

BC Science Chemistry 12
Chapter 1 – Reaction Kinetics Answer Key
September 20, 2012

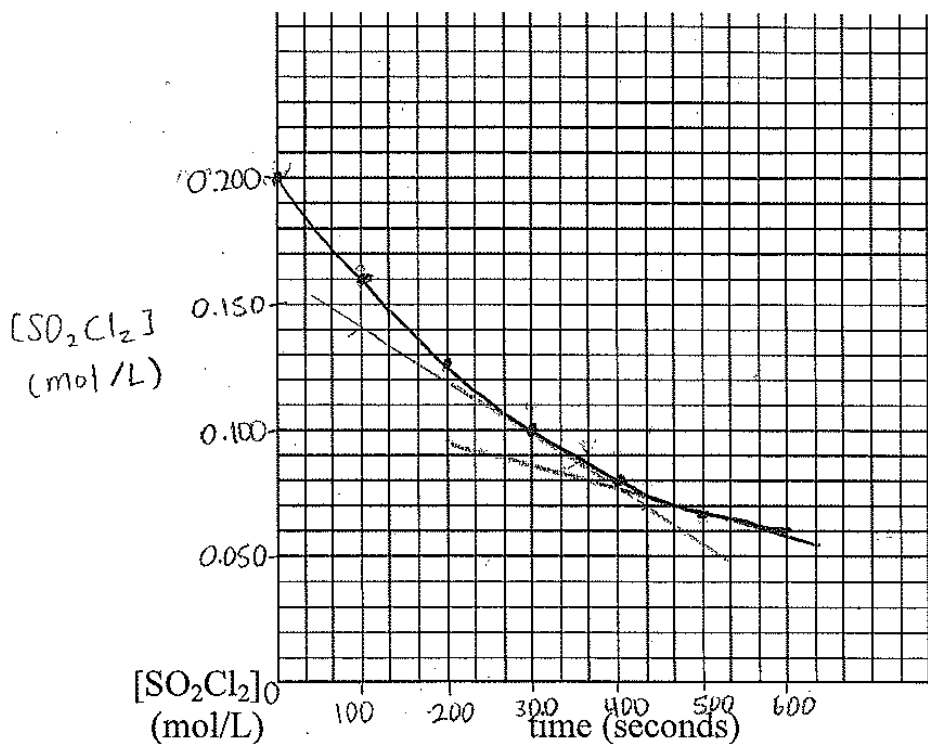
Section 1.1 Measuring the Rate of Chemical Reactions

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) $1.25 \frac{\text{km}}{\text{min}} \times \frac{60 \text{ min}}{1 \text{ h}} = 75.0 \text{ km/h}$
- 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)

[SO₂Cl₂] vs. Time



Graph:

- a) Rate of decomposition of SO_2Cl_2 .
- b) The slope becomes less and less steep.
- c) The rate decreases as the reaction proceeds.
- d) $\frac{0.060 \text{ mol/L} - 0.200 \text{ mol/L}}{600 \text{ seconds} - 0 \text{ seconds}} = \frac{-0.140 \text{ mol/L}}{600 \text{ s}} = -0.00023 \text{ mol/L/s}$ (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: $\frac{0.040 \text{ M}}{433 \text{ s}} = 9.2 \times 10^{-5} \text{ M/s}$ < 300 s: $\frac{0.100 \text{ M}}{467 \text{ s}} = 2.1 \times 10^{-4} \text{ M/s}$

Practice Problems (page 6)

1.
 - a) mass of Cu or mass of Ag, $[\text{Cu}(\text{NO}_3)_2]$ or $[\text{AgNO}_3]$, blue colour of $\text{Cu}(\text{NO}_3)_2$
 - 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: $\text{Zn}(s) + 2 \text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$

$$\text{rate} = \frac{25.0 \text{ mL H}_2}{150.0 \text{ s}} \times \frac{1 \text{ mol H}_2}{22,400 \text{ mL}} \times \frac{1 \text{ mol Zn}}{1 \text{ mol H}_2} \times \frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \times \frac{60 \text{ s}}{1 \text{ min}} = 0.0292 \text{ g/min}$$

- b) Rate is greatest at the beginning c) Rate = 0 g/min in the last increment
 d) This is because the HCl is all gone (limiting). Excess Zn left.

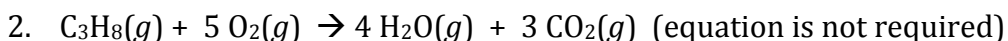


$$\text{rate} = \frac{3.45 \text{ g/L CaCO}_3}{4.50 \text{ min}} \times \frac{1 \text{ mol CaCO}_3}{100.1 \text{ g CaCO}_3} \times \frac{2 \text{ mol HCl}}{1 \text{ mol CaCO}_3} \times \frac{1 \text{ min}}{60 \text{ s}} = 2.55 \times 10^{-4} \text{ mol/L/s}$$

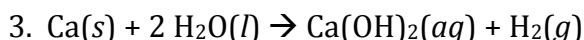
Practice Problems (page 11)

