Reflect on Your Learning

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1. (a) Some possibilities include increasing temperature, using a higher concentration of reactants, increasing the surface area of the reactants if the system is heterogeneous, or adding a catalyst.
   (b) Examples are, respectively: cooking food, using concentrated acid, starting a campfire with twigs, and using industrial catalysts.
2. Answers will vary but the mechanism of the reaction involves collisions of octane and oxygen molecules in which single carbon–carbon and single carbon–hydrogen bonds are broken in succession down the hydrocarbon chain with reformation of bonds to form carbon dioxide and water molecules.
3. Some reactant molecules have complex structures and strong chemical bonds which make reaction more difficult. Other reactions involve simple ions or molecules with weak or unstable chemical bonds in which most collisions result in reaction. Some reactions produce large amounts of heat that accelerate further reaction.

Try This Activity: Slowing the Browning Process

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(a) Apples react with oxygen from the air.
(b) The lemon juice is an antioxidant that slows the reaction.
(c) Temperature is the variable.
(d) Reducing the concentration of a reactant is investigated.
(e) Lemon juice, refrigeration, and removal of oxygen should all reduce rate.

6.1   RATE OF REACTION

PRACTICE

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Understanding Concepts

1. $r = \dfrac{\Delta c}{\Delta t}$

   $= \dfrac{(0.200 \text{ mol/L})}{40 \text{ s}}$

   $r = 0.0050 \text{ mol/(L} \cdot \text{s)}$

2. $r = \dfrac{\Delta c}{\Delta t}$

   $= \dfrac{(0.60 \text{ mol/L})}{5 \text{ min}}$

   $r = 0.12 \text{ mol/(L} \cdot \text{min)}$

PRACTICE

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Understanding Concepts

3. Rate of reaction with respect to
   $Fe^{+2}_{(aq)}$ consumption is 2.0×10^{-1} mol $Fe^{+2}_{(aq)}$/(L•min)

   $H^{+}_{(aq)}$ consumption is 3.2×10^{-1} mol $H^{+}_{(aq)}$/(L•min)

$Mn_{(aq)}^{+2}$ production is 4.0×10^{-2} mol $Mn_{(aq)}^{+2}/(L \cdot min)$

$Fe_{(aq)}^{+3}$ production is 2.0×10^{-1} mol $Fe_{(aq)}^{+3}/(L \cdot min)$

$H_2O_{(l)}$ production is 1.6×10^{-1} mol $H_2O_{(l)}/(L \cdot min)$

2. (a) $\dfrac{\Delta[O_{2(g)}]}{\Delta t} = \dfrac{5}{4} \times 2.0 \times 10^{-2}$ mol $O_{2(g)}/(L \cdot s)$

$= 2.5 \times 10^{-2}$ mol $O_{2(g)}/(L \cdot s)$

(b) $\dfrac{\Delta[H_2O_{(g)}]}{\Delta t} = \dfrac{6}{4} \times 2.0 \times 10^{-2}$ mol $H_2O_{(g)}/(L \cdot s)$

$= 3.0 \times 10^{-2}$ mol $H_2O_{(g)}/(L \cdot s)$

3. (a) Rate of production of NO_2:

$+\dfrac{\Delta[NO_2]}{\Delta t} = 4.0 \times 10^{-3}$ mol $NO_2/(L \cdot s)$

(b) Rate of consumption of NO:

$-\dfrac{\Delta[NO]}{\Delta t} = 4.0 \times 10^{-3}$ mol $NO/L \cdot s$

Rate of consumption of O_2:

$-\Delta\dfrac{[O_2]}{\Delta t} = 2.0 \times 10^{-3}$ mol $O_2/(L \cdot s)$

4. $2 NaHCO_3 + H_2SO_4 \rightarrow 2 CO_{2(g)} + 2 H_2O_{(l)} + Na_2SO_4$
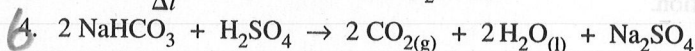
(a) Rate of consumption of $NaHCO_3$:

$\dfrac{\Delta m}{\Delta t} = 3.25$ g $NaHCO_3/20$ s

$\dfrac{\Delta m}{\Delta t} = 0.16(3)$ g $NaHCO_3/s$

(b) $n_{NaHCO_3} = 3.25g \times \dfrac{1 \text{ mol}}{84.0 \text{ g}}$

$n_{NaHCO_3} = 0.0387$ mol

$n_{H_2SO_4} = 0.0387$ mol $NaHCO_3 \times \dfrac{1 \text{ mol } H_2SO_4}{2 \text{ mol } NaHCO_3}$

