# AP Chemistry
Unit 6- Homework Problems
Kinetics

Collision Theory

1. In order for a reaction to occur, what three requirements are there according to the collision theory?
Molecules must (1) collide with (2) correct geometry and (3) minimum activation energy

2. Draw a graph of energy vs. reaction coordinate for an endothermic and an exothermic reaction. Label the activation energy and the ΔE for each.
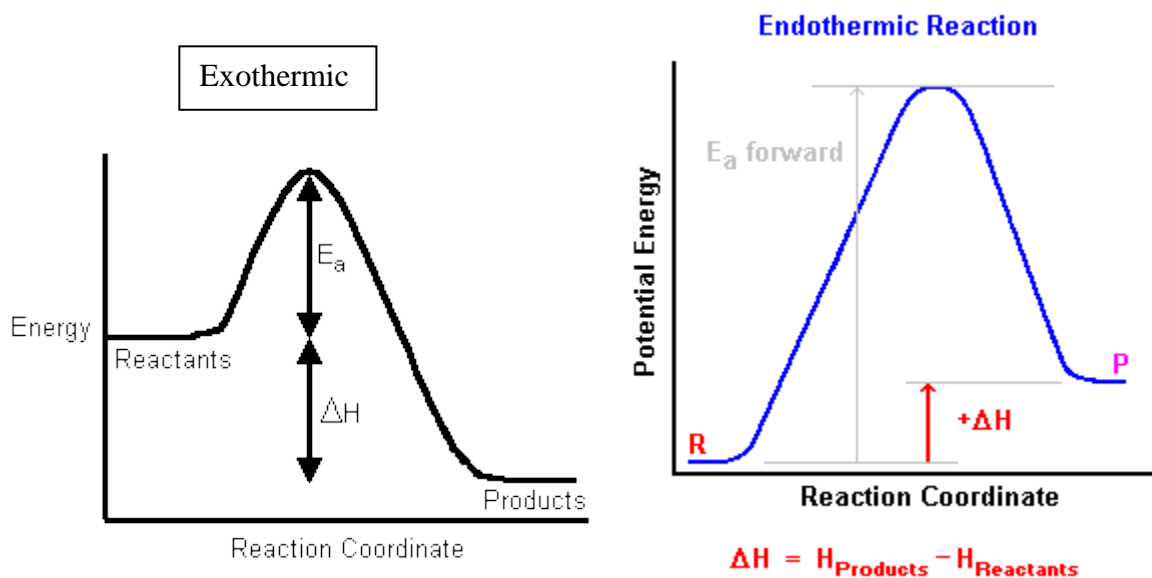
3. What are the four factors that can affect a chemical reaction's rate?
Temperature, Surface Area, Concentration, Catalysts

4. Explain why increasing the temperature generally increases the rate of a reaction?
Molecules move faster and collide more often. This means a greater chance of colliding with correct geometry. Also, because they move faster, they have more energy and have a better chance of overcoming the activation energy.

5. Draw a graph of fraction of molecules vs. energy and show the distribution of molecular energies at various temperatures. Also be sure to label the activation energy on the graph.
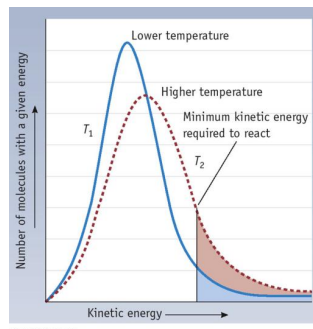
6. Explain why increasing the surface area of a sample generally increases the rate of a reaction.
Greater surface are a means a greater chance of colliding with correct geometry.

7. Explain why increasing the concentration of a sample generally increases the rate of a reaction.
More concentration means more collisions and so a greater chance of colliding with correct geometry.

8. What is a catalyst?
A catalyst lowers the activation energy by providing a different pathway for the reaction. The reaction speeds up because more molecules have the minimum activation energy. The catalyst is consumed and then re-produced in the reaction so does not appear in the overall equation.

9. On the graphs you drew from problems #2 and #5 above, show how a catalyst would affect each graph.

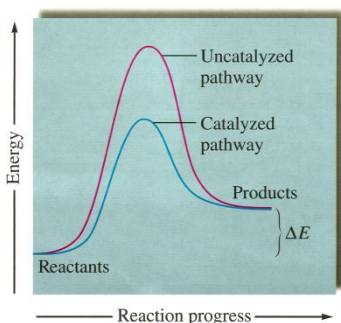**Figure 12.15** Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

Uncatalyzed pathway
Catalyzed pathway
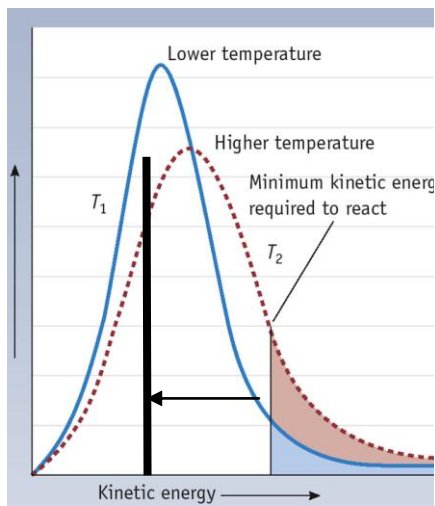Products
ΔE
Reactants
Energy
Reaction progress

Figure 12.15:
Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

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Zumdahl, Chemistry, Sixth Edition

Lower temperature
Higher temperature
Minimum kinetic energ
required to react
T_1
T_2
Kinetic energy

