## **KINETICS**

#### QUESTIONS

# **Multiple-Choice**

Ouestions 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 =  $k[A]^2[B]^2$
- 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.

A multistep reaction takes place by the following mechanism.

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

Which of the species shown above is an intermediate in the reaction?

- (A) A
- (B) B
- (C) C
- (D) D
- (E) E
- 8.  $2 \text{ NOCl} \rightarrow 2 \text{ NO} + \text{Cl}_2$

The reaction above takes place with all of the reactants and products in the gaseous phase. Which of the following is true of the relative rates of disappearance of the reactants and appearance of the products?

- (A) NO appears at twice the rate that NOCl disappears.
- (B) NO appears at the same rate that NOCl disappears.
- (C) NO appears at half the rate that NOCl disappears.
- (D) Cl<sub>2</sub> appears at the same rate that NOCl disappears.
- (E) Cl<sub>2</sub> appears at twice the rate that NOCl disappears.

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

When the reaction given above takes place in a sealed isothermal container, the rate law is:

Rate = 
$$k[H_{*}][I_{*}]$$

If a mole of H<sub>2</sub> gas is added to the reaction chamber, which of the following will be true?

- (A) The rate of reaction and the rate constant will increase.
- (B) The rate of reaction and the rate constant will not change.
- (C) The rate of reaction will increase and the rate constant will decrease.
- (D) The rate of reaction will increase and the rate constant will not change.
- (E) The rate of reaction will not change and the rate constant will increase.
- 10.  $A + B \rightarrow C$

When the reaction given above takes place, the rate law is:

Rate = k[A]

If the temperature of the reaction chamber were increased, which of the following would be true?

- (A) The rate of reaction and the rate constant will increase.
- (B) The rate of reaction and the rate constant will not change.
- (C) The rate of reaction will increase and the rate constant will decrease.
- (D) The rate of reaction will increase and the rate constant will not change.
- (E) The rate of reaction will not change and the rate constant will increase.

#### $A + B \rightarrow C$

Based on the following experimental data, what is the rate law for the hypothetical reaction given above?

Experiment	[A] (M)	[B] (M)	Initial Rate of Formation of C (mol/L-sec)
1	0.20	0.10	3 × 10 <sup>-2</sup>
2	0.20	0.20	$6 \times 10^{-2}$
3	0.40	0.20	$6 \times 10^{-2}$

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

#### 12.

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

The rate law for the hypothetical reaction shown above is as follows:

Rate = 
$$k[A]$$

Which of the following changes to the system will increase the rate of the reaction?

- I. An increase in the concentration of A
- II. An increase in the concentration of B
- III. An increase in the temperature
- (A) I only
- (B) I and II only
- (C) I and III only
- (D) II and III only
- (E) I, II, and III

$$A + B \rightarrow C$$

Based on the following experimental data, what is the rate law for the hypothetical reaction given above?

Experiment	[A] (M)	[B] (M)	Initial Rate of Formation of C (M/sec)
1	0.20	0.10	2.0 × 10 <sup>-6</sup>
2	0.20	0.20	$4.0 \times 10^{-6}$
3	0.40	0.40	$1.6 \times 10^{-5}$

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

$$A + B \rightarrow C$$

Based on the following experimental data, what is the rate law for the hypothetical reaction given above?

Experiment	[A] (M)	[B] (M)	Initial Rate of Formation of C (M/sec)
1	0.10	0.10	$1.5 \times 10^{-3}$
2	0.40	0.10	$6.0 \times 10^{-3}$
3	0.40	0.20	$2.4 \times 10^{-2}$

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

Time (Hours)	[A] M	[B] M
0	0.40	5.00
1	0.02	5.00
2	0.10	5.00
3	0.05	5.00

A reaction occurred in which A reacted with a large excess of B to form C. The concentrations of the reactants were measured periodically and recorded in the chart above. Based on the data in the chart, which of the following is the rate law for the reaction?

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

## **Problems**

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

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

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

- (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 will 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. 
$$2 \operatorname{NO}(g) + \operatorname{Br}_{2}(g) \rightarrow 2 \operatorname{NOBr}(g)$$

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

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

- (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, was consumed?
- (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)

$$N_2O_2 + Br_2 \rightarrow 2 \text{ NOBr}$$
 (slow)

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

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

3. 
$$2A+B\rightarrow C+D$$

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

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

- (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.
- (d) Which of the following possible reaction mechanisms is consistent with the rate law found in (a)?

I. 
$$A + B \rightarrow C + E$$
 (slow)

$$A + E \rightarrow D$$
 (fast)

II. 
$$B \rightarrow C + E$$
 (slow)

$$A + E \rightarrow F$$
 (fast)

$$A + F \rightarrow D$$
 (fast)

## Essays

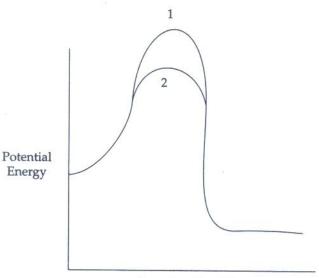
4.

