CHAPTER 14 – Chemical Kinetics

Define the term **reaction rate**.

Define the term **reaction mechanism**.

Section 14.1 – Factors That Affect Reaction Rates

(a) List the four factors that will cause the reaction rate to change.

__________________________________ __________________________________

__________________________________ __________________________________

(b) Explain why 10 g of powdered zinc will react with hydrochloric acid more quickly than a solid zinc strip that weighs 10 g.

(c) Explain why a sample of magnesium metal will react more quickly in 10 *M* HCl than it will react in 1 *M* HCl.

(d) Explain why an Alka-Seltzer tablet will dissolve more quickly in water @ 80°C than in water @ 20°C.

(e) Describe the role of a catalyst in a chemical reaction.

(f) As the frequency of collisions between reactant molecules increases, how will the rate of a chemical reaction be affected?

Section 14.2 – Reaction Rates

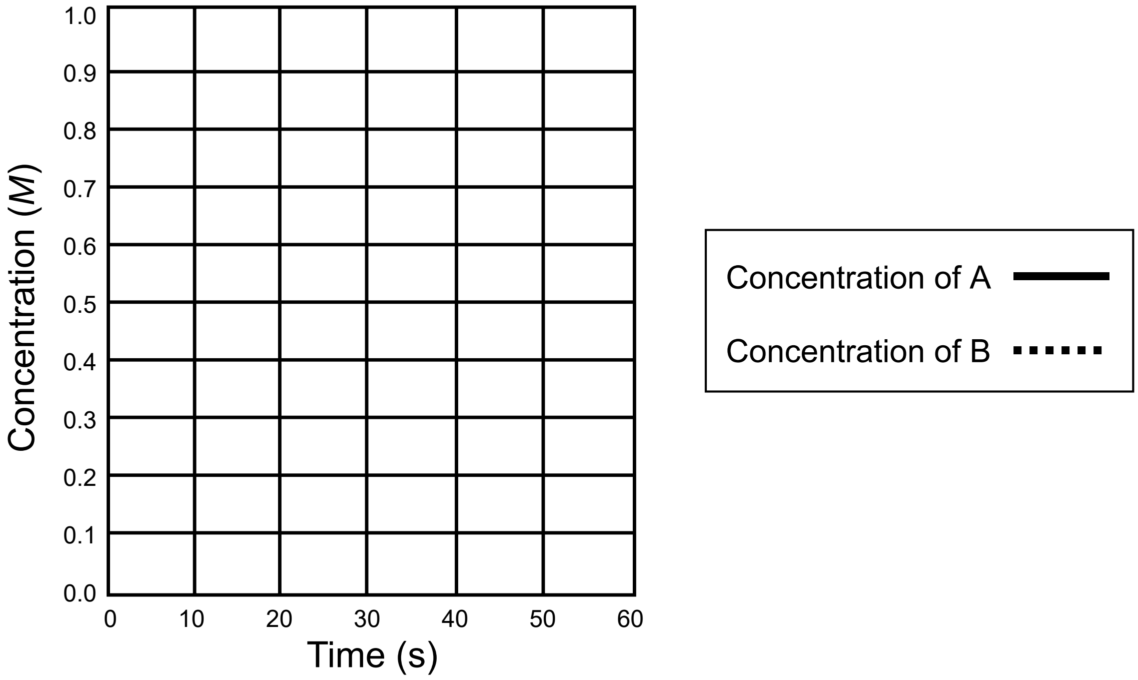
(a) What unit is used to measure the rate of a chemical reaction? ____________________

(b) In order to determine the reaction rate, the __________________________ of a reactant or a product is measured over time to see how fast it changes.

(c) The table below is based on the chemical reaction A → B as described in Figure 14.3 on page 559. Fill in the missing values for the amount of B produced.

Time (s)	0	10	20	30	40	50	60
Moles of A in the 1.0 L flask	1.00	0.73	0.54	0.40	0.30	0.21	0.16
Moles of B in the 1.0 L flask	0.00						

(d) Create a graph of the data from the table in part (c). Use a smooth line to connect the data points for each substance. Use a solid line for A and a dashed line for B.



(e) How is the average rate of a reaction calculated for a particular time interval? See Equation 14.1 on page 560.