Transparency #145

rooks/Cole - Thomson

10. For the following reaction, which species is acting as a catalyst? Which is an intermediate?

Overall: $O_3 + O \longrightarrow 2\ O_2$
Step 1: $Cl + O_3 \longrightarrow ClO + O_2$
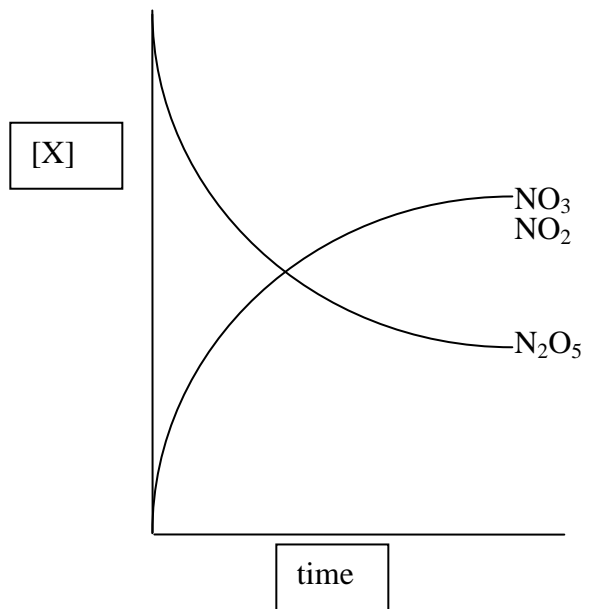Step 2: $ClO + O \longrightarrow Cl + O_2$
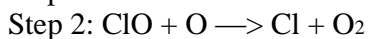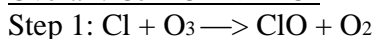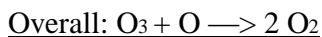
Cl is a catalyst. It is consumed and then re-made.
ClO is an intermediate. It is made and then re-consumed.

Relative Rate

For the following reactions, draw a graph showing concentration vs. time for each species. Assume you start with equal amounts of reactants, no products, and the reaction reaches equilibrium before any species runs out.

1. $CH_3Cl + 3 Cl_2 \rightarrow CCl_4 + 3 HCl$

[X]

CH$_3$Cl

HCl

Cl$_2$

CCl$_4$

time

2. $N_2O_5 \rightarrow NO_3 + NO_2$

[X]

NO$_3$
NO$_2$

N$_2$O$_5$

time

3. $2 NO_2 + F_2 \rightarrow 2 FNO_2$

[X]

F$_2$

NO$_2$

FNO

time
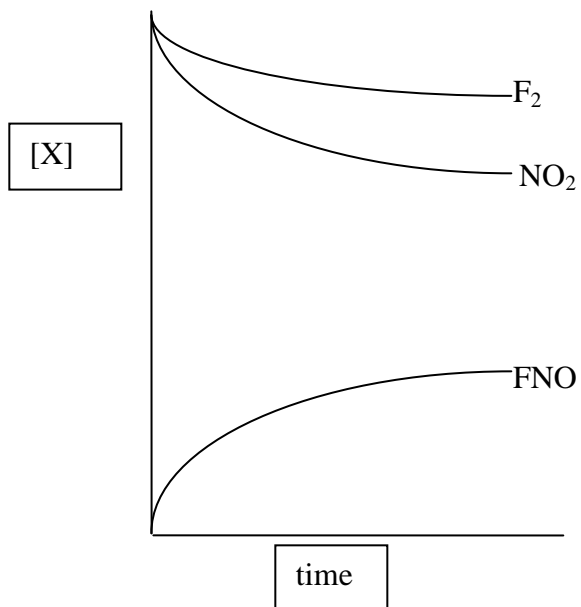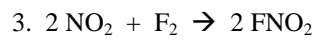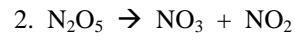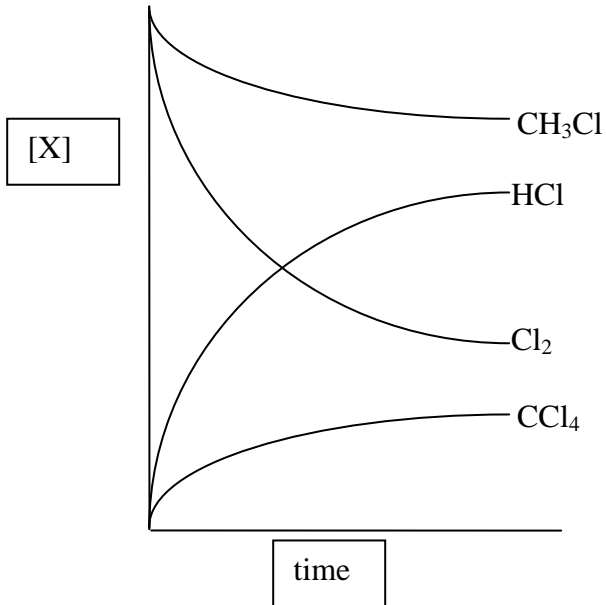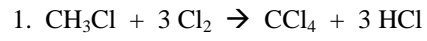
Rate Equations

1. Consider the following data for the reaction: A → B

[A] (M)	Initial Rate of Production of B (M/s)
0.100	0.053
0.200	0.210
0.300	0.473

    a) What is the order with respect to A? 2nd

    b) Write the rate law. Rate $= k[A]^2$

    c) What is the value of k (include units)? 5.3 $M^{-1}sec^{-1}$

    d) What would the initial rate be if [A] = 0.05 M? 0.01325 M/s

2. Consider the following data for the reaction: A → B

[A] (M)	Initial Rate of Production of B (M/s)
0.15	0.008
0.30	0.016
0.60	0.032

    a) What is the order with respect to A? 1st

    b) Write the rate law. Rate $= k[A]^1$

    c) What is the value of k (include units)? 0.0533 sec^{-1}

    d) What would the initial rate be if [A] = 0.75 M? 0.04 M/sec

3. Consider the following data for the reaction: $2 NO_2 + F_2 → 2 FNO_2$

$[NO_2]$ (M)	$[F_2]$ (M)	Initial Rate of Loss of NO_2 (M/s)
0.100	0.100	0.026
0.200	0.100	0.051
0.200	0.200	0.103
0.400	0.400	0.411

    a) What is the order with respect to NO_2? What is the order with respect to F_2? What is the overall order?

