Reaction Rates

Outline

1. Define reaction rate
Reaction rate is the rate at which the concentration (amount) of reactant decreases or the concentration (amount) of product increases over time.

For
Reactant → Products

\[
\text{Reaction Rate} = \frac{\Delta \text{conc Reactant}}{\Delta \text{time}} = \frac{-\Delta \text{conc Reactant}}{\Delta \text{time}}
\]

OR

\[
\text{Reaction Rate} = \frac{\Delta \text{conc product}}{\Delta \text{time}}
\]

In general, for the reaction
\[aA(g) + bB(g) \rightarrow \text{products}\]

\[
\text{Rate} = k[A]^m[B]^n
\]

This is called the rate expression.
Recall that \([\ ]\) means concentration of.

The powers to which the concentrations of reactants are raised in the rate expression is referred to as the order of the reaction. If \(m = 1\), reaction is first order with respect to A; if \(n = 2\), the reaction is said to be second order in B. The overall order of the reaction is the sum of the exponents \(m\) and \(n\).

1st order: \(m + n = 1\)
2nd order: \(m + n = 2\)

\(k\) is called the rate contant or the proportionality constant

For a particular reaction, \(k\) is a function only of temperature; it is independent of the concentrations of reactants. This means that \(k\) can only change for a reaction system only if the temperature is changed.
2. **Describe/Explain Collision Theory**

   Molecules must be properly oriented and collide with high frequency in order for a reaction to occur between reacting molecules.

3. **List 5 factors that affect reaction rates**
   a. Temperature  
   b. Nature of substance  
   c. Surface area  
   d. Concentration  
   e. Catalyst  
   f. Inhibitors

4. **Explain how each of these factors affect reaction rate**
   *Will discuss each factor in class*

5. **Define a catalyst, an inhibitor. How are they different?**

   A substance that speeds up the rate of a chemical reaction without being consumed (used up) during the reaction is called a catalyst.

   An inhibitor slows down the rate of a chemical reaction.

   They are different because they have opposite effects on reaction rate.

6. **Define activation energy**

   This is the energy that is required to form an activated complex. Activated complex is formed at the transition state. See Reaction Energy profile.

   ![Reaction Energy Diagram]

   - $E_p$: Potential Energy
   - $[\text{Activated Complex}]$: Transition State
   - $E_a$: Activation Energy
   - $E'_a$: Activation with Catalyst

   $E_a = \text{Activation Energy}$

   $E'_a = \text{Activation with Catalyst}$
7. Describe how a catalyst affects activation energy.

A catalyst reduces the activation energy thereby reducing the amount of time required to form an activated complex at the transition state. Therefore, the rate of reaction is faster. In the diagram above, the lower curve is the pathway in the presence of a catalyst. Note that the activation energy is lower with catalyst than without catalyst.

**Reaction Rates**

Identify the choice that best completes the statement or answers the question.

___ 1. Which of the following statements about a catalyst is true?
   a. A catalyst can initiate a reaction.
   b. A catalyst can accelerate a reaction.
   c. A catalyst can be consumed during a reaction.
   d. A catalyst can be changed during a reaction.

___ 2. Which of the following factors does NOT affect the rate of the reaction?
   a. the amount of the reactants
   b. the physical state of the reactants
   c. the size of the container used
   d. temperature

___ 3. A/An _____ is a substance that slows down the rate of a reaction.
   a. catalyst
   b. inhibitor
   c. reactant
   d. product

___ 4. A _____ exists in a physical state different than that of the reaction it catalyzes.
   a. heterogeneous catalyst
   b. homogeneous catalyst
   c. inhibitor
   d. product

___ 5. A collision requires _____ to be effective.
   a. only enough energy
   b. favorable orientation
   c. enough energy and favorable orientation
   d. a reaction mechanism
6. In a reaction of butyl chloride and water, the concentration of butyl chloride is 0.220M at the beginning of the reaction. After 4.00 seconds, the concentration of butyl chloride is 0.100M. Calculate the average reaction rate over the given time period expressed as moles of butyl chloride consumed per liter per second.

\[ \text{Rate} = k[A]^m[B]^n \]

7. Using the equation, calculate the instantaneous reaction rate when the reactant concentrations are \([\text{NO}] = 0.00200\text{M}\) and \([\text{H}_2] = 0.00400\text{M}\). The rate constant is \(2.9 \times 10^{-2} \text{ (L}^2/(\text{mol}^2\cdot\text{s}))\).

\[ 2\text{NO}(g) + \text{H}_2(g) \rightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \]

8. The decomposition of hydrogen peroxide in the presence of iodide ion is of the first order. The reaction is \(2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(g)\). Calculate the concentration of \(\text{H}_2\text{O}_2\) when the rate of the reaction is \(1.12 \times 10^{-2} \text{ (mol/(L}\cdot\text{s})\) and the rate constant is \(1.01 \times 10^{-2} \text{ s}^{-1}\).

Chemical Equilibrium

Definition: As it applies to a chemical reaction system: State of a reaction mixture at which the forward reaction rate is equal to the reverse reaction rate.

\[ 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]
Chemical Equilibrium

1. Reaction begins.  
   • No products yet formed.  
   • High rate of collisions between A & B.  
   • Rate of forward reaction HIGH.

2 & 3. Products formed  
   • Collisions between reactants decrease.  
   • Rate of forward reaction **DECREASES**  
   • Reverse reaction begins.