(f) Based on the data table from part (c), calculate the average rate of disappearance of A for each of the following time intervals. Units of rate should be *M* s^{-1}

0 s to 10 s ______________ 20 s to 30 s _____________ 40 s to 50 s _____________

10 s to 20 s _____________ 30 s to 40 s _____________ 50 s to 60 s _____________

(g) Examine the values for average rate that you calculated in part (f). How are these values changing over time? (e.g., increasing, decreasing, or staying constant)
You can see more examples of this trend in Table 14.1 and in Figure 14.4 on p. 561.

(h) Why is it typical for reaction rates to decrease over time as a reaction proceeds?

(i) Define the term **instantaneous rate** of reaction.

(j) The instantaneous rate at t = 0 is called the ______________ rate of the reaction.

(k) Suppose that, in a certain reaction, $\frac{\Delta[A]}{\Delta t} = 2 \times \frac{\Delta[B]}{\Delta t}$

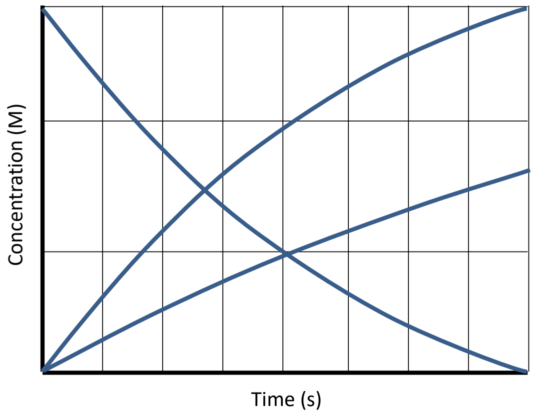
Which of the following reactions is consistent with this rate information? Explain.

$2A + B \rightarrow C$ $A + 2B \rightarrow C$

$$2\ HI(g) \rightarrow H_2(g) + I_2(g)$$

(l) At a certain moment in time, the rate of formation of H_2 is equal to 1.8 x 10^{-6} *M*/s. Calculate the rate of disappearance of HI at this moment in time.

(m) The graph below displays the change in concentration for each species in the following reaction: $2\ A \rightarrow 2\ B + C$ Label each curve on the graph below as A, B, or C.



Section 14.3 – Concentration and Rate Laws

Table 14.2 is shown below.

Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

(a) In experiments 1-3, the independent variable is the concentration of NH_4^+; the dependent variable is the observed initial rate of reaction. The concentration of NO_2^- is held constant. Discuss the relationship between the independent variable and the dependent variable in experiments 1 and 2.

(b) Discuss the relationship between the independent variable and the dependent variable in experiments 1 and 3.

(c) In experiments 4-6, the independent variable is the concentration of NO_2^-; the dependent variable is the observed initial rate of reaction. The concentration of NH_4^+ is held constant. Discuss the relationship between the independent variable and the dependent variable in experiments 4 and 5.

(d) Discuss the relationship between the independent variable and the dependent variable in experiments 4 and 6.

(e) Define the term **rate law**. Give an example of a rate law by using Equation 14.6 on p. 565.

(f) Discuss the meaning of the terms *k*, *m*, and *n* in Equation 14.7.

(g) Use Equation 14.6 and the data from Table 14.2 to calculate the value of the rate constant *k*. Include units in your answer.

(h) Does it matter which experimental data (1 – 6) we use in Table 14.2 in order to calculate the value of the rate constant *k*? Use data from several different experiments in order to justify your answer.

(i) Once we have both the rate law and the value of *k* for a reaction, we can calculate the rate of the reaction for any set of concentrations. Calculate the rate law at 25°C when the initial concentrations of NH_4^+ and NO_2^- are both 0.100 M.

The exponents *m* and *n* are called reaction orders. If the exponent is 1, we say that the reaction is 1st order with respect to that reactant. If the exponent is 2, we say that the reaction is 2nd order with respect to that reactant. The overall reaction order is the sum of the orders with respect to each reactant. In most of the rate laws that you will encounter in chemistry, the order with respect to a reactant will either be 0, 1, or 2.

(j) Is the statement below true or false? Explain.

