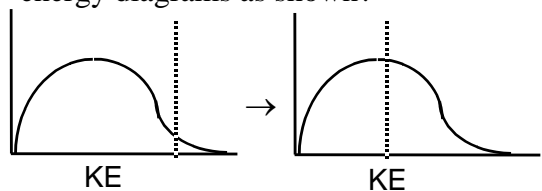


# 15 • Chemical Kinetics

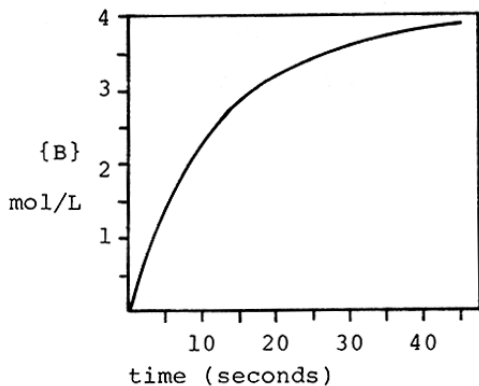
## PRACTICE QUIZ

- Which of the following does NOT influence the speed of a chemical reaction?
  - concentration of reactants
  - nature of reactants
  - temperature
  - presence of a catalyst
  - none of these

- What would cause the change in the kinetic energy diagrams as shown?



- increasing the  $\Delta H$
  - decreasing the temperature
  - increasing the surface area
  - addition of a catalyst
  - increasing the concentration of reactant
- A time vs. concentration graph is presented below for the reaction  $A \rightarrow B$ . What is the rate of appearance of 'B' 20 seconds after the start of the reaction?



- 0.050 mol/L·s
- 3.2 mol/L·s
- 2.2 mol/L·s
- 0.010 mol/L·s
- 9.8 mol/L·s

- The reaction  $3O_2 \rightarrow 2O_3$  is proceeding with a rate of disappearance of  $O_2$  equal to 0.60 mol/L·s. What is the rate of appearance of  $O_3$ , in mol/L·s?

- 0.60
- 0.40
- 0.10
- 0.90
- 1.20

- What is the rate constant for a first order reaction for which the half-life is 85.0 sec?

- 0.00814 sec<sup>-1</sup>
- 4.44 sec<sup>-1</sup>
- 0.170 sec<sup>-1</sup>
- 0.0118 sec<sup>-1</sup>
- 58.9 sec<sup>-1</sup>

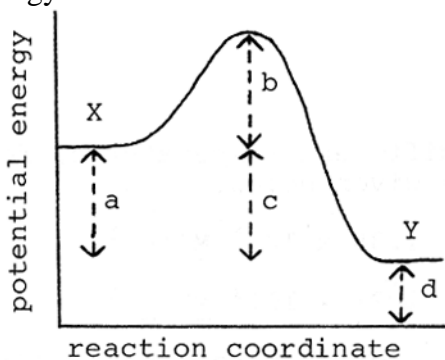
- What fraction of a reactant remains after 3 half-lives of a first order reaction?

- 1/2
- 1/3
- 1/6
- 1/8
- 1/12

- According to collision theory, which of the following factors does NOT influence the rate of reaction?

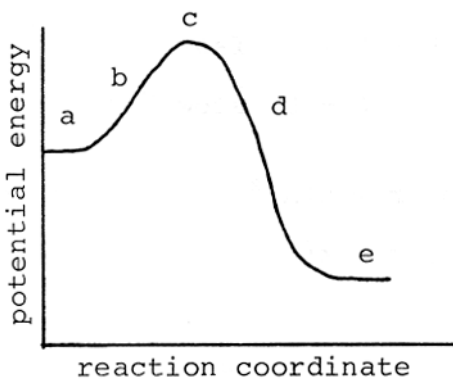
- collision frequency
- collision energy
- collision orientation
- collision rebound direction
- none of these

