*Chapter 13: Equilibrium*



*Important Vocabulary for Equilibrium*

Equilibrium

Equilibrium constant (Keq or K)

Heat of Reaction

Reaction Pathway

Rate of Reactions

The Law of Mass Action

Equilibrium Expression

Le Chatelier’s Principle

Reaction Quotient (Q)

RICE Table

*Chemical Equilibrium*

Not every reaction proceeds from reactants to products and then stops. Many reactions are reversible in certain conditions. A reversible reaction occurs when the products react to regenerate the original reactants. A reversible reaction is indicated by a double-headed arrow (⇌).The arrow pointing to the right represents the “forward” reaction and the arrow pointing to the left represents the “reverse” direction.

At ***chemical equilibrium***, ***the rate of the forward reaction equals the rate of the reverse reaction***. Since both reactions are happening simultaneously there is no net change in concentration of reactants or products. In other words, the concentrations of the reactants and products remain constant once a system has reached equilibrium. Remember, equilibrium is about the rate of the forward and reverse reactions being equal, not about concentrations being equal. Also, notice that the word rate keeps popping up.

This chapter will address 6 big questions concerning equilibrium (time permitting). The last two big questions will be addressed more thoroughly in AP chemistry.

1. How can we numerically express the equilibrium conditions of a given reaction?
2. What can we infer from an equilibrium constant?
3. How is equilibrium related to kinetics and thermochemistry?
4. How can we determine the direction a reaction will shift when equilibrium conditions are changed?
5. How can we determine the direction a reaction will proceed under non-equilibrium conditions?
6. How can we calculate initial and equilibrium concentrations from K and experimental data?
7. To address the first big question of this unit, we will derive an expression from a balanced equation. This expression is formally known as the ***Law of Mass Action***but more often it is referred to as an ***Equilibrium Constant Expression.*** Equilibrium position, or how far the reaction proceeds is measured by the ***equilibrium constant***, **Keq** or **K.** The equilibrium constant is a ratio of the relevant products to the relevant reactants, each of which is raised to a power indicated by their respective stoichiometric coefficients. Whew.
* For a given reaction a A + b B ⇌ y Y + z Z,

$$K= \frac{[Y]^{y}[Z]^{z}}{[A]^{a}[B]^{b}}$$

Where K is the unitless (for now) equilibrium constant; A, B, Y, and Z are molar concentrations of reactants and products; and a, b, y, and z are the molar coefficients from the balanced equation. Memorize how this was done. Products over reactants. Products over Reactants. Products over Reactants.

To calculate the value of the equilibrium constant K insert the equilibrium concentrations of reactants and products into the equation. Solids and liquids do not have molar concentrations therefore they are not included in the equilibrium expression. A few helpful tips follow:

* + [ ] = molarity (M, moles/liter). All numbers used in calculating K must be in molarity.
	+ Because pure liquids and solids do not have a concentration, they do not appear in the equilibrium constant expression. *Only species that are in the gas or aqueous state appear.*

Write the equilibrium constant expression for each of the following reactions.

1. Ba3(PO4)2(s) + 3 CO3-2(aq) ⇌ 3 BaCO3(s) + 2 PO4-3(aq)
2. Pb(s) + 2 H+1(aq) + 2 Cl-1(aq) ⇌ H2(g) + PbCl2(s)
3. 2 C6H6(l) + 15 O2(g) ⇌ 12 CO2(g) + 6 H2O(l)

The reaction involving hydroiodic acid, hydrogen, and iodine reaches equilibrium at 425°C. The reaction is 2 HI(g) ⇌ H2(g) + I2(g). The equilibrium concentrations of the three gases are [HI] = 0.0175 M, [H2] = 0.0045M, and [I2] = 0.00125 M. What is value of the equilibrium constant for this reaction?

Consider the reaction PCl5(g) ⇌ PCl3(g) + Cl2(g). A quantity of PCl5 was introduced to a closed 12-liter vessel and heated to 250°C until the above equilibrium was reached. At that time the vessel contained 0.21 mole PCl5, 0.32 mole PCl3, and 0.32 mole Cl2. Calculate K for the equilibrium at 250°C. How much PCl5 was originally introduced to the 12-liter vessel?

