Chapter 1 Answer Key

Page 3, Quick Check

1. Rate of decomposition of SO_2Cl_2.
2. The slope becomes less and less steep.
3. The rate decreases as the reaction proceeds.
4. -0.00023 mol/L/s (or +)
5. Rate is greater at 300 s than at 500 s.
6. Find the slope of a tangent drawn to the curve at that time.
7. 500 s: 09.2 x 10^{-5} M/s $<$ 300 s: = 2.1 x 10^{-4} M/s

Page 6, Practice Problems

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. Volume change is generally associated with the formation of a gas.
3. 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).

Page 8, Practice Problems

1. a) 0.0292 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.
2. 2.55 x 10-4 mol/L/s

Page 9, Practice Problems

1. 5.1 x 1025 molecules/L
2. 4.02 min
3. 52.5 s

Page 11, 1.1 Review Questions

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. a) i) 0.714 g/min ii) 0.172 g NO2/min iii) 0.0150 mol HNO3/min
   b) i) 840. mL ii) 0.450 mol/L
   c)

- Δ Conc HNO_3 by Titration using Buret, Flasks, Magnetic Mixer in *M* HNO_3/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 NO_2 by Manometer in closed system to measure P_f and P_i in units of kPa/s NO_2
- Δ Volume NO_2 by Eudiometer to measure V_f and V_i in units of mL/sNO_2
- Δ pH by pH meter to measure change in pH of HNO_3 per second
- Δ Mass of NO_2 gas by Balance to measure m_i and m_f in units of g/s
- Δ Conc $CuNO_3$ by Titration using buret, etc to find V_f and V_i in *M*/s

3.a)i) approx 32 mL/min
   ii) approx 16 mL/min
   iii) approx 3.3 mL/min
   b) (a) > (b) > (c) As the reaction proceeds there are less reactant particles available to collide and react. Consequently, the rate decreases with time.

4. a) 1.29 x 10^{-4} mol/s
   b) 0.282g Sr
   c) The [HCl] was decreasing. This led to less successful collisions.
   d) 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.

5.

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

a) 0.0014*M* HNO_3/s
b) 0.67 g
c) 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_2O_4(*g*) which is also brownish orange.)

Page 22, 1.2 Review Questions

1. Factors affecting heterogeneous and homogeneous reactions:
   Nature of reactants
   Temperature
   Concentration
   Presence of a catalyst
2. Surface Area. 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. $CaCO_3(s)$ + 2 $HNO_3(aq)$ → $Ca(NO_3)_2(aq)$ + $H_2O(l)$ + $CO_2(g)$
   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
5. 3.57×10^{-3} 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 C(*s*), temperature of system, $[O_2]$ (volume of container) (partial pressure of O_2), an appropriate catalyst
   ii) $[Pb^{3+}]$ and $[I^-]$, temperature of system, an appropriate catalyst
   iii) $[CuCl_2]$, surface area of 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.

Page 25, Quick Check

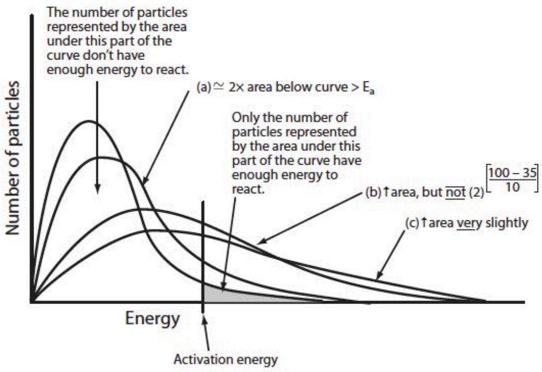
1. Rate = k[C][D]. This means that the rate of the reaction is directly related to the product of the concentrations of reactants C and D. Furthermore, it means the reaction is 1st order with respect to both reactants C and D.
   (The overall reaction order = 1 + 1 = 2.)
2. a) The rate would double.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

Page 27, Quick Check

1. Concentration (Volume of a Gas Sample), Surface Area, Temperature
2. Temperature, Presence of a Catalyst
3. Temperature

Page 29, Practice Problems

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).



2.

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

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

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

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

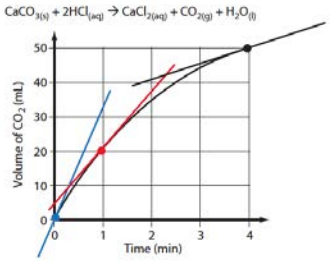
d) Increased frequency of collisions.

