**Learning Objectives:**

4.1 The student is able to design and/or interpret the results of an experiment regarding the factors (i.e., temperature, concentration, surface area) that may influence the rate of a reaction.

4.2 The student is able to analyze concentration vs. time data to determine the rate law for a zeroth-, first-, or second-order reaction.

4.3 The student is able to connect the half-life of a reaction to the rate constant of a first-order reaction and justify the use of this relation in terms of the reaction being a first-order reaction.

4.4 The student is able to connect the rate law for an elementary reaction to the frequency and success of molecular collisions, including connecting the frequency and success to the order and rate constant, respectively.

4.5 The student is able to explain the difference between collisions that convert reactants to products and those that do not in terms of energy distributions and molecular orientation.

4.6 The student is able to use representations of the energy profile for an elementary reaction (from the reactants, through the transition state, to the products) to make qualitative predictions regarding the relative temperature dependence of the reaction rate.

4.7 The student is able to evaluate alternative explanations, as expressed by reaction mechanisms, to determine which are consistent with data regarding the overall rate of a reaction, and data that can be used to infer the presence of a reaction intermediate.

4.8 The student can translate among reaction energy profile representations, particulate representations, and symbolic representations (chemical equations) of a chemical reaction occurring in the presence and absence of a catalyst.

4.9 The student is able to explain changes in reaction rates arising from the use of acid-base catalysts, surface catalysts, or enzyme catalysts, including selecting appropriate mechanisms with or without the catalyst present.

5.1 The student is able to create or use graphical representations in order to connect the dependence of potential energy to the distance between atoms and factors, such as bond order (for covalent interactions) and polarity (for intermolecular interactions), which influence the interaction strength.

5.2 The student is able to relate temperature to the motions of particles, either via particulate representations, such as drawings of particles with arrows indicating velocities, and/or via representations of average kinetic energy and distribution of kinetic energies of the particles, such as plots of the Maxwell-Boltzmann distribution.

5.3 The student can generate explanations or make predictions about the transfer of thermal energy between systems based on this transfer being due to a kinetic energy transfer between systems arising from molecular collisions.

**Kinetics Review**

1. In order for a reaction to occur the particles must \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_with proper \_\_\_\_\_\_\_\_\_\_\_\_\_\_ and \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. Therefore, the more collisions the reactant particle have, the faster the rate.
2. Recall 5 ways to increase the rate of reaction. Be specific.
3. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
4. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
5. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
6. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
7. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
8. Matches have the potential to burn on fire. But they will not without sufficient activation energy. Explain what activation energy means and what type of activation energy the matches need.
9. Which event must *always* occur for a chemical reaction to take place?
   * 1. formation of a precipitate
     2. formation of a gas
     3. effective collisions between reacting particles
     4. addition of a catalyst to the reaction system
10. Increasing the temperature increases the rate of a reaction by
    * 1. lowering the activation energy
      2. increasing the activation energy
      3. lowering the frequency of effective collisions between reacting molecules
      4. increasing the frequency of effective collisions between reacting molecules
11. After being ignited in a Bunsen burner flame, a piece of magnesium ribbon burns brightly, giving off heat and light. In this situation, the Bunsen burner flame provides
    * 1. ionization energy c) activation energy
      2. heat of reaction d) heat of vaporization
12. As the number of effective collisions between reacting particles increases, the rate of reaction
    * 1. Decreases b)increases c)remains the same
13. In most aqueous reactions as temperature increases, the effectiveness of collisions between reacting particles
    * 1. Decreases b) increases c) remains the same
14. Given the reaction: **Mg + 2 H2O 🡪 Mg(OH)2 + H2**

At which temperature will the reaction occur at the greatest rate?

1. 25ºC b) 50ºC c) 75ºC d) 100ºC
2. A 5.0-gram sample of zinc and a 50.-milliliter sample of hydrochloric acid are used in a chemical reaction. Which combination of these samples has the fastest reaction rate?
3. a zinc strip and 1.0 M HCl(aq)
4. a zinc strip and 3.0 M HCl(aq)
5. zinc powder and 1.0 M HCl(aq)
6. zinc powder and 3.0 M HCl(aq)
7. A 1.0-gram piece of zinc reacts with 5 milliliters of HCl(aq). Which of these conditions of concentration and temperature would produce the greatest rate of reaction?
   1. 1.0 M HCl(aq) at 20.°C c) 2.0 M HCl(aq) at 40.C
   2. 1.0 M HCl(aq) at 40.°C d) 2.0 M HCl(aq) at 20.°C
8. At STP, which 4.0-gram zinc sample will react fastest with dilute hydrochloric acid?
   * 1. lump c) bar
     2. powdered d) sheet metal
9. Given the reaction:

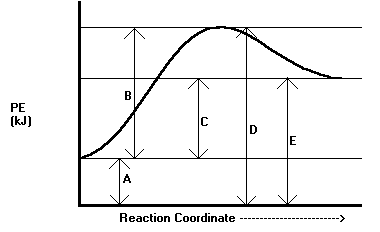
**Fe(s) + 2 HCl(aq) 🡪 FeCl2(aq) + H2(g)**

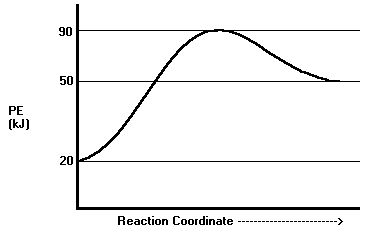
In this reaction, 5 grams of powdered iron will react faster than a 1-gram piece of solid iron because the powdered iron

* + 1. has less surface area c) is less dense
    2. has more surface area d) is more dense

1. Which statement best explains the role of a catalyst in a chemical reaction?
   * 1. A catalyst is added as an additional reactant and is consumed but not regenerated.
     2. A catalyst limits the amount of reactants used.
     3. A catalyst changes the kinds of products produced.
     4. A catalyst provides an alternate reaction pathway that requires less activation energy.

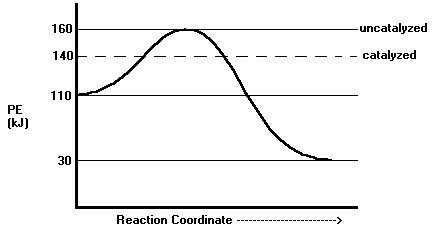
**Potential Energy Review**

****

1. Define potential energy (PE).
2. Using the first diagram to the right, record the letter that describes each statement:
   1. Reactants PE: \_\_\_
   2. Products PE: \_\_\_
   3. Activated complex PE: \_\_\_
   4. Activation Energy: \_\_\_
   5. Heat of Reaction: \_\_\_
3. Is the diagram above depicting an endothermic or exothermic reaction? Defend your answer.
4. On the second diagram to the right find the value of the following statements in kJ:
   1. Reactants PE: \_\_\_
   2. Products PE: \_\_\_
   3. Activated complex PE: \_\_\_
   4. Activation Energy: \_\_\_
   5. Heat of Reaction: \_\_\_
   6. Activation Energy of the

reverse reaction: \_\_\_

* 1. Enthalpy of reverse reaction: \_\_\_
  2. Is the diagram above depicting an endothermic or exothermic reaction? Defend your answer.



1. On the third diagram to the right find the value of the following statements in kJ for the uncatalyzed reaction:
   1. Reactants PE: \_\_\_\_\_
   2. Products PE: \_\_\_\_\_
   3. Activated complex PE: \_\_\_\_\_
   4. Activation Energy: \_\_\_\_\_
   5. Heat of Reaction: \_\_\_\_\_
   6. Activation Energy of the

reverse reaction: \_\_\_\_\_

* 1. Enthalpy of reverse reaction: \_\_\_\_\_
  2. Is the diagram above depicting an endothermic or exothermic reaction? Defend your answer.

1. On the third diagram, what values changed for the catalyzed reactions? Give the new values:
   1. Reactants PE: \_\_\_\_\_
   2. Products PE: \_\_\_\_\_
   3. Activated complex PE: \_\_\_\_\_
   4. Activation Energy: \_\_\_\_\_
   5. Heat of Reaction: \_\_\_\_\_
2. Using the graph below please draw a reaction potential energy diagram for a reaction with the following:

**Potential Energy of Reactants = 350 kJ/mole**

**Activation Energy of Forward Reaction = 100 kJ/mole**

**Potential Energy of Products = 150 kJ/mole**

Potential Energy (kJ)

Reaction Coordinate (X + Y → Z)

1. Is the reaction endothermic or exothermic?
2. Please identify the following on the diagram you created in question #1. Place this letter above its corresponding line segment on the graph and the value in the adjacent column.

|  |  |  |
| --- | --- | --- |
| **Component of Potential Energy Diagram** | **Symbol** | **Value** |
| Potential Energy of Reactants | A |  |
| Potential Energy of Products | B |  |
| Potential Energy of Activated Complex | C |  |
| Heat of Reaction | D |  |
| Activation Energy of Forward Reaction | E |  |
| Activation Energy of Reverse Reaction | F |  |

1. Using a dotted line, show how the reaction potential energy diagram would be altered upon the addition of a catalyst to the reaction in the graph above.
2. If a catalyst were added, which lettered quantities, if any would change?