**Questions to consider:**

1. What do you need in order to write an equilibrium expression?
2. What types of substances are NEVER included in an equilibrium expression?
3. Next we will examine the value of the equilibrium constant in order to address the second big question: “what can we infer from an equilibrium constant?” In other words, what does the magnitude of K tell us? The equilibrium constant (K) is a ratio of products over reactants so it tells us whether we have more products or more reactants at equilibrium. “How far did the reaction proceed to the right” or “how far did the reaction proceed before it came to equilibrium” are questions that can be resolved by just knowing the value of K.
* If K is larger than one, the amount of products at equilibrium will be more than the amount of reactants. **K > 1; products are favored. *This is a spontaneous reaction! That means it WILL occur…we just can’t say how long it will take. Kinetics answer that question.***
* If K is less than one, the amount of reactants at equilibrium will be more than the amount of products. **K < 1; reactants are favored**
* If K is equal to one (which rarely happens) then the amount products and reactants will be approximately equal. **K = 1, conditions do not favor either side of reaction.**
1. Equilibrium arises when the *rates* of the forward and reverse reactions are equal. Products and reactants are continually being converted back and forth however the overall concentration of reacting species is unchanged. This is important because it allows us to use our knowledge of chemical kinetics to evaluate or predict equilibrium conditions in some cases.
* Examine the following hypothetical reaction: A + 3B ⇌ C
	+ How difficult is the forward reaction?
	+ What do the concentration of the reactants have to be for it to happen?
	+ How difficult is the reverse reaction (what are the chances of it happening)?
	+ What do the concentration of the products have to be for it to happen?
	+ What does this tell us about K?
	+ What has to happen for the reaction to get to equilibrium?

**Questions to Consider:**

1. How can I use the value of K to determine whether or not products are favored in a reaction?
2. How is the equilibrium constant (K) related to the heat of reaction (ΔH)?
3. How can I use collision theory to evaluate or predict the relative value of K?
4. We will now address the fourth big question of this unit: “How can we determine the direction a reaction will shift when equilibrium conditions are changed? When a change or *stress* is imposed on a system that is in a state of dynamic equilibrium, *the position of the equilibrium will shift in the direction that tends to reduce that change*. This guiding principle is known as ***Le Chatelier’s Principle*.** This is very powerful tool for evaluating or predicting how a system will respond when conditions change.

We will examine 3 types of “stresses” that can be applied to a chemical reaction at equilibrium: **change in concentration** of reactant or product, **change in pressure** or a **change in temperature**. Note that solids and liquids do not appear in the equilibrium expression and do not affect equilibrium conditions UNLESS they are completely absent.

* A **change in concentration** can be caused by adding or removing reactants or products. The value of K does not change. Instead the reaction shifts in such a way that the new concentrations “math” up to K.
	+ Increasing the concentration of reactants causes the reaction to shift to the right in order to “eliminate” the stress that was placed on the system.
	+ Increasing the concentration of the products causes the reaction to shift to the left. More reactants are remade in order to “use up” the extra product that was added.
	+ Decreasing the concentration of reactants or products causes the opposite to occur.
	+ Ask your teacher what happens when a catalyst is added.

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called roasting) to form solid As4O6, which is then reduced using carbon:

As406 (s) + 6 C (s) ⇌ As4 (g) + 6 CO (g)

Predict whether each of the following changes in condition favors the forward or reverse reaction:

a. Addition of carbon monoxide. b. Removal of arsenic gas. c. Addition of carbon.

 Predict what will happen if the following chemicals are added to the following reaction that is at equilibrium.

HC2H3O2 (aq) ⇄ H+(aq) + C2H3O2-(aq)

 a. Addition of sodium acetate b. Addition of sodium chloride c. addition of hydrochloric acid

**Questions to consider**

1. How does the reaction shift when a catalyst is added?
2. How does the concentration of a reacting species change when *more* of that same species is added at equilibrium?
* A **change in pressure** of a system at equilibrium can be caused by changing the number of moles of reacting gases at constant volume or by altering the volume of the reaction vessel without changing the number of moles of gas. In both cases, assume that the temperature remains constant. Only gases are affected by changes in pressure or volume.
	+ When the pressure is increased by adding more moles of gas or decreasing the volume of the container, *the system will shift in the direction that reduces the pressure*. This occurs when the system shifts to the side of the reaction with the fewest number of moles of gas. The value of K is not altered.
	+ When the pressure is decreased, the opposite happens.
	+ Ask your teacher to explain what happens when an inert gas is added to the reaction vessel at equilibrium.

