Section 1.1 Measuring the Rate of Chemical Reactions

Warm Up (page 2)

a) Rate = \( \frac{\text{Change in Distance}}{\text{Change in Time}} = \frac{125 \text{ km}}{100.0 \text{ min}} = 1.25 \text{ km/min} \)

b) \( 1.25 \text{ km} \times 60 \text{ min} = 75.0 \text{ km/h} \)

min \quad 1 \text{ h}

c) As can be seen in the data, the rate is not consistent. It changes.

d) A unit of time is always in the denominator.

Quick Check (page 3)
a) Rate of decomposition of SO$_2$Cl$_2$.
b) The slope becomes less and less steep.
c) The rate decreases as the reaction proceeds.
d) $\frac{0.060 \text{ mol/L} - 0.200 \text{ mol/L}}{600 \text{ seconds} - 0 \text{ seconds}} = -0.140 \text{ mol/L} = -0.00023 \text{ mol/L/s (or +)}$
e) Rate is greater at 300 s than at 500 s.
f) Find the slope of a tangent drawn to the curve at that time.
g) 500 s: $0.040 \text{ M} = 9.2 \times 10^{-5} \text{ M/s} < 300 \text{ s: } 0.100 \text{ M} = 2.1 \times 10^{-4} \text{ M/s}$

**Practice Problems** (page 6)

1. a) mass of Cu or mass of Ag, [Cu(NO$_3$)$_2$] or [AgNO$_3$], blue colour of Cu(NO$_3$)$_2$
b) pressure of entire closed system will increase or green colour of chlorine gas
c) volume or mass of carbon dioxide gas or increased partial pressure of CO$_2$ (in a closed system).
d) mass of BaSO$_4$ ppt formed, [either reactant], conductivity as ions are consumed

2. There is a common misconception that a significant increase in the volume of water will occur as water is formed in a reaction that occurs in aqueous solution. This is, of course, nonsense! As the entire reaction occurs in the solvent water, there will simply be a small amount of water formed, replacing the hydrogen and oxygen atoms (actually hydrogen and hydroxide ions) reacted from the acid and base reactants. **Volume change is generally associated with the formation of a gas.**

3. The concentrations of pure solids and liquids are fixed. That is they do not change (appreciably for the liquid if it is the solvent and at all for the solid) during a chemical reaction. The amount (number of moles) certainly does change. However, we must realize that as more moles of solid or liquid are formed, the volume of the solid or liquid also increases, hence the molarity (the quotient of moles/volume) does not change. For aqueous species, increased numbers of moles in the same volume of solution certainly does increase the concentration. The same is true for gases being formed in a fixed size container. Hence, **concentration change is associated with the formation or use of an aqueous species or a gas, not a solid or a liquid (except in the rare case of solid or liquid mixtures).**

**Practice Problems** (page 9)

1. a) Balanced Equation: Zn(s) + 2 HCl(aq) $\rightarrow$ ZnCl$_2$(aq) + H$_2$(g)
rate = \frac{25.0 \text{ mL H}_2 \times 1 \text{ mol H}_2 \times 1 \text{ mol Zn} \times 65.4 \text{ g Zn} \times 60 \text{ s}}{150.0 \text{ s} \times 22,400 \text{ mL} \times 1 \text{ mol H}_2 \times 1 \text{ mol Zn} \times 1 \text{ min}} = 0.0292 \text{ g/min}

b) Rate is greatest at the beginning  

c) Rate = 0 \text{ g/min} in the last increment

d) This is because the HCl is all gone (limiting). Excess Zn left.

2. \text{CaCO}_3(s) + 2 \text{HCl(aq)} \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)

rate = \frac{3.45 \text{ g/L CaCO}_3 \times 1 \text{ mol CaCO}_3 \times 2 \text{ mol HCl} \times 1 \text{ min}}{4.50 \text{ min} \times 100.1 \text{ g CaCO}_3 \times 1 \text{ mol CaCO}_3 \times 60 \text{ s}} = 2.55 \times 10^{-4} \text{ mol/L/s}

**Practice Problems** (page 11)

1. \text{24 h x 3600 s x 6.5 x 10}^{-4} \text{ mol O}_3 \times 3 \text{ mol O}_2 \times 6.02 \times 10^{23} \text{ O}_2 \text{ molecules} = \frac{1 \text{ h}}{1 \text{ L s}} \times \frac{2 \text{ mol O}_3}{1 \text{ mole O}_2} \times \frac{5.1 \times 10^{25} \text{ molecules/L}}{1 \text{ mol CaCO}_3}

2. \text{C}_3\text{H}_8(g) + 5 \text{ O}_2(g) \rightarrow 4 \text{ H}_2\text{O}(g) + 3 \text{ CO}_2(g) \text{ (equation is not required)}

\text{6.75 L x 1 L C}_3\text{H}_8 \times \frac{44.0 \text{ g C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} \times \frac{1 \text{ min}}{2 \text{ mol O}_3} = \frac{60 \text{ s}}{1 \text{ mol O}_3} = 90.0 \text{ minutes}

\text{3. Ca(s) + 2 H}_2\text{O(l) \rightarrow Ca(OH)}_2(aq) + \text{H}_2(g)

\text{5.00 mL x 1.00 g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O} \times 1 \text{ mol Ca} \times 40.1 \text{ g Ca}}{18.0 \text{ g H}_2\text{O} \times 2 \text{ mol H}_2\text{O} \times 1 \text{ mol Ca} \times 2.65 \text{ g Ca}} = \frac{25.0 \text{ s}}{1 \text{ mL}} \times \frac{52.5 \text{ s}}{1 \text{ mol H}_2\text{O}} \times \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol Ca} \times 2 \text{ mol Ca} \times 2.65 \text{ g Ca}}