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

The reaction above is second order with respect to A and zero order with respect to B. Reactants A and B are present in a closed container. Predict how each of the following changes to the reaction system will affect the rate and rate constant.

- (a) More gas A is added to the container.
- (b) More gas B is added to the container.
- (c) The temperature is increased.
- (d) An inert gas D is added to the container.
- (e) The volume of the container is decreased.
- 5. Use your knowledge of kinetics to answer the following questions.

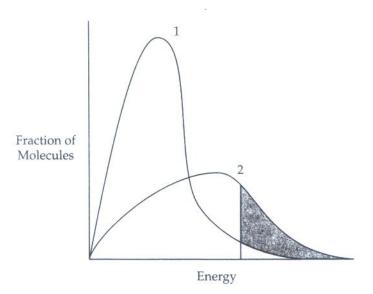
(a)



Reaction Coordinate

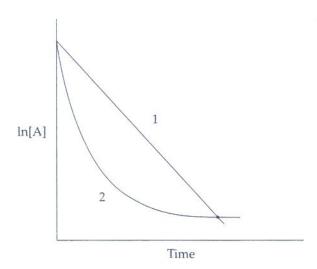
The two lines in the diagram above show different reaction pathways for the same reaction. Which of the two lines shows the reaction when a catalyst has been added? Explain.

(b)



Which of the two lines in the energy distribution diagram shows the conditions at a higher temperature?

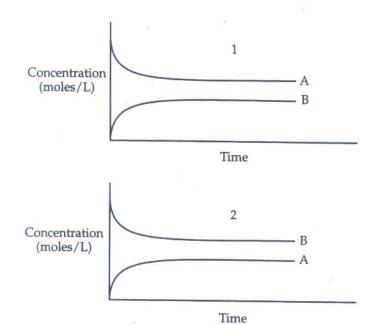
(c)



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:

Rate = 
$$k[A]$$

(d)



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

 $A \rightarrow B$ 

- 6. 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.

ANGWEDS AND EVELANATIONS

# **Practice Exercises**

## Multiple-Choice

Minetics Unit
Ap Avertions
#2 For the first four problems below, one or more of the following responses applies; each response may be used more than once or not at all in these questions.

- I. activation energy
- II. orientation
- III. potential energy curve
- IV. frequency
- V. activated complex
- 1. The heat of a reaction is best deduced from the
  - (A) I
  - (B) II
  - (C) III
  - (D) IV
  - (E) V

d

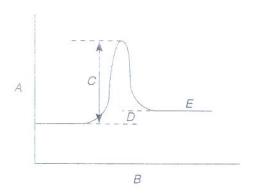
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- 2. The collision theory involves
  - (A) I and III
  - (B) II
  - (C) II and IV
  - (D) IV
  - (E) I, III, and V
- 3. The transition-state theory involves
  - (A) I and III
  - (B) III
  - (C) III and V
  - (D) IV
  - (E) I, III, and V

- 4. The rate of a chemical reaction is related to
  - (A) I and III
  - (B) II
  - (C) I, II, and IV
  - (D) IV
  - (E) I, III, and V
- 5. 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) a coordination state

- 6. A reaction in which the rate and the rate constant have the same units is
  - (A) a radioactive decay
  - (B) a second-order reaction
  - (C) a reaction with a one-step mechanism
  - (D) a first-order reaction
  - (E) a zero-order reaction

Questions 7-9 refer to the following diagram:



7. In the reaction profile, A, B, and C should be labeled as shown in

A

B

C

- (A) potential energy
- (B) heat of reaction
- (C) potential energy
- (D) heat of reaction
- (E) activation energy

reaction coordinate reaction coordinate

reaction coordinate

potential energy extent of reaction activation energy potential energy heat of reaction activation energy heat of reaction

- 8. In the reaction described by the reaction profile,
  - (A) forward  $E_a$  > reverse  $E_a$  and  $\Delta H$  is exothermic
  - (B) reverse  $E_a$  > forward  $E_a$  and  $\Delta H$  is endothermic
  - (C) forward  $E_a$  < reverse  $E_a$  and  $\Delta H$  is exothermic
  - (D) reverse  $E_a$  < forward  $E_a$  and  $\Delta H$  is endothermic
  - (E) reverse  $E_a$  = forward  $E_a$  and  $\Delta H$  is zero
- 9. Addition of a catalyst to the reaction mixture will affect only
  - (A) A
  - (B) B
  - (C) C
  - (D) D
  - (E) E