Predict whether the forward or reverse reaction will be favored when the volume is reduced for each of the following equilibrium conditions:

1. The preparation of liquid phosphorus trichloride by the reaction: P4 (s) + 6 Cl2 (g) ⇌ 4 PCl3(l)
2. The preparation of gaseous phosphorus pentachloride according to the equation: PCl3(g)    +    Cl2(g)    ⇌    PCl5(g)
3. The reaction of phosphorus trichloride with ammonia: PCl3(g)    +    3 NH3(g)    ⇌    P (NH2)3(g)    +    3 HCl (g)

**Questions to consider**

1. How does changing the volume affect the pressure?
2. Which direction does the reaction shift when an inert gas is added?
* To determine the effect of **temperature change,** treat heat as a product for exothermic reactions and as a reactant for endothermic reactions. If you heat a reaction up, it will try to cool itself back down. If you cool a reaction down, it will try to heat itself back up. For example, if

N2 (g) + 3 H2 (g) ⇌ 2 NH3 (g) and ΔH = -92 kJ, then N2 (g) + 3 H2 (g) ⇌ 2 NH3 (g) + **92 kJ**

* + Heating this system would be the same as adding products, causing the system to shift left (favoring the reverse reaction). The amount of products decreases and the amount of reactants increases. Since Keq is the ratio of the products to the reactants this would decrease Keq.
	+ Cooling the system would be the same as removing products and would have the opposite effect. **Temperature changes always alter Keq!**
	+ If you see “∆H = + number”, that is the same thing as saying a reaction is endothermic, and “ΔH = ‑ number” is the same thing as saying the reaction is exothermic.

For each of the following reactions, predict whether the forward or reverse reaction is favored as the *temperature is increased*.

1. N2 (g) + O2 (g) ⇌ 2 NO (g) ΔH= + 181 kJ
2. 2 SO2 (g) + O2 (g) ⇌ 2 SO3 (g) ΔH = -198 kJ
3. 3 A (g) + 3 B (g) ⇌ 2 C (s) + 3 D (g) ΔH = 0 kJ

Calcium hydroxide is less soluble in boiling water than in cold water. Is the dissolving of calcium hydroxide exothermic or endothermic?

 Ca(OH)2 (s) ⇌ Ca 2+ (aq) + 2OH- (aq)

**Questions to Consider**

1. How can you determine if heat is a reactant or product when you are only given the value of ΔH?
2. Does the equilibrium constant change with temperature?
3. There is also a mathematical method for determining how a reaction will reach equilibrium when it is not in that state. This allows us to determine which direction a reaction will shift under non-equilibrium conditions. The mathematical expression is identical to the equilibrium expression in how it is derived from a balanced equation but instead of entering equilibrium concentrations, the initial concentrations are used. And instead of solving for an equilibrium constant K, the calculations yield a new value – **Q** – the reaction quotient. Once you have solved for Q, evaluate its magnitude with respect to K. Remember, Q wants to be like K.
* If Q is larger than K, then Q will decrease to match K. Products will be converted to reactants and the reaction will shift to the left.
* If Q is smaller than K, then Q will increase to match K. Reactants will be converted into products and the reaction will shift to the right.
* If Q equals K, then the reaction is at equilibrium.

PCl5, PCl3, and Cl2 are introduced to a closed flask at the following initial concentrations: [PCl5] = 0.060M, [PCl3] = 0.080M, and [Cl2] = 0.040M. They react until equilibrium is reached according to this reaction:

PCl5 (g) ⇌ PCl3 (g) + Cl2 (g)

The equilibrium constant for the reaction above is 0.041. Which reaction, the forward or reverse will take place more often until equilibrium is reached again?

**Questions to Consider:**

1. How is the Reaction Quotient Q similar to Le Chatelier’s Principle?
2. Think up or discuss a scenario where the reaction quotient is more suitable than Le Chatelier’s Principle for predicting the direction a reaction will shift.

1. The last section in this chapter will give an overview of *how to calculate equilibrium concentrations when the equilibrium constant K is given along with some initial concentration*. This is a useful skill to pick up now because the strategies involved will be used in AP Chemistry as well as college level physics and biology classes where buffers must be prepared. Solving equilibrium problems is similar to solving stoichiometric problems, but the amount of substances that will be produced is determined by your equilibrium constant K, not just the balanced equation. Large values for K will yield greater quantities of products and smaller values of K will yield smaller quantities of product.

A problem solving format called a **RICE table** has been developed to aid in your equilibrium calculations. You will use this table whenever you have an equilibrium problem. *RICE stands for reaction, initial, change and equilibrium concentration*. The only type of value that may go into a RICE table is **Molarity** (for now). Many times, the initial concentrations are given in the problem, the change in concentration can be determined by the stoichiometry and equilibrium concentrations are calculated. It is important to note that this will not always be the case! You must become very familiar with the RICE table concept.