**Activity 1.1** (page 12)

<table>
<thead>
<tr>
<th>Property</th>
<th>State of Species</th>
<th>Apparatus Used</th>
<th>Units</th>
<th>Sample Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>solid</td>
<td>balance</td>
<td>g/min</td>
<td>(2 \text{ K(s) + 2 H}_2\text{O(l) \rightarrow 2 KOH(aq) + H}_2(g))</td>
</tr>
<tr>
<td>mass</td>
<td>gas</td>
<td>balance</td>
<td>g/min</td>
<td>(2 \text{ K(s) + 2 H}_2\text{O(l) \rightarrow 2 KOH(aq) + H}_2(g))</td>
</tr>
<tr>
<td>volume</td>
<td>gas</td>
<td>eudiometer</td>
<td>mL/min</td>
<td>(2 \text{ K(s) + 2 H}_2\text{O(l) \rightarrow 2 KOH(aq) + H}_2(g))</td>
</tr>
<tr>
<td>concentration</td>
<td>aqueous</td>
<td>titrimetry</td>
<td>M/min</td>
<td>(2 \text{ K(s) + 2 H}_2\text{O(l) \rightarrow 2 KOH(aq) + H}_2(g))</td>
</tr>
<tr>
<td>pH</td>
<td>aqueous</td>
<td>titrimetry</td>
<td>M/min</td>
<td>(2 \text{ K(s) + 2 H}_2\text{O(l) \rightarrow 2 KOH(aq) + H}_2(g))</td>
</tr>
<tr>
<td>colour</td>
<td>aqueous</td>
<td>spectrophotometer</td>
<td>/%</td>
<td>Ni(s) + 2 AuNO\textsubscript{3}(aq) \rightarrow Ni(NO\textsubscript{3})\textsubscript{4}(aq) + 2 Au\textsubscript{s} (Ni\textsuperscript{2+} is green)</td>
</tr>
<tr>
<td>pressure</td>
<td>gas</td>
<td>manometer</td>
<td>kPa/min</td>
<td>(2 \text{ K(s) + 2 H}_2\text{O(l) \rightarrow 2 KOH(aq) + H}_2(g))</td>
</tr>
<tr>
<td>Conductivity</td>
<td>aqueous</td>
<td>conductiv--</td>
<td>/s</td>
<td>(CH\textsubscript{3})\textsubscript{3}CBr(aq) + H\textsubscript{2}O(l) \rightarrow</td>
</tr>
</tbody>
</table>
1.1 Review Questions  (page 13)

1.
- The distance-time graph involves a vehicle changing position, while the rest of the data in this section involves a property of a chemical changing during a chemical reaction.
- The vehicle accelerates and then decelerates, while most reactions start at a maximum rate and decrease rate the entire time.
- The vehicle can stop moving entirely and then begin again. Once a reaction begins, it continues until it is finished.

2. Consider the following reaction, which could be done in either flask, using any of the equipment shown:

\[
6 \text{Cu}(s) + 8 \text{HNO}_3(aq) + \text{O}_2(g) \rightarrow 6 \text{CuNO}_3(aq) + 4 \text{H}_2\text{O}(l) + 2 \text{NO}_2(g)
\]

a) If 5.00 g of copper solid is completely reacted in 250.0 mL of excess nitric acid in 7.00 minutes at STP, calculate the rate of the reaction in:

i) g Cu / min
ii) g NO\textsubscript{2} / min
iii) mol HNO\textsubscript{3} / min

\[
5.00 \text{ g Cu} = 0.714 \text{ g/min}
\]

\[
\frac{5.00 \text{ g Cu}}{7.00 \text{ min}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times \frac{2 \text{ mol NO}_2}{6 \text{ mol Cu}} \times \frac{46.0 \text{ g NO}_2}{1 \text{ mol NO}_2} = 0.172 \text{ g NO}_2/\text{min}
\]

\[
5.00 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times 8 \text{ mol HNO}_3 = 0.0150 \text{ mol HNO}_3/\text{min}
\]
b) Determine the final: i) mL NO₂ formed at STP ii) molarity of CuNO₃ assuming the reaction continues at this average rate for 10.0 min total time.

\[
\begin{align*}
10.0 \text{ min} & \times \frac{5.00 \text{ g Cu}}{7.00 \text{ min}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times \frac{2 \text{ mol NO}_2}{6 \text{ mol Cu}} \times \frac{22.4 \text{ L NO}_2}{1 \text{ mol NO}_2} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 840. \text{ mL NO}_2 \\
250.0 \text{ mL} & \times \frac{5.00 \text{ g Cu}}{7.00 \text{ min}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times \frac{6 \text{ mol CuNO}_3}{6 \text{ mol Cu}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.450 \text{ mol/L NO}_3
\end{align*}
\]

c) Describe SIX ways you might measure the reaction rate. Include the equipment required, measurements made and units for the rate.