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

$$5.1 \times 10^{25} \text{ molecules/L}$$



$$6.75 \text{ L} \times \frac{1 \text{ mol CO}_2}{22.4 \text{ L CO}_2} \times \frac{1 \text{ mol C}_3\text{H}_8}{3 \text{ mol CO}_2} \times \frac{44.0 \text{ g C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} \times \frac{1 \text{ min}}{1.10 \text{ g C}_3\text{H}_8} = 4.02 \text{ min}$$



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

Activity 1.1 (page 12)

Property	State of Species	Apparatus Used	Units	Sample Reaction
mass	solid	balance	g/min	$2 \text{K}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{KOH}(aq) + \text{H}_2(g)$
mass	gas	balance	g/min	$2 \text{K}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{KOH}(aq) + \text{H}_2(g)$
volume	gas	eudiometer	mL/min	$2 \text{K}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{KOH}(aq) + \text{H}_2(g)$
concentration	aqueous	titrimetry	M/min	$2 \text{K}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{KOH}(aq) + \text{H}_2(g)$
pH	aqueous	titrimetry	M/min	$2 \text{K}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{KOH}(aq) + \text{H}_2(g)$
colour	aqueous	spectrophotometer	/min (%/min)	$\text{Ni}(s) + 2 \text{AuNO}_3(aq) \rightarrow \text{Ni}(\text{NO}_3)_2(aq) + 2 \text{Au}(s)$ (Ni ²⁺ is green)
pressure	gas	manometer	kPa/min	$2 \text{K}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{KOH}(aq) + \text{H}_2(g)$
Conduc-	aqueous	conductiv-	/s	$(\text{CH}_3)_3\text{CBr}(aq) + \text{H}_2\text{O}(l) \rightarrow$

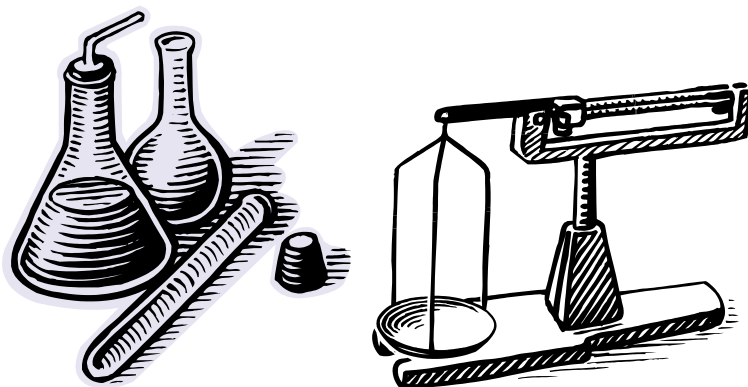
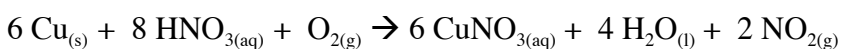
tivity		ity meter		$(\text{CH}_3)_3\text{COH}(aq) + \text{H}^+(aq) + \text{Cl}^-(aq)$

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:



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 NO₂ / min iii) mol HNO₃ / min

$$\frac{5.00 \text{ g Cu}}{7.00 \text{ min}} = 0.714 \text{ g/min}$$

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

$$\frac{5.00 \text{ g Cu}}{7.00 \text{ min}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times 8 \text{ mol HNO}_3 = 0.0150 \text{ mol HNO}_3/\text{min}$$

7.00 min 63.5 g Cu 6 mol Cu

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.

$$10.0 \text{ min} \times \frac{5.00 \text{ g Cu}}{7.00 \text{ min}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times \frac{2 \text{ mol NO}_2}{6 \text{ mol Cu}} \times \frac{22.4 \text{ L NO}_2}{1 \text{ mol NO}_2} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 840. \text{ mL}$$

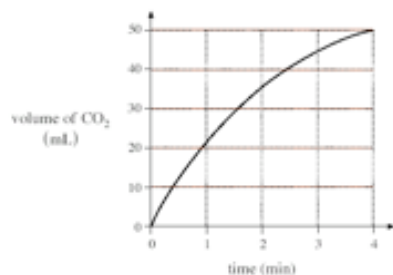
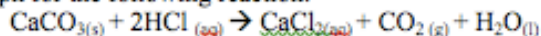
$$\frac{10.0 \text{ min}}{250.0 \text{ mL}} \times \frac{5.00 \text{ g Cu}}{7.00 \text{ min}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times \frac{6 \text{ mol CuNO}_3}{6 \text{ mol Cu}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.450 \text{ mol/L}$$

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

- Δ Conc HNO₃ by Titration using Buret, Flasks, Magnetic Mixer in *M* HNO₃/s to measure V_f and V_i
- Δ Mass Cu by Balance to measure m_f and m_i in units of g Cu/s
- Δ Pressure NO₂ by Manometer in closed system to measure P_f and P_i in units of kPa/s NO₂
- Δ Volume NO₂ by Eudiometer to measure V_f and V_i in units of mL/sNO₂
- Δ pH by pH meter to measure change in pH of HNO₃ per second
- Δ Mass of NO₂ gas by Balance to measure m_i and m_f in units of g/s
- Δ Conc CuNO₃ by Titration using buret, etc to find V_f and V_i in *M*/s

3.

