Chemical Equilibrium – Theory Review

1. What are the empirical characteristics of a system at equilibrium?

A system at equilibrium will have both reactants and products present after the reaction “appears” to stop. The amounts of these substances remain constant, so that no change is observed.

2. Why is the theory of equilibrium called “dynamic”?

Chemical equilibrium is considered dynamic because both the forward and reverse reactions are still occurring at the same rate, so that no net change is observed.

3. What three types of changes shift the position of a chemical equilibrium?

Changes in concentration (of reactants or products), temperature, and pressure/volume can shift the position of a chemical equilibrium.

4. For each of the following chemical systems at equilibrium, use Le Châtelier’s principle to predict the effect of the change imposed on the chemical system. Assume that the systems are closed and that they are initially at equilibrium.

   a) $\text{H}_2\text{O(l)} + \text{energy} \rightleftharpoons \text{H}_2\text{O(g)}$
   
   The container is heated.
   
   The equilibrium shifts to the right to produce more products.

   b) $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-\text{(aq)}$
   
   A few crystals of NaOH(s) are added to the container.
   
   The equilibrium shifts to the left to consume some of the additional hydroxide ions.

   c) $\text{CaCO}_3\text{(s)} + \text{energy} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$
   
   Carbon dioxide is removed from the container.
   
   The equilibrium shifts to the right to replace some of the removed carbon dioxide.

5. The following equation represents part of the industrial production of nitric acid. Predict the direction of the equilibrium shift for each of the following changes.

   $4 \text{NH}_3\text{(g)} + 5 \text{O}_2\text{(g)} \rightleftharpoons 4 \text{NO(g)} + 6 \text{H}_2\text{O(g)} + \text{energy}$

   a) Oxygen is added to the system.
   
   The equilibrium shifts to the right to consume some of the additional oxygen.

   b) The temperature of the system is increased.
   
   The equilibrium shifts to the left to consume some of the added heat and produce more reactants.
c) Nitrogen monoxide is removed from the system.

The equilibrium shifts to the right to replace some of the removed nitrogen monoxide.

d) The pressure of the system is increased by decreasing the volume.

The equilibrium shifts to the left to favour the side with fewer gas molecules.

6. Does a catalyst affect a state of equilibrium? What does it do?

A catalyst does not affect the state of equilibrium, it decreases the time required to reach equilibrium.

7. Chemical engineers use Le Châtelier’s principle to predict shifts in chemical systems at equilibrium resulting from changes in the reaction conditions. Predict the changes necessary to maximize the yield of product in each of the following industrial chemical systems.

   a) the production of ethene (ethylene) \( C_2H_6(g) + \text{energy} \rightleftharpoons C_2H_4(g) + H_2(g) \)

   high concentration of ethane, low concentration of ethene and hydrogen (constant removal of product as it forms), high temperature and low pressure

   b) the production of methanol \( CO(g) + 2 H_2(g) \rightleftharpoons CH_3OH(g) + \text{energy} \)

   high concentration of carbon monoxide and hydrogen, low concentration of methanol (constant removal of product as it forms), low temperature and high pressure

8. For the reaction: \( A + B \rightleftharpoons C \), the activation energy of the forward reaction is 5 kJ and the total energy change is \(-20\) kJ. What is the activation energy of the reverse reaction?

25 kJ
9. By means of a sketch, show that the activation energy of an endothermic reaction must be greater than or equal to the total energy change in the reaction. Does a similar relationship exist for exothermic reactions?

In an endothermic reaction, the products always have more energy than the reactants. By looking at the shape of the graph, $E_a \geq \Delta H_{rxn}$

In an exothermic reaction, no such relationship exists, the activation energy may be less than, equal to, or greater than the enthalpy of reaction.
10. Draw a potential energy diagram for a reaction in which the heat of reaction is: $\Delta H = -80 \text{ kJ/mol}$; and the activation is $28 \text{ kJ/mol}$. Label both axes, the activation energy, heat of reaction, site of activated complex, reactants and products. Show on the diagram, using a dashed line, how a catalyst is effective in increasing the reaction rate.
11. Name the factors that influence the rate of a chemical reaction. How are the effects of these factors explained by the collision theory?