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.

Page 33, 1.3 Review Questions

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 cm^2 + 6/6(6.00 cm^2) = 12.0 cm^2.
   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) 242 mL H_2
4. a) $3 \times 0.5 \times (3.10 \times 10^{-3}$ mol/L s) = 4.65×10^{-3} mol/L s
   b) $1 \times 4 \times (3.10 \times 10^{-3}$ mol/L s) = 1.24×10^{-2} mol/L s
   c) The temperature was increased, perhaps by approximately 10°C. Or a catalyst was added.
   d) $0.5 \times 0.5\ (3.10 \times 10^{-3}$ mol/L s) = 7.75×10^{-4} 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.

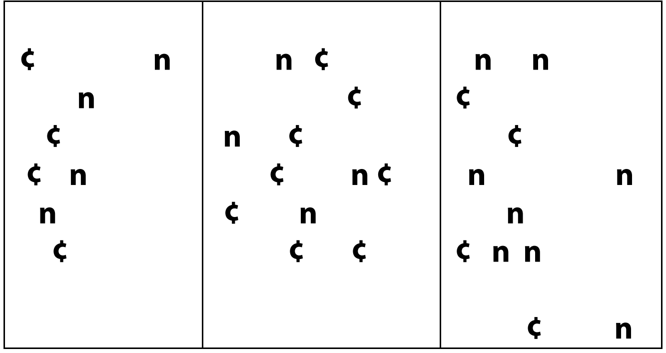
b)



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 Ea. 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 Ea.
   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.

Page 40, Practice Problems 1.4.1

1. Rate = k[NO][O_2]   Trial 1 = X x 10^6 l/mol · sec
2. Rate = k[Y]
   $k = 0.0070\ s^{-1}$
3. System 1: System 2: System 3:



Rate = 0.010 mol/L/s 0.020 mol/L/s 0.080 mol/L/s

Page 42, 1.4 Review Questions

1. a) Rate = $k[X]^2[Y]$
   b) k = 80 $L^2/mol^2/s$
   c) Rate = 0.4 mol/L/s
2. a) Rate = $k[NO_2][F_2]$
   b) k = 40.0 L/mol/s
3. a) Rate = $k[MnO_4^-]^2[H_2C_2O_4]$
   k = $2.0 \times 10^5\ L^2/mol^2/s$
   b) If all the concentrations of all three reactants were doubled, the initial reaction rate would be: $(2)^2(2)^1(2)^0$ = 8x.
   c) If the volume of the reaction system were doubled by adding distilled water, the reaction rate would be: $(½)^2(½)^1(½)^0$ = 1/8x.
4. a) Rate = $k[A]^2$
   b) k = 4.00×10^{-3} L/mol/s
   c) Trial 4: Rate = 3.60×10^{-4} mol/L/s

5. a) Rate = k$[MnO_4^-]^2$
   b) $k = 1.0 \times 10^2$ L/mol/min
   c) Rate = 1.0×10^{-5} mol/L/min
   d) $[MnO_4^-] = 4.8 \times 10^{-4}$ mol/L
   e) 5.2×10^{-6} mol/L/min MnO_4^-
6. Rate = k$[CH_3COCH_3][H^+]$
   $k = 0.0038$ L/mol/s

Page 48, Practice Problems

1. $k = 2.57 \times 10^{-3} s^{-1}$
2. $C = 0.982$ mol/L (0.98 mol/L)
3. $C = 2.16 \times 10^{-2}$ mol/L (2.2×10^{-2} mol/L)

Page 49, Practice Problems

1. t = 2900 s (48 min)
2. Mass = 140 mg
3. t = 24 h

Page 53, Practice Problems 1.

Pseudo integrated rate analysis

Time (s)	Concentration (mol/L)	ln Concentration	1/Concentration (L/mol)
0	0.100	- 2.30 (-2.303)	10.0
30	0.074	- 2.6 (-2.60)	14
60	0.055	- 2.9 (-2.90)	18
90	0.041	- 3.2 (-3.19)	24

The substitution reaction is 1st order with respect to $[(CH_3)_3CBr]$.
$k = 0.0100\ s^{-1}$

