

Key

Unit 5 Study guide

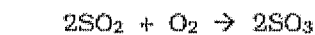
Reaction rate and rate laws

1. For this reaction, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$, and using the data in the table below, calculate the average rate of reaction, in M/s, for the time interval between each measurement.

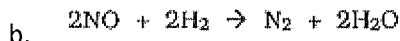
| Time (s) | $[\text{CH}_3\text{NC}]$ (M) | Average rate (M/s) |
|----------|------------------------------|----------------------|
| 0 | 0.0165 | $2.75 \cdot 10^{-6}$ |
| 2 000 | 0.0110 | $1.70 \cdot 10^{-6}$ |
| 5 000 | 0.00591 | $8.33 \cdot 10^{-7}$ |
| 8 000 | 0.00314 | $4.43 \cdot 10^{-7}$ |
| 12 000 | 0.00137 | $2.10 \cdot 10^{-7}$ |
| 15 000 | 0.00074 | |

$$\text{for } t=0 \rightarrow 2000 \\ \frac{-\Delta[\text{CH}_3\text{NC}]}{\Delta t} = \frac{0.0110 - 0.0165}{2000 - 0}$$

2. For each reaction shown below, write the rate expression in terms of the appearance of each product or the disappearance of each reactant (the rate expression has all the delta signs).



See key w/ work



3. $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. The rate law is first order in N_2O_5 . At 64 degrees, the rate constant is $4.82 \times 10^{-3} \text{ s}^{-1}$.

a. Write the rate law for the reaction. $\text{Rate} = k[\text{N}_2\text{O}_5]$

b. What is the rate of the reaction when $[\text{N}_2\text{O}_5] = 0.0240 \text{ M}$? $1.16 \cdot 10^{-4} \text{ M/s}$

c. What happens to the rate when the concentration of N_2O_5 is doubled to 0.0480 M ?

Rate is doubled, $2.32 \cdot 10^{-4} \text{ M/s}$

4. To study the rate of this reaction, $\text{A} + \text{B} \rightarrow \text{C}$, a student makes measurements of the initial rates under the following conditions:

| | |
|---------------------|-------------|
| Trial 1 [A] = 1.0 M | [B] = 1.0 M |
| Trial 2 [A] = 2.0 M | [B] = 1.0 M |

- a. What reactant concentration could be used for Trial 3 in order to determine the rate law, assuming that the rate law is of this form: $\text{rate} = k[\text{A}]^x[\text{B}]^y$
- b. For this reaction, $\text{A} + \text{B} + \text{C} \rightarrow \text{products}$, the following observations are made; doubling the concentration of A doubles the rate; tripling the concentration of B has no effect on the rate, and tripling the concentration of C increases the rate by a factor of 9. By what factor will the rate change if the concentrations of A, B, and C are all halved?

$\frac{1}{8}$

5. For this reaction, $\text{OCl}^- + \text{I}^- \rightarrow \text{OI}^- + \text{Cl}^-$, the following data were collected:

| $[\text{OCl}^-], \text{M}$ | $[\text{I}^-], \text{M}$ | Rate, M/s |
|---|---|--|
| $2 \times \begin{pmatrix} 1.5 \times 10^{-3} \\ 3.0 \times 10^{-3} \\ 1.5 \times 10^{-3} \end{pmatrix}$ | $\begin{pmatrix} 1.5 \times 10^{-3} \\ 1.5 \times 10^{-3} \\ 3.0 \times 10^{-3} \end{pmatrix} \times 2$ | $2 \times \begin{pmatrix} 1.36 \times 10^4 \\ 2.72 \times 10^4 \\ 2.72 \times 10^4 \end{pmatrix} \times 2$ |

- Write the rate law for this reaction. $\text{Rate} = k[\text{OCl}^-]^2[\text{I}^-]$
- Calculate the rate constant with units. $6.0 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$
- Calculate the rate when $[\text{OCl}^-] = 1.0 \times 10^{-3} \text{ M}$ and $[\text{I}^-] = 5.0 \times 10^{-4} \text{ M}$. $3.0 \cdot 10^3 \frac{\text{M}}{\text{s}}$

6. For this reaction, $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_3^- + \text{ClO}_2^- + \text{H}_2\text{O}$, the following data were collected:

| $[\text{ClO}_2], \text{M}$ | $[\text{OH}^-], \text{M}$ | Rate, M/s |
|---|---|--|
| $\begin{pmatrix} .080 \\ .020 \\ .020 \end{pmatrix} \times 3$ | $\begin{pmatrix} .030 \\ .030 \\ .090 \end{pmatrix} \times 3$ | $\begin{pmatrix} .0248 \\ .00276 \\ .00828 \end{pmatrix} \times 9$ |