**Concentration**: When the concentration of reactants is high, there are more particles in the same volume, which increases the chance of collision and the reaction rate increases. This effect is also observed when the volume is decreased or the pressure is increased for the same reason.

**Temperature**: When the temperature is increased, the particles are moving faster and collide more frequently, thus increasing the reaction rate. More importantly, more of the molecules have sufficient energy (activation energy) to form an activated complex, and more of the collisions are successful.

**Catalyst**: When a catalyst is added, the activation energy is lowered; therefore more of the particles have sufficient energy to react (form an activated complex) and the reaction rate increases.

**Nature of Reactants**: Ionic reactions tend to be faster than covalent reactions; reactions with strong acids or bases tend to be faster than reactions with weak acids or bases; and single displacement reactions with more active metals tend to be faster than single displacement reactions with less active metals. In general, the type of reaction, as well as the species involved in the reaction affect the rate of the reaction.

**Particle Size/Surface Area**: Increasing the surface area or decreasing the particle size increases the rate of reaction. By having a greater surface area (or smaller particle size) there is more area of contact between the reactants. Therefore the frequency of collisions should increase which should cause an increase in the reaction rate.

12. The following reaction is at equilibrium. Predict the effect (if any) that each of the following changes will have on (i) the equilibrium, and (ii) the reaction rate.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H = -92 \text{ kJ} \]

a) lowering the temperature  
   *shifts to the right*  
   *rate decreases*

b) adding hydrogen  
   *shifts to the right*  
   *rate increases*

c) adding a catalyst  
   *no shift*  
   *rate increases*

d) decreasing the pressure  
   *shifts to the left*  
   *rate decreases*

e) removing nitrogen  
   *shifts to the left*  
   *rate decreases*

f) decreasing the volume  
   *shifts to the right*  
   *rate increases*

33. Problem
Consider the following reaction. \[2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g) + 52 \text{kJ}\]
In which direction does the equilibrium shift if there is an increase in temperature?

What Is Required?
You need to determine whether increasing the temperature causes the equilibrium to shift to the left or to the right.

What Is Given?
You have the chemical equation. You know that heat is shown on the right of the equation. Therefore, the reaction is exothermic.

Plan Your Strategy
Use the chemical equation to determine the shift in equilibrium that will minimize the change.

Act on Your Strategy
The temperature is increased. Therefore, the equilibrium must shift in the direction in which the reaction is endothermic. From left to right, the reaction is endothermic. The reaction shifts to the left if the temperature is increased.

Check Your Solution
An increase in temperature must result in a shift in the reaction that minimizes the temperature increase. The shift must be in the direction in which the reaction is endothermic.
34. Problem
A decrease in the pressure of each equilibrium system below is caused by increasing the volume of the reaction chamber. In which direction does the equilibrium shift?

(a) \( \text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g) \)
(b) \( 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \)
(c) \( 2\text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) + \text{O}_2(g) \)
(d) \( \text{CH}_4(g) + 2\text{H}_2\text{S}(g) \rightleftharpoons \text{CS}_2(g) + 4\text{H}_2(g) \)

What Is Required?
You need to determine whether decreasing the pressure causes the equilibrium to shift to the left or the right, or whether it has no effect.

What Is Given?
You have each chemical equation.

Plan Your Strategy
Use the chemical equation to determine the shift in equilibrium that will minimize the decrease in pressure. The shift must be towards the side with the largest number of gas molecules.

Act on Your Strategy

(a) As the reaction proceeds there is no change in the number of gas molecules. Therefore, increasing the volume of the container has no effect on the position of equilibrium.

(b) There are more gas molecules on the left side of the equation. Therefore, increasing the volume of the container causes the reaction to shift to the left.

(c) There are more gas molecules on the right side of the equation. Therefore, increasing the volume of the container causes the reaction to shift to the right.