2. $2\ NO_2\ (g) \rightarrow 2\ NO\ (g) + O_2\ (g)$

Time (s)	Concentration (mol/L)	ln Concentration	1/Concentration (L/mol)
0	0.0100	- 4.61 (-4.605)	100.
50.	0.0079	- 4.8 (-4.84)	130
100.	0.0065	- 5.6 (-5.04)	150
200.	0.0048	- 5.3 (-5.34)	210
300.	0.0038	- 5.6 (-5.57)	260
400.	0.0032	- 5.7 (-5.75)	310

a) Rate = k$[NO_2]_2$
   $k = 0.54$ L/mol/s

b) i) If the initial concentration of NO2 increased, the reciprocal concentration would decrease, shifting the straight line graph down.
   ii) If the temperature of the decomposition were elevated further, the slope (k) of the straight line graph would become steeper (k increases as temperature raises).

Page 56, Practice Problems 1. a)

$t_{1/2} = 4.6\times10^4$ s (770 min) (13 h)
   b) $C = 0.094$ mol/L (0.09 mol/L)
2. a) $k = 5.8 \times 10^{-3}\ s^{-1}$
   b) $C = 0.038$ mol/L (0.04 mol/L)
   c) $t = 1.0 \times 10^2$ s

Page 58, Practice Problems

1. a) $t_{1/2} = 126$ s
   b) $\frac{1}{C} = 39.9$ L/mol
   $C = 2.51 \times 10^{-2}$ mol/L
2. If the half-life of a reaction is independent of the initial concentration of the reactants, then the reaction is first order.

Page 60, 1.5 Review Questions

1.

	a) first order	b) zero order	c) second order
i) rate of reaction	Decreases	Stays constant	Decreases
ii) rate constant	Stays constant	Stays constant	Stays constant
iii) half life	Stays constant	Decreases (half the previous)	Increases (double the previous)

2. $C = 0.222$ mol/L (0.22 mol/L)
3. $C = 0.14$ mol/L
4. $C = 0.41$ mol/L
5. a) $k = 0.050\ h^{-1}$
   b) t = 56 h
6. $k = 0.00212\ s^{-1}$
7. $t_{1/2} = 7.30$ s
8. Graphs for a 1st order equation are shown.
   a) decrease in the initial concentration by a factor of ½ as evident by examination of the y-axis
   b) decrease in the initial rate: a tangent drawn to the curves in the first graph at time zero now has about HALF the SLOPE
   c) rate constant, k (determined by finding the slope of the lnC vs t graph) remains the SAME
   d) temperature has increased. Only a change in temperature can change k.
   e) the slope of the initial tangent line (= the rate) has increased and the temperature could increase the rate constant

9. Graphs for a 2nd order equation are shown.

a) decrease in the initial concentration by a factor of ½ as evident by examination of the y-axis

b) decrease in the initial rate: a tangent drawn to the curves in the first graph at time zero now has about HALF the SLOPE

c) rate constant, k (determined by finding the slope of the 1/C vs t graph) remains the SAME

d) temperature has decreased. Only a change in temperature can change k.

e) the slope of the initial tangent line (= the rate) has decreased and the temperature could decrease the rate constant

10. Decomposition of aqueous sucrose to form the isomers glucose and fructose:

Time (min)	$[C_{12}H_{22}O_{11}]$ (mol/L)	ln$[C_{12}H_{22}O_{11}]$	$1/[C_{12}H_{22}O_{11}]$ (L/mol)
0	0.316	- 1.15 (- 1.152)	3.17
39	0.274	- 1.30 (- 1.295)	3.65
80	0.238	- 1.44 (- 1.435)	4.20
140	0.190	- 1.66 (- 1.661)	5.26
210	0.146	- 1.92 (- 1.924)	6.85

a) Rate = $k[C_{12}H_{22}O_{11}]$

b) $k = 0.004\ \text{min}^{-1}$. Approximate value from graph slope.

c) $t_{1/2}$ 1.13×10^{4} s (189 min) (3.14 h) . Approximate value from graph slope

d) $C = 0.166\ \text{mol/L}$ $(0.17\ \text{mol/L})$. Approximate value from graph slope.

11.

Time (s)	$[CH_3NC]$ (mol/L)	ln$[CH_3NC]$	$1/[CH_3NC]$ (L/mol)
2000	0.0110	- 4.51 (- 4.510)	90.0
5000	0.0059	- 5.1 (- 5.13)	170
8000	0.0031	- 5.8 (- 5.78)	320
12000	0.0014	- 6.6 (- 6.57)	710
15000	0.0007	- 7 (- 7.3)	1000

a) Rate = $k[CH_3NC]$

b) $k == 0.0002\ s^{-1}$. Approximate value from graph slope.

c) $t_{1/2} = 3000\ s$ $(50\ min)$ $(0.9\ h)$. Approximate value from graph slope.

d) $C = 2\times10^{-4}\ mol/L$ $(10^{-4}\ mol/L)$. Approximate value from graph slope.