- \( \Delta \text{ Conc HNO}_3 \) by Titration using Buret, Flasks, Magnetic Mixer in \( M \text{ HNO}_3/s \) to measure \( V_i \) and \( V_f \)
- \( \Delta \text{ Mass Cu} \) by Balance to measure \( m_f \) and \( m_i \) in units of g Cu/s
- \( \Delta \text{ Pressure NO}_2 \) by Manometer in closed system to measure \( P_f \) and \( P_i \) in units of kPa/s NO₂
- \( \Delta \text{ Volume NO}_2 \) by Eudiometer to measure \( V_f \) and \( V_i \) in units of mL/sNO₂
- \( \Delta \text{ pH} \) by pH meter to measure change in pH of HNO₃ per second
- \( \Delta \text{ Mass of NO}_2 \) gas by Balance to measure \( m_i \) and \( m_f \) in units of g/s
- \( \Delta \text{ Conc CuNO}_3 \) by Titration using buret, etc to find \( V_f \) and \( V_i \) in \( M/s \)

3. Consider the graph for the following reaction:

\[
\text{CaCO}_3(s) + 2\text{HCl(aq)} \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O(l)}
\]

Recall the discussion of the instantaneous rate on page 3. Determine the instantaneous rate at:

a) An instant after 0 min (this is the **initial rate**). b) 1 min c) 4 min

Find the slope of a tangent line drawn to the curve at these particular times.

a) approx 32 mL/min b) approx 16 mL/min c) approx 3.3 mL/min
How do these rates compare? What do you suppose causes this pattern?

(a) > (b) > (c)  As the reaction proceeds there are less reactant particles available to collide and react. Consequently, the rate decreases with time.

4. Here is a table indicating the volume of gas collected as a thin disk of strontium metal reacts in a solution of hydrochloric acid for one minute.

\[
\text{Sr}(s) + 2 \text{HCl}(aq) \rightarrow \text{SrCl}_2(aq) + \text{H}_2(g)
\]

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Volume of Hydrogen at STP (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 sec</td>
<td>0 mL</td>
</tr>
<tr>
<td>10.0</td>
<td>22.0</td>
</tr>
<tr>
<td>20.0</td>
<td>40.0</td>
</tr>
<tr>
<td>30.0</td>
<td>55.0</td>
</tr>
<tr>
<td>40.0</td>
<td>65.0</td>
</tr>
<tr>
<td>50.0</td>
<td>72.0</td>
</tr>
<tr>
<td>60.0</td>
<td>72.0</td>
</tr>
</tbody>
</table>

a. Calculate the average rate of reaction in moles of HCl consumed/second over the first 50.0 seconds.

\[
\frac{72.0 \text{ mL} - 0 \text{ mL} \text{H}_2}{50.0 \text{ s} - 0 \text{ s}} \times \frac{1 \text{ mol} \text{H}_2}{2 \text{ mol} \text{HCl}} \times \frac{1 \text{ mol} \text{Sr}}{2 \text{ mol} \text{HCl}} \times \frac{1 \text{ mol} \text{Sr}}{87.6 \text{ g} \text{Sr}} = 0.282 \text{ g} \text{Sr}
\]

b. Calculate the mass of strontium consumed in this 50.0 second period.

\[
\frac{50.0 \text{ s}}{1 \text{ s}} \times \frac{1.29 \times 10^{-4} \text{ mol} \text{HCl}}{2 \text{ mol} \text{HCl}} \times \frac{1 \text{ mol} \text{Sr}}{2 \text{ mol} \text{HCl}} \times \frac{87.6 \text{ g} \text{Sr}}{1 \text{ mol} \text{Sr}} = 0.282 \text{ g} \text{Sr}
\]

c. Why did the volume of gas collected, decrease in each increment until 50.0 seconds? - The [HCl] was decreasing. This led to less successful collisions.

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d. Why did the volume of gas remain unchanged from 50.0 to 60.0 seconds?
- One of the reactants (either the Sr disk or the HCl in solution) was completely consumed. Based on the reaction rate, the Sr disk was most likely the limiting reagent. The rate implies a reasonably large molarity of HCl.

4. \[ 3 \text{Cu}(s) + 8 \text{HNO}_3(aq) \rightarrow 3 \text{Cu(NO}_3)_2(aq) + 2 \text{NO}(g) + 4 \text{H}_2\text{O}(l) \]

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Absorbances (no unit)</th>
<th>Concentration of Copper(II) Ion (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 s</td>
<td>0 (this is a “blank”)</td>
<td>0 mol/L</td>
</tr>
<tr>
<td>20.</td>
<td>0.40</td>
<td>0.017</td>
</tr>
<tr>
<td>40.</td>
<td>0.70</td>
<td>0.030</td>
</tr>
<tr>
<td>60.</td>
<td>0.90</td>
<td>0.038</td>
</tr>
<tr>
<td>80.</td>
<td>1.00</td>
<td>0.042</td>
</tr>
</tbody>
</table>

Find the absorbances on the standard graph and record the corresponding concentrations of the copper(II) ions (equal to the concentration of Cu(NO$_3$)$_2$) in the table. (See Above)

a) Calculate the average rate of the reaction from time zero to 80 s in units of $M$ of HNO$_3(aq)$ /s.
\[
\left(\frac{0.042-0}{80-0}\right)\text{ mol L}^{-1}\text{ Cu}^{2+} \times \frac{1 \text{ mol Cu(NO}_3)_2}{1 \text{ mol Cu}^{2+}} \times \frac{8 \text{ mol HNO}_3}{3 \text{ mol Cu(NO}_3)_2} = 0.0014 M \text{ HNO}_3/s
\]

b) What mass of Cu(s) will be consumed during the 80. second trial?
\[
80. \text{ s } \times \frac{0.0014 \text{ mol L}^{-1} \text{ HNO}_3}{1 \text{ s}} \times \frac{3 \text{ mol Cu(s)}}{8 \text{ mol HNO}_3} \times \frac{63.5 \text{ g Cu(s)}}{1 \text{ mol Cu(s)}} = 2.667 \text{ g Cu/L}
\]