"*The exponent for each substance in a rate law should be the same as the coefficient for that substance in the overall balanced chemical equation.*"

(k) Is the statement below true or false? Explain.

"*The exponents in the rate law should always be determined from experimental data.*"

(l) The best way to determine if a reaction is fast or slow is to look at the magnitude of the

____

(m) The units of the rate constant will depend on the overall reaction order of the rate law.
For each rate law, assume that the units of the rate are *M*/s.
Fill in the missing information in the table below.

Rate Law	Overall reaction order	Units of the rate constant *k*
rate = k		
rate = k [A]		
rate = k [A]^2		
rate = k [A][B]		
rate = k [A]^2[B]		

(n) Suppose that the rate law for a reaction is as follows: rate = k
If you double the concentration of A,
what effect would this have on the rate? _______________________

(o) Suppose that the rate law for a reaction is as follows: rate = k [A]
If you double the concentration of A,
what effect would this have on the rate? _______________________

(p) Suppose that the rate law for a reaction is as follows: rate = k [A]^2
If you double the concentration of A,
what effect would this have on the rate? _______________________

(q) The following problem requires you to determine the rate law from experimental data.

$$2\ HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2\ Cl^-(aq) + 2\ CO_2(g) + Hg_2Cl_2(aq)$$

The equation for the reaction between mercury(II) chloride and the oxalate ion in aqueous solution is shown above. The initial rate of formation of chloride ion was calculated for various initial concentrations of the reactants as shown in the following table.

Experiment	Initial [$HgCl_2$] (*M*)	Initial [$C_2O_4^{2-}$] (*M*)	Initial Rate of Formation of Cl^- (*M*/min)
1	0.0836	0.202	5.20×10^{-5}
2	0.0836	0.404	2.08×10^{-4}
3	0.0418	0.404	1.04×10^{-4}
4	0.0316	0.514	?

(i) What is the order of the reaction with respect to $HgCl_2$? Justify your answer.

(ii) What is the order of the reaction with respect to $C_2O_4^{2-}$? Justify your answer.

(iii) Write the rate law for this reaction. ______________________________________

(iv) What is the overall order of this reaction? ________________

(v) Calculate the value of the rate constant *k*. Specify the units in your answer.

(vi) What is the value for the initial rate of disappearance of $C_2O_4^{2-}$ for Experiment 1?

(vii) Calculate the initial rate of formation of Cl^- for Experiment 4.

Section 14.4 – The Change of Concentration with Time

For a first-order reaction, the rate law can be written as follows: rate = k [A]

From calculus, the following integrated rate law can be obtained: $\ln[A]_t - \ln[A]_o = -kt$

(a) Define the meaning of each the following terms in the integrated rate law:

$[A]_o$

$[A]_t$

k

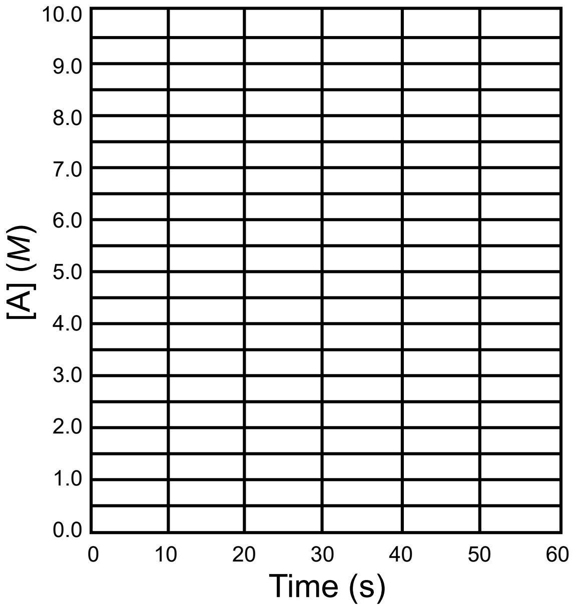
t

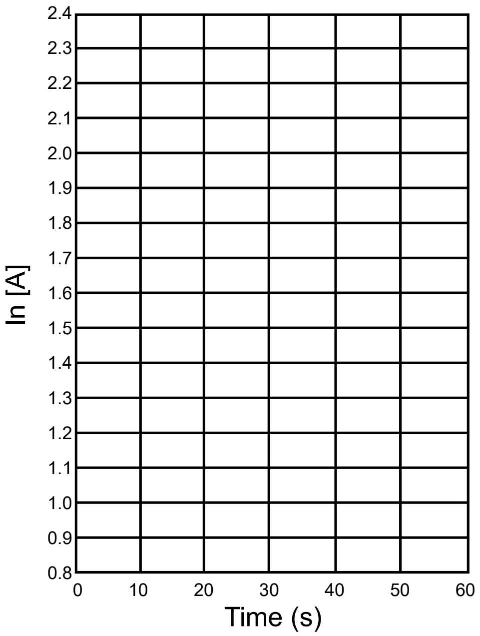
(b) Re-write the first-order integrated rate law so that it is the form "y = mx + b"

____

(c) The following represents data from a first-order reaction. Fill in the missing data in the table. Then plot the data on the two graphs below.

Time (s)	[A] (*M*)	ln[A]
0	10.0	
10	7.94	
20	6.30	
30	5.00	
40	3.97	
50	3.15	
60	2.50	





(d) For a first-order reaction, which of the following will generate a straight-line plot?

[A] vs. time   ln[A] vs. time   1/[A] vs. time

(e) Calculate the slope of the straight line that was generated from the data in part (c). Include units in your answer.

(f) What does the value of this slope represent in the first-order rate law equation? ___________

For a second-order reaction, the rate law can be written as follows: rate = $k\,[A]^2$

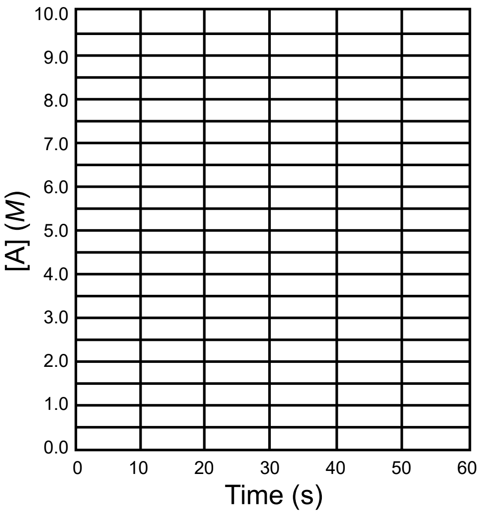
From calculus, the following integrated rate law can be obtained: $\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$

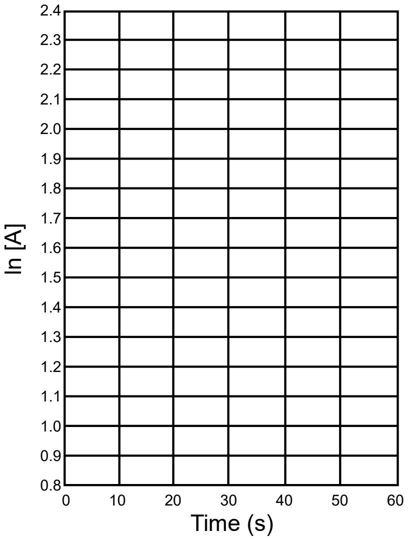
(g) Re-write the second-order integrated rate law so that it is the form "y = mx + b"

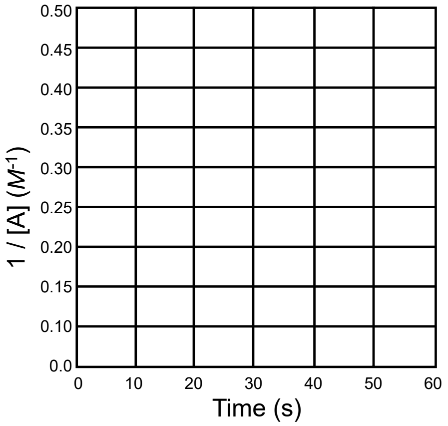
____

(h) The following represents data from a second-order reaction. Fill in the missing data in the table. Then plot the data on the three graphs below.

Time (s)	[A] (*M*)	ln[A]	1/[A] (M^{-1})
0	10.0		
10	6.67		
20	5.00		
30	4.00		
40	3.33		
50	2.86		
60	2.50		







(i) For a second-order reaction, which of the following will generate a straight-line plot?