          1st 1st 2nd

    b) Write the rate law. Rate $= k [NO_2]^1[F_2]$

    c) What is the value of k (include units)? K = 2.6 $M^{-1}sec^{-1}$

    d) What would the initial rate be if $[NO_2]$ = 0.050 M and $[F_2]$ = 0.075 M? 0.00975 M/sec

    e) For each line of the data table above, calculate the initial rate of loss of F_2.

| Initial Rate of Loss of NO_2 (M/s)	Rate of Loss of F_2
0.026	0.013
0.051	0.0255
0.103	0.0515
0.411	0.2055

Mechanisms

1. For the following reaction: $AB + C \rightarrow A + BC$, the following mechanism is proposed:

      Step 1: $AB + AB \rightarrow AB_2 + A$ slow

      Step 2: $AB_2 + C \rightarrow AB + BC$ fast

   a. Write the rate law based upon this information. $Rate = k[AB]^2$

   b. Which species is an intermediate in the above mechanism? AB_2

2. For the following reaction: $2\,NO_2 + Cl_2 \rightarrow 2\,ClNO_2$, the following mechanism is proposed:

      Step 1: $NO_2 + Cl_2 \rightarrow ClNO_2 + Cl$ slow

      Step 2: $NO_2 + Cl \rightarrow ClNO_2$ fast
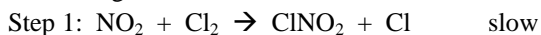
   a. Write the rate law based upon this information. $Rate = k[NO_2][Cl_2]$

   b. Which species is an intermediate in the above mechanism? Cl

3. For the following reaction: $X + Y \rightarrow XY$, the following mechanism is proposed:

      Step 1: $2\,X \leftrightarrow X_2$ fast

      Step 2: $X_2 + Y \rightarrow XY + X$ slow

   a. Write the rate law based upon this information. $Rate = k[X]^2[Y]$

   b. Which species is an intermediate in the above mechanism? X_2

4. For the following reaction: $H_2 + I_2 \rightarrow 2\,HI$, the following mechanism is proposed:

      Step 1: $I_2 \leftrightarrow 2\,I$ fast

      Step 2: $H_2 + 2\,I \rightarrow 2\,HI$ slow
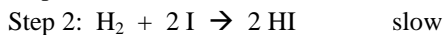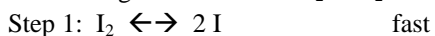
   a. Write the rate law based upon this information. $Rate = k[H_2][I_2]$

   b. Which species is an intermediate in the above mechanism? I

5. Why can't you tell what the rate equation is just from looking at the overall reaction?
The only step that matters is the slow step. The slow step is the rate law.

Integrated Rate Equations

1. The following is data for the reaction: AB → A + B

Time (sec)	[AB] (M)
0	0.95
50	0.459
100	0.302
150	0.225
200	0.180
250	.149
300	.128

a. What is the order of the reactant AB?

2nd

b. Write the rate law.

Rate = $k[AB]^2$

c. What is the value for k?

$0.0226\ M^{-1}sec^{-1}$

d. What would the concentration be at 1000 seconds?

$1/A = kt + 1/A_o$

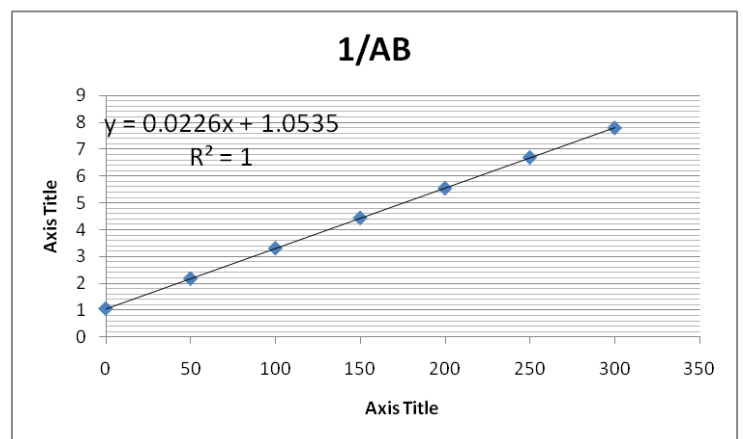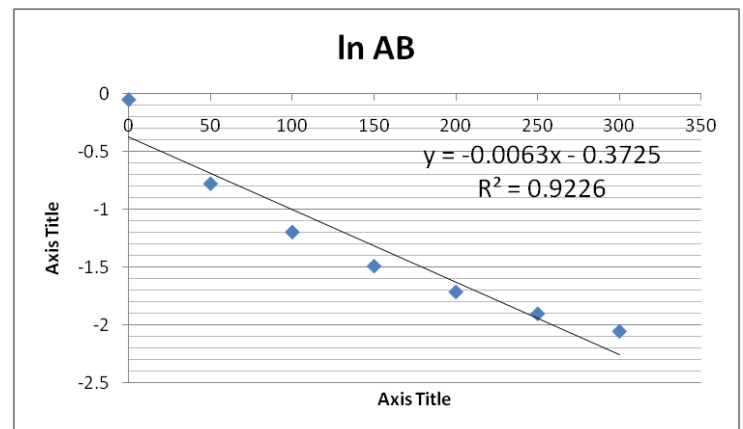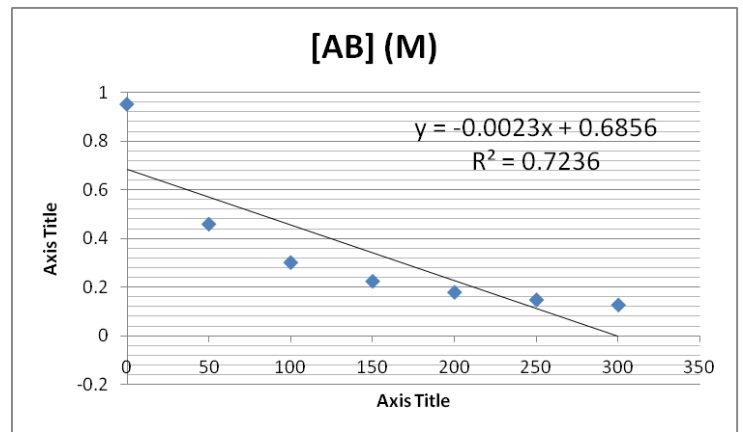$1/A = 0.0226\ (1000) + 1/0.95$

$1/A = 22.6 + 1.05$

$1/A = 23.6$

$A = 0.0424\ M$

e. What is the half-life of the reaction?