. Consider the graph for the following reaction:

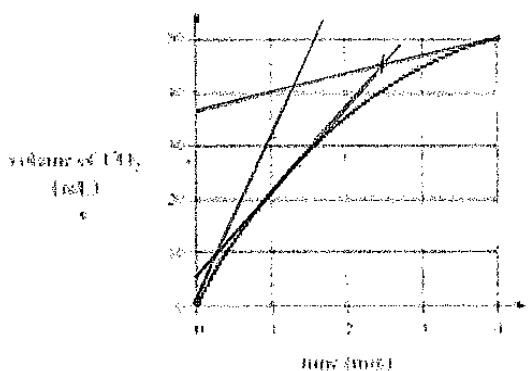


Recall the discussion of the *instantaneous rate* on page 3. Determine the instantaneous rate at:

- 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

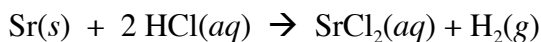
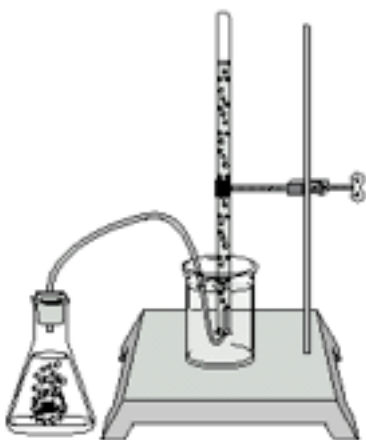


How do these rates compare? What do you suppose causes this pattern?

- (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.



Time (seconds)	Volume of Hydrogen at STP (mL)
0 sec	0 mL
10.0	22.0
20.0	40.0
30.0	55.0
40.0	65.0
50.0	72.0
60.0	72.0

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

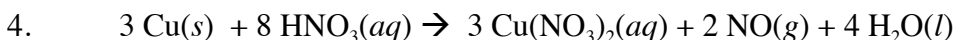
$$\frac{72.0 \text{ mL} - 0 \text{ mL H}_2}{50.0 \text{ s} - 0 \text{ s}} \times \frac{1 \text{ mol H}_2}{22400 \text{ mL}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol H}_2} = 1.29 \times 10^{-4} \frac{\text{mol}}{\text{s}}$$

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

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

- 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.

- 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.



Time (seconds)	Absorbances (no unit)	Concentration of Copper(II) Ion (mol/L)
0 s	0 (this is a "blank")	0 mol/L
20.	0.40	0.017
40.	0.70	0.030
60.	0.90	0.038
80.	1.00	0.042

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

- a) Calculate the average rate of the reaction from time zero to 80 s in units of M of $\text{HNO}_3(aq)$ /s.

$$\frac{(0.042 - 0) \text{ mol L}^{-1} \text{Cu}^{2+}}{(80. - 0) \text{ s}} \times \frac{1 \text{ mol Cu}(\text{NO}_3)_2}{1 \text{ mol Cu}^{2+}} \times \frac{8 \text{ mol HNO}_3}{3 \text{ mol Cu}(\text{NO}_3)_2} = 0.0014M \text{ HNO}_3/\text{s}$$

- b) What mass of $\text{Cu}(s)$ 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, $250 \text{ mL} \times \frac{2.667 \text{ g Cu}}{1000 \text{ mL}} = 0.67 \text{ g Cu}(s)$ reacts.

$$\text{EASY WAY: } 250 \text{ mL} \times \frac{0.042 \text{ mol Cu}^{2+}}{1000 \text{ mL}} \times \frac{1 \text{ mol Cu}(s)}{1 \text{ mol Cu}^{2+}} \times \frac{63.5 \text{ g Cu}(s)}{1 \text{ mol Cu}(s)} = 0.67 \text{ g}$$

- c) What will you observe in the main reaction flask as the reaction proceeds?
- $\text{Cu}(s)$ will decrease in size
 - Blue $\text{Cu}^{2+}(aq)$ 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 $\text{NO}(g)$ reacts immediately with oxygen in the air to form brownish orange $\text{NO}_2(g)$ or its dimer, $\text{N}_2\text{O}_4(g)$ which is also brownish orange.)