Since the flask is $\frac{1}{4}$ L, $250 \text{ mL } \times 2.667 \text{ g Cu} = 0.67 \text{ g Cu(s)}$ reacts.
\[
1000 \text{ mL}
\]

EASY WAY: $250 \text{ mL } \times 0.042 \text{ mol Cu}^{2+} \times \frac{1 \text{ mol Cu(s)}}{1 \text{ mol Cu}^{2+}} \times \frac{63.5 \text{ g Cu(s)}}{1 \text{ mol Cu(s)}} = 0.67 \text{ g}
\]

1000 mL

EASY WAY: $250 \text{ mL } \times 0.042 \text{ mol Cu}^{2+} \times \frac{1 \text{ mol Cu(s)}}{0.67 \text{ g Cu(s)}} = 0.67 \text{ g}

1000 mL

1 mol Cu$^{2+}$ 1 mol Cu(s)

b) What mass of Cu(s) will be consumed during the 80. second trial?
\[
80. \text{ s } \times \frac{0.0014 \text{ mol L}^{-1} \text{ HNO}_3}{1 \text{ s}} \times \frac{3 \text{ mol Cu(s)}}{8 \text{ mol HNO}_3} \times \frac{63.5 \text{ g Cu(s)}}{1 \text{ mol Cu(s)}} = 2.667 \text{ g Cu/L}
\]

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\[
1000 \text{ mL}
\]

EASY WAY: $250 \text{ mL } \times 0.042 \text{ mol Cu}^{2+} \times \frac{1 \text{ mol Cu(s)}}{1 \text{ mol Cu}^{2+}} \times \frac{63.5 \text{ g Cu(s)}}{1 \text{ mol Cu(s)}} = 0.67 \text{ g}
\]

1000 mL

EASY WAY: $250 \text{ mL } \times 0.042 \text{ mol Cu}^{2+} \times \frac{1 \text{ mol Cu(s)}}{0.67 \text{ g Cu(s)}} = 0.67 \text{ g}

1000 mL

1 mol Cu$^{2+}$ 1 mol Cu(s)

c) What will you observe in the main reaction flask as the reaction proceeds?
- Cu(s) will decrease in size
- Blue Cu$^{2+}(aq)$ will appear
- Bubbles will be seen as gas forms
- This is a very exothermic reaction so heat (and potentially some steam) will be given off
- (Colourless NO(g) reacts immediately with oxygen in the air to form brownish orange NO$_2(g)$ or its dimer, N$_2$O$_4(g)$ which is also brownish orange.)
As the values are graphic, answers may vary slightly in #3 and #4.

1.2 Factors Affecting Rates

Warm Up (page 18)

a) Powdered marble chips allow more successful collisions between reactants.
b) Hot water allows more energetic collisions (reactants hit each other more often and harder – with more energy) so more successful collisions will occur.
c) The potassium is more reactive than the sodium, which is more reactive than the lithium. (Potassium has a lower ionization energy, which allows it to lose its outer shell electron more easily.)

1.2 Activity (page 24)

\[
\text{Zn}(s) + 2 \text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)
\]
1. Fastest: Two > Four > Three > One: Slowest

(25°>Room T/1M) (Room T/1M/pwdr) (Room T/2M) (Room T/1M)

Most Influence: Temperature; Second Most Influence: Surface Area; Least: Conc

2. Trial One: \( \frac{29 \text{ mL} \text{ H}_2 \times 60 \text{ s}}{150 \text{ s}} = \frac{12 \text{ mL}}{1 \text{ min}} \) Two: \( \frac{65 \text{ mL} \times 60 \text{ s}}{90 \text{ s}} = \frac{43 \text{ mL}}{1 \text{ min}} \)

Trial Three: \( \frac{54 \text{ mL} \times 60 \text{ s}}{150 \text{ s}} = \frac{22 \text{ mL}}{1 \text{ min}} \) Four: \( \frac{65 \text{ mL} \times 60 \text{ s}}{120 \text{ s}} = \frac{33 \text{ mL}}{1 \text{ min}} \)

3. Trial One: At 90 seconds (1.5 minutes),

\[
24 \text{ mL} \text{ H}_2 \times \frac{1 \text{ mol} \text{ H}_2}{1 \text{ mol}} \times \frac{1 \text{ mol} \text{ Zn}}{65.4 \text{ g} \text{ Zn}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 64 \text{ mg} \text{ Zn}
\]

Trial Two: \( \frac{65 \text{ mL} \text{ H}_2 \times 1 \text{ mol} \text{ H}_2 \times 1 \text{ mol} \text{ Zn}}{26,500 \text{ mL}} \times \frac{65.4 \text{ g} \text{ Zn}}{1 \text{ mol}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 160 \text{ mg} \text{ Zn} \)

Trial Three: \( \frac{44 \text{ mL} \text{ H}_2 \times 1 \text{ mol} \text{ H}_2 \times 1 \text{ mol} \text{ Zn}}{24,500 \text{ mL} \text{ H}_2} \times \frac{65.4 \text{ g} \text{ Zn}}{1 \text{ mol} \text{ Zn}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 120 \text{ mg} \text{ Zn} \)

Trial Four: \( \frac{57 \text{ mL} \text{ H}_2 \times 1 \text{ mol} \text{ H}_2 \times 1 \text{ mol} \text{ Zn}}{24,500 \text{ mL} \text{ H}_2} \times \frac{65.4 \text{ g} \text{ Zn}}{1 \text{ mol} \text{ Zn}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 150 \text{ mg} \text{ Zn} \)

4. The temperature in most labs is < 25°C and the pressure would be very slightly < 101.3 kPa due to a higher elevation. The temperature difference would be much more significant than the pressure as we are very close to sea level. This means molar volume is likely a bit smaller than 24.5 L/mol (or 26.5 L/mol for trial two). Dividing by a smaller number would lead to a LARGER MASS of zinc expected.

