**Name ___________________________** **AP CHEM** **___/___/___**

**Collected AP Exam Essays for Chapter 12**

**1980 - #5**

$X(g) \Longleftrightarrow A(g) + B(g) \quad \Delta H° = +15$ kilocalories

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.

(c) If the temperature is increased, will the ratio kf / kr increase, remain the same, or decrease? Justify your answer with a one- or two-sentence explanation. (kf and kr are the specific rate constants for the forward and the reverse reactions, respectively.)

**1981 - #2**

$A(aq) + 2\ B(aq) \rightarrow 3\ C(aq) + D(aq)$

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

| Experiment | Initial concentration of Reactants mole liter$^{-1}$ $A_o$ | $B_o$ | Initial Rate of Reaction mole liter$^{-1}$ hour$^{-1}$ |
|---|---|---|---|
| 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.

(b) Calculate the value of the specific rate constant k at 30°C and specify its units.

(c) Calculate the value of the initial rate of this reaction at 30°C for the initial concentrations shown in experiment 6.

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

**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$^{-1}$·sec$^{-1}$) | Initial $[X]_o$, (mol·L$^{-1}$) | Initial $[Y]_o$, (mol·L$^{-1}$) |
|---|---|---|
| $7.0 \times 10^{-4}$ | 0.20 | 0.10 |
| $1.4 \times 10^{-3}$ | 0.40 | 0.20 |
| $2.8 \times 10^{-3}$ | 0.40 | 0.40 |
| $4.2 \times 10^{-3}$ | 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) |

**1985 - #8**

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

In the equation above, the forward reaction is first order in both $PCl_5$ and $Cl_2$ and the reverse reaction is first order in $PCl_5$

(a) Suppose that 2 moles of $PCl_3$ and 1 mole of $Cl_2$ are mixed in a closed container at constant temperature. Draw a graph that shows how the concentrations of $PCl_3$, $Cl_2$, and $PCl_5$ change with time until after equilibrium has been firmly established.

(b) Give the initial rate law for the forward reaction.

(c) Provide a molecular explanation for the dependence of the rate of the forward reaction on the concentrations of the reactants.

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

**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.

(b) $2\ XY \rightarrow X_2 + Y_2$

1. For the hypothetical reaction above, give a rate law that shows that the reaction is first order in the reactant XY.
2. Give the units for the specific rate constant for this rate law.
3. Propose a mechanism that is consistent with both the rate law and the stoichiometry.

**1987 - #2**

$$2\ HgCl_2\ (aq) + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2\ (g) + Hg_2Cl_2\ (s)$$

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 $[HgCl_2]$ | Initial $[C_2O_4^{2-}]$ | Initial Rate of formation of $Cl^-$ (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?

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

(c) What is the numerical value for the initial rate of disappearance of $C_2O_4^{2-}$ for Experiment 1?

(d) Calculate the initial oxalate ion concentration for Experiment 4.

**1989 - #8**

$$C_2H_4\ (g) + H_2\ (g) \rightarrow C_2H_6\ (g)$$

For the above reaction, $\Delta H° = -137$ 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.

(b) A small increase in temperature causes a large increase in the reaction rate.

(c) The presence of metallic nickel causes an increase in reaction rate.

(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.

**1990 - #7**

Consider the following general equation for a chemical reaction.

$A(g) + B(g) \rightarrow C(g) + D(g)$

(a) Describe the two factors that determine whether a collision between molecules of A and B results in a reaction.
(b) How would a decrease in temperature affect the rate of the reaction shown above? Explain your answer.
(c) Write the rate law expression that would result if the reaction proceeded by the mechanism shown below.

$A + B \rightleftharpoons [AB]$ (fast)
$[AB] + B \rightarrow C + D$ (slow)

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

**1991 - #3**

$2\ ClO_2(g) + F_2(g) \rightarrow 2\ ClO_2F(g)$

| Experiment | Initial $[ClO_2]$ mol $L^{-1}$ | Initial $[F_2]$ mol $L^{-1}$ | Initial Rate of Increase of $[ClO_2F]$ mol $L^{-1}$ $sec^{-1}$ |
|---|---|---|---|
| 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.
(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 $[F_2]$?
(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a)? Justify your choice.