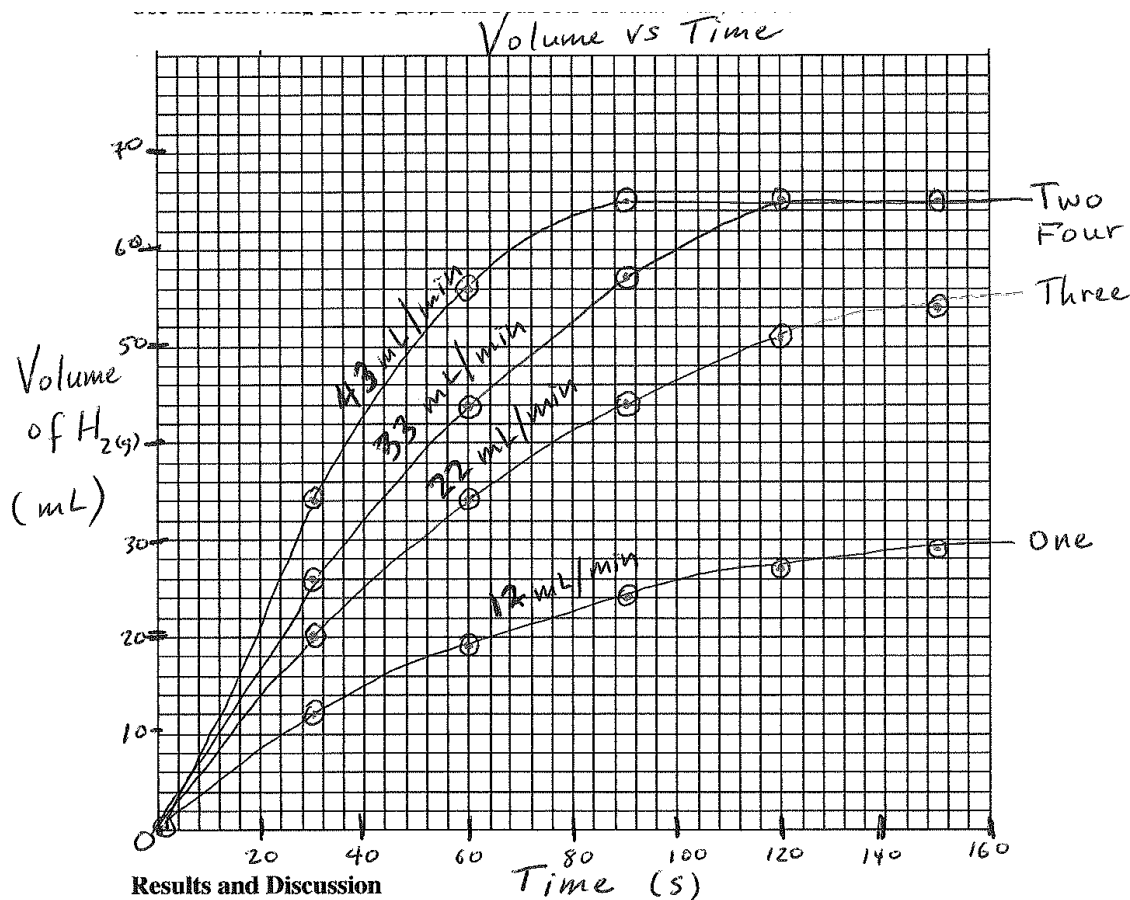
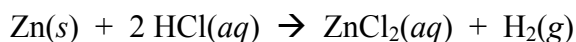
*As the values are graphic, answers may vary *slightly* in #3 and #4.

1.2 Factors Affecting Rates

Warm Up (page 18)

- Powdered marble chips allow more successful collisions between reactants.
- Hot water allows more energetic collisions (reactants hit each other more often *and harder* – with more energy) so more successful collisions will occur.
- 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)



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: $\frac{29 \text{ mL H}_2}{150 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ min}} = 12 \text{ mL/min}$ Two: $\frac{65 \text{ mL}}{90 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ min}} = 43 \text{ mL/min}$

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

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

$24 \text{ mL H}_2 \times \frac{1 \text{ mol H}_2}{24,500 \text{ mL}} \times \frac{1 \text{ mol Zn}}{1 \text{ mol H}_2} \times \frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 64 \text{ mg Zn}$

Trial Two: $65 \text{ mL H}_2 \times \frac{1 \text{ mol H}_2}{24,500 \text{ mL}} \times \frac{1 \text{ mol Zn}}{1 \text{ mol H}_2} \times \frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 160 \text{ mg Zn}$

Trial Three: $44 \text{ mL H}_2 \times \frac{1 \text{ mol H}_2}{26,500 \text{ mL}} \times \frac{1 \text{ mol Zn}}{1 \text{ mol H}_2} \times \frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 120 \text{ mg Zn}$

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

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:

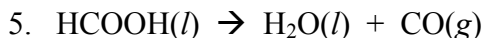
- Nature of reactants
- Temperature
- Concentration
- Presence of a catalyst

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. $\text{CaCO}_3(s) + 2 \text{HNO}_3(aq) \rightarrow \text{Ca}(\text{NO}_3)_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$
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 – CO_2 is a product so increased contact has no effect on forward rate



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

- 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 O_2), an appropriate catalyst

ii) $[\text{Pb}^{3+}]$ and $[\text{I}^-]$, 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 $2 \times 2 = 4$ times.
- 4] Increased T \rightarrow 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