$n_{H_2SO_4} = 0.0193$ mol H_2SO_4

$m_{H_2SO_4} = 0.0193$ mol $\times \dfrac{98.1 \text{ g}}{1 \text{ mol}}$

$m_{H_2SO_4} = 1.89$ g H_2SO_4

Rate of consumption of H_2SO_4:

$\dfrac{\Delta m}{\Delta t} = \dfrac{1.89 \text{ g } H_2SO_4}{20 \text{ s}}$

$\dfrac{\Delta m}{\Delta t} = 0.095$ g H_2SO_4/s

(c) $\dfrac{n_{H_2SO_4}}{\Delta t} = \dfrac{0.0193 \text{ mol } H_2SO_4}{20 \text{ s}}$

$\dfrac{n_{H_2SO_4}}{\Delta t} = 9.7 \times 10^{-4}$ mol H_2SO_4/s

(d) $\dfrac{n_{CO_2}}{\Delta t} = \dfrac{0.0387 \text{ mol } CO_2}{20 \text{ s}}$

$\dfrac{n_{CO_2}}{\Delta t} = 1.9 \times 10^{-3}$ mol CO_2/s

PRACTICE

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Understanding Concepts

5. Pressure or volume (of gases), colour, conductivity, or pH (of solutions) could all be used to measure a reaction rate.
6. (a) colour (Permanganate is purple.)
   (b) pressure or volume of hydrogen gas
7. Concentrations of reactants are highest at the beginning of a reaction, and rate depends on concentrations.
8.

Change of Concentration Over Time
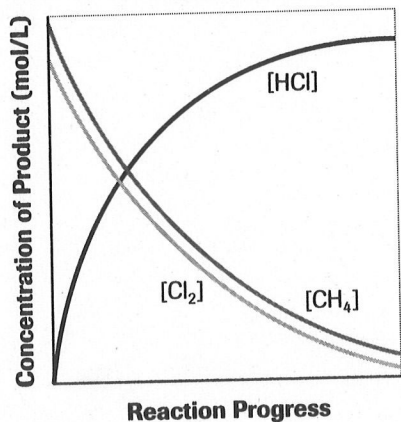
9. (a)
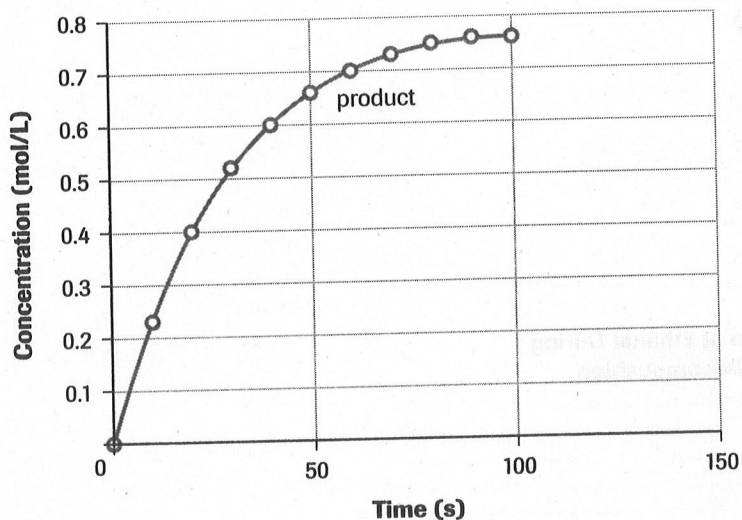
(b) $\dfrac{\Delta c_{\text{product}}}{\Delta t} = \dfrac{0.70 \text{ mol/L} - 0 \text{ mol/L}}{60 \text{ s} - 0 \text{ s}}$

$\dfrac{\Delta c_{\text{product}}}{\Delta t} = 0.011(7) \text{ mol/(L}\bullet\text{s)}$

(c) $\dfrac{\Delta c_{\text{product}}}{\Delta t} = \dfrac{0.70 \text{ mol/L} - 0.40 \text{ mol/L}}{60 \text{ s} - 20 \text{ s}}$

$\dfrac{\Delta c_{\text{product}}}{\Delta t} = 0.0075 \text{ mol/(L}\bullet\text{s)}$
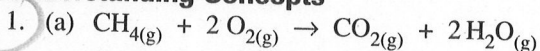
(d) $r = \dfrac{\Delta c_{product}}{\Delta t}$