8. What distance corresponds to the activation energy for the reaction of X to Y?



- a) a                                      d) d  
 b) b                                      e) e  
 c) c

9. At what point on the potential energy diagram given below does the transition state (activated complex) occur?



- a) a                                      d) d  
 b) b                                      e) e  
 c) c

10. Which of the following is NOT true about a catalyst?

- a) it speeds up the forward reaction  
 b) is acts as an inhibitor  
 c) it speeds up the reverse reaction  
 d) it may be homogeneous  
 e) it may be heterogeneous

**Answers:** (please use **CAPITAL** letters)

- |          |           |
|----------|-----------|
| 1. _____ | 6. _____  |
| 2. _____ | 7. _____  |
| 3. _____ | 8. _____  |
| 4. _____ | 9. _____  |
| 5. _____ | 10. _____ |

Useful Formulae:

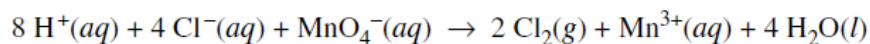
$$\ln \frac{[A]_o}{[A]_t} = kt$$

the special case of half-life

$$\ln(2) = 0.693 = kt_{1/2}$$

## Chemical Kinetics

### PRACTICE FRQ



$\text{Cl}_2(g)$  can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.

- (a) A 25.00 mL sample of 0.250 M NaCl reacts completely with excess  $\text{KMnO}_4(aq)$ . The  $\text{Cl}_2(g)$  produced is dried and stored in a sealed container. At 22°C the pressure of the  $\text{Cl}_2(g)$  in the container is 0.950 atm.
- Calculate the number of moles of  $\text{Cl}^-(aq)$  present before any reaction occurs.
  - Calculate the volume, in L, of the  $\text{Cl}_2(g)$  in the sealed container.

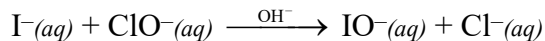
An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[\text{Cl}^-]$	$[\text{MnO}_4^-]$	$[\text{H}^+]$	Rate of Disappearance of $\text{MnO}_4^-$ in $M s^{-1}$
1	0.0104	0.00400	3.00	$2.25 \times 10^{-8}$
2	0.0312	0.00400	3.00	$2.03 \times 10^{-7}$
3	0.0312	0.00200	3.00	$1.02 \times 10^{-7}$

- (b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.
- $\text{Cl}^-$
  - $\text{MnO}_4^-$
- (c) The reaction is known to be third order with respect to  $\text{H}^+$ . Using this information and your answers to part (b) above, complete both of the following:
- Write the rate law for the reaction.
  - Calculate the value of the rate constant,  $k$ , for the reaction, including appropriate units.
- (d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

**15 • Reaction Kinetics****FRQ PRACTICE**

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

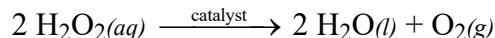


Iodide ion,  $\text{I}^{-}$ , is oxidized to hypoiodite ion,  $\text{IO}^{-}$ , by hypochlorite,  $\text{ClO}^{-}$ , in basic solution according to the equation above. Three initial-rate experiments were conducted; the results shown in the following table.

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.
- $\text{I}^{-}(aq)$
  - $\text{ClO}^{-}(aq)$
- (b) For the reaction,
- write the rate law that is consistent with the calculations in part (a);
  - calculate the value of the specific rate constant,  $k$ , and specify units.

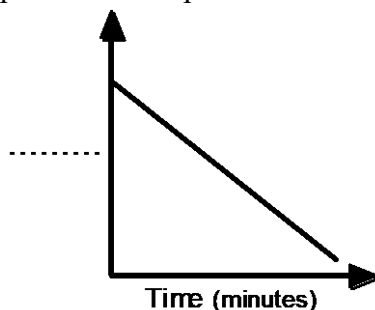
The catalyzed decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2(aq)$ , is represented by the following equation.



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.