- Write the rate law for this reaction. $\text{Rate} = k[\text{ClO}_2]^2[\text{OH}^-]$
- Calculate the rate constant with units. $k = 230 \text{ M}^{-2}\text{s}^{-1}$
- Calculate the rate when $[\text{ClO}_2] = 0.010 \text{ M}$ and $[\text{OH}^-] = 0.015 \text{ M}$. $3.4 \cdot 10^{-4} \text{ M s}^{-1}$

7. For this reaction, $\text{BF}_3 + \text{NH}_3 \rightarrow \text{F}_3\text{BNH}_3$, the following data were collected:

| Experiment | $[\text{BF}_3], \text{M}$ | $[\text{NH}_3], \text{M}$ | Initial Rate, M/s |
|------------|---------------------------|---------------------------|----------------------------|
| 1 | .250 | .250 | .2130 |
| 2 | .250 | .125 | .1065 |
| 3 | .200 | .100 | .0682 |
| 4 | .350 | .100 | .1193 |
| 5 | .175 | .100 | .0596 |

- Write the rate law for this reaction. $\text{Rate} = k[\text{BF}_3][\text{NH}_3]$
- What is the overall order of the reaction? 2nd
- What is the value of the rate constant for the reaction? $341 \text{ M}^{-1}\text{s}^{-1}$

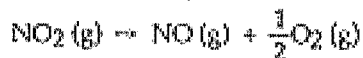
Half-life problems

The reaction $A \rightarrow B$ is first order in $[A]$. Consider the following data.

| time (s) | $[A]$ (M) |
|----------|-----------|
| 0.0 | 1.60 |
| 10.0 | 0.40 |
| 20.0 | 0.10 |

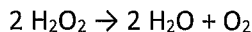
- The rate constant with units for this reaction is 0.13 s^{-1} .
- The half-life for this reaction is 5.3 s .
- The rate constant of a first-order process that has a half-life of 225 s is 0.00308 s^{-1} .

- At elevated temperatures, nitrogen dioxide decomposes to nitrogen oxide and oxygen:



The reaction is second order in NO_2 with a rate constant of $0.543 \text{ M}^{-1}\text{s}^{-1}$ at 300°C . If the initial $[\text{NO}_2]$ is 0.260 M , it will take 18.3 s for the concentration to drop to 0.100 M .

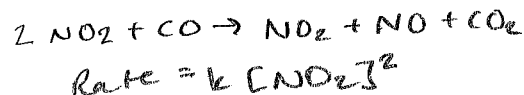
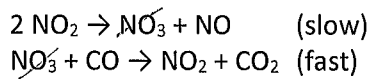
- The reaction below is first order in $[\text{H}_2\text{O}_2]$:



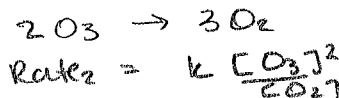
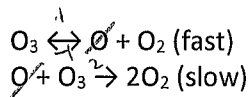
A solution originally at 0.600 M H_2O_2 is found to be 0.075 M after 54 min. The half-life for this reaction is 18 min.

- A second-order reaction has a half-life of 18 s when the initial concentration of reactant is 0.71 M . The rate constant for this reaction is 0.13 $\text{M}^{-1}\text{s}^{-1}$.

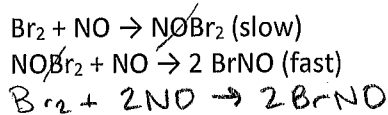
Mechanism practice



- Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

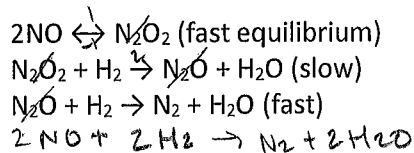


- Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute. (The rate law will look very strange, unlike anything you've seen. But it is correct.)