When using rice tables to analyze an equilibrium problem, you frequently end up with a polynomial that requires the use of the quadratic equation to solve. You will also learn a short-cut that lets you know when you skip this quadratic bizness.



* Consider the following equation: Fe2+ (aq) + 2 SCN- (aq) ⇌ Fe(SCN)2 (aq)

Solutions of 2.0 M Fe2+ and 2.0 M SCN- are mixed in a container. At equilibrium there is 0.60 M of Fe(SCN)2. Calculate the equilibrium constant for the reaction.

* The first step in solving any equilibrium problem is to write the equilibrium expression!!

That is so important that it shall be typed again…with caps lock on. And bolded. **THE FIRST STEP IN SOLVING ANY EQUILIBRIUM PROBLEM IS TO WRITE THE EQUILIBRIUM EXPRESSION!!**

$$K= \frac{[Fe\left(SCN\right)\_{2}]}{[Fe^{2+}] [SCN^{-}]^{2}}$$

We are solving for K so we must determine the equilibrium values for everything else. This is where the RICE table excels.

* Draw a RICE table and fill in the information you are given from the problem. Ensure that you understand which values are initial and equilibrium concentrations.

|  |  |
| --- | --- |
| R |  Fe2+ (aq) + 2 SCN- (aq) ⇌ Fe(SCN)2 (aq) |
| I | **2.0 M**  | **2.0 M**  |  |
| C |  |  |  |
| E |  |  | **0.60 M**  |

* Next fill out any squares based on some safe assumptions. Before the two solutions are mixed, it is safe to assume that zero product is made. We can assume that the initial concentration of the Fe(SCN)2 is zero and fill that in our RICE Table.

|  |  |
| --- | --- |
| R |  Fe2+ (aq) + 2 SCN- (aq) ⇌ Fe(SCN)2 (aq) |
| I | 2.0 M  | 2.0 M  | **0 M** |
| C |  |  |  |
| E |  |  | 0.60 M |

* Once you have an initial and equilibrium concentration for any species in the reaction, you can work out the **change** in concentration, then use the stoichiometric coefficients to determine the change for the remaining substances. The change in concentration for Fe(SCN)2 is 0.60 M – 0 M = 0.60 M. According to the stoichiometry for this reaction, if Fe(SCN)2  increases by any molar amount, the two reactants must decrease by the same molar amount. Fill out the **change** boxes.

|  |  |
| --- | --- |
| R |  Fe2+ (aq) + 2 SCN- (aq) ⇌ Fe(SCN)2 (aq) |
| I | 2.0 M | 2.0 M | 0 M |
| C | - 0.60 M | - 1.20 M | **+ 0.60 M** |
| E |  |  | 0.60 M  |

* Complete the RICE table by calculating the equilibrium concentrations from the initial and change values.

|  |  |
| --- | --- |
| R |  Fe2+ (aq) + 2 SCN- (aq) ⇌ Fe(SCN)2 (aq) |
| I | 2.0 M  | 2.0 M  | 0 M |
| C | - 0.60 M | - 1.20 M | + 0.60 M |
| E | **1.40 M** | **0.8 M** | 0.60 M  |

* Once the RICE table is completed, use the equilibrium concentrations and your original equilibrium expression to solve for the value of K.

$K= \frac{[Fe\left(SCN\right)\_{2}]}{[Fe^{2+}] [SCN^{-}]^{2}}$ = $\frac{[0.60]}{\left[1.40\right][0.8]^{2}}$ = **0.67**

* What does the magnitude of K suggest?

**Questions to Consider:**

1. How do you identify initial and equilibrium concentrations? What is the first thing you will do when solving an equilibrium problem?

1. Do you know what the C in RICE stands for and how to determine it?
* Consider the following reaction: H2 (g) + I2 (g) ⇌ 2HI (g) K=64

Calculate the molarity of each species at equilibrium if 0.040 M HI is placed in a flask and allowed to react until equilibrium is reached. Use the approximation rule and the quadratic equation to solve.

* Consider the following reaction: H2 (g) + I2 (g) ⇌ 2HI (g) K=64

If the starting concentrations are 0.050 M for HI and 0.027 for both H2 and I2, what are the equilibrium concentrations of all substances? You will use the quadratic equation to solve.

* What are the concentrations at equilibrium of all chemicals if 0.500M PCl5 is placed in a container and is allowed to come to equilibrium?