I. $ClO_2 + F_2 \rightleftharpoons ClO_2F_2$ (fast)
$ClO_2F_2 \rightarrow ClO_2F + F$ (slow)
$ClO_2 + F \rightarrow ClO_2F$ (fast)

II. $F_2 \rightarrow 2\ F$ (slow)
$2ClO_2 + 2F \rightarrow ClO_2F$ (fast)

**1992 - #5**

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$

For the exothermic reaction represented above, carried out at 298 K, the rate law is as follows.
Rate = k $[H_2]$ $[I_2]$
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.
(b) Increase in volume of the reaction vessel at constant temperature.
(c) Addition of a catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate.
(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

**1994 - #2**

$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$

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 | $1.8 \times 10^{-4}$ |
| 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 $H_2$, 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. $NO + NO \rightleftharpoons N_2O_2$

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

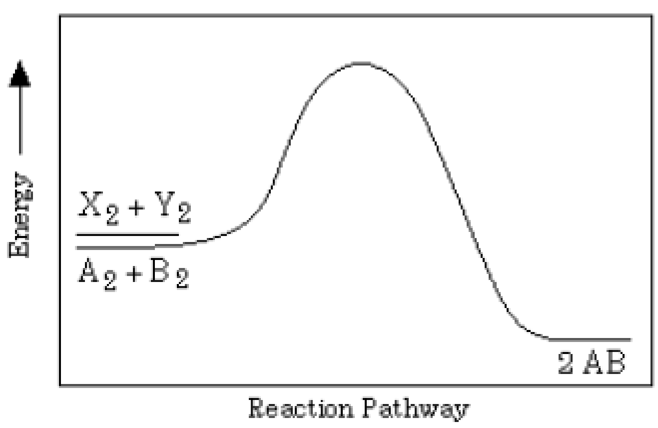
(ii) the overall stoichiometry of the reaction.

**1995 - #9**

(I) $A_2 + B_2 \rightarrow 2\ AB$

(II) $X_2 + Y_2 \rightarrow 2\ XY$

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.

(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

(ii) Heat of reaction

(c) For reaction II, the form of the rate law is 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.

(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.

**1996 - #8**

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

$NO + NO \rightleftharpoons N_2O_2$ (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).

**1997 - #4**

$2 A + B \rightarrow C + D$

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 (mol $L^{-1}min^{-1}$) |
|---|---|---|---|
| 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.
(b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.
(c) Determine the initial rate of change of [A] in Experiment 3.
(d) Determine the initial value of [B] in Experiment 4.
(e) Identify which of the reaction mechanisms represented below is consistent with the rate law developed in part (b). Justify your choice.

1. $A + B \rightarrow C + M$ (Fast)
   $M + A \rightarrow D$ (Slow)

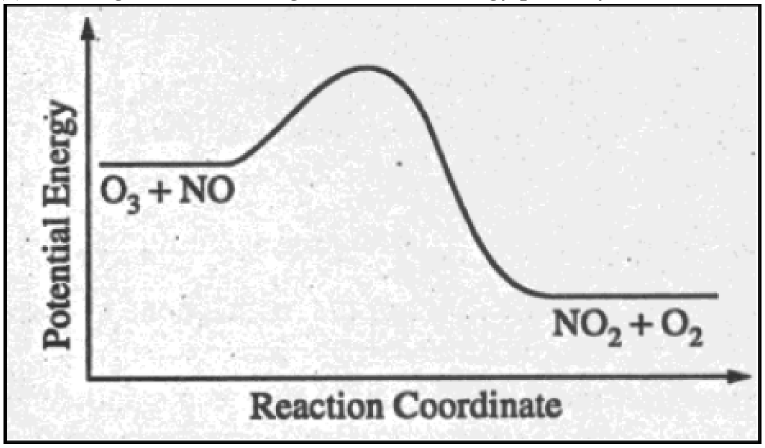
2. $B \rightleftharpoons M$ (Fast equilibrium)
   $M + A \rightarrow C + X$ (Slow)
   $A + X \rightarrow D$ (Fast)

