry that was given for the overall reaction.**

**(2) The rate-determining step (slow step) is consistent with the rate law because only reactant B occurs in the rate law and it occurs to the power of 2, which is the number of B molecules colliding in the rate-determining step.**



(3) The rate-determining step is consistent with the rate law because A is absent from the rate-determining step and the reaction is zero order—i.e., reactant A does not appear in the rate law.

(g) In the mechanism in part (f), is species E a catalyst, or is it an intermediate? Justify your answer.

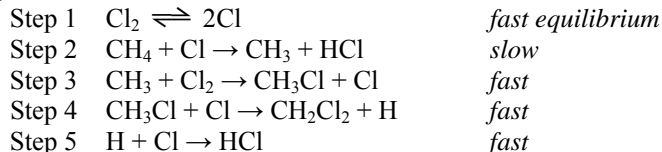
**Species E is an intermediate; it is formed in step 1 and consumed in step 2.**

**AND/OR**

**Species E is not a catalyst because a catalyst occurs as a reactant in an earlier step and is then reproduced as a product in a later step.**

### 2009 - #3 d-e

The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.



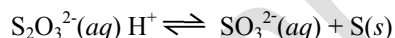
(d) In the mechanism, is  $\text{CH}_3\text{Cl}$  a catalyst, or is it an intermediate? Justify your answer.  **$\text{CH}_3\text{Cl}$  is an intermediate because it is produced in step 3 and consumed in step 4 of the reaction mechanism.**

(e) Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.

(i)  $\text{CH}_4(\text{g})$  **The order of the reaction with respect to  $\text{CH}_4$  is 1. The rate law for the slowest step in the reaction, step 2, is  $\text{rate} = k [\text{CH}_4] [\text{Cl}]$ . Because the exponent of  $\text{CH}_4$  in the rate law is 1, the order of the reaction with respect to  $\text{CH}_4$  is 1.**

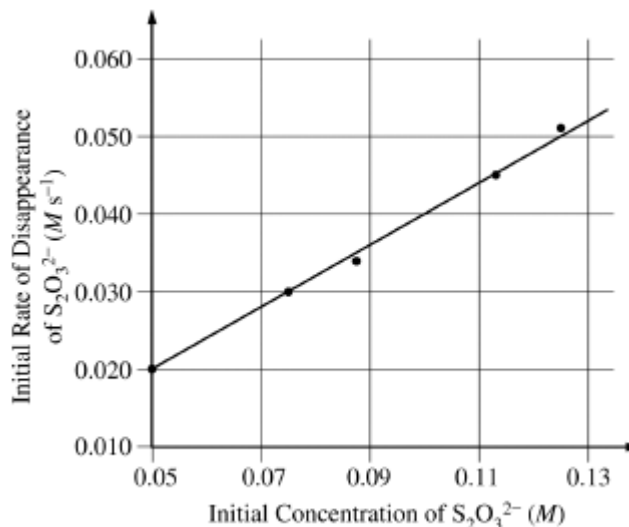
(ii)  $\text{Cl}_2(\text{g})$  **The order of the reaction with respect to  $\text{Cl}_2$  is  $\frac{1}{2}$ . Substituting into the rate law for step 2 (the slowest step in the mechanism) the exponent of  $\text{Cl}_2$  in the rate law is  $\frac{1}{2}$ , the order of the reaction with respect to  $\text{Cl}_2$  is  $\frac{1}{2}$ .**

### 2009B - #2



A student performed an experiment to investigate the decomposition of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of  $\text{S}_2\text{O}_3^{2-}(\text{aq})$ . Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ (M)	Initial Rate of Disappearance of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ ( $\text{M s}^{-1}$ )
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



(a) Identify the independent variable in the experiment.  **$\text{S}_2\text{O}_3^{2-}$ .**

(b) Determine the order of the reaction with respect to  $\text{S}_2\text{O}_3^{2-}$ . Justify your answer by using the information above.  **$1.5 = (1.5)^m$ , so  $m = 1$  and the reaction is first order with respect to  $\text{S}_2\text{O}_3^{2-}$ .**

(c) Determine the value of the rate constant,  $k$ , for the reaction. Include units in your answer. Show how you arrived at your answer.

Using the data from trial 1, (*show setup*) OR the rate constant is equal to the slope of the line.  $k = 0.40 \text{ s}^{-1}$

(d) In another trial the student mixed  $0.10 \text{ M Na}_2\text{S}_2\text{O}_3$  with hydrochloric acid. Calculate the amount of time it would take for the concentration of  $\text{S}_2\text{O}_3^{2-}$  to drop to  $0.020 \text{ M}$ . **4.0 s**

(e) On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials. **The line drawn should start on the y-axis at a lower point than the line already plotted and should have a less steep slope.**