**Average Reaction Rate**

1. Write rate expressions for the following reactions:
   1. H2 + O2 🡪 H2O
   2. N2 + H2 🡪 NH3
   3. PCl5 🡪 PCl3 + Cl2
   4. SF2 + 2F2 🡪 SF6
2. In the decomposition of dinitrogen pentoxide: 2N2O5 🡪 4NO2 + O2 at 45C, the following data was found:

|  |  |
| --- | --- |
| [N2O5] (M) | Time (s)   1. Calculate the average rate between 200 and 400s. 2. Calculate the average rate between 600 and 800s. 3. Calculate the average rate between 800 and 1000s. 4. Explain the trend in rate versus time. |
| 1.00 | 0 |
| 0.88 | 200 |
| 0.78 | 400 |
| 0.69 | 600 |
| 0.61 | 800 |
| 0.54 | 1000 |

1. Thiosulfate ions oxidized by Iodine: 2S2O32- + I2 🡪 S4O62- + 2I-
2. If 0.0080 moles of the S2O32- are consumed in 1L of solution each second, what is the rate of consumption of I2?
3. If 2.50M S4O6-2 is produced every 4.0 seconds, what is the rate of consumption of I2?

**Rate Laws**

1. The reaction gave the following data: 2ClO2 + 2OH- 🡪 ClO3- + ClO2- + H2O

|  |  |  |
| --- | --- | --- |
| [ClO2] (M) | [OH-] (M) | Rate (M/s)   1. What is the rate law? 2. Calculate the rate constant using the first experiment. 3. Calculate the rate constant using the second experiment. 4. Calculate the rate constant using the third experiment. |
| 0.050 | 0.10 | 0.0575 |
| 0.10 | 0.10 | 0.230 |
| 0.10 | 0.050 | 0.115 |

1. The following data was measured for the reaction: 2NO + O2 🡪 2NO2

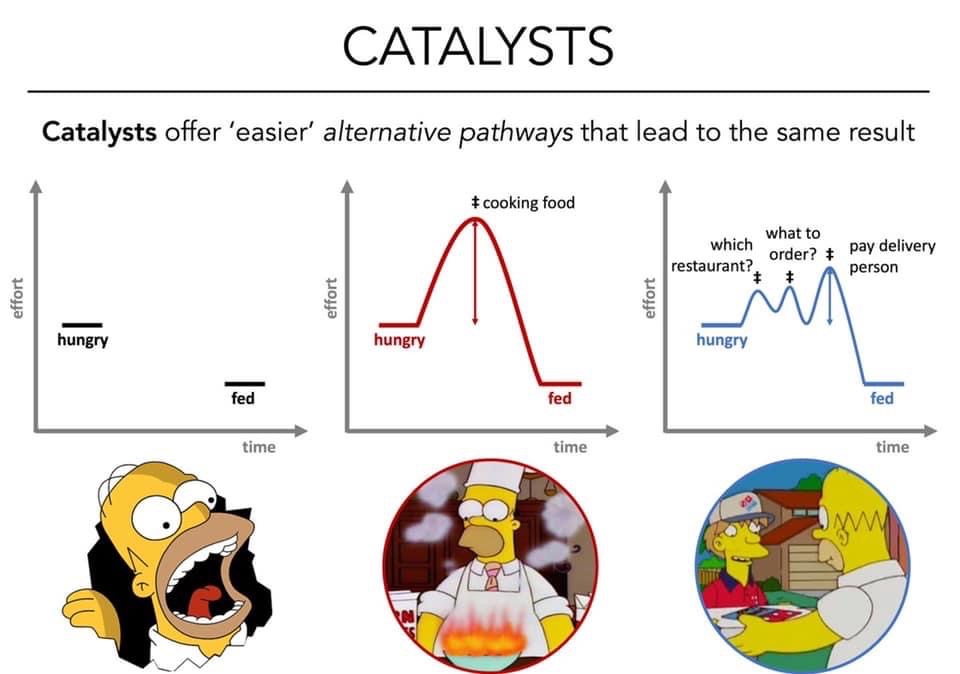
|  |  |  |
| --- | --- | --- |
| [NO] (M) | [O2] (M) | Rate (M/s)   1. Determine the rate law. 2. Calculate the average rate constant. |
| 0.0126 | 0.0125 | 0.0141 |
| 0.0252 | 0.0250 | 0.113 |
| 0.0252 | 0.0125 | 0.0564 |

1. The following data was measured for the reaction: I- + OCl- 🡪 IO- + Cl-

|  |  |  |  |
| --- | --- | --- | --- |
| [I-] (M) | [OCl-] (M) | [OH-] (M) | Rate (M/s)   1. Determine the reactant orders including OH-. (OH- will have a weird order since it is only a catalyst) 2. Write the rate law. 3. Determine the rate constant using any experiment. |
| 0.0013 | 0.012 | 0.10 | 9.40 |
| 0.0026 | 0.012 | 0.10 | 18.7 |
| 0.0013 | 0.006 | 0.10 | 4.70 |
| 0.0013 | 0.018 | 0.10 | 14.0 |
| 0.0013 | 0.012 | 0.05 | 18.7 |
| 0.0013 | 0.012 | 0.20 | 4.70 |
| 0.0013 | 0.018 | 0.20 | 7.00 |