3. $A + \rightleftharpoons M$ (Fast equilibrium)
   $M + A \rightarrow C + X$ (Slow)
   $X \rightarrow D$ (Fast)

**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 $O_3 + NO \rightarrow NO_2 + O_2$

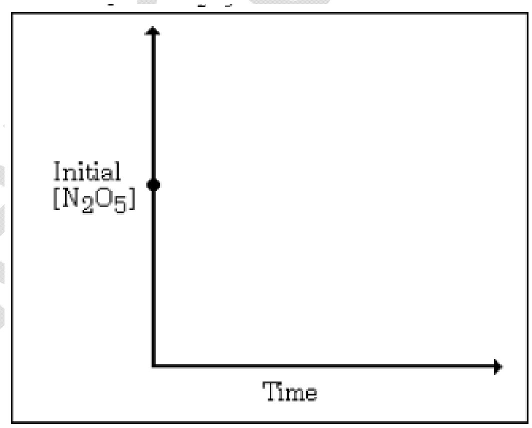



Clearly label the following directly on the diagram above.

(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 $N_2O_5$.



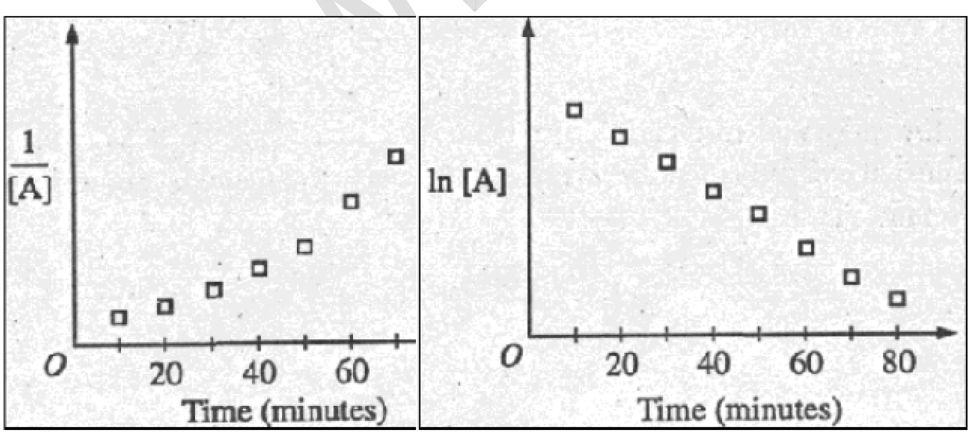

(i) Using the axes at right, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, t.

(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, k, could be determined.

(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.

(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.

(i) Write the rate-law expression for the reaction. Justify your answer.

(ii) Describe how to determine the value of the rate constant for the reaction.

**1999 - #3**

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

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 | $3.24 \times 10^{-4}$ |
| 2 | 0.0160 | 0.0240 | $6.38 \times 10^{-4}$ |
| 3 | 0.0320 | 0.0060 | $6.42 \times 10^{-4}$ |

(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,
(i) write the rate law that is consistent with the data, and
(ii) calculate the value of the specific rate constant, *k*, and specify units.
(d) The following mechanism was proposed for the reaction:
$Br_2(g) + NO(g) \rightarrow NOBr_2(g)$ *slow*
$NOBr_2(g) + NO(g) \rightarrow 2\ NOBr(g)$ *fast*
Is this mechanism consistent with the given experimental observations? Justify your answer.