12. a) $k = 0.0105\ L/mol/s$

b) $t_{1/2} = 316\ s$ this is the 1st half life

13. Assume 1.00 mol/L initial sample:

t = 34.2 years

14. a) $t_{1/2} = 20\ (C_o)s$

b) $C = 0.13\ \text{mol/L}$

15. t = 75.4 s

Page 66, Quick Check

2. $2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(l) + 2857.0\ kJ/mol_{rxn}$

$2\ C_2H_6(g) + 7\ O_2(g) \rightarrow 4\ CO_2(g) + 6\ H_2O(l)$ $\Delta H = -2857.0\ kJ/mol_{rxn}$

3. $72.2\ kJ/mol_{rxn} + 2\ HBr(g) \rightarrow H_2(g) + Br_2(l)$

$2\ HBr(g) \rightarrow H_2(g) + Br_2(l)$ $\Delta H = +72.2\ kJ/mol_{rxn}$

Page 70, Practice Problems

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.

Page 72, Quick Check

A) Reverse uncatalyzed activation energy. $E_{a(Reverse\ Uncatalyzed)}$ is #2 in Diagram 2.

B) Forward catalyzed activation energy. #3

C) Decrease in E_a due to catalysis. #4

D) ΔH. #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.)

Page 74, 1.6 Review Questions

1. a) $Fe_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Fe(s)$ $\Delta H = -852\ kJ/mol_{rxn}$

$Fe_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Fe(s) + 852\ kJ/mol_{rxn}$

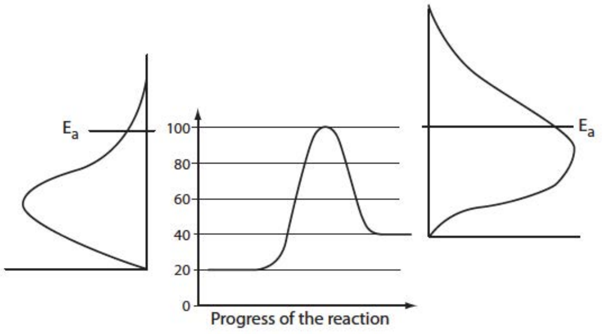
b) $Ca(s) + O_2(g) + H_2(g) \rightarrow Ca(OH)_2(s)$ $\Delta H = -986\ kJ/mol_{rxn}$

$Ca(s) + O_2(g) + H_2(g) \rightarrow Ca(OH)_2(s) + 986\ kJ/mol_{rxn}$

c) $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$ $\Delta H = +572\ kJ/mol_{rxn}$

$572\ kJ/mol_{rxn} + 2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$

2. a&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 = Δ*H*
C = Reverse uncatalyzed activation energy.
D = Forward uncatalyzed activation energy.
E = Reverse catalyzed activation energy.
b) Exothermic
c) No effect.

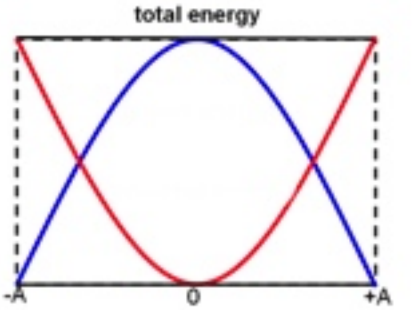
5. a) -50 kJ/mol
b) Q + S → T + 50 kJ/mol
Q + S → T Δ*H* = -50 kJ/mol
c) exothermic
d) 150 kJ/mol

6. The energy released as more $CO_2(g)$ and $H_2O(g)$ is formed provides the activation energy needed to continue decomposing the hydrocarbon fuel.

7. The energy released during bond forming is <u>greater</u> than the energy required for bond <u>breaking</u>. As a result, there is a net <u>release</u> of energy. The bonds formed have less potential energy than the <u>reactant</u> 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 (u-shape) 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.