1. The following data was obtained during the reaction: 5Br- + BrO3- + 6H+ 🡪 3Br2 + 3H2O
2. Determine the order for each reactant.
3. Determine the overall order of the reaction.
4. Determine the order of the rate constant, using the third experiment, with correct units.

|  |  |  |  |
| --- | --- | --- | --- |
| [Br-] (M) | [BrO3‑] (M) | [H+] (M) | Rate (M/s) |
| 0.00100 | 0.00500 | 0.100 | 2.50 x 10-4 |
| 0.00200 | 0.00500 | 0.100 | 5.00 x 10-4 |
| 0.00100 | 0.00750 | 0.100 | 3.75 x 10-4 |
| 0.00100 | 0.01500 | 0.200 | 3.00 x 10-3 |

****

**AP Rate Law Questions**

1. 2 A + 2 B  C + D

The following data about the reaction above were obtained from three experiments:

|  |  |  |  |
| --- | --- | --- | --- |
| Experiment | [A] | [B] | Initial Rate of Formation of C (mole.liter-1min-1) |
| 1 | 0.60 | 0.15 | 6.310-3 |
| 2 | 0.20 | 0.60 | 2.810-3 |
| 3 | 0.20 | 0.15 | 7.010-4 |

(a) What is the rate equation for the reaction?

(b) What is the numerical value of the rate constant k? What are its dimensions?

1. For a hypothetical chemical reaction that has the stoichiometry 2 X + Y  Z, the following initial rate data were obtained. All measurements were made at the same temperature.

|  |  |  |
| --- | --- | --- |
| Initial Rate of Formation of Z, (mol.L-1.sec-1) | Initial [X]o, (mol.L-1) | Initial [Y]o, (mol.L-1) |
| 7.010-4 | 0.20 | 0.10 |
| 1.410-3 | 0.40 | 0.20 |
| 2.810-3 | 0.40 | 0.40 |
| 4.210-3 | 0.60 | 0.60 |

(a) Give the rate law for this reaction from the data above.

(b) Calculate the specific rate constant for this reaction and specify its units.

(c) How long must the reaction proceed to produce a concentration of Z equal to 0.20 molar, if the initial reaction concentrations are [X]o = 0.80 molar, [Y]o = 0.60 molar and [Z]0 = 0 molar?

2 HgCl2*(aq)* + C2O42-  2 Cl- + 2 CO2*(g)* + Hg2Cl2*(aq)*

1. The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table

|  |  |  |  |
| --- | --- | --- | --- |
| Experi-ment | Initial [HgCl2] | Initial [C2O42-] | Initial Rate of Formation of Cl-  (mol.L-1.min-1) |
| (1) | 0.0836 M | 0.202M | 0.5210-4 |
| (2) | 0.0836 M | 0.404M | 2.0810-4 |
| (3) | 0.0418 M | 0.404M | 1.0610-4 |
| (4) | 0.0316 M | ? | 1.2710-4 |

(a) According to the data shown, what is the rate law for the reaction above?

(b) On the basis of the rate law determined in part (a), calculate the specific rate constant. Specify the units.

(c) What is the numerical value for the initial rate of disappearance of C2O42- for Experiment 1?

(d) Calculate the initial oxalate ion concentration for Experiment 4.

C2H4*(g)* + H2*(g)*  C2H6*(g)* H = -137 kJ

1. Account for the following observations regarding the exothermic reaction represented by the equation above.

(a) An increase in the pressure of the reactants causes an increase in the reaction rate.

(b) A small increase in temperature causes a large increase in the reaction rate.

(c) The presence of metallic nickel causes an increase in reaction rate.

(d) The presence of powdered nickel causes a larger increase in reaction rate than does the presence of a single piece of nickel of the same mass.

2 A + B  C + D

1. The following results were obtained when the reaction represented above was studied at 25C.

|  |  |  |  |
| --- | --- | --- | --- |
| Experiment | Initial [A] | Initial [B] | Initial Rate of Formation of C (mol L-1 min-1) |
| 1 | 0.25 | 0.75 | 4.310-4 |
| 2 | 0.75 | 0.75 | 1.310-3 |
| 3 | 1.50 | 1.50 | 5.310-3 |
| 4 | 1.75 | ? | 8.010-3 |

(a) Determine the order of the reaction with respect to A and to B. Justify your answer.

(b) Write the rate law for the reaction. Calculate the value of the rate constant, specifying units.

(c) Determine the initial rate of change of [A] in Experiment 3.

(d) Determine the initial value of [B] in Experiment 4.