$t_{1/2} = \dfrac{1}{k[A]_0}$

$t_{1/2} = 1/(0.0226)(0.95)$

$t_{1/2} = 46.6\ sec$

[AB] (M)

y = -0.0023x + 0.6856
$R^2 = 0.7236$

ln AB

y = -0.0063x - 0.3725
$R^2 = 0.9226$

1/AB

y = 0.0226x + 1.0535
$R^2 = 1$

2. The following is data for the reaction: $N_2O_5 \rightarrow NO_3 + NO_2$

Time (sec)	$[N_2O_5]$ (M)
0	1.00
25	0.822
50	0.677
75	0.557
100	0.458
125	0.377
150	0.310

a. What is the order of the reactant N_2O_5?

1st

b. Write the rate law.

Rate = $k[N_2O_5]$

c. What is the value for k?

k = 0.0078 sec^{-1}

d. What would the concentration be at 500 seconds?

Ln A = -kt + ln A_o

Ln A = -(0.0078)(500)

Ln A = -3.9

A = 0.0202 M

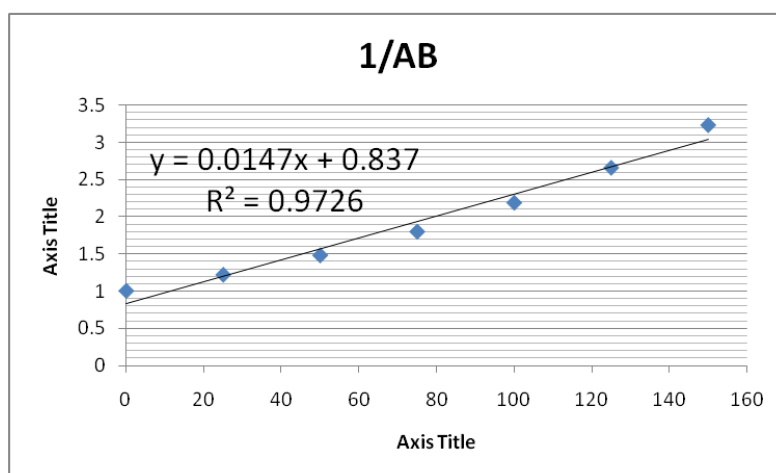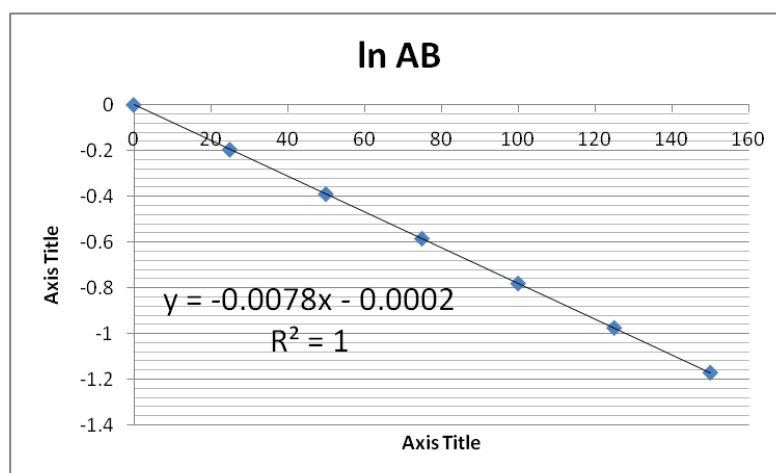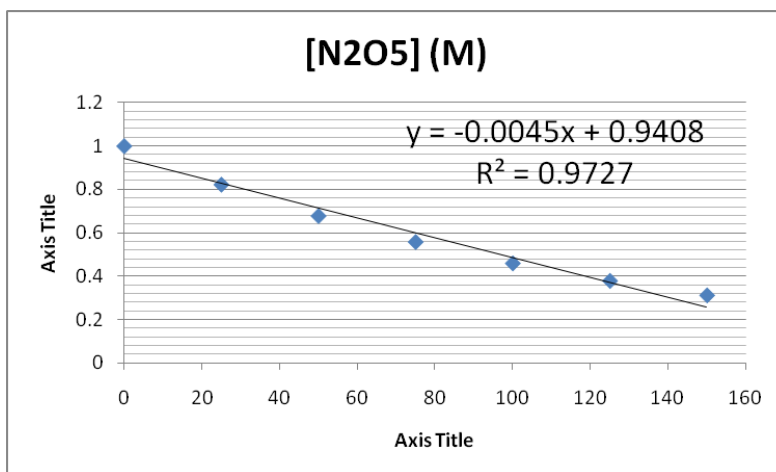e. What is the half-life of the reaction?

$t_{1/2}$ = 0.693/K

$t_{1/2}$ = 0.693/0.0078

$t_{1/2}$ = 88.9 sec

[N2O5] (M)

y = -0.0045x + 0.9408
R^2 = 0.9727

ln AB

y = -0.0078x - 0.0002
R^2 = 1

1/AB

y = 0.0147x + 0.837
R^2 = 0.9726

3. The following is data for the reaction: $C_4H_8 \rightarrow 2 C_2H_4$

Time (sec)	$[C_4H_8]$ (M)
0	1.00
10	0.894
20	0.799
30	0.714
40	0.638
50	0.571
60	0.510

a. What is the order of the reactant C_4H_8?

1st

b. Write the rate law.

Rate = $k[C_4H_8]$

c. What is the value for k?

0.0112 sec^{-1}

d. What would the concentration be at 100 seconds?