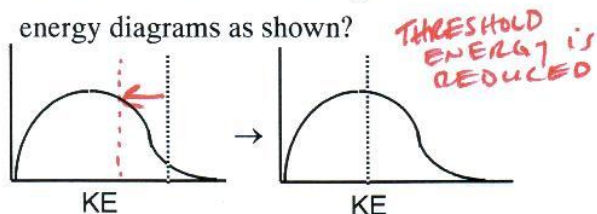
- Label the vertical axis of the graph
- What are the units of the rate constant,  $k$ , for the decomposition of  $\text{H}_2\text{O}_2(aq)$ ?
- On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 M  $\text{H}_2\text{O}_2(aq)$ .

# 15 • Chemical Kinetics

## PRACTICE TEST

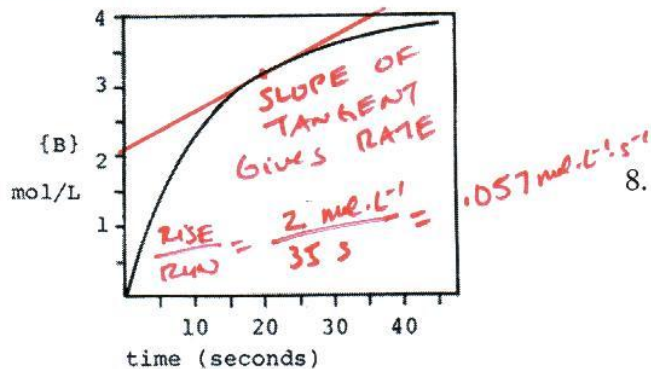
1. Which of the following does NOT influence the speed of a chemical reaction?
- concentration of reactants
  - nature of reactants
  - temperature
  - presence of a catalyst
  - none of these**

2. What would cause the change in the kinetic energy diagrams as shown?



- increasing the  $\Delta H$
- decreasing the temperature
- increasing the surface area
- addition of a catalyst**
- increasing the concentration of reactant

3. A time vs. concentration graph is presented below for the reaction  $A \rightarrow B$ . What is the rate of appearance of 'B' 20 seconds after the start of the reaction?



- 0.050 mol/L-s**
- 3.2 mol/L-s
- 2.2 mol/L-s
- 0.010 mol/L-s
- 9.8 mol/L-s

4. The reaction  $3O_2 \rightarrow 2O_3$  is proceeding with a rate of disappearance of  $O_2$  equal to 0.60 mol/L-s. What is the rate of appearance of  $O_3$ , in mol/L-s?

- 0.60
  - 0.40**
  - 0.10
  - 0.90
  - 1.20
- Handwritten:  $\frac{3O_2}{2O_3} = \frac{.60}{x}$*

5. A reaction has the rate law  $Rate = k[A]^2[B]$ . What is the overall order of the reaction?

- 0
- 2
- 1
- 4
- 3**

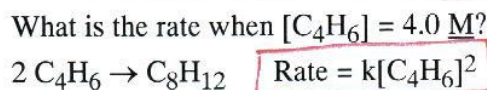
6. What are the correct units for a second order rate constant?

- mol/L-s
  - 1/s
  - L/mol-s**
  - $L^2/mol^2 \cdot s$
  - $mol^2/L^2 \cdot s$
- Handwritten:  $Rate = k[A]^2$   $k = \frac{Rate}{[A]^2} = \frac{mol \cdot L^{-1} \cdot s^{-1}}{mol^2 \cdot L^{-2}} = mol^{-1} \cdot L^1 \cdot s^{-1} = L \cdot mol^{-1} \cdot s^{-1}$*

7. The reaction  $I^- + OCl^- \rightarrow IO^- + Cl^-$  is first order with respect to  $I^-$  and first order with respect to  $OCl^-$ . The rate constant is  $6.1 \times 10^{-2} L/mol \cdot s$ . What is the rate of reaction when  $[I^-] = 0.10 M$  and  $[OCl^-] = 0.20 M$ ?