[A] vs. time   ln[A] vs. time   1/[A] vs. time

(j) Calculate the slope of the straight line that was generated from the data in part (h). Include units in your answer.

(k) What does the value of this slope represent in the second-order rate law equation? ________

For a zero-order reaction, the rate of the reaction (i.e., the disappearance of A) does NOT depend on the concentration of the reactant A. The rate law for a zero-order reaction can be written as follows: rate = k

The following integrated rate law can be obtained: $[A]_t - [A]_o = -kt$

(l) For a zero-order reaction, which of the following will generate a straight-line plot?

[A] vs. time   ln[A] vs. time   1/[A] vs. time

(m) Define the term **half-life ($t_{½}$)**.

(n) The following exercise will help you to understand the concept of half-life for a first-order reaction.

(i) Write the integrated rate law for a first-order reaction: ______________________________

(ii) Substitute the following values for $[A]_o$ and $[A]_t$ into the equation: $[A]_o = 100$ $[A]_t = 50$

(iii) Simplify the equation and solve for t: ____

(o) Notice that the half-life for a first-order rate law does NOT depend on the initial concentration of the reactant. The half-life remains constant over time throughout the reaction.
Go back to the first-order data table in part (c).

How much time was required for the reactant
concentration to change from 10.0 M to 5.0 M? ___________

How much time was required for the reactant
concentration to change from 5.0 M to 2.5 M? ____________

(p) You may recall that the rate constant for that first-order reaction in part (c) was equal to

$0.023\ s^{-1}$. Verify that $\frac{0.693}{k} = t_{½}$

If a decomposition reaction yields data that shows that the half-life is constant over time, then the reaction must be a first-order reaction.

(q) The half-life for a second-order reaction is NOT constant over time. To verify this, go back to the second-order data table in part (h).

How much time was required for the reactant concentration to change from 10.0 M to 5.0 M? ___________

How much time was required for the reactant concentration to change from 5.0 M to 2.5 M? ____________

Section 14.5 – Temperature and Rate

(a) Most chemical reactions will occur at a _______________ rate when the temperature of the reaction is increased.

(b) If the temperature of a chemical reaction is increased, the value of the rate constant

should __________________.

(c) Use the collision model to explain why increasing the concentration of a reactant should normally cause the reaction rate to increase.

(d) Use the collision model to explain why increasing the temperature of a reaction causes the reaction rate to increase.

(e) Consider the reaction between hydrogen and iodine to form hydrogen iodide.

Is it true that every time a hydrogen molecule collides with an iodine molecule,

a molecule of HI is formed? __________

(f) In most reactions, reactant molecules must be ____

during a collision in order for a reaction to occur.

(g) In 1888, the Swedish chemist Arrhenius suggested that molecules must __________________