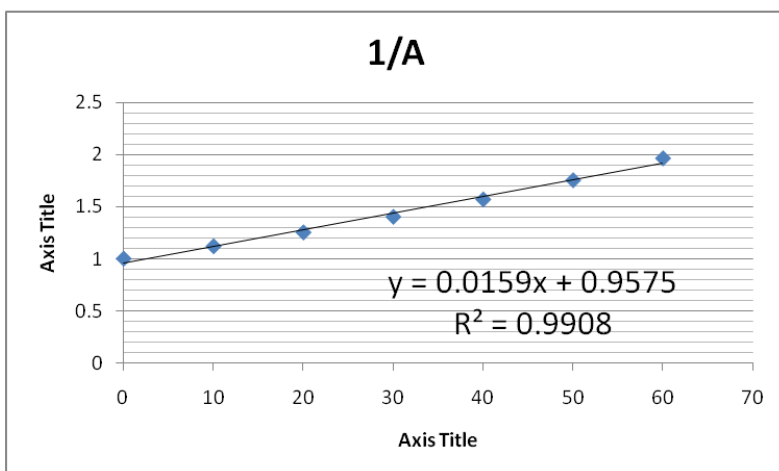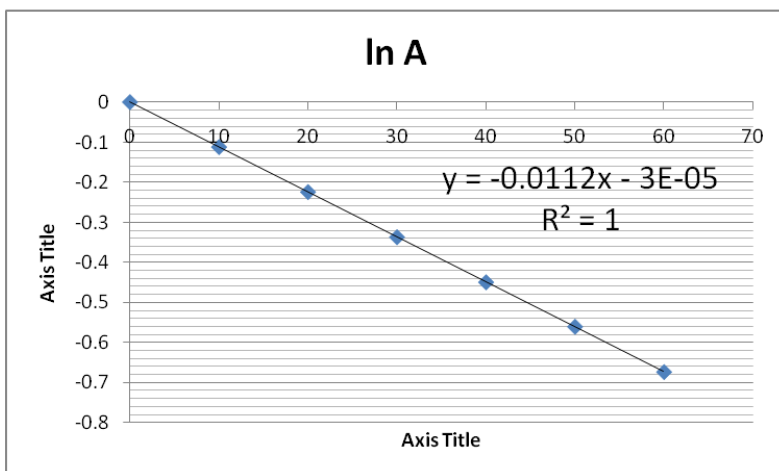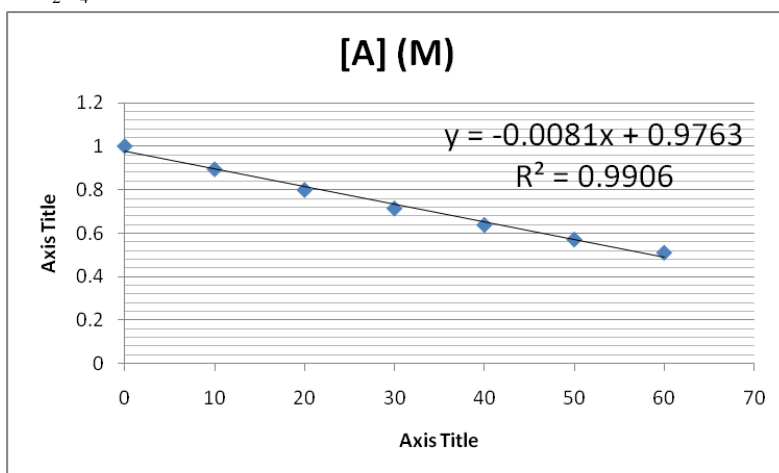Ln A = -kt + ln A_o

Ln A = -(0.0112)(100)

Ln A = -1.12

A = 0.326 M

e. What is the half-life of the reaction?

$t_{1/2}$ = 0.693/K

$t_{1/2}$ = 0.693/0.0112

$t_{1/2}$ = 61.9 sec

[A] (M)

y = -0.0081x + 0.9763
R^2 = 0.9906

ln A

y = -0.0112x - 3E-05
R^2 = 1

1/A

y = 0.0159x + 0.9575
R^2 = 0.9908

4. The following is data for the reaction: A → B

Time (sec)	[A] (M)
0	1.00
25	0.914
50	0.829
75	0.744
100	0.659
125	0.573
150	0.488

a. What is the order of the reactant A?

zero order

b. Write the rate law.

Rate = k

c. What is the value for k?

0.0034 M/sec

d. What would the concentration be at 200 seconds?
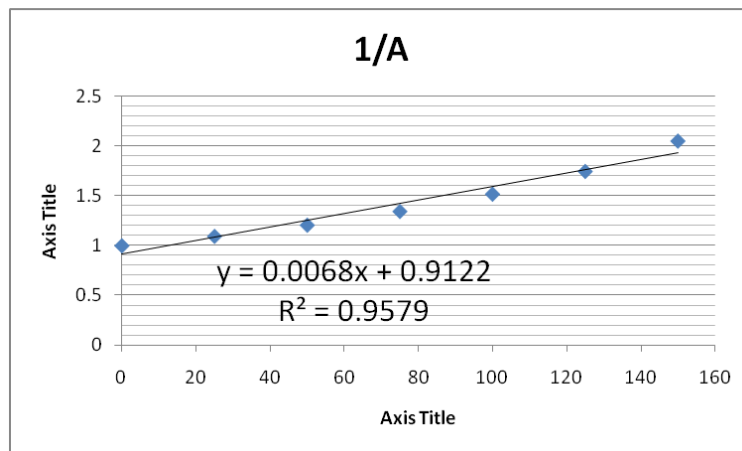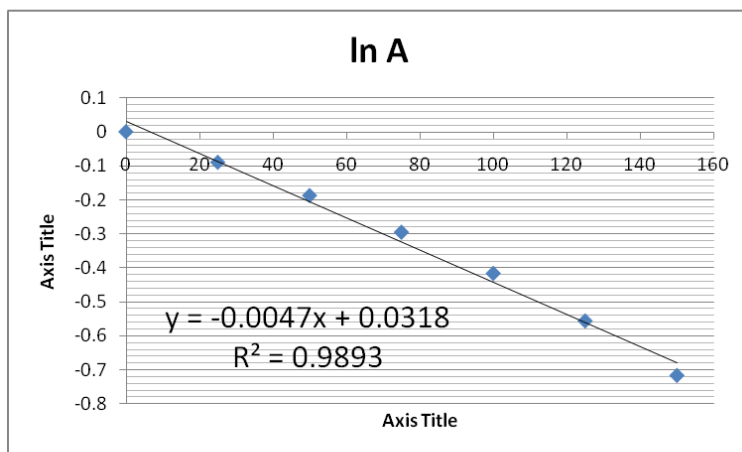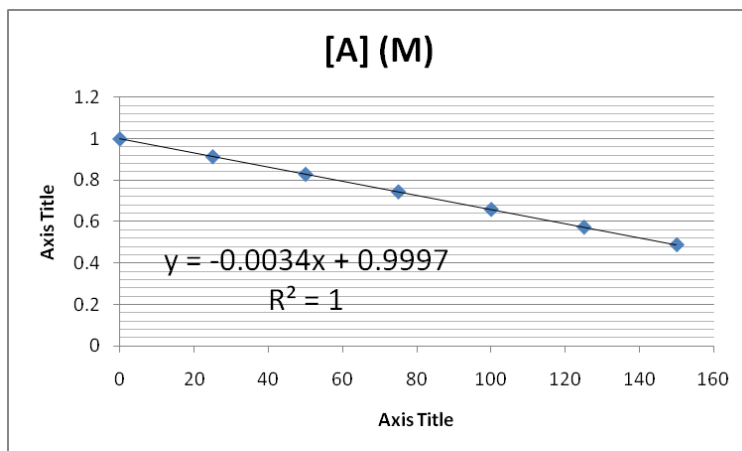
[A] = -kt + [A]0

A = -(0.0034)(200) + 1

A = 0.32 M

e. What is the half-life of the reaction?