- $2.4 \times 10^{-4} M/s$
  - $1.2 \times 10^{-3} M/s$**
  - $6.1 \times 10^{-3} M/s$
  - $1.2 \times 10^{-4} M/s$
  - $2.4 \times 10^{-5} M/s$
- Handwritten:  $Rate = k[I^-]^1[OCl^-]^1 = (6.1 \times 10^{-2})(.10)(.20) = .00122$*

8. A reaction and its rate law are given below. When  $[C_4H_6] = 2.0 M$ , the rate is 0.106 M/s.



- 0.053 M/s
- 0.212 M/s
- 0.106 M/s
- 0.424 M/s**
- 0.022 M/s

*Handwritten: 2nd order. When [ ]^2 is DOUBLED Rate is QUADRUPLED  $4 \times .106 = .424 M/s$*



9. The rate law for the reaction  
 $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$   
 is  $\text{Rate} = k[\text{NO}]^2[\text{O}_2]$ . What happens to the rate when the concentration of NO is doubled?

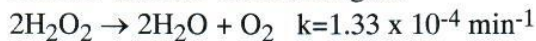
- a) the rate doubles    d) the rate is halved  
 b) the rate triples    e) none of these  
 c) the rate quadruples

10. Below is some rate data for the hypothetical reaction,  $2\text{A} + \text{B} \rightarrow \text{C}$ . What is the rate law for this reaction?

Experiment	[A] <sub>0</sub>	[B] <sub>0</sub>	Rate (M/s)
1	2.0 M	1.0 M	0.100
2	2.0 M	2.0 M	0.400
3	4.0 M	1.0 M	0.100

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

11. The acid catalyzed decomposition of hydrogen peroxide is a first order reaction with the rate constant given below. For an experiment in which the starting concentration of hydrogen peroxide is 0.110 M, what is the concentration of  $\text{H}_2\text{O}_2$  450 minutes after the reaction begins?



- a) 0.0961 M    d) 0.00658 M  
 b) 0.104 M    e) 0.0156 M  
 c) 0.117 M

*use 1st order integrated rate law*

12. What is the rate constant for a first order reaction for which the half-life is 85.0 sec?

- a)  $0.00814 \text{ sec}^{-1}$     d)  $0.0118 \text{ sec}^{-1}$   
 b)  $4.44 \text{ sec}^{-1}$     e)  $58.9 \text{ sec}^{-1}$   
 c)  $0.170 \text{ sec}^{-1}$

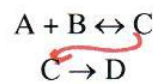
*$\ln 2 = k t_{1/2}$   
 $0.693 = k(85 \text{ s})$   
 solve for k*

13. What fraction of a reactant remains after 3 half-lives of a first order reaction?

- a) 1/2    d) 1/8  
 b) 1/3    e) 1/12  
 c) 1/6



14. Assume a reaction occurs by the mechanism given below. What is the rate law for the reaction?



*SUBSTITUTE A+B for C in the 2nd step*

- a)  $\text{Rate} = k[\text{A}][\text{B}][\text{C}]$   
 b)  $\text{Rate} = k[\text{A}]^2$   
 c)  $\text{Rate} = k[\text{A}][\text{B}]$   
 d)  $\text{Rate} = k[\text{A}][\text{B}]/[\text{D}]$   
 e)  $\text{Rate} = k[\text{A}]$

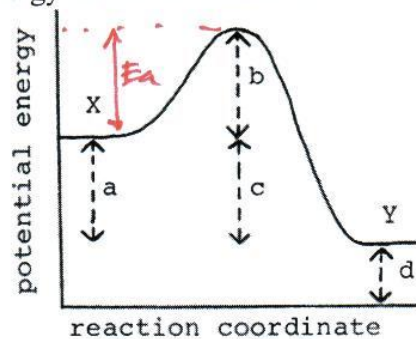
*slow step is: A+B → D*

15. According to collision theory, which of the following factors does NOT influence the rate of reaction?

- a) collision frequency  
 b) collision energy  
 c) collision orientation  
 d) collision rebound direction  
 e) none of these