$$\text{Rate} = k [\text{Br}_2] [\text{NO}]$$

3. Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

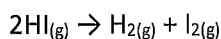


$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

4. Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

MC practice

1. Hydrogen iodide decompose to give a mixture of hydrogen and iodine:

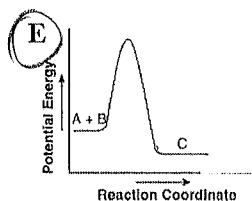
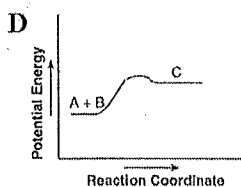
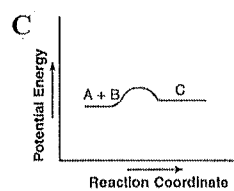
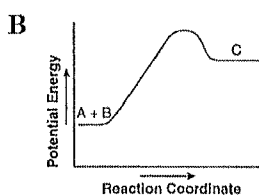
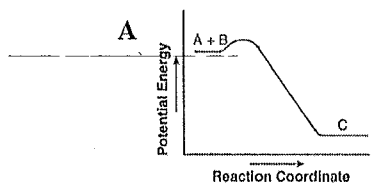


The order of the decomposition of HI in the gas phase is

- a. 0
b. 1
c. 2
d. 3
e. 4

| Trial | [HI] (M) | Initial Rate (M/sec) |
|-------|----------------------|----------------------|
| 1 | 1.0×10^{-2} | 4.0×10^{-6} |
| 2 | 2.0×10^{-2} | 1.6×10^{-5} |
| 3 | 3.0×10^{-2} | 3.6×10^{-5} |

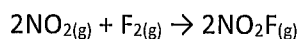
2. Which of the following is a graph that describes the pathway of reaction that is exothermic and has relatively high activation energy?



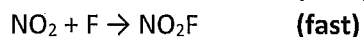
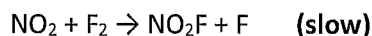
4. Which of the following, if increased, does not increase reaction rate?
- a. Reactant concentration
 - b. Surface area
 - c. Pressure
 - d. Activation energy
 - e. Temperature

5. The rate constant
- a. Always shows an exponential increase with the Kelvin or absolute temperature
 - b. Increase with increasing concentration
 - c. Usually increases with increased pressure for gases
 - d. Never changes (it is constant)
 - e. Is the same for a given reaction at the same Kelvin or absolute temperature

6. The reaction



Follows the mechanism below:



The rate law would be consistent with

- a. Rate = $k[\text{NO}_2]^3[\text{F}_2]^2$
 - b. Rate = $k[\text{NO}_2]^2[\text{F}_2]$
 - c. Rate = $k[\text{NO}_2][\text{F}_2]$
 - d. Rate = $k[\text{NO}_2]^2[\text{F}_2]^2$
 - e. Rate = $k[\text{NO}_2][\text{F}_2]^2$
7. A reaction is first order with respect to [X] and second order with respect to [Y]. When [X] is 0.20 M and [Y] is 0.20 M the rate is 8.00×10^{-3} M/min. the value of the rate constant, including units, is
- a. 1.00 M min^{-1}
 - b. $1.00 \text{ M}^{-2} \text{ min}^{-1}$
 - c. $2.00 \text{ M}^{-1} \text{ min}^{-1}$
 - d. $2.0 \text{ M}^{-2} \text{ min}^{-1}$
 - e. $8.00 \times 10^{-3} \text{ min}^{-3}$

8. Which of the following rate laws has a rate constant with units of $\text{L mol}^{-1} \text{ sec}^{-1}$?

- a. Rate = $k[\text{A}]$
- b. Rate = $k[\text{A}]^2$
- c. Rate = $k[\text{A}]^2[\text{B}]$
- d. Rate = $k[\text{A}][\text{B}]^2$
- e. Rate = $k[\text{A}]^0$

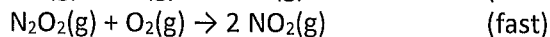
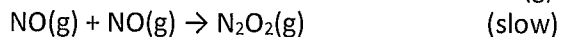
9. A first order reaction has a half-life of 85 s. What factors of the reactant is ^{left} after 255 s?

- a. $\frac{1}{2}$
- b. $\frac{1}{4}$
- c. $\frac{1}{8}$
- d. $\frac{1}{3}$
- e. $\frac{1}{6}$