**2000 - #6**

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

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

| | $O_3(g)$ | $NO(g)$ | $NO_2(g)$ |
|---|---|---|---|
| Standard enthalpy of formation, $\Delta H_f°$, at 25°C (kJ $mol^{-1}$) | 143 | 90. | 33 |

(b) Make a qualitative prediction about the magnitude of the standard entropy change, $\Delta S°$, for the reaction at 25°C. Justify your answer.
(c) On the basis of your answers to parts (a) and (b), predict the sign of the standard free-energy change, $\Delta G°$, for the reaction at 25°C. Explain your reasoning.
(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 [$O_3$] (mol $L^{-1}$) | Initial [NO] (mol $L^{-1}$) | Initial Rate of Formation of $NO_2$ (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 1 | 0.0010 | 0.0010 | *x* |
| 2 | 0.0010 | 0.0020 | 2*x* |
| 3 | 0.0020 | 0.0010 | 2*x* |
| 4 | 0.0020 | 0.0020 | 4*x* |

(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 I: $O_3 + NO \rightarrow O + NO_3$
Step II: $O + O_3 \rightarrow 2\ O_2$
Step III: $NO_3 + NO \rightarrow 2\ NO_2$

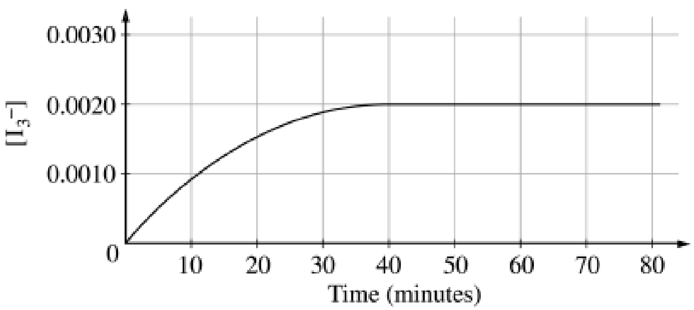
**2001 - #6**

$3\ I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_3^-(aq) + 2\ SO_4^{2-}(aq)$

Iodide ion, $I^-(aq)$, reacts with peroxydisulfate ion, $S_2O_8^{2-}(aq)$, 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 $I^-(aq)$ to $I_3^-$ $(aq)$.

(b) In an experiment, equal volumes of 0.0120 *M* $I^-(aq)$ and 0.0040 *M* $S_2O_8^{2-}(aq)$ are mixed at 25°C. The concentration of $I_3^-(aq)$ over the following 80 minutes is shown in the graph below.



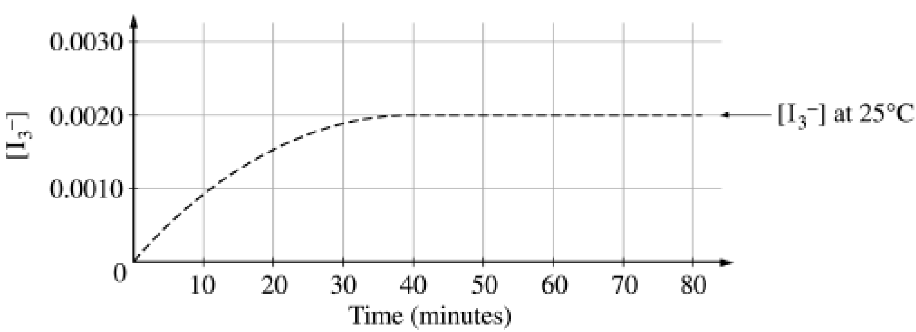

(i) Indicate the time at which the reaction first reaches completion by marking an "X" on the curve above at the point that corresponds to this time. Explain your reasoning.

(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.

(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 $S_2O_8^{2-}(aq)$.

(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.

(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°C rather than at 25°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.

Step I $\quad O_3 + Cl \rightarrow O_2 + ClO$

Step II $\quad ClO + O \rightarrow Cl + O_2$

(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

**2003 - #3**

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

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 | $2.50 \times 10^{-4}$ |
| 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) $Br^-$

(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.