____ in order to react.

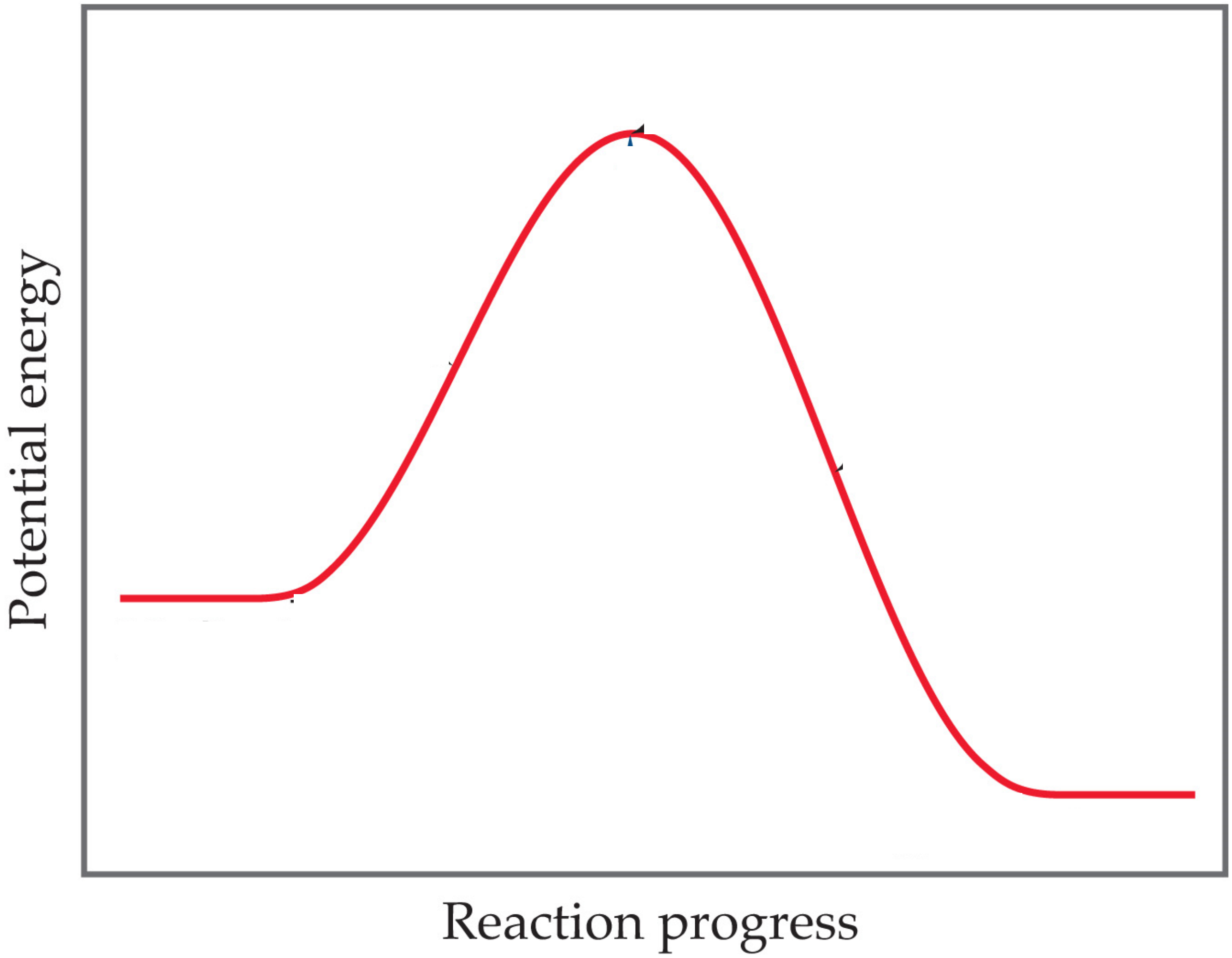
This is known as the _______________________ energy, E_a.

The top of the "hill" in an energy diagram represents the **activated complex** or **transition state**. This represents a situation where bonds are partially broken and partially formed.

(h) In the diagram below, label the following

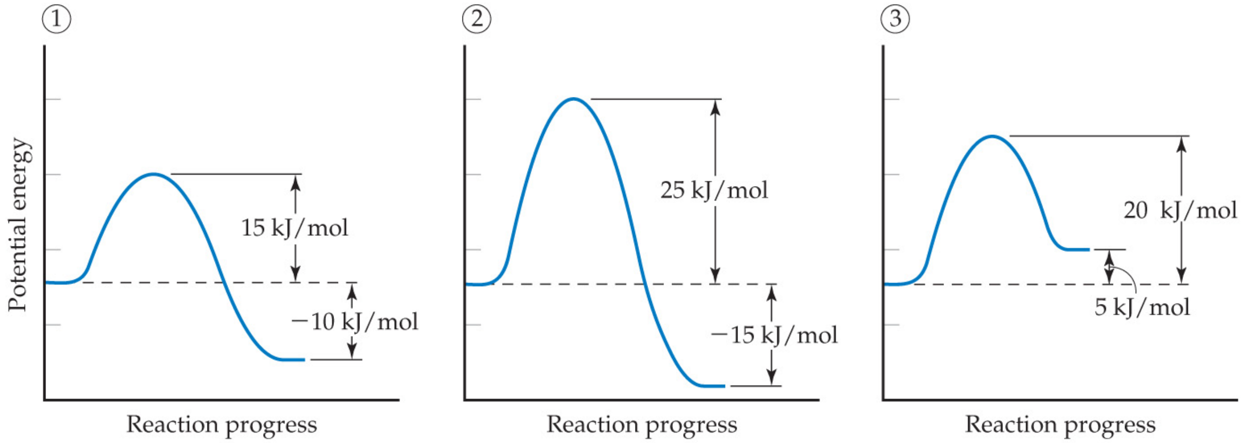
potential energy of $CH_3N{\equiv}C$	activation energy
potential energy of $CH_3C{\equiv}N$	overall ΔE for the reaction
activated complex	