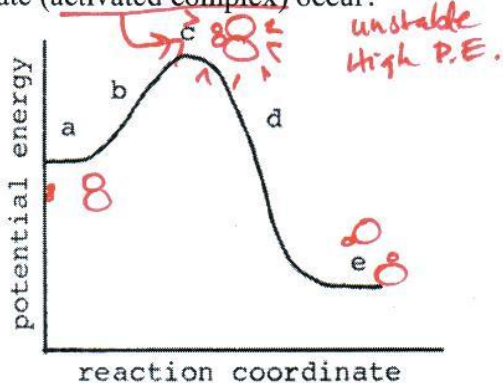
*important*  
*who cares where the particle goes AFTER the collision*

16. What distance corresponds to the activation energy for the reaction of X to Y?



- a) a    d) d  
 b) b    e) e  
 c) c

17. At what point on the potential energy diagram given below does the transition state (activated complex) occur?



- a) a  
b) b  
**c) c**  
d) d  
e) e

18. The rate constants, at two different temperatures, for the reaction



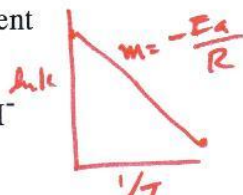
are given below.

$t = 30^\circ\text{C}$        $k = 1.38 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$

$t = 49^\circ\text{C}$        $k = 1.21 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$

What is the activation energy for this reaction?  $R = 8.314 \text{ J/mol}\cdot\text{K}$ .

- a) **92.7 kJ/mol**  
b) 200 kJ/mol  
c) 40.3 kJ/mol  
d) 343 kJ/mol  
e) none of these



19. Which of the following is NOT true about a catalyst?

- a) it speeds up the forward reaction  
**b) is acts as an inhibitor**  
c) it speeds up the reverse reaction  
d) it may be homogeneous  
e) it may be heterogeneous

*an "inhibitor" is like an anti-catalyst... it slows DOWN a reaction.*

20. In the reaction,  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ , the step  $\text{Br}\cdot + \text{H}_2 \rightarrow \text{HBr} + \text{H}\cdot$  is what step?

- a) initiation  
b) completion  
c) inhibition  
d) **propagation**  
e) termination

*CHAIN REACTION MECHANISM*

21. In the reaction,  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ , the step  $\text{Br}\cdot + \text{Br}\cdot \rightarrow \text{Br}_2$  is what step?

- a) initiation  
b) completion  
c) inhibition  
d) propagation  
**e) termination**

22. A free radical is a chemical species that possesses

- a) a positive charge  
b) a negative charge  
**c) an unpaired electron**  
d) an oxygen atom  
e) unconventional political views

*Br· H· are examples*

**Answers:** (please use CAPITAL letters)

- |              |              |
|--------------|--------------|
| 1. <u>E</u>  | 11. <u>B</u> |
| 2. <u>D</u>  | 12. <u>A</u> |
| 3. <u>A</u>  | 13. <u>D</u> |
| 4. <u>B</u>  | 14. <u>C</u> |
| 5. <u>F</u>  | 15. <u>D</u> |
| 6. <u>C</u>  | 16. <u>B</u> |
| 7. <u>B</u>  | 17. <u>C</u> |
| 8. <u>D</u>  | 18. <u>A</u> |
| 9. <u>C</u>  | 19. <u>B</u> |
| 10. <u>E</u> | 20. <u>D</u> |
| 21. <u>E</u> |              |
| 22. <u>C</u> |              |