$\quad = \dfrac{(0.40 - 0.13)\ \text{mol/L}}{(20 - 0)\ \text{s}}$

$\dfrac{\Delta c_{product}}{\Delta t} = 0.014\ \text{mol/(L} \cdot \text{s)}$

SECTION 6.1 QUESTIONS

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Understanding Concepts

1. (a) $CH_{4(g)} + 2\,O_{2(g)} \rightarrow CO_{2(g)} + 2\,H_2O_{(g)}$

Rate of consumption of methane:

$\dfrac{-\Delta[CH_4]}{\Delta t} = \dfrac{8.0\ \text{mol}}{2.00\ \text{L} \times 3.2\ \text{s}}$

$\dfrac{-\Delta[CH_4]}{\Delta t} = 1.2(5)\ \text{mol/(L} \cdot \text{s)}$

(b) Rate of consumption of oxygen:

$\dfrac{-\Delta[O_2]}{\Delta t} = \dfrac{2}{1} \times 1.2(5)\ \text{mol/(L} \cdot \text{s)}$

$\dfrac{-\Delta[O_2]}{\Delta t} = 2.5\ \text{mol/(L} \cdot \text{s)}$

(c) Rate of production of carbon dioxide:

$\dfrac{+\Delta[CO_2]}{\Delta t} = \dfrac{1}{1} \times 1.2(5)\ \text{mol/(L} \cdot \text{s)}$

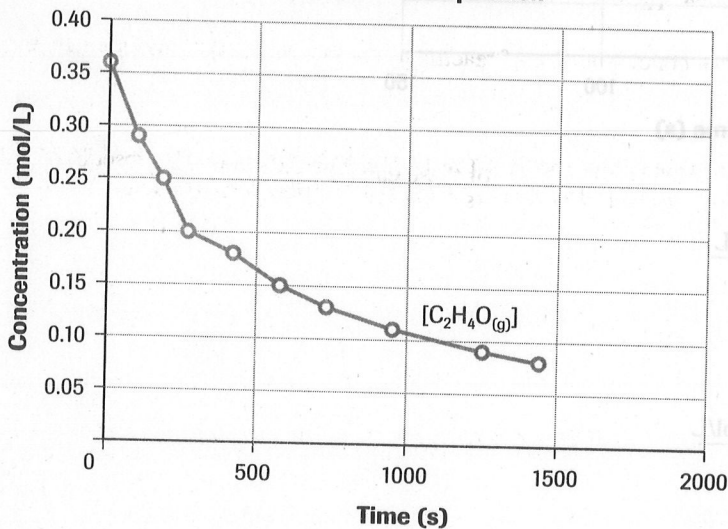$\dfrac{+\Delta[CO_2]}{\Delta t} = 1.2(5)\ \text{mol/(L} \cdot \text{s)}$

(d) Rate of production of water vapour:

$\dfrac{+\Delta[H_2O]}{\Delta t} = \dfrac{2}{1} \times 1.2(5)\ \text{mol/(L} \cdot \text{s)}$

$\dfrac{+\Delta[H_2O]}{\Delta t} = 2.5\ \text{mol/(L} \cdot \text{s)}$

2. (a)

Concentration of Ethanal During Thermal Decomposition

$[C_2H_4O_{(g)}]$

(b) $\text{rate}_{(t = 0 \text{ to } 420 \text{ s})} = \dfrac{(0.360 - 0.180) \text{ mol/L}}{(420 - 0) \text{ s}}$

$= 4.3 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$

(c) $\text{rate}_{(t = 420 \text{ to } 1250 \text{ s})} = \dfrac{(0.180 - 0.090) \text{ mol/L}}{(1250 - 420) \text{ s}}$

$= 1.1 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$

(d) Rate falls as the concentration of the reactant(s) falls.

(e) Extrapolation yields a value of about 2000 s.

(f) From slopes of the appropriate tangents, approximate rates are:

$\text{rate}_{(c = 0.20 \text{ mol/L})} = 2.8 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}$

$\text{rate}_{(c = 0.10 \text{ mol/L})} = 8.3 \times 10^{-5} \text{ mol/(L}\cdot\text{s)}$

Making Connections

3. (a) (Answers will vary.) Some possibilities include increasing temperature, using a higher concentration of reactants, increasing the surface area of the reactants if the system is heterogeneous, or adding a catalyst.
   (b) Examples are, respectively: baking a cake, using pure oxygen gas in an oxyacetylene torch, dust explosions, and using a catalyst disc in contact lens solution.
   (c) (Answers will vary, depending on individual student responses.)