4. Rate of forward reaction **EQUAL** to rate of reverse reaction.  
   • **Dynamic equilibrium** established.  
   • Concentrations constant.
Fig. 1: shows measurable physical parameters for a system as it approaches equilibrium, starting from a condition of only reactants and no products.

The Upper graph is a comparison of the magnitudes of the rates of forward and reverse reactions in the system as it approaches equilibrium.

At the start of the reaction, there is only a forward reaction since there are no products yet to react.

As time progresses, the magnitude of the forward rate diminishes and that of the reverse rate increases.

Eventually (only after infinite time) the two magnitudes are equal and the chemical system has reached equilibrium.
By definition, the forward rate must be the negative of the reverse rate at equilibrium.

The Lower graph shows the amounts of Reactants and Products of the same system as it approaches equilibrium.

Initially, there are only reactants but as time progresses, products are formed and reactants are used up.

When equilibrium is reached the amounts of reactants and products no longer changes but are not necessarily equal to each other.

The law of mass action (equilibrium constant)

Consider the reaction \[ jA + kB \rightleftharpoons lC + mD \]

\[ K_c = \frac{[C]^l[D]^m}{[A]^j[B]^k} \]

Note:
the square brackets [ ] indicate concentration in mol/L (M)
the subscript c on the K indicates this value derived using concentration units.

**Le Châtelier's Principle**

A chemical system at equilibrium has many factors affecting the position of that equilibrium.

- the amount of each of the components,
- the temperature
- the pressure
- volume

**Le Châtelier's Principle states:**
If a change (stress) is applied to a system at equilibrium the system will adjust to try to reduce the change.

Animations

http://www.dlt.ncssm.edu/tiger/Flash/equilibrium/CaO-CaCO3.html


Name: __________________________  Date: _____________

1. What is the expression for the equilibrium constant for the reaction: \(2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightleftharpoons 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})\)?
   A) \(K = \frac{[\text{CO}_2][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_6][\text{O}_2]}\)

   B) \(K = \frac{[\text{CO}_2]^4[\text{H}_2\text{O}]^6}{[\text{C}_2\text{H}_6]^7[\text{O}_2]^7}\)

   C) \(K = \frac{[\text{C}_2\text{H}_6][\text{O}_2]}{[\text{CO}_2][\text{H}_2\text{O}]}\)

   D) \(K = \frac{[\text{C}_2\text{H}_6]^7[\text{O}_2]^7}{[\text{CO}_2]^5[\text{H}_2\text{O}]^6}\)
2. An equilibrium constant with a value of $8.0 \times 10^6$ indicates that at equilibrium
   A) the reactants are favored.
   B) the products are favored.
   C) approximately equal concentrations of reactants and products are present.
   D) there are more reactants present than products.

3. An equilibrium constant with a value of $1.5 \times 10^{-9}$ indicates that at equilibrium
   A) the reactants are favored.
   B) the products are favored.
   C) approximately equal concentrations of reactants and products are present.
   D) there are more products present than reactants.

4. When the pressure of a reaction at equilibrium decreases, in which direction does the equilibrium shift?
   A) The equilibrium shifts in the direction that increases the number of moles of gas.
   B) The equilibrium shifts in the direction that decreases the number of moles of gas.
   C) The equilibrium does not shift.
   D) The equilibrium shifts always shifts to the right.
   E) The equilibrium shifts always shifts to the left.

5. For an endothermic reaction at equilibrium, increasing the temperature
   A) does not shift the equilibrium since $K$ is a constant.
   B) increases the rate of the reverse reaction to form more reactants.
   C) increases the rate of the forward reaction to form more products.
   D) increases the rate of the reverse reaction to form more products.

6. Consider the reaction: $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$. If $[\text{PCl}_3] = 0.78 \text{ M}$, $[\text{Cl}_2] = 0.44 \text{ M}$, and $[\text{PCl}_5] = 0.88$ at equilibrium, what is the value of $K$?
   A) 0.39
   B) 1.4
   C) 2.6
   D) 0.72

7. Consider the reaction: $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$. If $[\text{N}_2] = 0.520 \text{ M}$, $[\text{O}_2] = 0.0662 \text{ M}$, and $[\text{NO}] = 0.00956$ at equilibrium, what is the value of $K$?
   A) 3.60
   B) 0.278
   C) 377
   D) 0.00265
8. Consider the reversible reaction at equilibrium: \( \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \). What is the effect of removing some \( \text{N}_2(\text{g}) \) from the equilibrium system?
A) the concentration of \( \text{O}_2(\text{g}) \) increases
B) the concentration of \( \text{O}_2(\text{g}) \) decreases
C) the concentration of \( \text{NO}(\text{g}) \) increases
D) the equilibrium system shifts to the right

9. One step in the metabolism of glucose is depicted below. Which statement best describes how the equilibrium system would respond if the amount of dihydroxyacetone phosphate is decreased?

\[
\text{fructose 1,6-bisphosphate} \rightleftharpoons \text{dihydroxyacetone phosphate} + \text{glyceraldehyde 3-phosphate}
\]

A) The system would shift to the left, consuming more dihydroxyacetone phosphate.
B) The system would shift to the right, producing more dihydroxyacetone phosphate and glyceraldehyde 3-phosphate.
C) The system would shift to the left, producing more fructose 1,6-bisphosphate.
D) The system would shift to the right, consuming some glyceraldehyde 3-phosphate and producing more dihydroxyacetone phosphate.