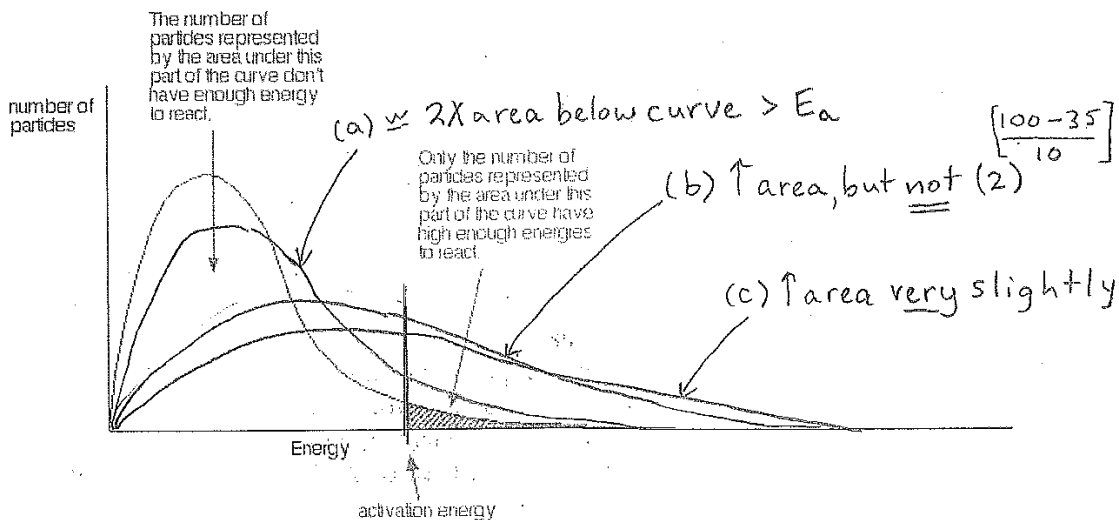
Practice Problems – Collision Theory (page 35)

- 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]

Temperature	100°C	300°C
Frequency of Collisions	$2.00 \times 10^{15} \text{ s}^{-1}$	$3.00 \times 10^{15} \text{ s}^{-1}$
Force of Collisions (% Possessing E_a)	95.0%	97.0%
Frequency of Collisions Possessing Activation Energy	$1.90 \times 10^{15} \text{ s}^{-1}$	$2.91 \times 10^{15} \text{ s}^{-1}$

a) $\frac{97.0\%}{95.0\%} = 1.02\text{X}$ greater

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

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

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)

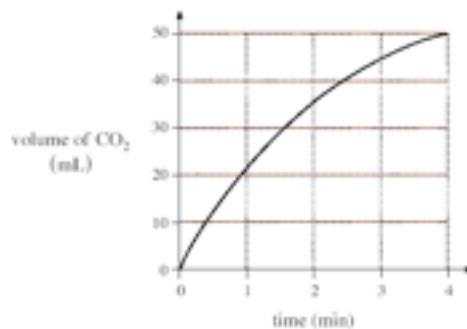
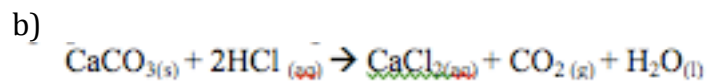
1.

The Number of Collisions per Unit Time	Snapshot (a)	Snapshot (b)	Snapshot (c)
Snapshot Series 1 (Effect of Concentration)	2	4	7
Snapshot Series 2 (Effect of Temperature)	4	7	13
Snapshot Series 3 (Effect of Volume/Pressure)	2	4	9

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 (E_a) and proper collision geometry.
3. a) Original surface area + $6/6$ (original surface area) since six new faces have been exposed. Thus $6.00 \text{ cm}^2 + 6/6(6.00 \text{ cm}^2) = 12.0 \text{ cm}^2$.
b) $6/6 + 6/6 = 12/6$ or 2X as many collisions as before.
c) $2 (0.00120 \text{ mol Zn/min}) = 0.00240 \text{ mol Zn/min}$
d) $\text{Zn}(s) + 2 \text{HCl}(aq) \rightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$
$$4.50 \text{ min} \times \frac{0.00240 \text{ mol Zn}}{1 \text{ min}} \times \frac{1 \text{ mol H}_2}{1 \text{ mol Zn}} \times \frac{22.4 \text{ L H}_2}{1 \text{ mol}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 242 \text{ mL H}_2$$
4. a) $3 \times 0.5 \times (3.10 \times 10^{-3} \text{ mol/L s}) = 4.65 \times 10^{-3} \text{ mol/L s}$
b) $1 \times 4 \times (3.10 \times 10^{-3} \text{ mol/L s}) = 1.24 \times 10^{-2} \text{ mol/L s}$
c) The temperature was increased, perhaps by approximately 10°C . Or a catalyst was added.
d) $0.5 \times 0.5 (3.10 \times 10^{-3} \text{ mol/L s}) = 7.75 \times 10^{-4} \text{ mol/L s}$
(note that both concentrations were halved)
5. a) The greatest concentration of HCl and the greatest surface area of CaCO_3 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 1.0M acid has the greatest number of particles available for collisions.
7. The Cl atoms must be able to contact one another to produce Cl₂ and NO₂. 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 N₂. 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)

Reaction Type	Endothermic	Exothermic
Most Synthesis (Combination) Reactions		X
Most Decomposition Reactions	X	
Neutralization Reactions		X
Combustion Reactions		X

Quick Check (page 44)

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

$$2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l}) \quad \Delta H = -2857.0 \text{ kJ/mol}_{\text{rxn}}$$
- $$72.2 \text{ kJ/mol}_{\text{rxn}} + 2 \text{HBr}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{Br}_2(\text{l})$$

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

Practice Problems 1.41 (page 48)

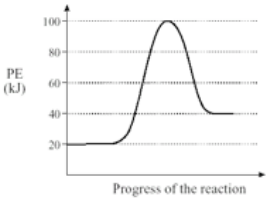
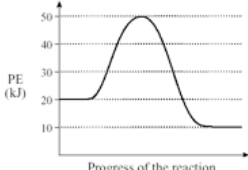
- endothermic
 - 30 kJ/mol
 - +20 kJ/mol
 - 130 kJ/mol
 - 140 kJ/mol
- Activation energy for the forward reaction.
 - Potential energy for the reactants.
 - Activation energy for the reverse reaction.
 - Enthalpy change.