1.2 Review Questions (page 25)

1. Factors affecting heterogeneous and homogeneous reactions:
   - Nature of reactants
   - Temperature
   - Concentration
   - Presence of a catalyst

You can impact any of these EXCEPT the “nature of the reactants” as this is determined once you’ve selected the reaction you want to study.

2. Surface Area - In a heterogeneous reaction, the reactants are able to come into contact with each other only where they meet at the interface between the two phases. The size of the area of contact determines the rate of the reaction. Decreasing the size of the pieces of solid reactant will increase the area of contact.
You can only increase this area of contact for solids and rarely, liquids.

3. a) Platinum in the catalytic converter of a car.
   b) Iron is used in the Haber Process to make ammonia.
   c) Platinum is used in contact lens disinfectant disks to decompose hydrogen peroxide producing oxygen gas. The bubbling process helps clean the surface of the lenses.
   d) A Magnesium Complex called Chlorophyll assists in photosynthesis.

4. \( \text{CaCO}_3(s) + 2 \text{HNO}_3(aq) \rightarrow \text{Ca(NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \)
   a) Increase – more frequent contact between reactants
   b) Increase – more surface area leads to more contact between reactants
   c) Decrease – less energetic collisions due to lower temperature
   d) no effect – \( \text{CO}_2 \) is a product so increased contact has no effect on forward rate

5. \( \text{HCOOH}(l) \rightarrow \text{H}_2\text{O}(l) + \text{CO}(g) \)

\[
\frac{80.0 \text{ mL CO(g)}}{1.00 \text{ min}} \times \frac{1 \text{ mol CO}}{22,400 \text{ mL}} \times \frac{1 \text{ mol HCOOH}}{1 \text{ mol CO}} = 3.57 \times 10^{-3} \text{ mol HCOOH/min}
\]

a) Less than half as much time (rxn most rapid a start) – under 30 seconds.
   b) Considerably more time – much > 1 minute.
   c) Approximately half as much time for each 10°C increase – about 30 seconds.

6. a) i) slow (due to solid C)
   ii) fast (ionic species)
   iii) slow (due to solid Mg)

   Fastest: (ii) > (iii) > (i) Slowest

   b) i) surface area of \( \text{C(s)} \), temperature of system, \([\text{O}_2]\) (volume of container) (partial pressure of \( \text{O}_2 \)), an appropriate catalyst

   ii) \([\text{Pb}^{3+}]\) and \([\Gamma]\), temperature of system, an appropriate catalyst

   iii) \([\text{CuCl}_2]\), surface area of \( \text{Mg(s)} \), temperature of system, an appropriate catalyst

7. c > b > a

The greatest opportunity for contact between reactant particles is in system c. It appears to have the highest concentration/greatest partial pressure of each reactant gas. The next would be system b and the least opportunity would be system a.
1.3 Collision Theory

Warm Up (page 29)

1] a) 1  b) 2  c) 6  d) 12

2] Number of possible collisions = Number of A particles x Number of B particles

3] Increased number of A & B particles leads to an increased reaction rate.

Quick Check (page 30)

1] Rate = k[C][D]. This means that the rate of the reaction is directly related to the product of the concentrations of reactants C and D. Furthermore, it means the reaction is 1st order with respect to both reactants C and D. (The overall reaction order = 1 + 1 = 2.)

2] a) The rate would double.  b) The rate would half.

3] If the volume of the container were halved, the concentrations of both A and B would be doubled. Hence, the rate would be increased by a factor of 2 x 2 = 4 times.

4] Increased T → Increased Rate. Increased T must cause increased rate constant, k.

Quick Check (Page 32)

1] Concentration (Volume of a Gas Sample), Surface Area, Temperature

2] Temperature, Presence of a Catalyst

3] Temperature

Practice Problems – Collision Theory (page 35)

1] a) The added curve should have the same total area below it. The area below the curve and to the right of the vertical line representing $E_a$ should be DOUBLED.

b) The added curve should have the same total area below it. The area below the curve and to the right of the vertical line representing $E_a$ should be SIGNIFICANTLY INCREASED.

c) The added curve should have the same total area below it. The area below the curve and to the right of the vertical line representing $E_a$ should be INCREASED BUT CLEARLY LESS THAN DOUBLE THAT IN CURVE (b).

SEE DIAGRAM:
2]  

<table>
<thead>
<tr>
<th>Temperature</th>
<th>100°C</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency of Collisions</td>
<td>2.00 \times 10^{15} \text{ s}^{-1}</td>
<td>3.00 \times 10^{15} \text{ s}^{-1}</td>
</tr>
<tr>
<td>Force of Collisions (% Possessing ( E_a ))</td>
<td>95.0%</td>
<td>97.0%</td>
</tr>
<tr>
<td>Frequency of Collisions Possessing Activation Energy</td>
<td>1.90 \times 10^{15} \text{ s}^{-1}</td>
<td>2.91 \times 10^{15} \text{ s}^{-1}</td>
</tr>
</tbody>
</table>

a) 97.0% = 1.02X greater  
95.0%

b) \( 3.00 \times 10^{15} \text{ s}^{-1} = 1.50X \) greater  
\( 2.00 \times 10^{15} \text{ s}^{-1} \)

c) \( 2.91 \times 10^{15} \text{ s}^{-1} = 1.53X \) greater  
\( 1.90 \times 10^{15} \text{ s}^{-1} \)

d) Increased frequency of collisions.

e) Extremely forceful collisions may be too forceful to transfer KE of collisions into PE of new bonds. These forceful collisions may be unsuccessful resulting in reactants that simply bounce off one another.