PCl3 (g) + Cl2 (g) ⇌ PCl5 (g) K=0.041

* 0.100M H2, 0.100M I2, and 0.800M HI are mixed in a container. What are the concentrations of all chemicals at equilibrium? Helpful tip: This requires the use of the reaction quotient Q in order to determine which way the reaction will shift.

H2(g) + I2(g) ⇄ 2HI(g) K = 2.00

Homework #1: Reaction Pathways, Kinetics and Equilibrium

1. Based on the following reaction draw an energy diagram and label the following: reactants, products, activated complex (AC), energy of activation (Ea), and ΔH.

**Ca + 2 H20 ⇌ Ca(OH)2 + H2**

The potential energy of the reactants is 450 kJ/mol. The potential energy of the activated complex is 700 kJ/mol and the potential energy of the products is 225 kJ/mole.

Is this an endothermic or exothermic reaction? Justify your answer.

Is the value of K greater than or less than 1? Justify your answer.

1. Use the following reaction to answer the questions that follow: **2 AB ⇌ A2 + B2 + heat**

Suppose this reaction has been found to take place in these two steps:

**2AB ⇌ A2 + 2B + heat (slow)**

**2B ⇌ B2 (fast)**

* 1. Show that by adding these two reactions you obtain the overall reaction.
	2. Which of the two steps in this reaction mechanism is likely to have the higher activation energy? Why?
1. Hydrogen peroxide reacts with hydrogen ions and iodide ions according to the following equation:

**H+ + I- + H2O2 ⇌ H2O + HOI**

A possible reaction mechanism for reaction is:

**H+ + H2O2 ⇌ H3O2+ (fast)**

**H3O2 +  + I- ⇌ H2O + HOI (slow)**

* 1. Show that adding the two steps of the reaction mechanism gives the overall equation.
	2. How would you expect the overall reaction to be affected if the concentration of I- was doubled?

*Homework #2: Equilibrium Constant Expressions*

1. Write the equilibrium constant expressions for the following reactions then use the given equilibrium concentrations to calculate the value of K. Identify whether the reactants or products are favored for each reaction. Write a comment about letter (c).
	1. **N2 (g) + 3 H2 (g) ⇌ 2 NH3 (g);** [NH3] = 0.0100 M, [N2] = 0.0200 M, [H2] = 0.0200 M
	2. **2 KClO3 (s) ⇌ 2 KCl (s) + 3 O2**(g); [O2] = 0.0500 M
	3. **H2O (l) ⇌ H+1 (aq) + OH-1**(aq); [H+1] = 1 x 10-8 M, [OH-1] = 1 x 10-6 M
	4. **2 CO (g) + O2 (g) ⇌ 2 CO2**(g); [CO] = 2.0 M, [O2] = 1.5 M, [CO2] = 3.0 M
	5. **Li2CO3 (s) ⇌ 2 Li+1 (aq) + CO3-2**(aq); [Li+1] = 0.2 M, [CO3-2] = 0.1 M
	6. **2 S02 (g) + 02 (g) ⇌ 2 S03** (g) [SO2] = 0.3 M, [O2] = 0.6 M, [SO3] = 0.12 M
2. Use the following hypothetical reaction to answer the questions: **A ⇌ C + 5B**
	1. Are the chances high or low that the forward reaction will happen?
	2. Does the concentration of the reactants need to be high or low for the reaction to happen?
	3. Are the chances high or low that the reverse reaction will happen?
	4. Do the concentrations of the products need to be high or low for the reaction to happen?
	5. What has to happen for the reaction to reach equilibrium?
	6. Based on your answers in a - e, should the value of Keq be less than or greater than one?
3. The reaction involving ammonia, hydrogen, and nitrogen reaches equilibrium at 225°C. The reaction is represented by the following equation:

**2 NH3 (g) ⇌ 3 H2 (g) + N2 (g).**

The equilibrium concentration of the three gases are: [NH3] = 0.065 M, [H2] = 0.0025 M, [N2] = 0.00125 M.