Quick Check (page 50)

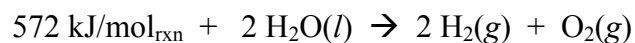
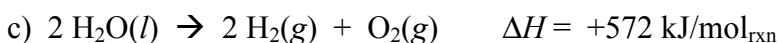
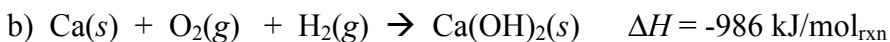
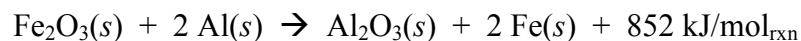
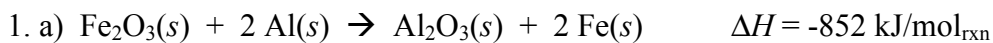
- Reverse uncatalyzed activation energy. $E_{\text{a(Reverse Uncatalyzed)}}$ is #2 in Diagram 2.
 - Forward catalyzed activation energy. #3
 - Decrease in E_{a} due to catalysis. #4
 - ΔH . #7
 - Forward uncatalyzed activation energy. #6
 - Reverse catalyzed activation energy. #1
- (Note that #5 is the PE of the activated complex – forward and reverse - uncatalyzed.)

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

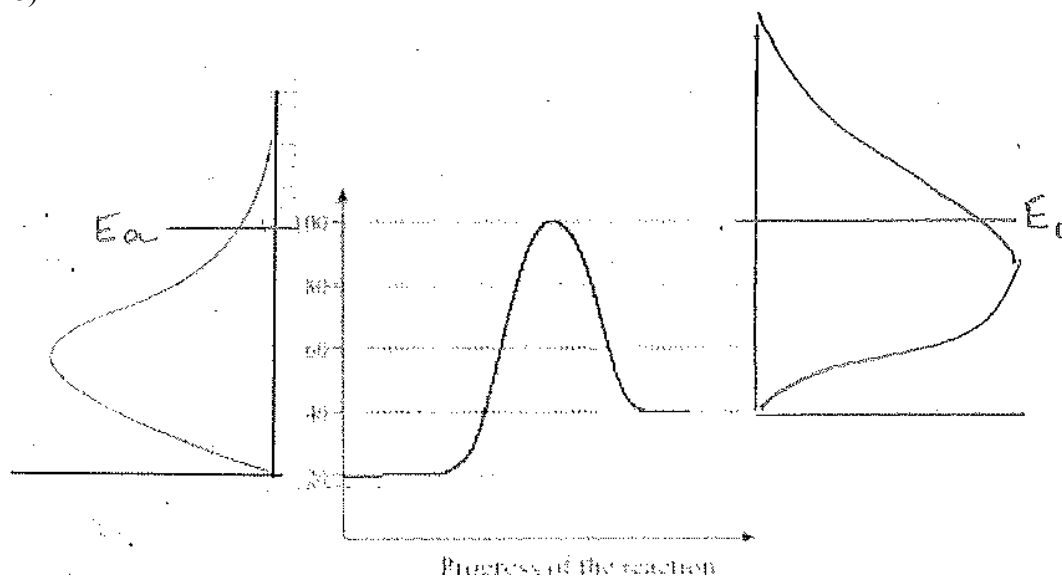
Characteristic	Endothermic	Exothermic
Sensation	Feels cold	Feels hot
Sign of ΔH	+	-
Change in Enthalpy	Increases	Decreases

P.E. \leftrightarrow K.E. Transformation	K.E. \rightarrow P.E.	P.E. \rightarrow K.E.
Sample Thermochemical Eqn	$AB + \text{heat} \rightarrow A + B$	$A + B \rightarrow AB + \text{heat}$
Sample Equation Using ΔH	$AB \rightarrow A + B \quad \Delta H = +\text{heat}$	$A + B \rightarrow AB \quad \Delta H = -\text{heat}$
Bond Energy Comparisons	strong, low energy reactant bonds \rightarrow weak, high energy product bonds	Weak, high energy reactant bonds \rightarrow strong, low energy product bonds
Breaking Bonds vs Forming Energy	Energy released by forming product bonds is less than energy required to break reactant bonds.	Energy released by forming product bonds is greater than the energy required to break reactant bonds.
Sample PE Diagram [numbers on axes not necessary, y axis unit is kJ/mol]		

1.4 Review Questions (page 52)



2. b)



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 = Activation energy for forward catalyzed reaction.