$t_{1/2} = \dfrac{[A]0}{2k}$

$t_{1/2} = \dfrac{1}{2(0.0034)}$

$t_{1/2} =$ 147 sec

[A] (M)

y = -0.0034x + 0.9997
R² = 1

ln A

y = -0.0047x + 0.0318
R² = 0.9893

1/A

y = 0.0068x + 0.9122
R² = 0.9579

Nuclear Half Life and Integrated Rate Equations

1. I-131 has a half-life of 8 days. If you start with 200 micrograms of I-131, how much will be left after 40 days?

40 days is exactly 5 half-lives. Each ½ life reduces the amount by ½ so:

$200 \rightarrow 100 \rightarrow 50 \rightarrow 25 \rightarrow 12.5 \rightarrow 6.25$ micrograms

2. Radon-222 has a half-life of 4 days. How long does it take for the sample to be less than 1% of the original amount?

Since nuclear radiation is always first order, you can use:

$t\,½ = 0.693/K$ and $\ln A = -kt + \ln A_o$

$k = 0.693/4 = 0.173$ so $\ln 1 = -(0.173)(t) + \ln 100$ $t = 26.6$ days

3. The half-life of C-14 is 5700 years. If the activity of C-14 in an ancient sample is 1.75 dpm/g and living tissue has an activity of 14 dpm/g, how old is the sample?

Since nuclear radiation is always first order, you can use:

$t\,½ = 0.693/K$ and $\ln A = -kt + \ln A_o$

$k = 0.693/5700 = 1.216 \times 10^{-4}$ so $\ln 1.75 = -(1.216 \times 10^{-4})(t) + \ln 14$ $t = 17,100$ yrs

4. The half-life of I-123 is 13.2 hrs. If a sample starts with an acitivty of 4.5 dpm/g, what will be the activity in 48 hrs?

Since nuclear radiation is always first order, you can use:

$t\,½ = 0.693/K$ and $\ln A = -kt + \ln A_o$

$k = 0.693/13.2 = 0.0525$ so $\ln x = -(0.0525)(48) + \ln 4.5$ $x = 0.362$ dpm/g

5. The half-life of C-14 is 5700 yrs. If a living plant tissue sample is about 16 dpm/g but the ancient sample has an activity of about 5 dpm/g, how old is the sample?

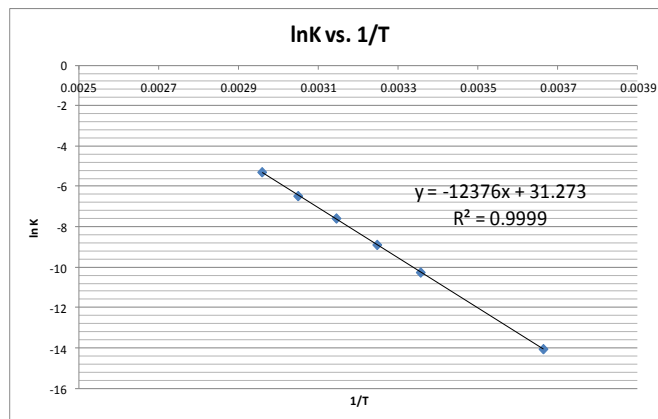Since nuclear radiation is always first order, you can use:

$t\,½ = 0.693/K$ and $\ln A = -kt + \ln A_o$

$k = 0.693/5700 = 1.216 \times 10^{-4}$ so $\ln 5 = -(1.216 \times 10^{-4})(t) + \ln 16$ $t = 9565$ yrs

Arrhenius Equation

1. The following is data for the reaction: $N_2O_5 \rightarrow 2\ NO_2\ +\ \frac{1}{2}\ O_2$

T (K)	K
338	4.87×10^{-3}
328	1.50×10^{-3}
318	4.98×10^{-4}
308	1.35×10^{-4}
298	3.46×10^{-5}
273	7.87×10^{-7}

Calculate the activation energy of this reaction.

1/T	ln K
0.002959	-5.324661342
0.003049	-6.502290171
0.003145	-7.604910481
0.003247	-8.91023578
0.003356	-10.27165688
0.003663	-14.05503759

InK vs. 1/T

y = -12376x + 31.273
R² = 0.9999

slope = -E*/R or E* = -mR   E* = -(-12376)(8.314 J) = 103 kJ

2. A + B $\rightarrow$ C + D

T (K)	K
298	0.0409
308	0.0818
318	0.157
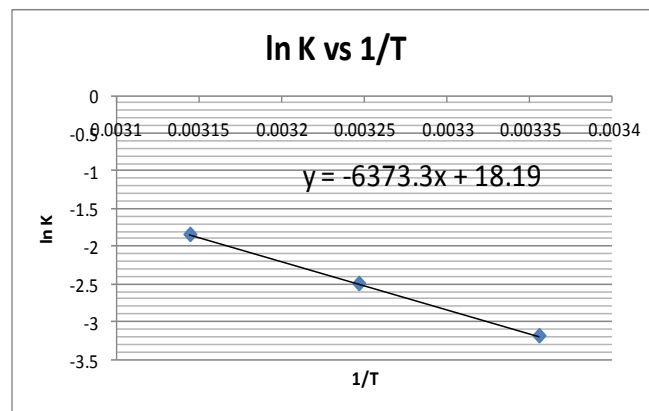
Calculate the activation energy of this reaction.