**First and Second Order Reactions**

1. Cyclopropane converts to propene in a first order reaction at 500C with k=6.7x10-4s-1.
   1. Draw cyclopropane and propene.
   2. If the initial concentration of cyclopropene is 0.25M, what is the concentration after 8.8 minutes?
   3. How long will it take the concentration of cyclopropane to decrease from 0.25M to 0.15M?
2. The rate constant for the second order reaction given equals 0.80/Ms at 300C. 2NOBr 🡪 2NO + Br2

The starting concentration of NOBr equals 0.086M, what is the concentration after 22 seconds?

1. The rate constant for the reaction is 0.54/Ms at 300C. How long does it take the NO2 to decrease from 0.62M to 0.28M? 2NO2  🡪 2NO + O2
2. The following reaction is a first order reaction: SO2Cl2 🡪 SO2 + Cl2
   1. At 600K the half life is 2.x105s. What is the rate constant at that temperature?
   2. At 320C the rate constant is 2.2x10-5/s. What is the half life?
3. Answer the following questions regarding the kinetics of chemical reactions.

(a)The diagram below at right shows the energy pathway for the reaction O3 + NO  NO2 + O2. Clearly label the following directly on the diagram.



(i) The activation energy *(Ea)* for the forward reaction

(ii) The enthalpy change (*H*) for the reaction

(b) The reaction 2 N2O5  4 NO2 + O2 is first order with respect to N2O5.

(i) Using the axes at right, complete the graph that represents the change in [N2O5] over time as

the reaction proceeds.



(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, *t*.

(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, *k,* could be determined.

(iv) If more N2O5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, *k* ? Explain.

1. Kinetic results for a reaction involving substance A are shown below.

Time (mins) [A] in mol L-1

0.000 1.00

2.00 0.82

4.00 0.67

7.00 0.49

10.0 0.37

14.0 0.24

20.0 0.14

25.0 0.08

(a) Plot and record data from a graph of these results.

(b) What is the order of this reaction with respect to A?

(c) Use your graph to calculate the half-life for this reaction.

(d) Given that in this reaction, A reacts with G, and that the order with respect to G is second, write

the rate equation for this reaction.

1. Time in minutes [B] in mol L-1

0.00 1.00

2.00 0.790

4.00 0.590

7.00 0.300

(a) Plot and record data from a graph of these results.

(b) What is the order with respect to B in this reaction?

(c) What can be said about the rate of consumption of B in this reaction?

1. [X] in mol L-1 0.0032 0.0064 0.0096 0.0100 0.0111 0.0200

Rate in m min-1 9.2 9.2 9.2 9.2 9.2 9.2

(a) Plot and record data from a graph of these results.

(b) What is the order with respect to X in this reaction?

**Reaction Mechanisms**

1. A mechanism is proposed for the decomposition of hydrogen peroxide:

H2O2 🡪 2OH

H2O2 + OH 🡪 H2O + HO2

HO2 + OH 🡪 H2O + O2

* 1. Write the overall reaction for the decomposition of hydrogen peroxide.
  2. Identify any intermediates and catalysts in the mechanism.
  3. Identify the molecularity of each of the e steps in the mechanism.
  4. Write the skeletal rate law for each elementary step.
  5. Write the skeletal rate law for the overall reaction written in part a.
  6. Which step seems to be the rate determining step?
  7. Write the rate expressions for the overall reaction.
  8. Determine the rate order by graphing.
  9. Write the overall rate law.
  10. Calculate the rate constant.
  11. Find the half-life of this reaction.

|  |  |
| --- | --- |
| Time (s) | [H2O2](M) |
| 0 | 1.27 |
| 100 | 1.23 |
| 300 | 1.15 |
| 600 | 1.04 |
| 1200 | 0.85 |
| 1800 | 0.70 |
| 2400 | 0.58 |
| 3600 | 0.39 |

**AP Rates Questions**

**AP Problems**

1. Some alkyl halides, such as (CH3)3CCl, (CH3)3CBr, and (CH3)3CI, represented by RX are believed to react

with water according to the following sequence of reactions to produce alcohols:

RX  R+ + X- (slow reaction)

R+ + H2O  ROH + H+ (fast reaction)

(a) For the hydrolysis of RX, write a rate expression consistent with the reaction sequence above.

(b) When the alkyl halides RCl, RBr, and RI are added to water under the same experimental conditions, the rates are in the order RI > RBr > RCl.

Construct properly labeled potential energy diagrams that are consistent with the information on the rates of hydrolysis of the three alkyl halides. Assume that the reactions are exothermic.

1. The decomposition of compound X is an elementary process that proceeds as follows:



The forward reaction is slow at room temperature but becomes rapid when a catalyst is added.

(a)Draw a diagram of potential energy *vs* reaction coordinate for the uncatalyzed reaction. On this diagram label:

(1) the axes

(2) the energies of the reactants and the products

(3) the energy of the activated complex

(4) all significant energy differences

(b)On the same diagram indicate the change or changes that result from the addition of the catalyst. Explain the role of the catalyst in changing the rate of the reaction.