## Kinetics

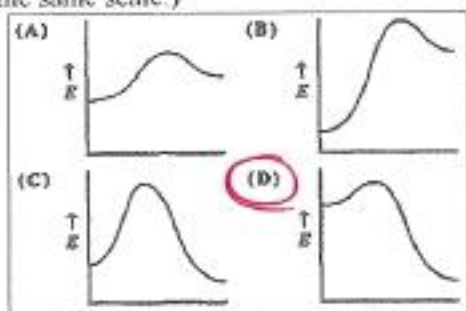
### NChO Practice Problems

1999 NChO Exam *Rate = k[A]<sup>1</sup>[B]<sup>2</sup>*

28. The rate of a reaction with just two reactants is observed to double when the concentration of one reactant is doubled and the second reactant is held constant. The rate is also observed to increase by a factor of nine when the concentration of the second reactant is tripled, holding the concentration of the first reactant constant. What is the overall order for this reaction?

- (A) 2 (C) 5  
(B) 3 (D) 6

29. Which energy diagram represents a highly exothermic reaction that has a small activation energy? (Assume that all curves are plotted on the same scale.)



30. Tritium decays by a first-order process that has half-life of 12.5 years. How many years will it take to reduce the radioactivity of a tritium sample to 15% of its original value?

- (A) 64 y (C) 34 y  
(B) 54 y (D) 24 y

31. What is the overall order of a reaction with a rate constant having the units  $L \cdot mol^{-1} \cdot s^{-1}$ ?

- (A) 0 (C) 2 *as we learned in class.*  
(B) 1 (D) 3

32. In a reaction with several steps, which step limits the rate of the reaction? *Rate Determining step*

- (A) first (C) fastest  
(B) last (D) slowest

### 1998 NChO Exam



What is the ratio of the rate of decomposition of  $N_2O_5$  to the rate of the formation of  $NO_2$ ?

- (A) 1:2 (C) 1:4 *2:4*  
(B) 2:1 (D) 4:1 *≈ 1:2*

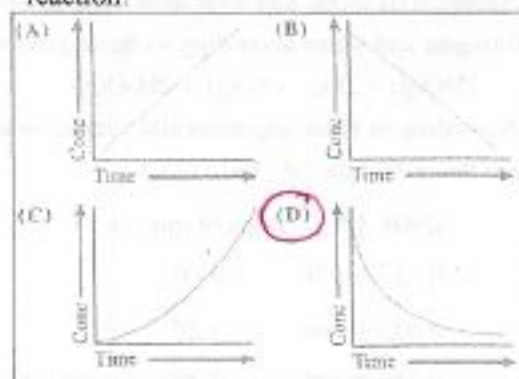
28. When reacted with water, the insecticides DDT decomposes with a half-life of 10 years. Approximately how many years will it take for 99% of a given sample to decompose once exposed to water in the environment?

- (A) 50 yr (C) 500 yr  
(B) 70 yr (D) 700 yr

29. Which property, if decreased, will cause an increase in the rate of a reaction involving a solid? *more surface area*

- (A) temperature (C) concentration  
(B) pressure (D) particle size

30. Which graph corresponds to the change in concentration of a reactant that is a first order reaction?



31. Which reaction characteristics are changing by the addition of a catalyst to a reaction at constant temperature?

- activation energy *YES*
  - equilibrium concentrations *NO CHANGE*
  - reaction enthalpy *ΔH, NO CHANGE*
- (A) 1 only (C) 1 and 2 only  
(B) 3 only (D) 1, 2, and 3



1997 NChO Exam

27. A plot of reactant concentration versus time gives a straight line. What is the order of the reaction for this reactant?

- (A) zero (C) second  
(B) first (D) some other value

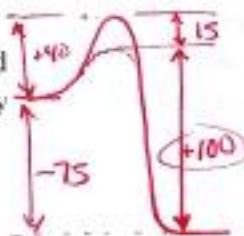
28. Which change does not increase the value of the rate constant for a reaction?