1/T	ln K
0.003356	-3.19663
0.003247	-2.50348
0.003145	-1.85151

ln K vs 1/T

y = -6373.3x + 18.19

slope = -E*/R or E* = -mR   E* = -(-6373)(8.314 J) = 56 kJ

Combination Problems

1. For the equations:

$$2\,A + B \rightarrow C + D$$
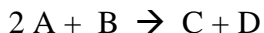
Experiment	Initial [A]	Initial [B]	Initial Rate of formation of C (M/min)
1	0.25	0.75	$4.2\mathrm{x}10^{-4}$
2	0.75	0.75	$1.3\mathrm{x}10^{-3}$
3	1.50	1.50	$5.3\mathrm{x}10^{-3}$
4	1.75	???	$8.0\mathrm{x}10^{-3}$

a) Determine the order of the reaction with respect to A and to B. Justify your answer.

Exp 1→2 triple [A] and rate triples; therefore A is 1st order

Exp 2→ 3 double both [A] and [B] and rate goes up by 4 times

   Since we know A is 1st order, then 2 of the 4 times is from increasing A

   This leaves us with doubling [B] and the rate effectively doubles so its 1st order

b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.

Rate = k[A][B]   k = Rate/[A][B] = $4.2\mathrm{x}10^{-4}$ /(0.25)(0.75) = 0.00224 1/Mmin

c) Determine the initial rate of change of [A] in experiment #3

From the balanced eq, A changes twice as fast as C so rate A = 2*$5.3\mathrm{x}10^{-3}$ = 0.0106 M/min

d. Determine the initial value of [B] in Experiment #4

[B] = Rate/k[A] = $8.0\mathrm{x}10^{-3}$/(0.00224)(1.75) = 2.04 M

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

   i) A + B → C + M   Fast
       M + A → D   Slow

   ii) B ←→ M   Fast equilibrium
       M + A → C + X   Slow
       A + X →   Fast

   iii) A + B ←→ M   Fast equilibrium
        M + A → C + X   Slow
        X → D   Fast

Mechanism 2 is the best.

Since the first line is a fast equilibrium, [B]k' = [M]

Since the 2nd line is the slow step, it is the rate law: Rate = k[M][A]

Substitute in for [M] and you get: Rate = kk'[B][A]

Combine the 2 k values to get: Rate = k''[A][B] which matches rate law above

2. The first-order decomposition of a colored species, X, into a colorless product is monitored with a spectrophotometer. The following table shows the results:

[X] M	Absorbance	Time (min)
????	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	???

a) Calculate the initial concentration of the colored species.

Absorbance is directly related to [X] by Beer's law so because 0.600 Abs is triple that of 0.200 abs, the [X] should be triple 4.00×10^{-5} so 1.2×10^{-4} M

b) Calculate the rate constant for the 1st-order reaction using the values given for concentration and time. Include units.

Ln [X] = -kt + ln [X]$_o$

Pick the first line and the second line to substitute:

Ln (4×10^{-5}) = -k(35) + ln (1.2×10^{-4})

-10.13 = -k(35) -9.03

k = 0.0314 1/min

c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075

Ln [X] = -kt + ln [X]$_o$

Pick the first line and the last line to substitute:

Ln (1.5×10^{-5}) = -(0.0314)t + ln (1.2×10^{-4})

-11.11 = -(0.0314)(t) -9.03

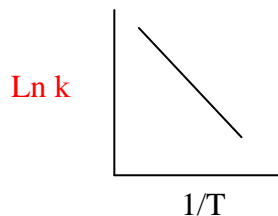t = 66.2 min

d) Calculate the half-life of the reaction. Include units.

$t_{1/2}$ = 0.693/k
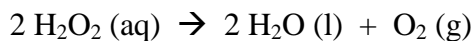
$t_{1/2}$ = 22.1 min

e) Label the vertical axis of the following graph which will be able to calculate E_a.

Ln k

1/T

3. For the equation:

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

a. An aqueous solution of H_2O_2 that is 6% H_2O_2 by mass has a density of 1.03 g/mL.
   i) Calculate the original moles of H_2O_2 in a 125 mL sample of the solution
   (125 mL)(1.03 g/mL) = 128.75 g *(0.06) = 7.725 g H_2O_2
   ii) The number of moles of O_2 that are made when all of the sample from a reacts
   7.725 g H_2O_2 *(1 mole/34 g) = 0.2272 moles H_2O_2
   0.2272 moles H_2O_2 *(1 mole O_2/2 mole H_2O_2) = 0.1136 moles O_2

b. The graphs below show results from a study of the decomposition of H_2O_2
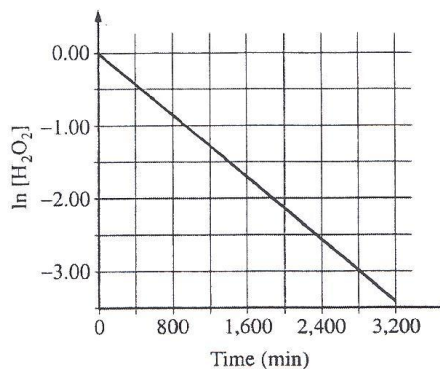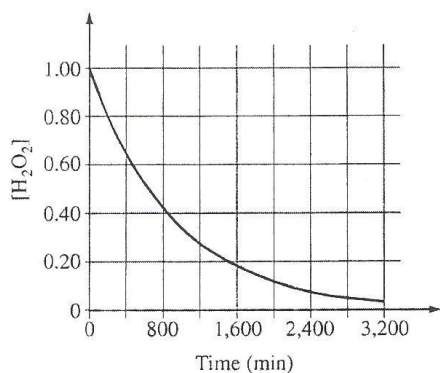
   i) Write the rate law for the reaction. Justify your answer
   Rate = k[H_2O_2]
   A straight line comes from the ln [H_2O_2] vs. time so that means it must be first
      order
   ii) Determine the half-life of the reaction.
   From the 1st graph, it appears that it starts at 1.00 M and is reduced to 0.50 M by
      about 600 min
   Using information from part iii, knowing that k = 0.00107 1/min
   $T_{1/2}$ =0.693/k = 0.693/0.00107 = 648 min
   iii) Calculate the value of the rate constant, k. Include units.
   Pick 2 points on graph 2
   0, 0   and   2800, -3
   Slope = $\Delta Y/\Delta X$ 0-(-3)/0-2800 = -0.00107
   So k = 0.00107 1/min
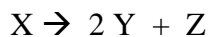   iv) Determine [H_2O_2] after 2000 minutes elapse from the time it began
   Ln [X] = -kt + ln [X]$_o$
   Ln [X] = -(0.00107)(2000) + ln (1)
   Ln [X] = -2.14
   [X] = e$^{-2.14}$ = 0.1176 M