- 10. A fast reaction should have
  - (A) a high activation energy
  - (B) a catalyst present
  - (C) a large equilibrium constant
  - (D) a low activation energy
  - (E) an exothermic heat of reaction
- 11. Which of the following rate laws has a rate constant with units of L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>?
  - (A) Rate = k[A]
  - (B) Rate =  $k [A]^2$
  - (C) Rate = k [A] [B]
  - (D) Rate =  $k [A][B]^2$
  - (E) Rate =  $k [A]^0$
- 12. Which of the following is LEAST effective in increasing the rate of a reaction?
  - (A) increasing the pressure by adding an inert gas
  - (B) grinding a solid reactant into small particles
  - (C) increasing the temperature
  - (D) eliminating reverse reactions
  - (E) adding a catalyst
- 13. A first-order reaction has a half-life of 36 min. What is the value of the rate constant?
  - (A)  $3.2 \times 10^{-4} \,\mathrm{s}^{-1}$
  - (B)  $1.9 \times 10^{-3} \,\mathrm{L \, mol^{-1} \, s^{-1}}$
  - (C)  $1.2 \text{ s}^{-1}$
  - (D)  $0.028 \text{ s}^{-1}$
  - (E)  $9.3 \times 10^{-4} \,\mathrm{L \, mol^{-1} \, s^{-1}}$
- 14. 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) 0
  - (B) 1
  - (C) 2
  - (D) 3
  - (E) 1/2

- 15. If the temperature of a reaction is raised from 300 K to 320 K, the reaction rate will increase by a factor of approximately
  - (A)  $\frac{320 \text{ K}}{300 \text{ K}}$
  - (B)  $\frac{22^{\circ}C}{2^{\circ}C}$
  - (C) 4
  - (D) 2
  - (E) 20
- 16. 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)
- 17. The rate at which CO<sub>2</sub> is produced in the following reaction:

$$2C_6H_6(g) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(\ell)$$

- is  $2.2 \times 10^{-2}$  mol L<sup>-1</sup> s<sup>-1</sup>. What is the rate at which O<sub>2</sub> is consumed?
- (A)  $2.2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
- (B)  $1.3 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$
- (C)  $2.8 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$
- (D)  $1.8 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
- (E)  $-2.2 \times 10^{-2} \text{ mol } L^{-1} \text{ s}^{-1}$
- 18. Which of the following will be most helpful in determining the stability or shelf life of a new drug?
  - (A) the reaction mechanism for its decomposition
  - (B) the rate law for its decomposition
  - (C) the Arrhenius plot of the decomposition reaction
  - (D) the integrated rate law plot
  - (E) the overall chemical reaction

- 19. An Arrhenius plot is a graph of
  - (A) the rate constant versus concentration
  - (B) the natural logarithm (ln) of the rate constant versus concentration
  - (C) the reciprocal of the rate constant versus  $\ln T$
  - (D) the rate constant versus  $\ln (1/T)$
  - (E) the natural logarithm (ln) of the rate constant versus 1/T
- 20. A first-order reaction has a half-life of 85 s. What fraction of the reactant is left after 255 s?
  - $(A)^{-1}/2$
  - (B)  $^{1}/_{4}$
  - $(C)^{-1}/8$
  - (D)  $\frac{1}{3}$
  - $(E)^{-7}/8$
- 21. A rate law is found to be

Rate = 
$$k[A]^2[B]$$

The order of the reaction is

- (A) first order
- (B) second order
- (C) third order
- (D) fourth order
- (E) The rate order cannot be determined.

#### 22. A rate law is found to be

### Rate = $k[A]^2[B]$

Which of the following actions will NOT change the initial reaction rate?

- (A) doubling the concentrations of both A and B
- (B) doubling the concentration of A and halving the concentration of B
- (C) halving the concentration of A and doubling the concentration of B
- (D) halving the concentration of A and quadrupling the concentration of B
- (E) doubling the concentration of A and quadrupling the concentration of B
- 23. Using the rule of thumb that the reaction rate doubles for each 10°C, increase in temperature, estimate the shelf life (stability) of a new product at 25°C if it takes 2 days to decompose at 125°C.
  - (A) 2048 days
  - (B) 20 days
  - (C) 200 days
  - (D) 11,585 days
  - (E) 365 days
- 24. Modern automobiles use a catalytic converter to
  - (A) increase horsepower by burning more gasoline
  - (B) absorb pollutants from the exhaust
  - (C) complete the combustion of unburned gases
  - (D) cool the exhaust gases
  - (E) convert pollutants into water

# Free-Response

- (a) Sketch and label a potential energy diagram (reaction profile) and discuss its implications for chemical reactions. How does the addition of a catalyst alter the diagram? What effect will a change in temperature have?
- (b) Describe the collision theory.
- (c) Describe the transition-state theory.
- (d) How are rate laws and reaction mechanisms related?
- (e) Use the table of data below to determine the rate law for the reaction

$$3F + 2H \rightarrow P + 2S$$

Experimen	t Concentration F (mol/L)	Concentration H (mol/L)	Initial Reaction Rate (mol/L s)
1	0.000345	0.000765	3.24 × 10 <sup>-8</sup>
2	0.000690	0.000765	3.24 × 10 <sup>-8</sup>
3	0.000537	0.00765	3.24 × 10 <sup>-7</sup>

(f) Calculate the rate constant and give its units.

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