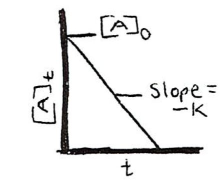
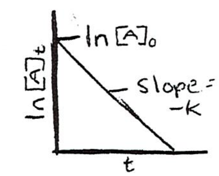
Chapter 12

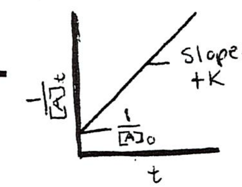
Kinetics

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$ *Units for k M/s*	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = k [A]	$\ln[A] = \ln[A]_0 - kt$ Units for k s-1	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = k $[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ *Units for k 1/M•s*	$t_{1/2} = \frac{1}{k[A]_0}$







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• Kinetics

Graphical Methods of Determining Reaction Order and the Rate Constant

First-Order Reactions: (rate is directly proportional to the concentration)

$$\text{Rate} = -\frac{\Delta[R]}{\Delta t} = k[R]$$

using calculus, as the Δt approaches 0, the Rate equation becomes

$$ln\left(\frac{[R]_o}{[R]_t}\right) = kt$$

which can be rearranged into the "y = mx + b" format

$$ln[R]_t = -kt + ln[R]_o$$

so… IF the reaction is **first-order** with respect to R,
plotting ***ln*[R]$_t$ versus time** results in a straight line with **k = -slope**

Summary:

Order	Rate Equation	Integrated Rate Equation	Straight Line Plot	Slope	k Units
0	Rate = $k[R]^0$	$[R]_o - [R]_t = kt$	$[R]_t$ *vs. t*	$-k$	mol/L·s
1	Rate = $k[R]^1$	$ln([R]_o/[R]_t) = kt$	$ln[R]_t$ *vs. t*	$-k$	s^{-1}
2	Rate = $k[R]^2$	$(1/[R]_t) - (1/[R]_o) = kt$	$1/[R]_t$ *vs. t*	k	L/mol·s
			memorize this!		

Second-Order Reactions	Zero-Order Reactions:
$\text{Rate} = -\frac{\Delta[R]}{\Delta t} = k[R]^2$	$\text{Rate} = -\frac{\Delta[R]}{\Delta t} = k[R]^0$
$\frac{1}{[R]_t} - \frac{1}{[R]_o} = kt$	$[R]_o - [R]_t = kt$
$1/[R]_t = kt - (1/[R]_o)$	$[R]_t = -kt + [R]_o$

Half-Life and First-Order Reactions: ***(radioactivity is a first-order reaction)***

Recall (from the Nuclear Chemistry chapter) the special case of half-life ($t_{½}$)

$$ln\left(\frac{[R]_o}{[R]_t}\right) = kt \text{ becomes } ln(2) = kt_{½}$$

$$ln(2) = 0.693$$

so… $k = 0.693/t_{½}$ and $t_{½} = 0.693/k$

Practice Problem:

Data for the decomposition of N_2O_5 in a particular solvent at 45°C are as follows:

$[N_2O_5]$ (mol/L)	*t* (min)
2.08	3.07
1.67	8.77
1.36	14.45
0.72	31.28

$ln[N_2O_5]$	$1/[N_2O_5]$

Plot $[N_2O_5]$, $ln[N_2O_5]$, and $1/[N_2O_5]$ versus time, *t*.
What is the order of the reaction? What is the rate constant, *k*, for the reaction?

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RATE LAWS

1. Consider the reaction: $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

The following data were obtained from three experiments using the method of initial rates:

	Initial [NO] mol L^{-1}	Initial [O_2] mol L^{-1}	Initial rate NO mol $L^{-1}s^{-1}$
Experiment 1	0.010	0.010	2.5×10^{-5}
Experiment 2	0.020	0.010	1.0×10^{-4}
Experiment 3	0.010	0.020	5.0×10^{-5}

a. Determine the order of the reaction for each reactant.

b. Write the rate equation for the reaction.

c. Calculate the rate constant.

d. Calculate the rate (in mol $L^{-1}s^{-1}$) at the instant when [NO] = 0.015 mol L^{-1} and [O_2] = 0.0050 mol L^{-1}

e. At the instant when NO is reacting at the rate 1.0×10^{-4} mol $L^{-1}s^{-1}$, what is the rate at which O_2 is reactant and NO_2 is forming?