B = ΔH

C = Reverse uncatalyzed activation energy.

D = Forward uncatalyzed activation energy.

E = Reverse catalyzed activation energy.

b) Exothermic

c) No effect.

5. a) -50 kJ/mol

b) $Q + S \rightarrow T + 50 \text{ kJ/mol}$

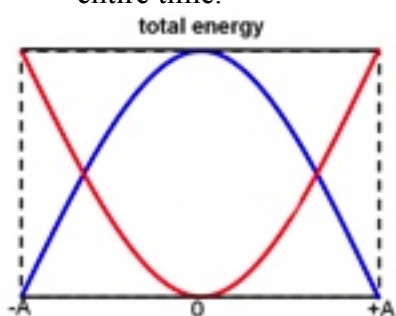
$Q + S \rightarrow T \quad \Delta H = -50 \text{ kJ/mol}$

c) exothermic

d) 150 kJ/mol

6. The energy released as more $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ 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 → 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.



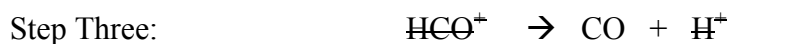
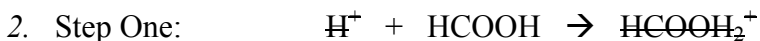
blue is PE, red is KE

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)

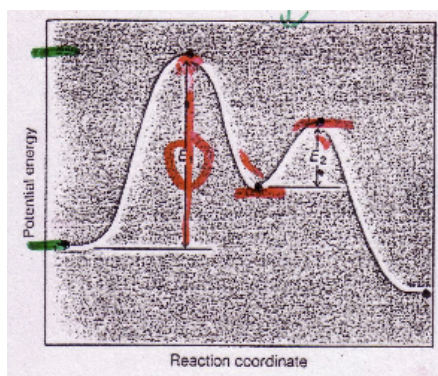
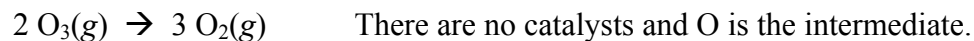
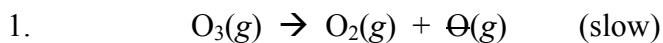
1. There are three reactions in the series.



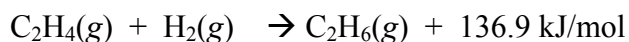
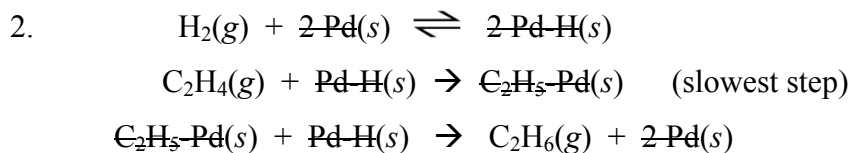
Quick Check (page 58)

- $\text{NO}(g) + \text{Br}_2(g) \rightarrow \text{NOBr}_2(g)$ Bimolecular – Elementary Process
- $\text{HCOOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}(g)$ Unimolecular – Elementary Process
- $2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g)$ Termolecular – Overall Reaction

Practice Problems (page 62)

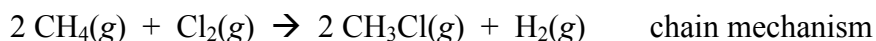
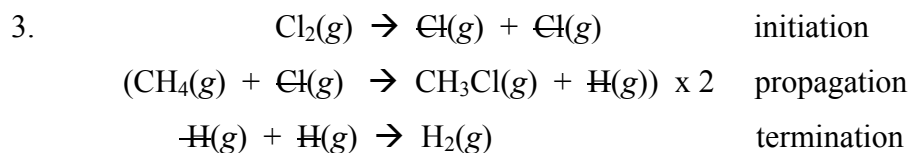
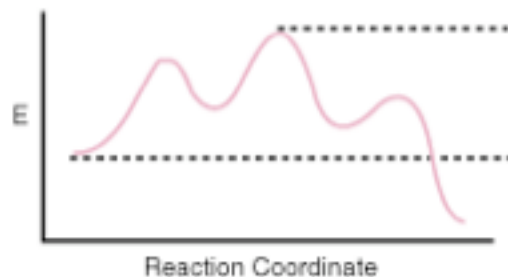


Overall E_a is shown on the y-axis.



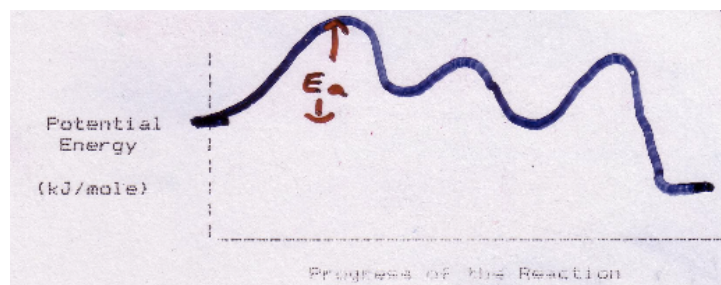
Catalyst is: Pd Intermediates are: Pd-H and $\text{C}_2\text{H}_5\text{Pd}$

Activation energy is between the dotted lines.