(c)If the temperature is increased, will the ratio kf/kr increase, remain the same, or decrease? Justify your answer with a one or two sentence explanation. [kf and kr are the specific rate constants for the forward and the reverse reactions, respectively.]

2 ClO2*(g)* + F2*(g)*  2 ClO2F*(g)*

1. The following results were obtained when the reaction represented above was studied at 25C.

|  |  |  |  |
| --- | --- | --- | --- |
| Experiment | Initial [ClO2], (mol.L-1) | Initial [F2], (mol.L-1) | Initial Rate of Increase of [ClO2F],  (mol.L-1.sec-1) |
| 1 | 0.010 | 0.10 | 2.410-3 |
| 2 | 0.010 | 0.40 | 9.610-3 |
| 3 | 0.020 | 0.20 | 9.610-3 |

(a) Write the rate law expression for the reaction above.

(b) Calculate the numerical value of the rate constant and specify the units.

(c) In experiment 2, what is the initial rate of decrease of [F2]?

(d) Which of the following reaction mechanisms is consistent with the rate law developed in (a).

Justify your choice.

I. ClO2 + F2  ClO2F2 (fast)

ClO2F2  ClO2F + F (slow)

ClO2 + F  ClO2F (fast)

II. F2  2 F (slow)

2 (ClO2 + F  ClO2F) (fast)

H2*(g)* + I2*(g)*  2 HI*(g)*

1. For the exothermic reaction represented above, carried out at 298K, the rate law is as follows.

Rate = k[H2][I2]

Predict the effect of each of the following changes on the initial rate of the reaction and explain your prediction.

(a) Addition of hydrogen gas at constant temperature and volume

(b) Increase in volume of the reaction vessel at constant temperature

(c) Addition of catalyst. In your explanation, include a diagram of potential energy versus reaction coordinate.

(d) Increase in temperature. In your explanation, include a diagram showing the number of molecules as a function of energy.

2 NO*(g)* +2 H2*(g)*  N2*(g)* + 2 H2O*(g)*

1. Experiments were conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Initial Concentration (mol/L) | | Initial Rate of Formation of N2 |
| Experiment | [NO] | [H2] | (mol/L**.**min) |
| 1 | 0.0060 | 0.0010 | 1.8 10-4 |
| 2 | 0.0060 | 0.0020 | 3.6 10-4 |
| 3 | 0.0010 | 0.0060 | 0.30 10-4 |
| 4 | 0.0020 | 0.0060 | 1.2 10-4 |

(a) (i) Determine the order for each of the reactants, NO and H2, from the data given and show your reasoning.

(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, *k*, for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H2 had been consumed.

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. NO + NO  N2O2

II. N2O2 + H2  H2O + N2O

III. N2O + H2  N2 + H2O

Based on the data presented, which of the above is the rate-determining step? Show that the mechanism is consistent with

(i) the observed rate law for the reaction, and

(ii) the overall stoichiometry of the reaction.

**Review 1st and 2nd Order Reactions**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Equation** | **X** | **Y** | **Slope** | **k** |
| **First Order** |  |  |  |  |  |
| **Second Order** |  |  |  |  |  |

1. Find the final concentration of reactant A after 50 seconds when the initial concentration is 2.50M at 230C. k=5.60x10-6s-1.

2. Find the initial concentration of reactant Cl2 after 120 seconds when the final concentration is 0.350M at 400C. k=2.30x10-5s-1.

3. Find the rate constant of a first order reaction when reactant M decreases from 5.0M to 3.0M in 125 seconds.

4. Find the time it takes reactant B to decrease from 2.3M to 1.4M. k=1.23x10-2s-1.

5. Find the final Molarity of reactant NO2 after 230 seconds when the initial concentration is 1.57M at 20C. k=3.75x10-8M-1s-1.

6. Find the initial Molarity of reactant X after 2.0 minutes when the final concentration is 2.150M at 580C. k=1.50x10-3 M-1s -1.