* 1. What is the value of the equilibrium constant for this reaction? Does this reaction favor the reactants or the products?
	2. At a different temperature, the equilibrium concentrations of the substances involved in the reaction are as follows: [NH3] = 0.0035 M, [H2] = [N2] = 0.00078 M. What is the new value of Keq?
1. For the reaction**: 2 KClO3­(s) ⇌ 2 KCl (s) + 3 O2 (g),** K is equal to 1.25 x 10-4. Calculate the concentration of O2.
2. For the reaction **PCl5(g) ⇌ PCl3(g) + Cl2(g),** K = 0.041. If a 7.5 liter flask is found to contain 0.16 mole PCl5 and 0.052 mol PCl3, how many moles of Cl2 are present?
3. For the reaction **2 CO(g) + O2(g) ⇌ 2 CO2(g)**, K equals 1.5 when the concentrations of CO = 2.0 M and O2= 1.5 M. Calculate the concentration of CO2.
4. For the reaction **Li2CO3(s) ⇌ 2 Li+1(aq) + CO3-2(aq)**, K equals 0.004 when the concentration of CO3-2 = 0.1 M. Calculate the concentration of Li+1.

*Homework #3: Applying Le Chatelier’s Principle*

1. What is the effect on the concentration of NH3 in the reaction below in a closed system at equilibrium for each of the given stresses? **N2 (g) + 3 H2 (g) ⇌ 2 NH3 (g) ΔH = -92 kJ**

a. addition of nitrogen c. the volume is doubled

b. increase in temperature d. hydrogen is removed

1. If the following reaction is at equilibrium in a closed system, what effect will the following changes have on the concentration of carbon monoxide? **2 CO (g) + O2 (g) ⇌ 2 CO2 (g)**

a. oxygen is removed c. carbon dioxide is removed

b. pressure is increased d. a catalyst is added

1. What is the effect on the concentration nitrogen on the following equilibrium when each stress (change) is applied? **N2 (g) + 2 O2 (g) ⇌ 2 NO2 (g) + heat**

a. addition of N2 d. removal of O2

b. decrease in temperature e. addition of a catalyst

c. increase in volume f. increase in pressure

1. Predict whether each of the following concentration changes would favor the forward or reverse reactions.

 **2 HI (g) ⇌ H2 (g) + I2 (g)**

a. addition of HI d. removal of I2

b. addition of H2 e. removal of HI

c. decrease in volume f. decrease in pressure

1. What will be the effect of each of the following changes on the new equilibrium concentration of water vapor? **4 HCl (g) + O2 (g) ⇌ 2 H2O (g) + 2 Cl2 (g)**

a. addition of HCl d. removal of O2 b. removal of Cl2 e. addition of Cl2 c. increase in volume f. increase in pressure

1. Predict the effect of each of the following on the indicated equilibrium system in terms of which reaction will be favored (forward, reverse, or neither): **H2 (g) + Cl2 (g) ⇌ 2 HCl (g) + 184 kJ**

a. addition of Cl2 f. removal of H2

b. removal of HCl g. decreased pressure

c. increased pressure h. addition of a catalyst

d. decreased temperature i. increased volume

e. decreased volume f. increased temperature

1. Predict the effect of each of the following on the indicated equilibrium system in terms of which reaction will be favored (forward, reverse, or neither): **2 NO2 (g) ⇌ 2 NO (g) + O2 (g) ΔH = +57 kJ**

a. removal of oxygen d. addition of catalyst

b. increased temperature e. addition of NO2

c. decreased volume f. decreased pressure

*Homework #4: Applying Le Chatelier’s Principle*

1. Rust is flushed from radiators using oxalic acid according to the equation:

**Fe2O3 (s) + 6 H2C2O4 (aq) ⇌ 2 Fe2(C2O4)3 (aq) + 3 H2O (l) + 6 H+**

What is the effect on the dissolving of the rust if:

* 1. More concentrated oxalic acid is used?
	2. The solution is made more acidic?
	3. More Fe2O3 is added?
1. After flushing a radiator with oxalic acid, excess acid is neutralized with sodium carbonate by the reaction:

**H2C2O4 (aq) + Na2CO3 (s) ⇌ H2O (l) + CO2 (g) + 2 Na+ (aq) + C2O42- (aq)**

Will this equilibrium left or right if:

* 1. The oxalic acid I s made more concentrated?
	2. Sodium hydroxide is added?
	3. More sodium carbonate is added?
1. Gypsum, CaSO4, is slightly soluble in acid. To increase the solubility of gypsum, should the acid concentration be increased or decreased? Explain using Le Chatelier's principle.

**CaSO4 (s) + H+ (aq) ⇌ Ca2+ (aq) + HSO4- (aq)**

1. Potassium hydroxide dissolves exothermically. Is KOH more or less soluble at higher temperatures? Explain using Le Chatelier’s Principle as your justification.
2. The enthalpy change for the reaction in which sulfur precipitates from volcanic fumes is ΔH = +42.2 kJ mol-1.