(d) There are more gas molecules on the right side of the equation. Therefore, increasing the volume of the container causes the reaction to shift to the right.

Check Your Solution
An increase in volume must result in a decrease in pressure. The reaction must shift in the direction that minimizes the pressure decrease. The shift must be in the direction in which more gas molecules are formed.
35. Problem
The following reaction is exothermic. \(2\text{NO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{N}_2(g) + 2\text{H}_2\text{O}(g)\)

In which direction does the equilibrium shift as a result of each change?

(a) removing the hydrogen gas
(b) increasing the pressure of gases in the reaction vessel by decreasing the volume
(c) increasing the pressure of gases in the reaction vessel by pumping in argon gas while keeping the volume of the vessel constant
(d) increasing the temperature
(e) using a catalyst

What Is Required?
You need to determine whether each change causes the equilibrium to shift to the left or the right, or whether it has no effect.

What Is Given?
You have the chemical equation. You know the reaction is exothermic.

Plan Your Strategy
Identify the change. Then use the chemical equation to determine the shift in equilibrium that will minimize the change.

Act on Your Strategy
(a) \([\text{H}_2]\) is reduced. Therefore, the equilibrium must shift to increase \([\text{H}_2]\). The reaction shifts to the left.

(b) The pressure is increased by decreasing the volume of the reaction vessel. Therefore, the equilibrium must shift to decrease the pressure. Because there are fewer gas molecules on the right of the equation, the reaction shifts to the right.

(c) Argon does not react with any of the gases in the mixture. The position of equilibrium does not change.

(d) The temperature increases. Therefore, the equilibrium must shift in the direction in which the reaction is endothermic. From left to right, the reaction is exothermic. Therefore, the reaction is endothermic from right to left. The reaction shifts to the left if the temperature is increased.

(e) A catalyst has no effect on the position of equilibrium.

Check Your Solution
Check the changes. Any change that affects the equilibrium reaction must result in a shift that minimizes it.
36. Problem
In question 35, which changes affect the value of $K_c$? Which changes do not affect the value of $K_c$?

What Is Required?
You must determine which changes affect the value of $K_c$.

What Is Given?
You have the chemical equation. You know the reaction is exothermic.

Plan Your Strategy
For a given reaction at equilibrium, $K_c$ depends on temperature.

Act on Your Strategy
Change (d) is the only one that affects the temperature of the reaction. Therefore, change (d) is the only one that affects the value of $K_c$. Therefore, changes (a), (b), (c), and (e) have no effect on the value of $K_c$.

Check Your Solution
The value of $K_c$ for a particular equilibrium system depends on temperature.
37. Problem
Toluene, C7H8, is an important organic solvent. It is made industrially from methyl cyclohexane.

\[ C_7H_{14}(g) \rightleftharpoons C_7H_8(g) + 3H_2(g) \]

The forward reaction is endothermic. State three different changes to an equilibrium mixture of these reacting gases that would shift the equilibrium toward greater production of toluene.

**What Is Required?**
You must identify three different changes that would shift the equilibrium toward greater production of toluene.

**What Is Given?**
You have the chemical equation. You know the reaction is endothermic.

**Plan Your Strategy**
Each change must shift the reaction to the right. Use the chemical equation to identify changes that will shift the equilibrium to the right as the change is minimized.

**Act on Your Strategy**
- The equilibrium will shift to the right if any chemical on the left is added. Therefore, increasing [C7H14] increases the production of toluene.
- The equilibrium will shift to the right if any chemical on the right is removed. Therefore, decreasing either [C7H8] or [H2], or both, increases the production of toluene.
- The number of gas molecules increases as the reaction proceeds from left to right. Therefore, decreasing the pressure of the gases in the reaction vessel increases the production of toluene.
- The reaction is endothermic from left to right. Therefore, increasing the temperature increases the production of toluene.

**Check Your Solution**
Check each change. Minimizing each change must result in a shift in the reaction to the right.