4. For the reaction:

$$X \rightarrow 2\,Y + Z$$

In a certain experiment, the reaction took place in a 5.00 L flask at 428 K. Data from the experiment were used to produce the table below which is then plotted in the graphs that follow:

Time (min)	[X] mol/L	Ln [X]	1/[X] L/mol
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
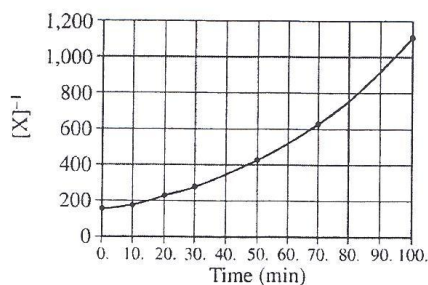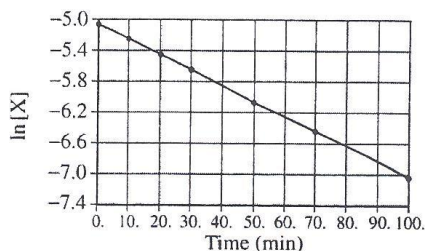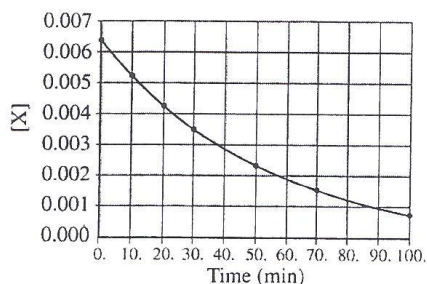
a. How many moles of X were initially in the flask? 0.03165 moles
b. How many molecules of Y were produced in the first 20. minutes of the rxn
   0.00633 M – 0.00427 M = 0.00206 mole/L *(5 L) = 0.0103 moles X reacted
   0.0103 moles X *(2 moles Y/mole X) = 0.0206 moles Y
c. What is the order of this reaction with respect to X? Justify your answer.
   A straight line comes from the ln [X] vs. time so that means it must be 1st order
d. Write the rate law for the reaction. Rate = k[X]
e. Calculate the specific rate constant for this reaction. Specify units.
   Pick 2 points: 0, 0.00633   and   100, 0.0009
   Ln [X] = -kt + ln [X]$_0$ ln (0.0009) = -k(100) + ln (0.00633) k = 0.0195 1/min
f. Calculate the concentration of X in the flask after a total of 150 min of rxn.
   Ln [X] = -kt + ln [X]$_0$ ln (X) = -(0.0195)(150) + ln (0.00633)
                                      Ln (X) = -7.987   X = e$^{-7.987}$ = 3.40x10^{-4} M

5. For the reactions:

      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
    $O_3 + O \rightarrow 2\ O_2$
    b. Clearly identify the catalyst in the mechanism above. Justify.
    The catalyst is Cl. It is used in step I and then regenerated in step 2.
    c. Clearly identify the intermediate in the mechanism above. Justify.
    The intermediate is ClO. It is made in step I and then re-used in step 2
    d. If the rate law for the above reaction is $rate = k[O_3][Cl]$, determine:
      i) The overall order of the reaction
      Overall order is 2nd. It is 1st in O_3 and 1st in Cl according to the rate law
      ii) Appropriate units for the rate constant, k
      k = 1/Mtime
      iii) The rate-determining step of the reaction, along with justification of your answer.
      The slow step of the mechanism IS the rate law molecularity. Since the rate law is 1st
        order in each O_3 and Cl then the slow step must be unimolecular in each. Step I
   clearly matches these requirements so the slow step is step I.

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.
  (i)   The activation energy (E_a) for the forward reaction
  (ii) The enthalpy change (ΔH) for the reaction
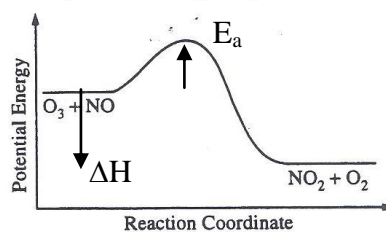
(b) The reaction $2 N_2O_5 \rightarrow 4 NO_2 + O_2$ is first order with respect to N_2O_5.

  (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.
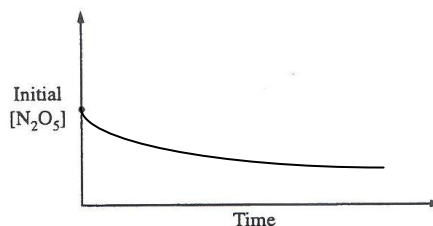
ii) Draw a tangent line at any given time. Calculate the slope of the tangent line.
iii) Graph ln $[N_2O_5]$ vs. time on one graph and graph $1/[N_2O_5]$ vs. time on another graph. Whichever graph gives a straight line will tell you the order of the reaction. If the straight line is for the ln graph, it is 1st order. If the straight line if for the inverse graph, then it is 2nd order. Once you get the straight line, take the slope of that straight line. For 1st order reactions, k = - slope. For 2nd order reactions, k = slope.
iv) The rate constant, k, would not be effected by this. It may change the rate of reaction, etc., but the only way to change the rate constant is to change the temperature.

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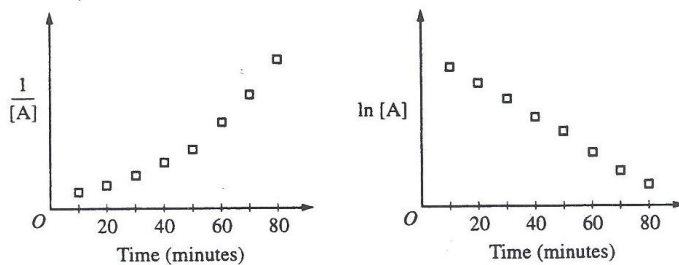
Use the information in the graphs above to answer the following.

  (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.

i) Since the straight line is for the ln graph, the rate must be 1st order. Thus the rate law is:
 Rate = k[A]
ii) Calculate the slope of the straight line. k = -slope