 **SO2 (g) + 2 H2S (g) ⇌ 3 S (s) + 2 H2O (g)**

Will this equilibrium be shifted more to the right or to the left at the higher temperatures of a volcano?

1. NO2 (g) is red-brown and N2O4 (g) is colorless. An equilibrium mix of the two, **2 NO2 (g) ⇌ N2O4 (g)**, is observed to become more red-brown as it is heated. Is ΔH positive or negative for this reaction?
2. The air around electrical generating equipment often smells of ozone from the endothermic reaction **3 O2 (g)    ⇌    2 O3** **(g).** If the total pressure around the equipment is dropped will this equilibrium shift left or right?
3. Oxides of nitrogen are often formed in the atmosphere during lightning discharges: **N2 (g)    +    2 O2 (g)    ⇌    2 NO2 (g)**. Would this reaction be shifted more to the right or to the left in the upper atmosphere where the total pressure is lower?
4. For each reaction listed, state whether the equilibrium would be shifted to the right by a volume increase or by a volume decrease.
	1. 4 NO (g) + 6 H2O (l) ⇌    4 NH3 (g) + 5O2 (g)
	2. 2 CaCO3 (s) + 2 SO2 (g) + O2 (g) ⇌    2 CaSO4 (s) + 2 CO2 (g)
	3. CH4 (g) + 2 O2 (g) ⇌ CO2 (g) + 2 H2O (g)
5. For the reaction 2 NO (g) + Cl2 (g) ⇌ 2 NOCl (g), K = 10.0 at a certain temperature. If the initial concentrations are 0.15 M NO, 0.050 M Cl2, and 0.10 M NOCl, will the reaction favor the products or reactants?

*Homework #5: Equilibrium Calculations*

1. Initially, a 25 liter flask contains 0.050 mol SO2, 0.10 mol O2, and 0.075 mol SO3. Will more or less SO3 be present at equilibrium? Think about what this question is asking before you create a rice table.

2 SO2 (g) + O2 (g) ⇌ 2 SO3 (g) K = 280

2. The nerve gas phosgene decomposes according to the following reaction COCl2 (g) ⇌ CO (g) + Cl2 (g), K = 0.32 at 1000 K. If the initial concentration of phosgene is 0.015 M, what are the equilibrium concentrations of all gases?

3. The equilibrium 2 NO2 (g) ⇌ N2O4 (g) is reached after 1.50 moles of N2O4 are introduced to a 3.6 liter container. K = 0.50 at the temperature of the system. Find the concentration of both gases.

4. The formation of nitrogen monoxide, ½ N2 (g) + ½ O2 (g) ⇌ NO (g), has an equilibrium constant of 0.050. If a flask initially contains 0.100 moles per liter of NO at these conditions, what will the equilibrium concentrations be for all gases?

5. Find the concentrations of all species in a 1.0 liter flask if 0.72 mol H2 reacts with 0.72 mol CO2, until the equilibrium CO2(g)    +    H2(g)    ⇌    CO (g)    +    H2O (g) is reached. K = 0.34 at the existing temperature.

6. A flask is initially 0.050 M in NO2 and 0.010 M in N2O4. What will the equilibrium concentrations be if K = 0.50 for 2 NO2(g)    ⇌    N2O4(g) at the conditions of the flask?

7. When solid ammonium chloride is put in a reaction vessel at 323 K, equilibrium concentrations of ammonia and hydrogen chloride are found to 0.0660 M. Calculate K for the reaction: NH4Cl (s)    ⇌    NH3(g)    +    HCl (g)

8. K is 1.60 at 933 K for this reaction: H2(g)    +    CO2(g)    ⇌    H2O (g)    +    CO (g). Calculate the equilibrium concentration of hydrogen when [CO2] = 0.320 M, [H2O] = 0.240 M, and [CO] = 0.280 M at equilibrium.

9. At 2273 K, Keq = 6.2 x 10-4 for the reaction N2(g)    +    O2(g)    ⇌    2 NO (g). If [N2] = 0.05200 M and [O2] = 0.00120 M initially, what is the concentration of NO at equilibrium?