Page 80, Quick Check

2. a)Bimolecular – Elementary Process
b) Unimolecular – Elementary Process
c) Termolecular – Overall Reaction

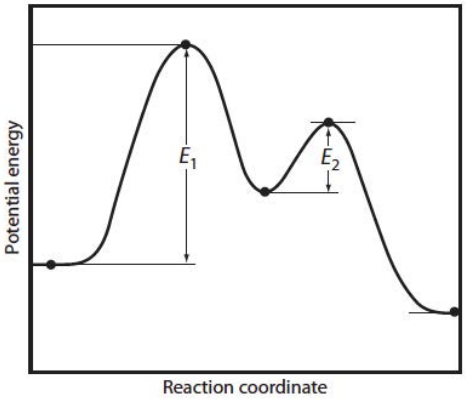
Page 83, Practice Problems

1. $O_3(g) \rightarrow O_2(g) + \cancel{O}(g)$ (slow)

$\cancel{O}(g) + O_3(g) \rightarrow 2\,O_2(g)$
(Δ*H* value for entire reaction = - 284.6 kJ/mol)

$2\,O_3(g) \rightarrow 3\,O_2(g)$
There are no catalysts and O is the intermediate.

Overall E_a is shown on the y-axis.

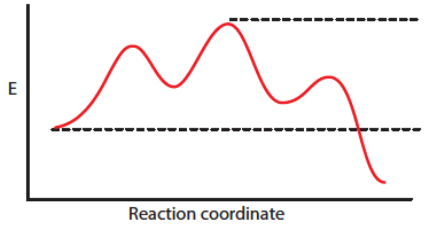


2. $H_2(g) + \cancel{2\,Pd}(s) \rightleftharpoons \cancel{2\,Pd\text{-}H(s)}$
$C_2H_4(g) + \cancel{Pd\text{-}H}(s) \rightarrow \cancel{C_2H_5\text{-}Pd}(s)$ (slowest step)
$\cancel{C_2H_5\text{-}Pd}(s) + \cancel{Pd\text{-}H}(s) \rightarrow C_2H_6(g) + \cancel{2\,Pd}(s)$

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) + 136.9\text{ kJ/mol}$

Catalyst is: Pd   Intermediates are: Pd-H and C_2H_5Pd

Activation energy is between the dotted lines.



3.

$Cl_2(g) \rightarrow \cancel{Cl}(g) + \cancel{Cl}(g)$ initiation
$CH_4(g) + \cancel{Cl}(g) \rightarrow CH_3Cl(g) + \cancel{H}(g))$ x 2   propagation
$\cancel{H}(g) + \cancel{H}(g) \rightarrow H_2(g)$ termination
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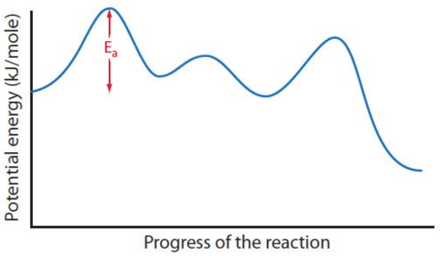
$2\,CH_4(g) + Cl_2(g) \rightarrow 2\,CH_3Cl(g) + H_2(g)$ chain mechanism

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.)

Page 87, Practice Problems

1. a) intermediates: HOCl, OH^-, HIO; catalyst: H_2O
   b) Rate = $k[I^-][OCl^-]/[OH^-]$
2. a) $Cl_2 \leftrightarrow \cancel{2\,Cl}$
   $\cancel{Cl} + CHCl_3 \rightarrow HCl + \cancel{CCl_3}$
   $\cancel{Cl} + \cancel{CCl_3} \rightarrow CCl_4$
   $Cl_2 + CHCl_3 \rightarrow CCl_4 + HCl$
   b) intermediates: Cl, CCl_3
   c) Rate = $k[Cl_2]^{1/2}[CHCl_3]$

Page 91, 1.7 Review Questions

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: $H_2O_2(aq) + \cancel{I^-(aq)} \rightarrow H_2O(l) + \cancel{IO^-(l)}$ slow

2nd $H_2O_2(aq) + \cancel{IO^-(aq)} \rightarrow H_2O(l) + O_2(g) + \cancel{I^-(aq)}$ fast

   a) Overall Rxn: $2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$
   b) Intermediates: IO^-
   c) catalyst is I^-

6. $NO_2 + F_2 \rightarrow NO_2F + \cancel{F}$ (RDS)
   $NO_2 + \cancel{F} \rightarrow NO_2F$

   $2\,NO_2 + F_2 \rightarrow 2\,NO_2F$
7. a) 3
   b) 2nd step (middle step or step C)
   c) C
   d) B
   e) F
   f) endothermic
8.
   a) Mechanism One:
   Step 1:
   $2\,NO_2(g) \rightarrow NO_3(g) + NO(g)$ slow

   Step 2:
   $CO + NO_3 \rightarrow CO_2 + NO_2$ fast
   Overall Rxn:
   $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$
   (Note that this is an example of ***authocatalysis.*** The reactant, NO_2, also acts as a catalyst for the reaction. Some autocatalyzed reactions involve the formation of the catalyst from the reactants in an early step.)