- (A) decreasing the activation energy  
(B) raising the temperature  
(C) adding a catalyst  
(D) increasing the concentration of reactants

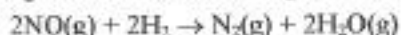
THOSE CHANGE "k"

29. A certain reaction has a  $\Delta H = -75$  kJ and an activation energy of 40 kJ. A catalyst is found that lowers the activation energy of the forward reaction by 15 kJ. What is the activation energy of the reverse reaction in the presence of this same catalyst?

- (A) 25 kJ (C) 90 kJ  
(B) 60 kJ (D) 100 kJ



30. Nitrogen(II) oxide and hydrogen react to form nitrogen and water according to this equation.



According to these experimental results, what are the orders for NO and H<sub>2</sub>?

[NO]	[H <sub>2</sub> ]	Rate (M min <sup>-1</sup> )
0.015	0.020	0.60
0.015	0.040	1.20
0.030	0.020	2.40

$[\text{H}_2] \times 2$  Rate  $\times 2$   
 $[\text{NO}] \times 2$  Rate  $\times 4$

$[\text{H}_2]^1$  1ST ORDER

$[\text{NO}]^2$  2ND ORDER

Answer 2, 1

Order, NO Order, H<sub>2</sub>

- (A) 1 1  
(B) 1 2  
(C) 2 1  
(D) 2 2

31. At a certain temperature the first-order decomposition of hydrogen peroxide exhibits these data.

time (seconds, s)	[H <sub>2</sub> O <sub>2</sub> ](mol L <sup>-1</sup> )
0	2.0
15	1.0

At what time will the [H<sub>2</sub>O<sub>2</sub>] = 0.50 mol L<sup>-1</sup>?

- (A) 30 s (C) 22 s  
(B) 25 s (D) 20 s

Answers to the Practice FRQ:

Practice FRQ

a) Expt  $\frac{2}{1}$   $[I^-]$   $\frac{.052}{.017}$   $[CeO^-]$  same Rate  $\frac{.474}{.156}$  order = 1  
 i)  $[I^-]$  "x3" "x3"

ii)  $CeO^-$   
 Expt  $\frac{3}{1}$   $[I^-]$   $\frac{same}{x1}$   $[CeO^-]$  4x Rate  $\frac{.594}{.154} \times 4$  order = 1

b) (i) Rate = k  $[I^-][CeO^-]$

(ii)  $k = \frac{Rate}{[I^-][CeO^-]} = \frac{.156 \text{ M} \cdot \text{s}^{-1}}{(.017)(.015) \text{ M}^2} = \boxed{611.7 \text{ M}^{-1} \cdot \text{s}^{-1}}$   
 $= \boxed{610 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}}$

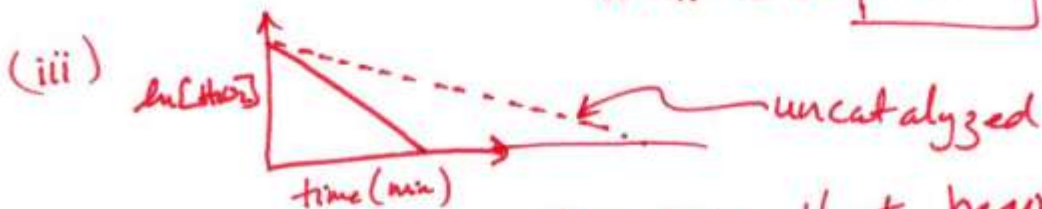
c) First order is a straight line if  $y = \ln [H_2O_2]$

(i)  $\ln [H_2O_2]$

(ii) Rate = k  $[H_2O_2]$

$k = \frac{Rate}{[H_2O_2]} = \frac{\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \text{ min}^{-1}}{\text{mol} \cdot \text{L}^{-1}}$

units =  $\boxed{\text{min}^{-1}}$



Any line that begins at the same point and takes more time to react.