2. The reaction $2\,NO(g) + 2\,H_2(g) \rightarrow N_2(g) + 2\,H_2O(g)$ was studied at 904 °C, and the data in the table were collected.

	Initial [NO] mol L^{-1}	Initial [H_2] mol L^{-1}	Initial rate N_2 mol $L^{-1}s^{-1}$
Experiment 1	0.420	0.122	0.136
Experiment 2	0.210	0.122	0.0339
Experiment 3	0.210	0.244	0.0678
Experiment 4	0.105	0.488	0.0339

a. Determine the order of the reaction for each reactant.

b. Write the rate equation for the reaction.

c. Calculate the rate constant at 904 °C.

d. Find the rate of appearance of N_2 at the instant when [NO] = 0.350 M and [H_2] = 0.205 M.

3. The reaction of ^{t}butyl-bromide $(CH_3)_3CBr$ with water is represented by the equation:

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

The following data were obtained from three experiments using the method of initial rates:

	Initial [$(CH_3)_3CBr$] mol L^{-1}	Initial [H_2O] mol L^{-1}	Initial rate mol $L^{-1}min^{-1}$
Experiment 1	5.0×10^{-2}	2.0×10^{-2}	2.0×10^{-6}
Experiment 2	5.0×10^{-2}	4.0×10^{-2}	2.0×10^{-6}
Experiment 3	1.0×10^{-1}	4.0×10^{-2}	4.0×10^{-6}

a. What is the order with respect to $(CH_3)_3CBr$?

b. What is the order with respect to H_2O?

c. What is the overall order of the reaction?

d. Write the rate equation.

e. Calculate the rate constant, k, for the reaction.

CHAPTER 12 QUESTIONS

MULTIPLE-CHOICE QUESTIONS

Questions 1–3

$$A + B \rightarrow C$$

The following are possible rate laws for the hypothetical reaction given above.

(A) Rate = $k[A]$
(B) Rate = $k[A]^2$
(C) Rate = $k[A][B]$
(D) Rate = $k[A]^2[B]$
(E) Rate = $k[A]^2[B]^2$

1. This is the rate law for a first order reaction.

2. This is the rate law for a reaction that is second order with respect to B.

3. This is the rate law for a third order reaction.

Questions 4–6

$$A + B \rightarrow C$$

The following are possible rate laws for the hypothetical reaction given above.

(A) Rate = $k[A]$
(B) Rate = $k[B]^2$
(C) Rate = $k[A][B]$
(D) Rate = $k[A]^2[B]$
(E) Rate = $k[A]^2[B]^2$

4. When [A] and [B] are doubled, the initial rate of reaction will increase by a factor of eight.

5. When [A] and [B] are doubled, the initial rate of reaction will increase by a factor of two.

6. When [A] is doubled and [B] is held constant, the initial rate of reaction will not change.

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PROBLEMS

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

The following results were obtained in experiments designed to study the rate of the reaction above:

Experiment	Initial Concentration (mol/L) [A]	[B]	Initial Rate of Disappearance of A (M/sec)
1	0.05	0.05	3.0×10^{-3}
2	0.05	0.10	6.0×10^{-3}
3	0.10	0.10	1.2×10^{-2}
4	0.20	0.10	2.4×10^{-2}

(a) Determine the order of the reaction with respect to each of the reactants, and write the rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include the units.

(c) If another experiment is attempted with [A] and [B], both 0.02-molar, what would be the initial rate of disappearance of A?

(d) The following reaction mechanism was proposed for the reaction above:

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

(i) Show that the mechanism is consistent with the balanced reaction.

(ii) Show which step is the rate-determining step, and explain your choice.

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

The following results were obtained in experiments designed to study the rate of the reaction above:

Experiment	Initial Concentration (mol/L) [NO]	$[Br_2]$	Initial Rate of Appearance of NOBr (M/sec)
1	0.02	0.02	9.6×10^{-2}
2	0.04	0.02	3.8×10^{-1}
3	0.02	0.04	1.9×10^{-1}

(a) Write the rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include the units.

(c) In experiment 2, what was the concentration of NO remaining when half of the original amount of Br_2 was consumed?

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(d) Which of the following reaction mechanisms is consistent with the rate law established in (a)? Explain your choice.