$CH_3N{\equiv}C \rightarrow CH_3C{\equiv}N$



(i) The rate of a reaction depends on the magnitude of E_a. Explain.

(j) In terms of the activation energy, explain why the reaction rate tends to increase at higher temperatures.



(k) Which reaction above (1, 2, or 3) is endothermic? __________

(l) Which reaction should occur at the slowest rate? __________

Which reaction should occur at the fastest rate? ___________

(m) Calculate the activation energy for the <u>reverse</u> reactions.

1: ________ kJ/mol 2: ________ kJ/mol 3: ________ kJ/mol

Section 14.6 – Reaction Mechanisms

(a) At the beginning of this chapter, the term **reaction mechanism** was defined as

____

Each event in a reaction mechanism is called an elementary reaction or an **elementary step**. If there is only one molecule as the reactant in an elementary step, the reaction is said to be **unimolecular**. If an elementary step involves two reactant molecules, the reaction is said to be **bimolecular**. Termolecular reactions that involve the simultaneous collision of three particles are rare.

Consider the following two-step mechanism:

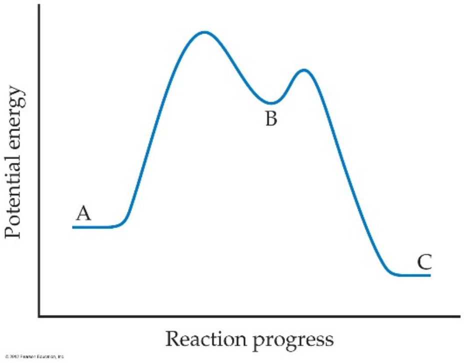
Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

(b) What is the overall reaction that is described by this two-step mechanism?

(c) The species NO_3 is neither a reactant nor a product in this reaction. It is formed in Step 1 and consumed in Step 2. This is an example of an ______________________.

(d) An intermediate is not the same as a transition state, because intermediates can be stable and can sometimes be isolated. Transition states are always unstable and can never be isolated. If an intermediate can be detected in an experiment, it can help to support why a particular reaction mechanism is likely to occur. Label the intermediate on the diagram at right.



Step 1: $Mo(CO)_6 \rightarrow Mo(CO)_5 + CO$

Step 2: $Mo(CO)_5 + P(CH_3)_3 \rightarrow Mo(CO)_5P(CH_3)_3$

(e) In the proposed two-step reaction mechanism shown above, $Mo(CO)_5$ is classified as

a(n) ________________________ and CO is classified as a(n) ________________________.

In Section 14.3, it was mentioned that a rate law must be determined from experimental data. One cannot determine the order with respect to a reactant by simply looking at its coefficient in the overall balanced chemical equation. However, the rate law can be determined by examining the elementary steps of a reaction mechanism. If the experimentally-determined rate law is consistent with the rate law from a reaction mechanism, it supports the fact that the mechanism is valid.

(f) The rate law of an elementary step is based directly on its molecularity. This means that the

rate of a unimolecular step is ________________ and the rate of a bimolecular step is

_________________.

(g) A reaction mechanism often involves two or more steps. Each elementary step has its own rate, rate constant, and activation energy. It is often true that one step is much slower than the others in the mechanism. The overall reaction rate cannot be any faster than the rate of the slowest elementary step. Because the slow step limits the overall reaction rate, it is called the

____, and this step governs the rate law for

the overall reaction.

Consider the following two-step mechanism again. It has been labeled with a <u>slow initial step</u>.

Step 1: $NO_2 + NO_2 \rightarrow NO_3 + NO$ (slow)

Step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

(h) Based on this mechanism, write the balanced equation for the overall reaction and write the rate law for the overall reaction.