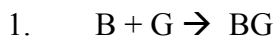
There are no catalysts. LIGHT provides E_a for the reaction.

Intermediates include H's and 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.)

Activity 1.5 A Molecular View of a Reaction Mechanism (page 65)



2. They are the same.

3. The catalyst is R.

4. The only intermediate is BR.

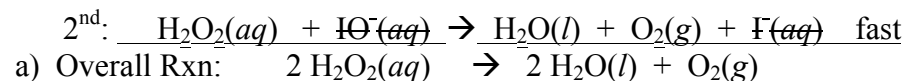
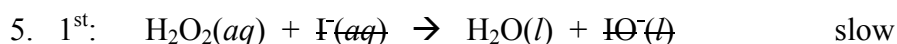
5. Much shorter for the catalyzed series.

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).

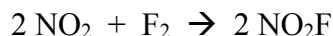
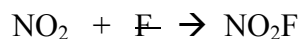
Review Questions (page 67)

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

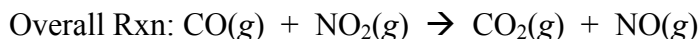
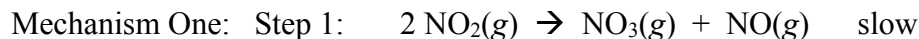


- b) Intermediates: IO^- c) catalyst is I^-

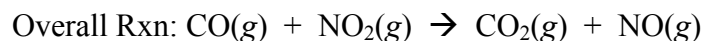
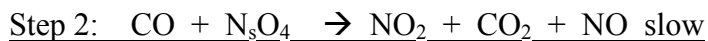


7. a) 3
- b) 2nd step (middle step or step C)
- c) C
- d) B
- e) F
- f) endothermic

8.

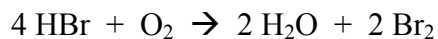
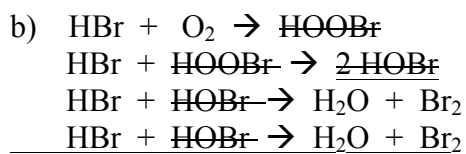


(Note that this is an example of *autocatalysis*. The reactant, NO₂, also acts as a catalyst for the reaction. Some autocatalyzed reactions involve the formation of the catalyst from the reactants in an early step.)



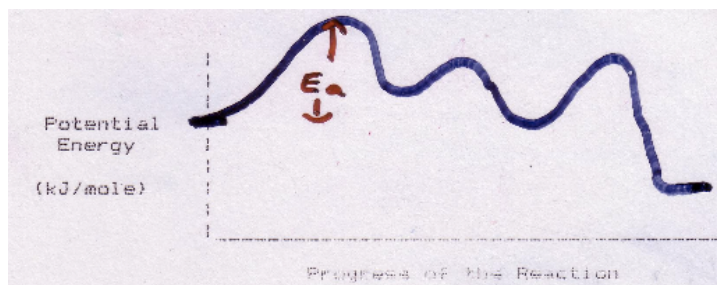
b) Mechanism 1 is correct as the CO is NOT in the RDS!

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

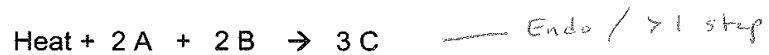


c) Step One (both HBr and O₂ influence reaction rate).

d)

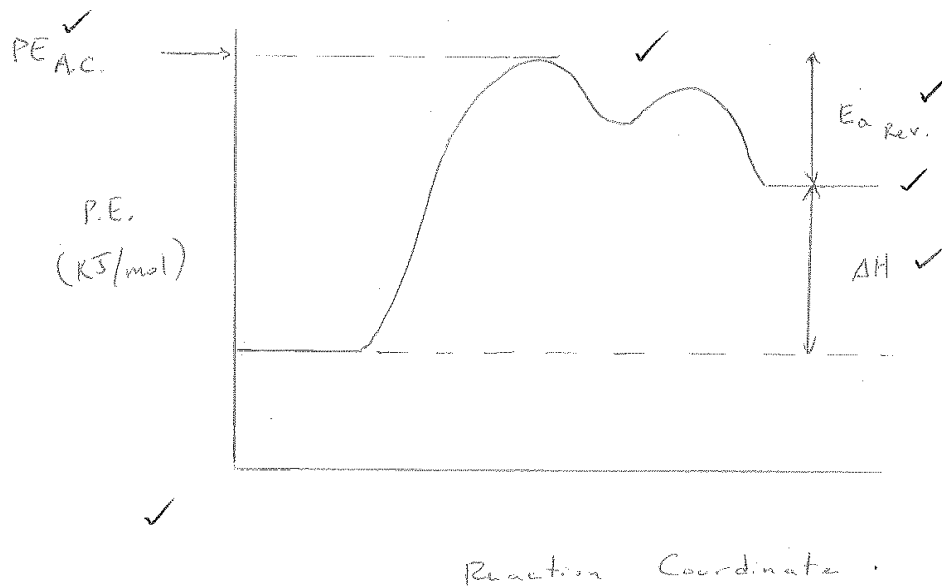


10.



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.)