I. $NO + NO \rightleftharpoons N_2O_2$ (fast)

$N_2O_2 + Br_2 \rightarrow 2\,NOBr$ (slow)

II. $Br_2 \rightarrow Br + Br$ (slow)

$2(NO + Br \rightarrow NOBr)$ (fast)

3. $N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

Dinitrogen pentoxide gas decomposes according to the equation above. The first-order reaction was allowed to proceed at 40°C and the data below were collected.

$[N_2O_5]$ (M)	Time (min)
0.400	0.0
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(a) Calculate the rate constant for the reaction using the values for concentration and time given in the table. Include units with your answer.

(b) After how many minutes will $[N_2O_5]$ be equal to 0.350 M?

(c) What will be the concentration of N_2O_5 after 100 minutes have elapsed?

(d) Calculate the initial rate of the reaction. Include units with your answer.

(e) What is the half-life of the reaction?

4. $2A + B \rightarrow C + D$

The following results were obtained in experiments designed to study the rate of the reaction above:

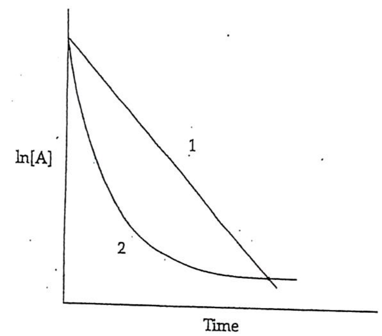
Experiment	Initial Concentration (moles/L) [A]	[B]	Initial Rate of Formation of D (M/min)
1	0.10	0.10	1.5×10^{-3}
2	0.20	0.20	3.0×10^{-3}
3	0.20	0.40	6.0×10^{-3}

(a) Write the rate law for the reaction.

(b) Calculate the value of the rate constant, k, for the reaction. Include the units.

(c) If experiment 2 goes to completion, what will be the final concentration of D? Assume that the volume is unchanged over the course of the reaction and that no D was present at the start of the experiment.

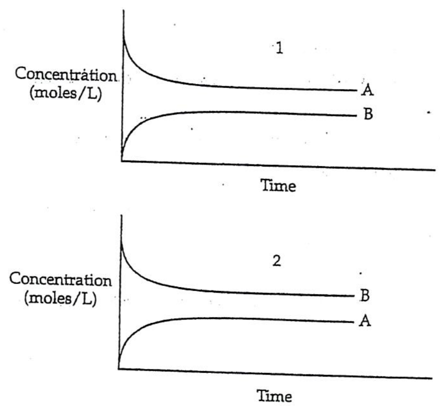
(c)



Which of the two lines in the diagram above shows the relationship of ln[A] to time for a first-order reaction with the following rate law?

$$\text{Rate} = k[\text{A}]$$

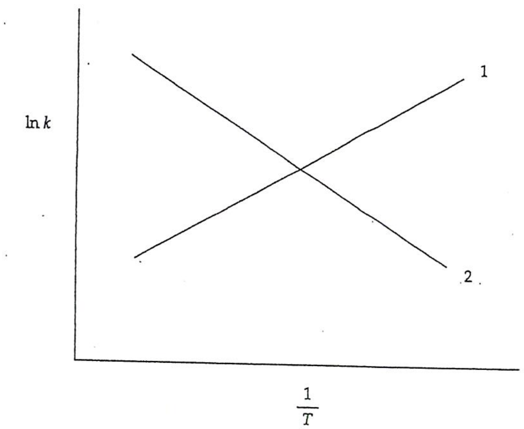
(d)



Which of the two graphs above shows the changes in concentration over time for the following reaction?

$$\text{A} \rightarrow \text{B}$$

(e)



Which of the two lines in the diagram above shows the relationship of $\ln k$ to $\frac{1}{T}$ for a reaction? How is the slope of the line related to the activation energy for the reaction?

7. Use your knowledge of kinetics to explain each of the following statements:

(a) An increase in the temperature at which a reaction takes place causes an increase in reaction rate.

(b) The addition of a catalyst increases the rate at which a reaction will take place.

(c) A catalyst that has been ground into powder will be more effective than a solid block of the same catalyst.

(d) Increasing the concentration of reactants increases the rate of a reaction.