**2004B - #3**

$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

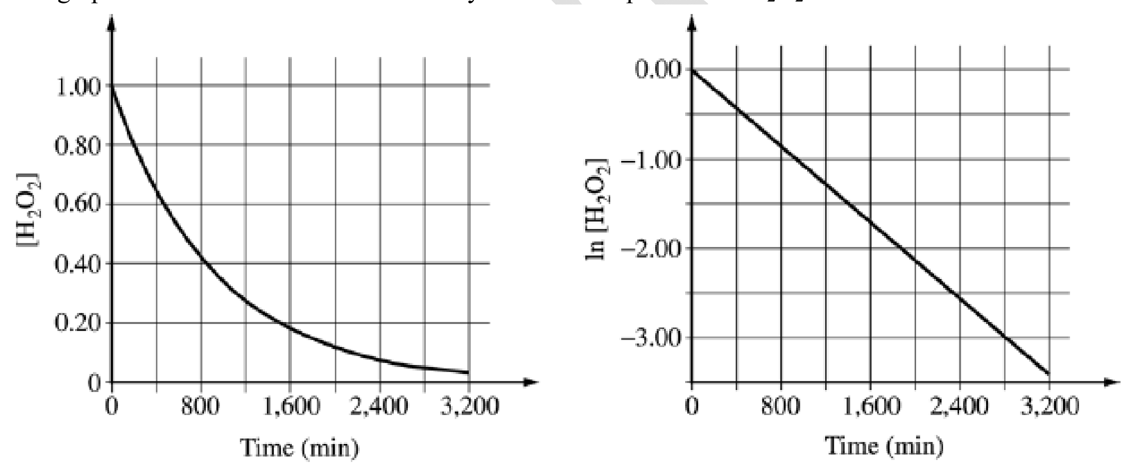
Hydrogen peroxide decomposes according to the equation above.

(a) An aqueous solution of $H_2O_2$ that is 6.00 percent $H_2O_2$ by mass has a density of 1.03 g $mL^{-1}$. Calculate each of the following.

(i) The original number of moles of $H_2O_2$ in a 125 mL sample of the 6.00 percent $H_2O_2$ solution

(ii) The number of moles of $O_2(g)$ that are produced when all of the $H_2O_2$ in the 125 mL sample decomposes

(b) The graphs below show results from a study of the decomposition of $H_2O_2$.




(i) Write the rate law for the reaction. Justify your answer.

(ii) Determine the half-life of the reaction.

(iii) Calculate the value of the rate constant, *k*. Include appropriate units in your answer.

(iv) Determine $[H_2O_2]$ after 2,000 minutes elapse from the time the reaction began.

**2005 - #3**

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

$$I^-(aq) + ClO^-(aq) \rightarrow IO^-(aq) + Cl^-(aq)$$

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

| Experiment | $[I^-]$ (mol $L^{-1}$) | $[ClO^-]$ (mol $L^{-1}$) | Initial Rate of Formation of $IO^-$ (mol $L^{-1}s^{-1}$) |
|---|---|---|---|
| 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) $I^-(aq)$

(ii) $ClO^-(aq)$

(b) For the reaction,

(i) write the rate law that is consistent with the calculations in part (a);

(ii) calculate the value of the specific rate constant, k, and specify units.

The catalyzed decomposition of hydrogen peroxide, $H_2O_2(aq)$ , is represented by the following equation.

$$2\ H_2O_2(aq) \xrightarrow{\text{catalyst}} 2\ H_2O(l) + O_2(g)$$

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.

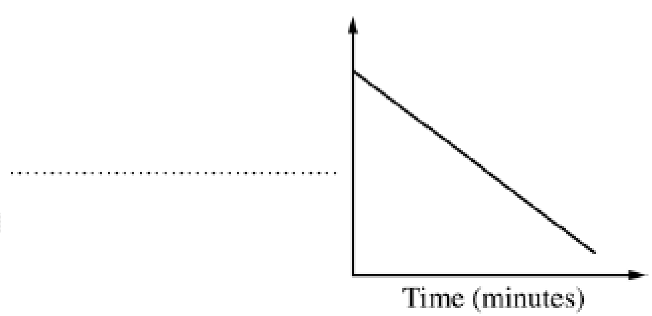
| $[H_2O_2]$ (mol $L^{-1}$) | Time (minutes) |
|---|---|
| 1.00 | 0.0 |
| 0.78 | 5.0 |
| 0.61 | 10.0 |

(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 $H_2O_2(aq)$ ?