6.2 FACTORS AFFECTING REACTION RATE

PRACTICE

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Understanding Concepts

1. The five factors are: the chemical nature of reactants (gold vs. sodium in water); temperature (burning wood); surface area (steel wool burning in pure oxygen); concentration (magnesium into dilute or concentrated acid); catalysis (manganese dioxide in hydrogen peroxide).
2. Only one factor — surface area — applies to heterogeneous systems (e.g., grain dust explodes whereas grain smoulders).
3. The rate would double or triple for each increase of 10°C; for a 20°C rise, the rate would increase by a factor of roughly 4 to 10 times.
4. Increased surface area increases reaction rate. The lump of coal has a very small surface area, compared to that of a similar mass of coal dust.
5. Possible leaks of these gases would increase concentrations of reactants, thus increasing the possible rate of combustion of fuels.

Making Connections

6. Enzymes are key catalysts in metabolic reactions. "Poisoning" of these catalysts can seriously upset body chemistry.
7. BHT is an antioxidant or inhibitor (negative catalyst) that decreases the rate of food decay reactions.

SECTION 6.2 QUESTIONS

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Understanding Concepts

1. (a) chemical nature of reactant
   (b) temperature
   (c) catalysis
   (d) surface area
   (e) concentration

2. Hydrochloric acid has a much higher concentration of reactive hydrogen ions in solution than carbonic acid. Most of the carbonic acid remains in solution undissociated.

Making Connections

3. To be suitable for starting a campfire, fuel should be flammable (chemical nature), and have a high surface area (more subdivided if a solid).

4. Heterogeneous catalysts are easier to separate from the products and reuse. Since many catalysts are very expensive, reuse is very important economically. For example, vanadium(V) oxide is a solid catalyst used in the industrial production of millions of tonnes of sulfuric acid; platinum is used in the manufacture of nitrogen dioxide, and so on.

5. Catalytic converters are used to remove carbon monoxide, VOCs (volatile organic compounds), and NOx (nitrogen oxides) from exhaust. Two separate types of catalysts, reduction and oxidation catalysts, are arranged in a honeycomb pattern. Nitrogen oxides are reduced to nitrogen and oxygen by the reduction catalyst. The oxidation catalyst changes carbon monoxide and unburned hydrocarbons (VOCs) into carbon dioxide and water.

6.3 RATE LAWS AND ORDER OF REACTION

PRACTICE

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Understanding Concepts

1. Order of reaction refers to the rate dependence or exponential index of one species in the rate law, whereas overall order is the sum of all the indices. If a rate law were $r = k[A][B]^2$, the order of reaction with respect to A would be 1, the order of reaction with respect to B would be 2, and the overall order would be 3.

2. This is a first-order reaction, so doubling the initial concentration should double the initial rate.

3. (a) $k = \dfrac{r}{([NH_{4(aq)}^+][NO_{2(aq)}^-])}$

   $= \dfrac{2.40 \times 10^{-7}\ mol/(L \bullet s)}{(0.200\ mol/L \times 0.00500\ mol/L)}$

   $k = 2.4 \times 10^{-4}\ L/(mol \bullet s)$

   (b) $r = k[NH_{4(aq)}^+][NO_{2(aq)}^-]$

   $= 3.20 \times 10^{-4}\ L/(mol \bullet s) \times 0.100\ mol/L \times 0.0150\ mol/L$

   $r = 4.8 \times 10^{-7}\ mol/(L \bullet s)$

4. (a) Rate is second order with respect to A, first order with respect to B, zeroth order with respect to C.
   (b) $r = k[A]^2[B]$

5. (a) The reaction rate constant increases.
   (b) The reaction rate constant is unchanged.

6. (a) When we compare Trials 1 and 2, we see that as [A] is doubled, rate is multiplied by 4; therefore, rate depends on $[A]^2$.
   When we compare Trials 1 and 3, we see that as [B] is tripled, rate is multiplied by 1; therefore, rate depends on $[B]^0$.
   When we compare Trials 2 and 4, we see that as [C] is doubled, rate is multiplied by 2; therefore, rate depends on $[C]^1$.
   (b) $r = k[A]^2[C]^1$

   (c) When we use data from Trial 1,

   $k = \dfrac{r}{[A]^2[C]}$

   $= \dfrac{3.0 \times 10^{-4}\ mol/(L \bullet s)}{(0.10\ mol/L)^2 \times 0.10\ mol/L}$

   $k = 0.30\ L^2/(mol^2 \bullet s)$