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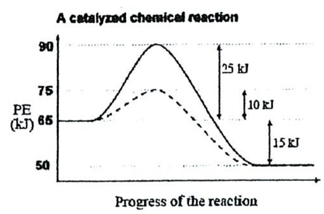
Name ______________________________

AP Chemistry Chapter 12 Kinetics review

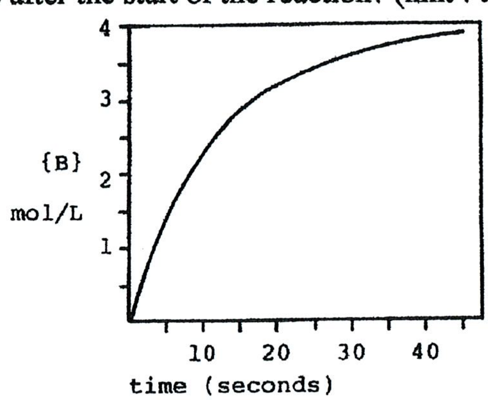
1. Which of the following does NOT influence the speed of a chemical reaction?
   a) concentration of reactants
   b) nature of reactants
   c) temperature
   d) presence of a catalyst
   e) none of these

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



   a) increasing the ΔH
   b) decreasing the temperature
   c) increasing the surface area
   d) addition of a catalyst
   e) 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? (hint : tangent)



   a) 0.050 mol/L·s
   b) 3.2 mol/L·s
   c) 2.2 mol/L·s
   d) 0.010 mol/L·s
   e) 9.8 mol/L·s

(8)

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?

a) 0.60   d) 0.90
b) 0.40   e) 1.20
c) 0.10

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

a) 0   b) 2   c) 1   d) 4   e) 3

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

a) mol/L·s   d) $L^2/mol^2 \cdot s$
b) 1/s   e) $mol^2/L^2 \cdot s$
c) L/mol·s

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 6.1×10^{-2} L/mol·s. What is the rate of reaction when $[I^-] = 0.10$ M and $[OCl^-] = 0.20$ M?

a) 2.4×10^{-4} M/s   d) 1.2×10^{-4} M/s
b) 1.2×10^{-3} M/s   e) 2.4×10^{-5} M/s
c) 6.1×10^{-3} M/s

8. A reaction and its rate law are given below. When $[C_4H_6] = 2.0$ M, the rate is 0.106 M/s. What is the rate when $[C_4H_6] = 4.0$ M?

$2\ C_4H_6 \rightarrow C_8H_{12}$ Rate = $k[C_4H_6]^2$

a) 0.053 M/s   d) 0.424 M/s
b) 0.212 M/s   e) 0.022 M/s
c) 0.106 M/s

9. The rate law for the reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

is Rate = $k[NO]^2[O_2]$. 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

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

Experiment	$[A]_o$	$[B]_o$	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) Rate = k[A][B]
b) Rate = k[A]^2[B]
c) Rate = k[A][B]^2
d) Rate = k[A]^2[B]^2
e) Rate = k[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 H_2O_2 450 minutes after the reaction begins?

$2H_2O_2 \rightarrow 2H_2O + O_2$ $k = 1.33 \times 10^{-4}$ min^{-1}

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

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

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

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

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

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

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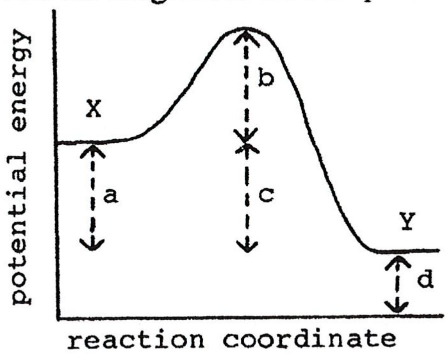
Use the Diagram to answer questions 16-19



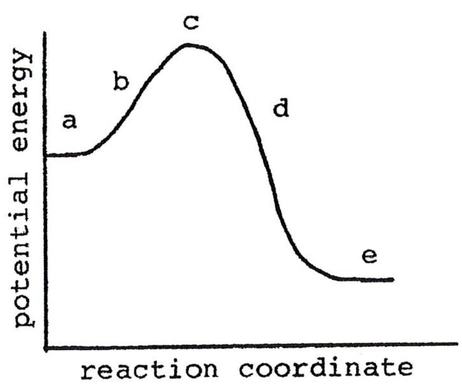
16. What distance corresponds to the activation energy for the reaction of X to Y? __________

17. What letter represents the Reactants? __________

18. What letter represents the products? __________

19. What letter represents the enthalpy for this reaction? ______________

20. 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

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