Activity 1.3 – Tracking a Collision  
(page 37)

1.  

<table>
<thead>
<tr>
<th>The Number of Collisions per Unit Time</th>
<th>Snapshot (a)</th>
<th>Snapshot (b)</th>
<th>Snapshot (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Snapshot Series 1 (Effect of Concentration)</td>
<td>2</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Snapshot Series 2 (Effect of Temperature)</td>
<td>4</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>Snapshot Series 3 (Effect of Volume/Pressure)</td>
<td>2</td>
<td>4</td>
<td>9</td>
</tr>
</tbody>
</table>
2. Concentration (series 1) and Volume/Pressure (series 2)

3. Temperature

4. Not only do collisions occur more frequently, but they also occur with more energy (the particles strike each other more forcefully).

5. a. More effective collisions.
   b. More frequent collisions.

**1.3 Review Questions** (page 39)

1. The frequency of collisions and the fraction of these collisions that succeed.

2. Sufficient energy (Eₐ) and proper collision geometry.

3. a) Original surface area + 6/6(original surface area) since six new faces have been exposed. Thus 6.00 cm² + 6/6(6.00 cm²) = 12.0 cm².

   b) 6/6 + 6/6 = 12/6 or 2X as many collisions as before.

   c) 2 (0.00120 mol Zn/min) = 0.00240 mol Zn/min

   d) Zn(s) + 2 HCl(aq) → ZnCl₂(aq) + H₂(g)

      4.50 min x 0.00240 mol Zn x 1 mol H₂ x 22.4 L H₂ x 1000 mL = 242 mL H₂

      1 min   1 mol Zn   1 mol   1 L

4. a) 3 x 0.5 x (3.10 x 10⁻³ mol/L s) = 4.65 x 10⁻³ mol/L s

   b) 1 x 4 x (3.10 x 10⁻³ mol/L s) = 1.24 x 10⁻² mol/L s

   c) The temperature was increased, perhaps by approximately 10°C. Or a catalyst was added.

   d) 0.5 x 0.5 (3.10 x 10⁻³ mol/L s) = 7.75 x 10⁻⁴ mol/L s
   (note that both concentrations were halved)

5. a) The greatest concentration of HCl and the greatest surface area of CaCO₃ exists at the beginning of the reaction. Consequently, the reaction rate is greatest at the beginning as these circumstances allow for more successful collisions. As the reaction proceeds, there are less particles and surface available to collide and so the reaction rate decreases.
6. III > I > II The powdered zinc allows for the greatest contact at the surface and the 1.0\(M\) acid has the greatest number of particles available for collisions.

7. The Cl atoms must be able to contact one another to produce Cl\(_2\) and NO\(_2\). The particles must be drawn to allow this contact to directly occur.

8. a) Low temperatures decrease the frequency of collisions and decrease the fraction of collisions reaching \(E_a\). This keeps the food from spoiling.

b) Fine bits of magnesium in the shavings (more surface area) allow more frequent collisions with the oxygen molecules. This allows a fire to start more readily. Its “nature” allows magnesium to react readily with oxygen with a low \(E_a\).

c) Pt acts as a catalyst in the conversion of NO\(_x\)’s into N\(_2\). This means the collisions required for a successful reaction can occur with less energy or at lower temperatures.

1.4 Potential Energy Diagrams

Warm Up (page 42)
Quick Check  (page 44)

1. \[ 2 \text{C}_2\text{H}_6(g) + 7 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) + 2857.0 \text{kJ/mol}_{\text{rxn}} \]

\[ 2 \text{C}_2\text{H}_6(g) + 7 \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l) \quad \Delta H = -2857.0 \text{kJ/mol}_{\text{rxn}} \]

2. \[ 72.2 \text{kJ/mol}_{\text{rxn}} + 2 \text{HBr}(g) \rightarrow \text{H}_2(g) + \text{Br}_2(l) \]

\[ 2 \text{HBr}(g) \rightarrow \text{H}_2(g) + \text{Br}_2(l) \quad \Delta H = +72.2 \text{kJ/mol}_{\text{rxn}} \]

Practice Problems 1.41  (page 48)

1. a) endothermic  
   b) i) 30 kJ/mol  
   ii) +20 kJ/mol  
   iii) 130 kJ/mol  
   iv) 140 kJ/mol

2. I) Activation energy for the forward reaction.  
   II) Potential energy for the reactants.  
   III) Activation energy for the reverse reaction.  
   IV) Enthalpy change.

Quick Check  (page 50)

A) Reverse uncatalyzed activation energy.  \( E_a(\text{Reverse Uncatalyzed}) \) is #2 in Diagram 2.

B) Forward catalyzed activation energy. #3

C) Decrease in \( E_a \) due to catalysis. #4

D) \( \Delta H \). #7

E) Forward uncatalyzed activation energy. #6

F) Reverse catalyzed activation energy. #1

(Note that #5 is the PE of the activated complex – forward and reverse - uncatalyzed.)