7. Find the rate constant of a second order reaction when reactant O2 decreases from 5.8M to 3.2M in 87s.

8. Find the time it takes reactant Cu(NO3)2 to decrease from 3.8M to 0.25M. k=3.50x10-4 M-1s -1.

9. Find the half-life of a first order reaction if k=2.30x10-5s-1

10. Find the half-life of a second order reaction if k=2.30x10-5 M-1s -1

11. Find the rate constant of a first order reaction if the half-life is 65 seconds.

12. Find the rate constant of a second order reaction if the half-life is 23 seconds.

**AP Chemistry: Kinetics Multiple Choice**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Questions 25-26  H3AsO4 + 3I−+ 2 H3O+ 🡪 H3AsO3 + I3− + H2O | | | | | | | | | | | | | |
| The oxidation of iodide ions by arsenic acid in acidic aqueous solution occurs according to the stoichiometry shown above. The experimental rate law of the reaction is: Rate = k [H3AsO4] [I−] [H3O+] | | | | | | | | | | | | | |
| 25. What is the order of the reaction with respect to I−? | | | | | | | | | | | | | |
| (A) 1 (B) 2 (C) 3 (D) 5 (E) 6 | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 26. According to the rate law for the reaction, an increase in the concentration of hydronium ion has what effect on this reaction? | | | | | | | | | | | | | |
| (A) The rate of reaction increases. (B) The rate of reaction decreases. | | | | | | | | | | | | | |
| (C) The value of the equilibrium constant increases. (D) The value of the equilibrium constant decreases. | | | | | | | | | | | | | |
| (E) Neither the rate nor the value of the equilibrium constant is changed. | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 28. 2 A(g) + B(g) ⇄ 2 C(g) | | | | | | | | | | | | | |
| When the concentration of substance B in the reaction above is doubled, all other factors being held constant, it is found that the rate of the reaction remains unchanged. The most probable explanation for this observation is that… | | | | | | | | | | | | | |
| (A) the order of the reaction with respect to substance B is 1. | | | | | | | | | | | | | |
| (B) substance B is not involved in any of the steps in the mechanism of the reaction. | | | | | | | | | | | | | |
| (C) substance B is not involved in the rate-determining step of the mechanism, but is involved in subsequent steps. | | | | | | | | | | | | | |
| (D) substance B is probably a catalyst, and as such, its effect on the rate of the reaction does not depend on its concentration. | | | | | | | | | | | | | |
| (E) the reactant with the smallest coefficient in the balanced equation generally has little or no effect on the rate of the reaction. | | | | | | | | | | | | | |
|  | | | |  | |  | |  |  |  |  | | |
| Step 1) N2H2O2 ⇄ N2HO2− + H+ | | | | fast equilibrium | |  | |  |  |  |  | | |
| Step 2) N2HO2− 🡪 N2O + OH− | | | | (slow) | |  | |  |  |  |  | | |
| Step 3) H+ + OH− 🡪 H2O | | | | (fast) | |  | |  |  |  |  | | |
|  | | | | | | | | | | | | | |
| 82. Nitramide, N2H2O2, decomposes slowly in aqueous solution. This decomposition is believed to occur according to the reaction mechanism above. The rate law for the decomposition of nitramide that is consistent with this mechanism is given by which of the following? | | | | | | | | | | | | | |
| (A) Rate = k [N2H2O2] (B) Rate = k [N2H2O2] [H+] (C) Rate = (k [N2H2O2]) / [H+] | | | | | | | | | | | | | |
| (D) Rate = (k [N2H2O2]) / [N2HO2−] (E) Rate = k [N2H2O2] [OH−] | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 57. rate = k[X] | | | | | | | | | | | | | |
| For the reaction whose rate law is given above, a plot of which of the following is a straight line? | | | | | | | | | | | | | |
| (A) [X] versus time (B) ln [X] versus time (C) 1/[X] versus time | | | | | | | | | | | | | |
| (D) [X] versus 1/time (E) ln [X] versus 1/time | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 58. (CH3)3CCl(aq) + OH− 🡪 (CH3)3COH(aq) + Cl−  For the reaction represented above, the experimental rate law is given as follows:  Rate = k [(CH3)3CCl] | | | | | | | | | | | | | |
| If some solid sodium solid hydroxide is added to a solution that is 0.010-molar in (CH3)3CCl and 0.10-molar in NaOH, which of the following is true? (Assume the temperature and volume remain constant.) | | | | | | | | | | | | | |
| (A) Both the reaction rate and k increase. (B) Both the reaction rate and k decrease. | | | | | | | | | | | | | |
| (C) Both the reaction rate and k remain the same. (D) The reaction rate increases but k remains the same. | | | | | | | | | | | | | |
| (E) The reaction rate decreases but k remains the same. | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 17. Relatively slow rates of chemical reaction are associated with which of the following? | | | | | | | | | | | | | |
