

Answers

Key

MULTIPLE-CHOICE QUESTIONS

- A** This is an example of an acid-catalyzed reaction. A catalyst is a reactant in the first step of the mechanism and a product in the last step of the mechanism. LO 4.9
- B** Activation energy is calculated by performing a reaction using the same concentrations of reactants at different temperatures. By graphing $\ln k$ vs $1/T$, E_a can be calculated from the slope (*Chemistry* 8th ed. pages 565–570/9th ed. pages 577–583). LO 4.6
- D** Chances that three particles will collide with correct energy and orientation is very rare so this reaction most likely involves at least one intermediate (*Chemistry* 8th ed. pages 562–565/9th ed. pages 574–577). LO 4.7
- B** The temperature and orientation are both favorable for a reaction to occur (*Chemistry* 8th ed. pages 565–567/9th ed. pages 577–579). LO 4.4
- B** At a given temperature, the free energy of particles remains constant. The enzyme lowers E_a so more of the particles have sufficient energy to overcome the energy barrier (*Chemistry* 8th ed. pages 570–576/9th ed. pages 583–588). LO 4.9
- C** Examine the diagram on p. 216. The E_a of the reverse reaction must equal the E_a of the forward reaction plus ΔH of the reaction (*Chemistry* 8th ed. pages 565–568/9th ed. pages 577–581). LO 4.6
- D** It takes half as much time for A to form B as for X to form Y, as seen by the smaller half-life. Note that option "B" would be incorrect as the grams of A and the grams of X are not the same number of moles (*Chemistry* 8th ed. pages 555–556/9th ed. pages 567–568). LO 4.3
- B** From these data, it follows that the rate law is $\text{Rate} = k[X][Y]^2$. Solving for the rate constant and substituting data for this reaction:

$$k = \text{Rate} / [X][Y]^2$$

$$= 8.00 \times 10^{-3} \text{ M/min} / (0.200 \text{ M})(0.200 \text{ M})^2$$

$$= 0.008 \text{ M/min} / 0.008 \text{ M}^3$$

$$= 1.00 \text{ M}^{-2} \text{ min}^{-1}$$
 (*Chemistry* 8th ed. pages 548–554, 562/9th ed. pages 560–566, 574) LO 4.2
- D** Adding a catalyst suitable for this reaction will lower the energy barrier (activation energy) by forming a different activated complex which has a lower potential energy (*Chemistry* 8th ed. pages 565–572/9th ed. pages 577–585). LO 4.8

10. **D** For zero-order reactions, $\text{Rate} = k[X]^0$. Because anything raised to the zero power is equal to one, $\text{Rate} = k$. This is another way of saying that the rates of zero-order reactions do not change; they do not speed up and they do not slow down, they either take place or they do not (*Chemistry* 8th ed. page 559/9th ed. page 571). LO 4.2
11. **D** Compare experiments 1 and 2, doubling the concentration of CO has caused the initial rate to increase by a factor of 4 or 2^2 . Therefore $m = 2$. And comparing experiments 1 and 3, doubling the concentration of O_2 , keeping the $[CO]$ the same, resulted in the initial rate also being doubled, or 2^1 . Therefore $n = 1$ (*Chemistry* 8th ed. pages 549–551/9th ed. pages 561–563). LO 4.2
12. **D** The overall order is simply the sum of $m + n$ or $2 + 1 = 3$ (*Chemistry* 8th ed. pages 549–551/9th ed. pages 561–563). LO 4.2
13. **B** Using experiment 1, $\text{rate} = k[CO]^2[O_2]$; $3.68 \times 10^{-5} = k(0.020)^2(0.020)$
- Solving for k , $k = 4.60 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$.
- (*Chemistry* 8th ed. pages 549–551/9th ed. pages 561–563) LO 4.2
14. **B** According to the balanced equation 2 moles of H_2 are used up for every mole of O_2 , so during the same time period, the rate of disappearance of the H_2 would be twice as great (*Chemistry* 8th ed. pages 540–545/9th ed. pages 553–557). LO 4.1
15. **C** Collision theory states that the molecules colliding must not only have the minimum combined activation energy required for reaction, they must also have the proper spatial orientation when they collide (*Chemistry* 8th ed. pages 565–568/9th ed. pages 577–581). LO 4.5

FREE-RESPONSE QUESTIONS

1. (a) To determine how each of the concentrations of the reactants is related to the reaction rate, only the one reactant concentration may change.
- (i) Compare $[A]_0$ in Trial 1 and 3. Doubling the concentration increases the rate by a factor of about 4 which indicates the reaction is second order in A. Compare $[B]_0$ in Trials 1 and 2. Doubling the concentration doubles the rate which means that the reaction is first order in B.

$$\text{Rate} = k[A]^x[B]^y$$

$$\text{Trial 1} \quad 0.332 = k[0.040]^x[0.060]^y$$

$$\text{Trial 3} \quad 1.32 = k[0.080]^x[0.060]^y$$

$$0.252 = 0.5^x$$

$$x = 2$$

$$\begin{array}{l} \text{Trial 1} \quad 0.332 = k(0.040)^2(0.060)^y \\ \text{Trial 2} \quad 0.662 = k(0.040)^2(0.12)^y \end{array}$$

$$\begin{array}{l} 0.502 = 0.50^y \\ y = 1 \end{array}$$

(ii) The rate law is rate = $k[A]^2[B]$.

(b) Solving the rate law for k yields:

$$\begin{aligned} k &= \text{Rate}/([A]^2[B]) \\ &= 0.332 \text{ mol L}^{-1} \text{ min}^{-1} / (0.040 \text{ mol L}^{-1})^2(0.060 \text{ mol L}^{-1}) \\ &= 3.5 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1} \end{aligned}$$

(c) $-1/2\Delta[B]/\Delta t = \Delta[C]/\Delta t$

$$\begin{aligned} \Delta[B]/\Delta t &= -2\Delta[C]/\Delta t \\ &= (-2)(1.32 \text{ mol L}^{-1} \text{ min}^{-1}) \\ &= -2.64 \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

(d) (i) Intermediates are X and Y because they are made in one step and used in the next. There are no catalysts.

(ii) The rate law must match the rate determining step. Step 1 cannot be the RDS because that rate law would be rate = $k[A]^2$ which does not match the experimentally determined rate law.

The rate law for Step 2 would be rate = $k[X][B]$. At first glance this does not appear to agree with the experimental rate law, either. However, intermediates are not included in the rate law. Since the first reaction is an equilibrium rate forward = rate reverse.

$$\text{Rate} = k_f[A]^2 = k_r[X]$$

$$[X] = k_f[A]^2 / k_r$$

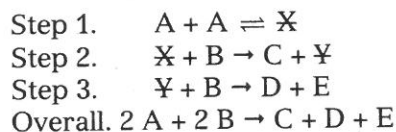
$$k_f / k_r = k'$$

$$[X] = k'[A]^2$$

Substituting into the rate law for the RDS,

$$\text{Rate} = k_2 k'[A]^2[B] \text{ or } \text{Rate} = k[A]^2[B]$$

(iii) The experimental rate law and the rate law of the slowest step are the same. The overall stoichiometry of the mechanism is the same as reaction which indicates the mechanism is plausible,



(Chemistry 8th ed. pages 547–565/9th ed. pages 559–577)
LO 4.2, LO 4.7