Activity 1.4  Comparing and Contrasting Concepts in Kinetics  (page 51)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Endothermic</th>
<th>Exothermic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensation</td>
<td>Feels cold</td>
<td>Feels hot</td>
</tr>
<tr>
<td>Sign of ( \Delta H )</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Change in Enthalpy</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
<tr>
<td>P.E. ↔ K.E. Transformation</td>
<td>K.E. → P.E.</td>
<td>P.E. → K.E.</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Sample Thermochemical Eqn</td>
<td>AB + heat → A + B</td>
<td>A + B → AB + heat</td>
</tr>
<tr>
<td>Sample Equation Using ΔH</td>
<td>AB → A + B ΔH = +heat</td>
<td>A + B → AB ΔH = -heat</td>
</tr>
<tr>
<td>Bond Energy Comparisons</td>
<td>strong, low energy reactant bonds → weak, high energy product bonds</td>
<td>Weak, high energy reactant bonds → strong, low energy product bonds</td>
</tr>
<tr>
<td>Breaking Bonds vs Forming Energy</td>
<td>Energy released by forming product bonds is less than energy required to break reactant bonds.</td>
<td>Energy released by forming product bonds is greater than the energy required to break reactant bonds.</td>
</tr>
<tr>
<td>Sample PE Diagram</td>
<td><img src="image" alt="Sample PE Diagram" /></td>
<td><img src="image" alt="Sample PE Diagram" /></td>
</tr>
</tbody>
</table>

**1.4 Review Questions** (page )

1. a) \( \text{Fe}_2\text{O}_3(s) + 2 \text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2 \text{Fe}(s) \quad \Delta H = -852 \text{ kJ/mol}_\text{rxn} \)

\[ \text{Fe}_2\text{O}_3(s) + 2 \text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2 \text{Fe}(s) + 852 \text{ kJ/mol}_\text{rxn} \]

b) \( \text{Ca}(s) + \text{O}_2(g) + \text{H}_2(g) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta H = -986 \text{ kJ/mol}_\text{rxn} \)

\[ \text{Ca}(s) + \text{O}_2(g) + \text{H}_2(g) \rightarrow \text{Ca(OH)}_2(s) + 986 \text{ kJ/mol}_\text{rxn} \]

c) \( 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \quad \Delta H = +572 \text{ kJ/mol}_\text{rxn} \)

\[ 572 \text{ kJ/mol}_\text{rxn} + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{H}_2(g) + \text{O}_2(g) \]
2. b) [Diagram showing energy levels and reaction rates]

c) The particles above the $E_a$ line in the first graph represent the particles whose collisions are successful (have energy $> E_a$ and have good geometry).

e) An endothermic reaction has a greater number of successful collisions than the corresponding exothermic reaction. This indicates that the endothermic reaction is much more sensitive to an increase OR decrease in temperature’s effect on its reaction rate. (Will find in Chapter 2 that an increase in T will always cause a shift in the ENDO direction.)

3. a) Endothermic sketch.
   b) 60 kJ/mol
   c) -35 kJ/mol

4. a) $A = \text{Activation energy for forward catalyzed reaction.}$
   $B = \Delta H$
   $C = \text{Reverse uncatalyzed activation energy.}$
   $D = \text{Forward uncatalyzed activation energy.}$
   $E = \text{Reverse catalyzed activation energy.}$
   b) Exothermic
   c) No effect.

5. a) -50 kJ/mol
   b) $Q + S \rightarrow T + 50 \text{ kJ/mol}$
   c) exothermic
   d) 150 kJ/mol

6. The energy released as more CO$_2$(g) and H$_2$O(g) is formed provides the activation energy needed to continue decomposing the hydrocarbon fuel.
7. Fill in the blanks for an EXOthermic reaction: The energy released during bond forming is __greater__ than the energy required for bond __breaking__. As a result, there is a net __release__ of energy. The bonds formed have _less_ potential energy than the __reactant__ bonds did.

8. The diagrams would be the same. The potential bond energy would be the same. The “reaction coordinate” is NOT a time axis!!

9. As particles approach one another their KE DECREASES (bond breaking requires energy – KE \( \rightarrow \) PE). Meanwhile, their PE INCREASES (see above). Once an activated complex has formed, the KE INCREASES (bond forming releases energy) and their PE decreases). The sum of KE and PE remains constant the entire time.

![Energy Diagram](image)

blue is PE, red is KE

10. a) exothermic  
   b) 10 kJ/mol  
   c) 25 kJ/mol  
   d) -15 kJ/mol - no change at all when catalyzed.  
   e) 15 kJ/mol lower with a catalyst.  
   f) increases the reaction rate.

1.5 Mechanisms and Catalysis

**Warm Up** (page 57)

1. There are three reactions in the series.

2. Step One: \( \text{H}^+ + \text{HCOOH} \rightarrow \text{HCOOH}_2^+ \)

   Step Two: \( \text{HCOOH}_2^+ \rightarrow \text{H}_2\text{O} + \text{HCO}^+ \)

   Step Three: \( \text{HCO}^+ \rightarrow \text{CO} + \text{H}^+ \)

   Overall Rxn: \( \text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO} \)
Quick Check (page 58)

1. NO(g) + Br₂(g) → NOBr₂(g)  Bimolecular – Elementary Process
2. HCOOH(aq) → H₂O(l) + CO(g)  Unimolecular – Elementary Process
3. 2 NO(g) + Cl₂(g) → 2 NOCl(g)  Termolecular – Overall Reaction