(iii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M $H_2O_2(aq)$ .

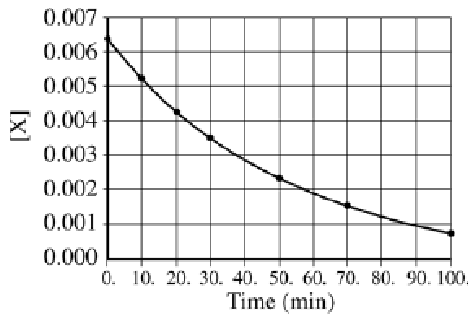


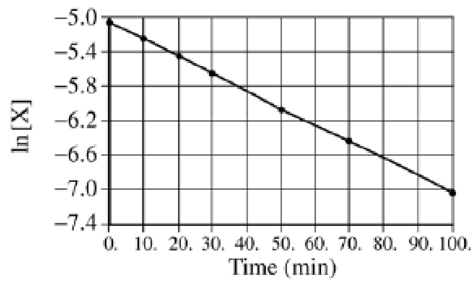
**2005B - #3**

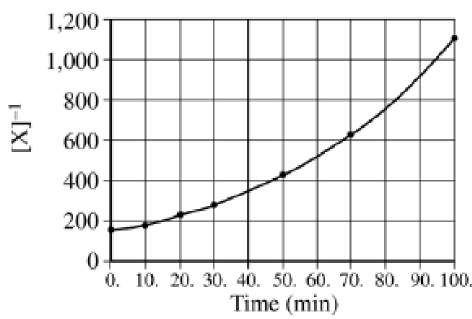
X → 2 Y + Z

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

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




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

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

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

(d) Write the rate law for this reaction.

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

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

**2006 - #6d**
(d) Consider the four reaction-energy profile diagrams shown below.

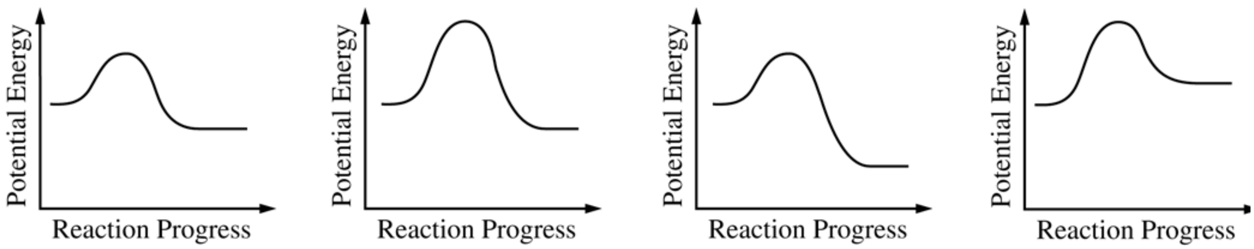



Diagram 1 Diagram 2 Diagram 3 Diagram 4

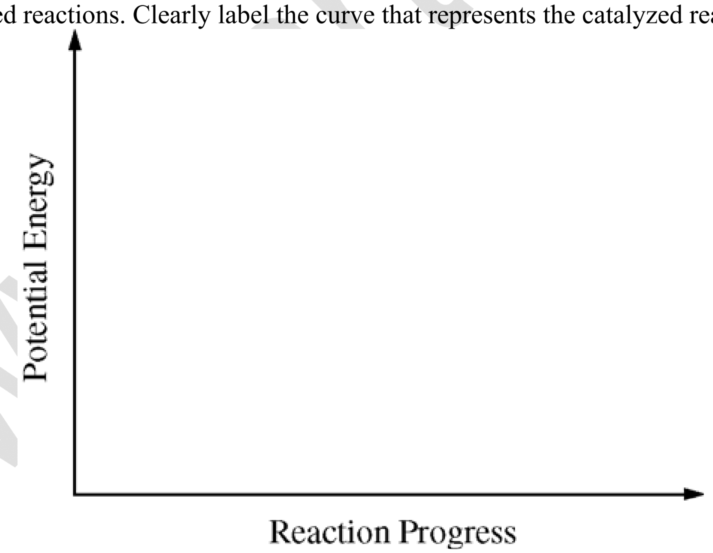
(i) Identify the two diagrams that could represent a catalyzed and an uncatalyzed reaction pathway for the same reaction. Indicate which of the two diagrams represents the catalyzed reaction pathway for the reaction.
(ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