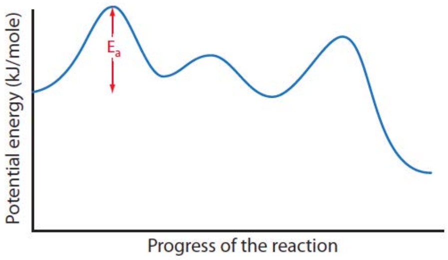
   Mechanism Two:
   Step 1:
   $2\,NO_2(g) \rightarrow N_2O_4(g)$ fast
   Step 2:
   $CO + N_sO_4 \rightarrow NO_2 + CO_2 + NO$ slow
   Overall Rxn:
   $CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g)$

   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) $HBr + O_2 \rightarrow \cancel{HOOBr}$

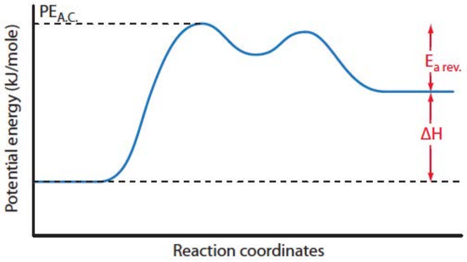
$$HBr + \cancel{HOOBr} \rightarrow \cancel{2\,HOBr}$$
$$HBr + \cancel{HOBr} \rightarrow H_2O + Br_2$$
$$\underline{HBr + \cancel{HOBr} \rightarrow H_2O + Br_2}$$
$$4\,HBr + O_2 \rightarrow 2\,H_2O + 2\,Br_2$$

c) Step One (both HBr and O_2 influence reaction rate).

d)



10.



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

11. a) intermediate: N_2O_2

b) Rate = $k[NO]^2[O_2]$

12. Starting with each mechanism's temporary rate law based upon the slow step:

Mechanism One: inconsistent with the provided rate law, rate = $k[A][B]$

Rate = $k'[M][A]$

$$K_{eq} = \frac{[C][M]}{[A][B]}$$

$[M] = K_{eq}[A][B]/[C]$

Rate = $k'K_{eq}[A]^2[B]/[C]$

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

N/A: if [M] in the rate law was substituted with the statement above, non-reactant species are also included

Mechanism Two: consistent with the provided rate law, rate = $k[A][B]$

Rate = $k'[M][A]$

$$K_{eq} = \frac{[M]}{[B]}$$

$[M] = K_{eq}[B]$

Rate = $k'K_{eq}[A][B]$

Rate = $k[A][B]$

Mechanism Three: inconsistent with the provided rate law, rate = $k[A][B]$

Rate = $k'[M][A]$

$$K_{eq} = \frac{[M]}{[A][B]}$$

$[M] = K_{eq}[A][B]$

Rate = $k'K_{eq}[A]^2[B]$

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

13. a) Step 1: $NO + O2 \leftrightarrow \cancel{NO_3}$

$\underline{\text{Step 2: } \cancel{NO_3} + NO \rightarrow 2\,NO_2}$

$2\,NO + O_2 \rightarrow 2\,NO_2$

b) Rate = $k[NO]^2[O_2]$

14. a) $NH_3 + OBr^- \leftrightarrow \cancel{NH_2Br} + \cancel{OH^-}$

$\cancel{NH_2Br} + NH_3 \rightarrow \cancel{N_2H_5^+} + Br^-$

$\underline{\cancel{N_2H_5^+} + \cancel{OH^-} \rightarrow N_2H_4 + H_2O}$

$2\,NH_3 + OBr^- \rightarrow N_2H_4 + Br^- + H_2O$ (basic)

b) intermediates: NH_2Br, OH^-, $N_2H_5^+$

c) Rate = $k[NH_3]^2[OBr^-]/[OH^-]$