Practice Problems (page 62)

1. O₃(g) → O₂(g) + Q(g)  (slow)
   Q(g) + O₃(g) → 2 O₂(g)  \( \Delta H \) value for entire reaction = -284.6 kJ/mol

2. H₂(g) + 2Pd(s) ⇌ 2Pd-H(s)
   C₂H₄(g) + Pd-H(s) → C₂H₅-Pd(s)  (slowest step)
   C₂H₅-Pd(s) + Pd-H(s) → C₂H₆(g) + 2Pd(s)

   \[ \text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) + 136.9 \text{ kJ/mol} \]

   Catalyst is: Pd  Intermediates are: Pd-H and C₂H₅Pd

   Activation energy is between the dotted lines.
3. $\text{Cl}_2(g) \rightarrow \text{Cl}(g) + \text{Cl}(g)$ \hspace{1cm} \text{initiation}$

$(\text{CH}_4(g) + \text{Cl}(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{H}(g)) \times 2$ \hspace{1cm} \text{propagation}$

$\text{H}(g) + \text{H}(g) \rightarrow \text{H}_2(g)$ \hspace{1cm} \text{termination}$

-----------------------------------------------------------

$2 \text{CH}_4(g) + \text{Cl}_2(g) \rightarrow 2 \text{CH}_3\text{Cl}(g) + \text{H}_2(g)$ \hspace{1cm} \text{chain mechanism}$

There are no catalysts. \text{LIGHT} provides $E_a$ for the reaction.

Intermediates include $\text{H}$’s and $\text{Cl}$’s (free radicals).

(The relative heights of the second and third step are not actually known from the information provided. The reaction is only slightly exothermic. Though the propagation step occurs twice, the reactant and product energies are the same, so it is shown only once.)

\textbf{Activity 1.5 A Molecular View of a Reaction Mechanism} (page 65)

1. $\text{B} + \text{G} \rightarrow \text{BG}$
2. $\text{B} + \text{R} \rightarrow \text{BR}$
   \hspace{1cm} $\text{BR} + \text{G} \rightarrow \text{BG} + \text{R}$ \hspace{1cm} \text{Assumed RDS (slow)}$

-----------------------------------------------------------

1. $\text{B} + \text{G} \rightarrow \text{BG}$
2. They are the same.
3. The catalyst is $\text{R}$.
4. The only intermediate is $\text{BR}$.
5. Much shorter for the catalyzed series.
6. Less time passes between one and two than between two and three.
7. B would NOT affect the rate; G would increase the rate (because G is the reactant in the RDS).

**Review Questions (page 67)**

1. A series of steps that may be added together to give an overall chemical reaction.

2. The slowest elementary process in a reaction mechanism determines the overall reaction rate and is called the RATE-DETERMINING STEP.

3. Chemists determine these models by altering the concentration of species involved in the mechanism and examining the effects these alterations produce. Computer models are also very useful in the pursuit of mechanisms.

4. a) Hetero  
   b) Homo  
   c) Hetero

5. 1st:  \( \text{H}_2\text{O}_2(aq) + \text{F}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{IO}(l) \)  
   slow

   2nd:  \( \text{H}_2\text{O}_2(aq) + \text{IO}^-(aq) \rightarrow \text{H}_2\text{O}(l) + \text{O}_2(g) + \text{F}(aq) \)  
   fast

   a) Overall Rxn:  \( 2 \text{H}_2\text{O}_2(aq) \rightarrow 2 \text{H}_2\text{O}(l) + \text{O}_2(g) \)

   b) Intermediates: \( \text{IO}^- \)

   c) catalyst is \( \Gamma \)

6. \( \text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F} \)  
   (RDS)

   \[
   \text{NO}_2 + \text{F}^- \rightarrow \text{NO}_2\text{F} \\
   \text{------------------------------------} \\
   2 \text{NO}_2 + \text{F}_2 \rightarrow 2 \text{NO}_2\text{F}
   \]

7. a) 3
   b) 2nd step (middle step or step C)
   c) C
   d) B
   e) F
   f) endothermic

8. Mechanism One: Step 1:  \( 2 \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \)  
   slow

   Step 2:  \( \text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}_2 \)  
   fast

   Overall Rxn:  \( \text{CO}(g) + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \)
(Note that this is an example of **autocatalysis**. The reactant, NO₂, also acts as a catalyst for the reaction. Some autocatalyzed reactions involve the formation of the catalyst from the reactants in an early step.)

Mechanism Two: Step 1: \(2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)\) fast

Step 2: \(\text{CO} + \text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{CO}_2 + \text{NO}\) slow

Overall Rxn: \(\text{CO}(g) + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO}(g)\)

b) Mechanism 1 is correct as the CO is NOT in the RDS!

9. a) No – too many reactant particles (five) for a single step.

   b) \(\text{HBr} + \text{O}_2 \rightarrow \text{HOBr}\)

   \(\text{HBr} + \text{HOBr} \rightarrow 2\text{HOBr}\)

   \(\text{HBr} + \text{HOBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2\)

   \(\text{HBr} + \text{HOBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2\)

   \(4 \text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2\)

   c) Step One (both HBr and O₂ influence reaction rate).

   d) [Diagram of potential energy and progress of the reaction]

10. 
Heat + 2 A + 2 B → 3 C

Be sure to label the axes. Indicate the following features on the diagram:

a) Reverse Activation Energy
b) Delta H
c) Potential Energy of Activated Complex  (6 marks)

(Note the relative heights of steps one and two don’t matter, but there must be AT LEAST two steps.)