(i) A reaction mechanism can never be "proved." It can only be stated that the rate law predicted by the proposed mechanism is ____

Consider the following two-step mechanism with a <u>slow initial step</u>.

Step 1: $N_2O \rightarrow N_2 + O$ (slow)

Step 2: $N_2O + O \rightarrow N_2 + O_2$ (fast)

(j) Based on this mechanism, write the balanced equation for the overall reaction and write the rate law for the overall reaction.

Consider the following two-step mechanism with a <u>slow second step</u>.

Step 1: $NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2$ (fast)

Step 2: $NOBr_2 + NO \xrightarrow{k_2} 2\ NOBr$ (slow)

(k) Since Step 2 is the rate-determining step, the rate law for that step governs the rate of the overall reaction. Write this rate law based on the bimolecular step 2 reaction.

____

(l) We cannot accept the rate law written in part (k) as our final answer, because intermediates are usually _________________ and have a low, unknown concentration. We need to rewrite this rate law so that it is expressed in terms of the reactants.

Since the first step in the mechanism is a fast, reversible process, we can write the following.

$$k_1\,[NO][Br_2] = k_{-1}[NOBr_2]$$

(m) The equation above is true because the rate of the forward reaction in step 1 ________________________ the rate of the reverse reaction.

(n) Solving for $[NOBr_2]$, we get

$[NOBr_2] =$

(o) Substituting this relationship into the equation written in part (k), we get

rate =

In general, when a fast step precedes a slow step in a mechanism, we can solve for the concentration of the intermediate by assuming that an equilibrium is established in the first step.

Section 14.7 – Catalysis

(a) Define the term **catalyst**.

Step 1: $2\ Br^- + H_2O_2 + 2\ H^+ \rightarrow Br_2 + 2\ H_2O$

Step 2: $Br_2 + H_2O_2 \rightarrow 2\ Br^- + 2\ H^+ + O_2$

(b) Based on the mechanism above, write the balanced equation for the overall reaction.

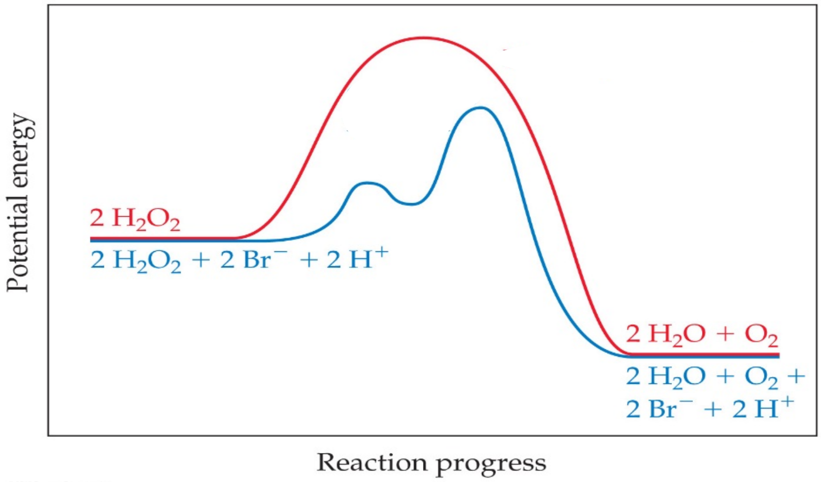
(c) In this mechanism, Br_2 is classified as a(n) ________________________ because it is formed as a product in Step 1 and later consumed as a reactant in Step 2.

(d) In this mechanism, Br^- is classified as a(n) ________________________ because it is present as a reactant in Step 1 and it is formed as a product in Step 2.

(e) Catalysts may function by stabilizing a transition state. This would ___________________ the activation energy of an elementary step, increasing the rate of that step but leave the mechanism otherwise unchanged.

(f) Catalysts may also participate in the formation of a new ___________________________, which provides a new mechanism that provides a faster pathway between reactants and products.

(g) Label the catalyzed pathway and the uncatalyzed pathway in the diagram at right.



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(h) A biological catalyst is known as an _________________. They can form a bond to the substrate molecules at the active site. The lock-and-key model provides a simple explanation for how a particular substrate molecule can bind very specifically to the active site.