| (A) The presence of a catalyst (B) High temperature (C) High concentration of reactants | | | | | | | | | | | | | |
| (D) Strong bonds in reactant molecules (E) Low activation energy | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| Step 1: Ce4+ + Mn2+ 🡪 Ce3+ + Mn3+ | | | | | | | | | | | | | |
| Step 2: Ce4+ + Mn3+ 🡪 Ce3+ + Mn4+ | | | | | | | | | | | | | |
| Step 3: Mn4+ + Tl+ 🡪 Tl3+ + Mn2+ | | | | | | | | | | | | | |
| 23. The proposed steps for a catalyzed reaction between Ce4+ and Tl+ are represented above. The products of the overall catalyzed reaction are… | | | | | | | | | | | | | |
| (A) Ce4+ and Tl+ | | | | | | | | | | | | | |
| (B) Ce3+ and Tl3+ | | | | | | | | | | | | | |
| (C) Ce3+ and Mn3+ | | | | | | | | | | | | | |
| (D) Ce3+ and Mn4+ | | | | | | | | | | | | | |
| (E) Tl3+ and Mn2+ | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 49. The isomerization of cyclopropane to propylene is a first-order process with a half-life of 19 minutes at 500 °C. The time it takes for the partial pressure of cyclopropane to decrease from 1.0 atmosphere to 0.125 atmospheres at 500 °C is closest to… | | | | | | | | | | | | | |
| (A) 38 minutes (B) 57 minutes (C) 76 minutes (D) 152 minutes (E) 190 minutes | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| http://chem.neopages.com/quiz/apchem/mc1999g.gif63. The graph to the right shows the results of a study of the reaction of X with a large excess of Y to yield Z. The concentrations of X and Y were measured over a period of time. According to the results, which of the following can be concluded about the rate of law for the reaction under the conditions studied?  (A) It is zero order in [X]. (B) It is first order in [X].  (C) It is second order in [X]. (D) It is the first order in [Y].  (E) The overall order of the reaction is 2. | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
|  | |  |  | |  | |  | | | | |  |  |
| Experiment | | Initial [NO] | Initial [O2] | | Initial Rate of Formation of NO2 | |  | | | | |  |  |
| (mol L−1) | (mol L−1) | | (mol L−1 s−1) | |  | | | | |  |  |
|  |  | |  | |  | | | | |  |  |
| 1 | | 0.1 | 0.1 | | 2.5 x 10−4 | |  | | | | |  |  |
| 2 | | 0.2 | 0.1 | | 5.0 x 10−4 | |  | | | | |  |  |
| 3 | | 0.2 | 0.4 | | 8.0 x 10−3 | |  | | | | |  |  |
|  | | | | | | | | | | | | | |
| 36. The initial-rate data in the table above were obtained for the reaction represented below. What is the experimental rate law for the reaction? | | | | | | | | | | | | | |
| (A) rate = k[NO] [O2] (B) rate = k[NO] [O2]2 (C) rate = k[NO]2 [O2] | | | | | | | | | | | | | |
| (D) rate = k[NO]2 [O2]2 (E) rate = k[NO] / [O2] | | | | | | | | | | | | | |
|  | | | | | | | | | | | | | |
| 57. Rate = k[M][N]2  The rate of a certain chemical reaction between substances M and N obeys the rate law above. The reaction is first studied with [M] and [N] each 1 × 10−3 molar. If a new experiment is conducted with [M] and [N] each 2 × 10−3 molar, the reaction rate will increase by a factor of …  (A) 2 (B) 4 (C) 6 (D) 8 (E) 16 | | | | | | | | | | | | | |
| 27. 2 NO(g) + O2(g) → 2 NO2(g)  A possible mechanism for the overall reaction represented above is the following:  (1) NO(g) + NO(g) → N2O2(g) *slow*  (2) N2O2(g) + O2(g) → 2 NO2(g) *fast*  Which of the following rate expressions agrees best with this possible mechanism?  (A) Rate = k[NO]2 (D) Rate = k[NO]2[O2](B) Rate = k[NO] (E) Rate = k[N2O2][O2]  [O2]  (C) Rate = k[NO]2  [O2] | | | | | | | | | | | | |
|  | | | | | | | | | | | | |
| 47. Which of the following is a correct statement about reaction order?  (A) Reaction order can only be a whole number (B) Reaction order can be determined only from the coefficients of the balanced equation for the reaction (C) Reaction order can be determined only by experiment (D) Reaction order increases with increasing temperature (E) A second-order reaction must involve at least two different compounds as reactants | | | | | | | | | | | | |
|  | | | | | | | | | | | | |
| 54. Which of the following must be true for a reaction for which the activation energy is the same for both the forward and the reverse reactions?  (A) A catalyst is present. (B) The reaction order can be obtained directly from the balanced equation. (C) The reaction order is zero. (D) ΔH° for the reaction is zero. (E) ΔS° for the reaction is zero. | | | | | | | | | | | | |
|  | | | | | | | | | | | | |
| 55. Time (days) 0 1 2 3 4 5 6 7 … 10 … 20  % Reactant Remaining 100 79 63 50 40 31 25 20 … 10 … 1    A reaction was observed for 20 days and the percentage of the reactant remaining after each day was recorded in the table above. Which of the following best describes the order and the half-life of the reaction?  Reaction Order Half-life(days) (A) First 3 (B) First 10 (C) Second 3 (D) Second 6 (E) Second 10 | | | | | | | | | | | | |