11. If a reactant's concentration is doubled and the reaction rate increases by a factor of 8, the exponent for that reactant in the rate law should be
- a. 3
 - b. 2
 - c. 1
 - d. 0
 - e. $\frac{1}{2}$
12. A graph of the reciprocal of reactant concentration versus time will give a straight-line for
- a. A zero order reaction
 - b. A first order reaction
 - c. A second order reaction
 - d. Both A and C
 - e. A, B and C
13. The activated complex may be described as
- a. An elementary reaction in a mechanism
 - b. The shape of the molecules at the moment of collision
 - c. The shape of the reaction product
 - d. The phase- liquid, solid, or gas- in which a reaction takes place
 - e. The final state
14. The Molecularity of an elementary step
- a. Specifies that the particles taking part in the reaction are molecules
 - b. Indicates the order of the reaction
 - c. Specifies the number of reacting species participating in that step
 - d. Is a measure of the energy released or absorbed in the reaction
 - e. Indicates the size of the reacting particles; a high Molecularity meaning a small particle size
15. Which of the following statements is false?
- a. An exothermic reaction always goes faster than an endothermic reaction
 - b. A catalyst provides a different route by which the reaction can occur
 - c. Some reactions may never reach completion (100% products)
 - d. The rate of a reaction depends upon the height of the energy barrier
 - e. Increase in temperature usually increases the rate of a reaction
16. A graph of the natural log of reactant concentration versus time will give a straight-line for
- a. A zero order reaction
 - b. A first order reaction
 - c. A second order reaction
 - d. Both A and C
 - e. A, B and C
17. Addition of a catalyst to a reaction mixture
- a. Increases the activation energy of a reaction
 - b. Decreases the energy required to activate the reaction
 - c. Has no effect of the activation energy of a reaction
 - d. Decreases the frequency of collisions that are effective
 - e. Has no effect on the frequency of collisions that are effective

* I ignore highlighting!

19. A possible mechanism for the overall reaction $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$ is the following:

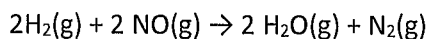


Which of the following rate expressions agrees best with this possible mechanism?

- a. Rate = $k[\text{NO}]^2$
- b. Rate = $k[\text{NO}]/[\text{O}_2]$
- c. Rate = $k[\text{NO}]^2/[\text{O}_2]$
- d. Rate = $k[\text{NO}]^2[\text{O}_2]$
- e. Rate = $k[\text{N}_2\text{O}_2][\text{O}_2]$

For questions 17-20 - 20 - 23

Consider the following reaction between hydrogen gas and nitrous oxide:



The rate law for this reaction is

Rate = $k[\text{H}_2][\text{NO}]^2$

20. What is the order of this reaction in respect to NO?

- a. 0
- b. 1
- c. 2
- d. 3
- e. 4

21. What is the overall order of the reaction?

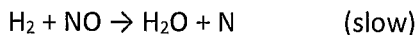
- a. 0
- b. 1
- c. 2
- d. 3
- e. 4

22. If the concentration of NO is tripled, the reaction rate will increase by a factor of

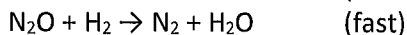
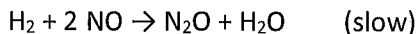
- a. 3
- b. 9
- c. 27
- d. 54
- e. 81

23. The following are three mechanisms by which the reaction can proceed. On the basis of the observed rate law, which mechanism(s) can be ruled out?

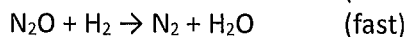
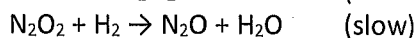
Mechanism I



Mechanism II



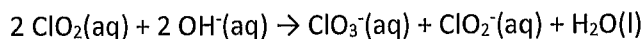
Mechanism III



- a. I only
- b. II only
- c. III only
- d. I and II
- e. II and III

FRQ practice

Free response 1:



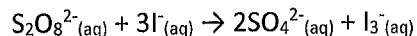
A series of experiments were conducted to study the above reaction. The initial concentrations and rates are reported in the table below.

| EXPERIMENT | INITIAL CONCENTRATION (mol/L) | | INITIAL RATE OF FORMATION OF ClO_3^- (mol/L. min) |
|------------|-------------------------------|------------------|--|
| | $[\text{OH}^-]$ | $[\text{ClO}_2]$ | |
| 1 | 0.030 | 0.020 | 0.166 |
| 2 | 0.060 | 0.020 | 0.331 |
| 3 | 0.030 | 0.040 | 0.661 |