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

**2007 - #6e**
The reaction between $SO_2(g)$ and $O_2(g)$ to form $SO_3(g)$ is represented below.

$$2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$$

The reaction is exothermic. The reaction is slow at 25°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. $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(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 $L^{-1}$) | Initial Concentration of $O_2$ (mol $L^{-1}$) | Initial Rate of Formation of $NO_2$ (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 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
(ii) $O_2$
(e) Write the expression for the rate law for the reaction as determined from the experimental data.
(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

**2008B - #2**

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

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

| Experiment | Initial [A] (mol $L^{-1}$) | Initial [B] (mol $L^{-1}$) | Initial Reaction Rate (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 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.
(b) Determine the order of the reaction with respect to reactant B . Justify your answer.
(c) Write the rate law for the overall reaction.
(d) Determine the value of the rate constant, *k* , for the reaction. Include units with your answer.
(e) Calculate the initial reaction rate for experiment 4.
(f) The following mechanism has been proposed for the reaction.

Step 1: $B + B \rightarrow E + D$ *slow*
Step 2: $E + A \rightleftharpoons B + C$ *fast equilibrium*

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

**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.

| | | |
|---|---|---|
| Step 1 | $Cl_2 \rightleftharpoons 2Cl$ | *fast equilibrium* |
| Step 2 | $CH_4 + Cl \rightarrow CH_3 + HCl$ | *slow* |
| Step 3 | $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$ | *fast* |
| Step 4 | $CH_3Cl + Cl \rightarrow CH_2Cl_2 + H$ | *fast* |
| Step 5 | $H + Cl \rightarrow HCl$ | *fast* |

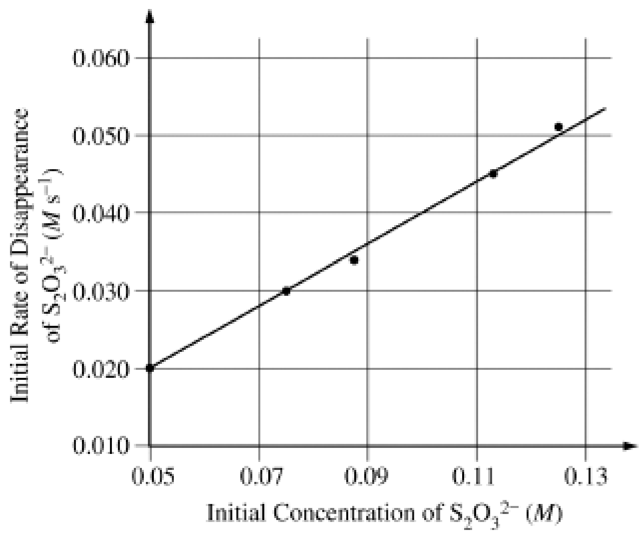
(d) In the mechanism, is $CH_3Cl$ a catalyst, or is it an intermediate? Justify your answer.
(e) Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.
(i) $CH_4(g)$
(ii) $Cl_2(g)$

**2009B - #2**

$$S_2O_3^{2-}(aq)\ H^+ \rightleftharpoons SO_3^{2-}(aq) + S(s)$$

A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, 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 $S_2O_3^{2-}(aq)$. 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 $S_2O_3^{2-}$ $(aq)$ $(M)$ | Initial Rate of Disappearance of $S_2O_3^{2-}$ $(aq)$ $(M\ s^{-1})$ |
|---|---|---|
| 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.
(b) Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.
(c) Determine the value of the rate constant, *k*, for the reaction. Include units in your answer. Show how you arrived at your answer.
(d) In another trial the student mixed 0.10 $M$ $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 $M$.
(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.