- a.
- Determine the order of the reaction with respect to each reactant. Make sure you explain your reasoning. *1st order OH^- 2nd order ClO_2*
 - Give the rate law for the reaction. *rate = $k[\text{OH}^-][\text{ClO}_2]^2$*
- b. Determine the value of the rate constant. Include units. *$1.4 \cdot 10^4 \text{ M}^{-2} \text{ min}^{-1}$*
- c. Calculate the initial rate of disappearance of ClO_2 in experiment 1. *0.332 M min^{-1}*
- d. The following has been proposed as a mechanism for this reaction. Which step is the rate-determining step?
- Step 1: $\text{ClO}_2 + \text{ClO}_2 \leftrightarrow \text{Cl}_2\text{O}_4$ (fast equilibrium)
- Step 2: $\text{Cl}_2\text{O}_4 + \text{OH}^- \rightarrow \text{ClO}_3^- + \text{HClO}_2$ (slow)
- Step 3: $\text{HClO}_2 + \text{OH}^- \rightarrow \text{ClO}_2^- + \text{H}_2\text{O}$ (fast)
- e. Show that this mechanism is consistent with:
- The overall rate law for the reaction, and *see work*
 - The overall stoichiometry of the reaction

Free response 2:

Initial rate data were collected for the following reaction in which iodide ion is oxidized to triiodide by peroxydisulfate ion:

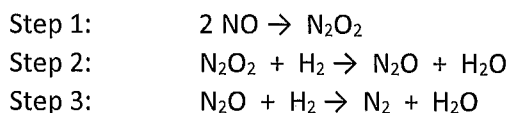


| Experiment | $[\text{S}_2\text{O}_8^{2-}]$ (M) | $[\text{I}^-]$ (M) | Initial rate (M/sec) |
|------------|-----------------------------------|--------------------|----------------------|
| 1 | 0.080 | 0.034 | 2.2×10^{-4} |
| 2 | 0.080 | 0.017 | 1.1×10^{-4} |
| 3 | 0.160 | 0.017 | 2.2×10^{-4} |
| 4 | 0.280 | ??? | 5.7×10^{-4} |

- a. Write the rate law for the overall reaction. $Rate = k[S_2O_8^{2-}][I^-]$
- b. Determine the value of the rate constant, k , for the reaction. Include units with your answer. $k = 8.1 \cdot 10^{-2} M^{-1}s^{-1}$
- c. Calculate the initial concentration of I^- for experiment 4. $[I^-] = 2.5 \cdot 10^{-2} M$
- d. What is the overall order of this reaction? 2^{nd}
- e. What does the overall order indicate about the slow step of the reaction mechanism?
bimolecular

Free response 3:

Consider the proposed mechanism for the reaction between nitrogen monoxide and hydrogen gas. Assume the mechanism is correct



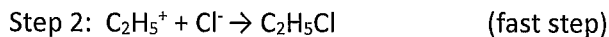
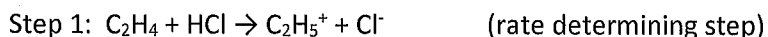
- a. Use the steps in the mechanism to determine the overall balanced equation for the reaction. Clearly show your method $2NO + 2H_2 \rightarrow 2H_2O + N_2$
- b. If step 2 is the rate-determining step, write the rate law for the reaction, explain your answer
 $Rate = k[NO]^2[H_2]$
- c. If the observed rate law is $rate = k[NO]^2[H_2]^2$, which step is rate determining? Explain your reasoning
step 3, see work
- d. If the first step is the rate-determining step, what is the order of reaction with respect to each reactant?
NO - 2nd order
H₂ - 0 order

Free response 4:

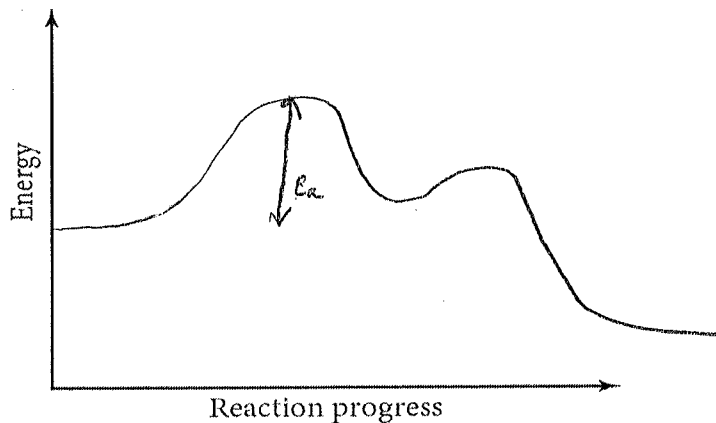
$C_2H_4(g)$ reacts readily with $HCl(g)$ to produce $C_2H_5Cl(g)$, as represented by the following equation:



It is proposed that the formation of $C_2H_5Cl(g)$ proceeds via the following two step reaction mechanism:



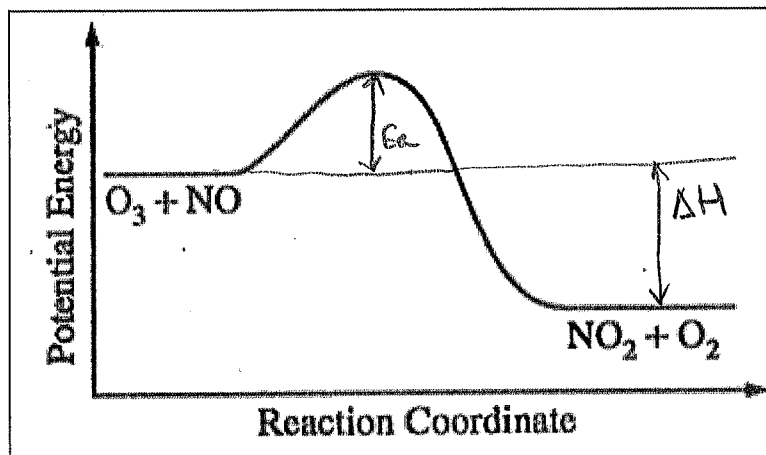
- a. Write the rate law for the reaction that is consistent with the reaction mechanism above. $Rate = k[C_2H_4][HCl]$
- b. Identify an intermediate in the reaction mechanism above. $C_2H_5^+ \quad Cl^-$
- c. Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two step mechanism and the enthalpy change of the reaction.



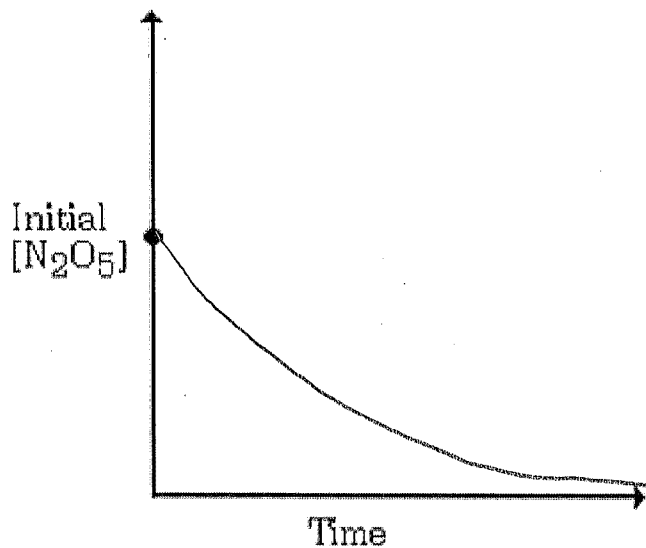
- d. On the diagram above, clearly indicate the activation energy, E_a , for the rate determining step in the reaction.

Free response 5:

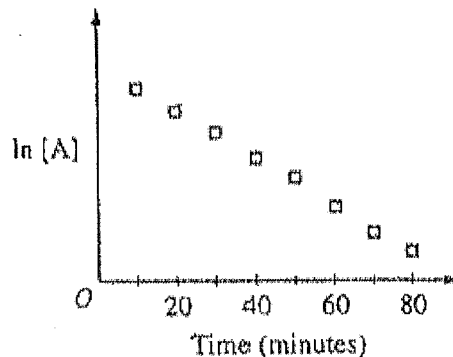
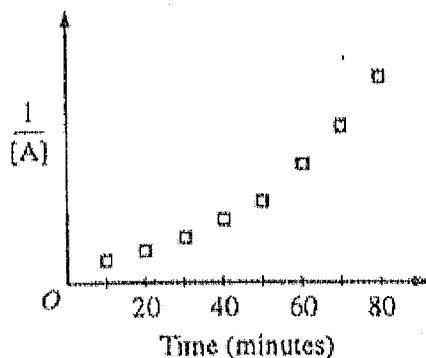
Answer the following questions regarding the kinetics of chemical reactions.



- a. The diagram above 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 axis, 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 .
tangent line
- iii. Considering the rate law and the graph in (i), describe how the value of the rate constant, k , could be determined. *graph in $[N_2O_5]$ vs t*
determine $t_{1/2}$; $t_{1/2} = \frac{0.693}{k}$
- 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.
no change in 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 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.
Rate = $k[A]^2$
- ii. Describe how to determine the value of the rate constant for the reaction.
slope of $\ln[A]$ vs $t = -k$