*Review: Equilibrium Vocabulary Concepts*

1. The change in concentration of reactants or products divided by the change in time is called the \_\_\_\_\_.
2. When one graphs a speed or rate, what variable is plotted on the X-axis?
3. The reaction has reached \_\_\_\_\_ when the forward and reverse reactions are taking place at the same rate.
4. In the equilibrium constant expression is a ratio of the \_\_\_\_\_ (continued in #5)
5. over the \_\_\_\_\_.
6. The [ ] used in the equilibrium constant expression indicate the \_\_\_\_\_ of the substances in the reaction
7. In the equilibrium constant expression, only substances in the \_\_\_\_\_ phase (continued in # 8)
8. and the \_\_\_\_\_ phase are used.
9. If the Keq is greater than 1, then the \_\_\_\_\_ are favored.
10. The value of the equilibrium constant changes only when the \_\_\_\_\_ is changed

*Review Questions: Multiple Choice*

**Choose one best answer to each of the following questions.**

Questions 1 through 5 refer to a hypothetical reversible chemical reaction in which reactant Y is a bright yellow color, reactant C is colorless, and the product B is a bright blue color. The reaction is exothermic with a Keq of 1.5. The system is initially at equilibrium and has a green color. **C(g) + Y(g) ⇌ 3B(g)**

1. Adding a large quantity of C gives a

 a. blue color. b. yellow color. c. green color. d. no color

1. Cooling the system gives a

 a. blue color. b. yellow color. c. green color. d. no color

1. Adding a catalyst gives a

 a. blue color. b. yellow color. c. green color. d. no color

1. Increasing the pressure on the system gives a

 a. blue color. b. yellow color. c. green color. d. no color

1. Removing B from the system gives a

 a. blue color. b. yellow color. c. green color. d. no color

1. What is the effect of adding more water to the following equilibrium reaction? **CO2 + H2O ⇌ H2CO3**

 a. more H2CO3 is produced b. equilibrium is pushed in the direction of the reactants

 c. the CO2 concentration increases d. nothing

1. Two opposing reactions (A + B **⇌** C + D) occurring simultaneously at the same rate is an example of a

 a. cancellation reaction. b. chemical equilibrium.

c. both a and b. d. neither a nor b.

1. The Keq of a reaction is 4 x 10-7. At equilibrium,

 a. the reactants are favored.

 b. the products are favored.

 c. the reactants and products are present in equal amounts.

 d. the rate of the forward reaction is much greater than the rate of the reverse reaction.

1. Assuming that the products in a reaction have a total heat content of 0 kJ and that the reactants have a total heat content of 100 kJ, the value of ∆H for the reaction is

 a. -393.5 kJ b. -100 kJ. c. 0 kJ. d. +100 kJ.

1. Assuming that the products in a reaction have a total enthalpy of 458 kJ and the reactants have a total energy of 858 kJ, what is ∆H for the reaction?

 a. -1116 kJ b. -400 kJ c. +400 kJ d. +1116 kJ

1. In an endothermic reaction, which of the following is true?

 a. energy content of products < activation energy < energy content of reactants

 b. energy content of reactants < activation energy < energy content of products

 c. energy content of products < energy content of reactants < activation energy

 d. energy content of reactants < energy content of products < activation energy

1. At equilibrium,

 a. forward reaction rate < reverse reaction rate. b. forward reaction rate > reverse reaction rate.

 c. forward reaction rate = reverse reaction rate. d. no reactions take place.

1. In the expression K = [W][X] the reactant concentrations are expressed as

 [Y][Z]

 a. [W][X] b. [Y][Z] c. [W][X] d. K = [W][X]

 [Y][Z] [Y][Z]

1. A change in which of the following affects the value of the equilibrium constant?

 a. pressure only. b. concentration only. c. temperature only d. pressure, conc., and temp.

1. What symbol in a chemical equation indicates equilibrium?

 a. → b. ← c. →← d. none of these

1. A value of Keq close to 1 indicates that it is likely that at equilibrium

 a. only products will be present. b. only reactants will be present.

 c. quantities of products & reactants will be present. d. the reactions occur at a moderate rate.

1. A reaction in which products can react to re-form reactants is said to be

 a. at equilibrium b. reversible c. buffered d. impossible

1. Where are the coefficients in a chemical equilibrium equation placed in a chemical equilibrium expression?

 a. as coefficients b. as exponents c. as subscripts d. nowhere

1. What is the effect on concentrations if the temp. of the equilibrium system **X + Y ⇌ Z + 25 kJ** is decreased?

 a. [X] decreases and [Z] increases b. [X] increases and [Z] decreases

 c. [X] decreases and [Z] decreases d. there is no effect

1. The chemical equilibrium expression for the equation **L + 2 M ⇌ 4 N + 3 O** is

 a. K = [N]4[O]3 b. K = [L][M]2 c. K = 4[N]3[O] d. K = [L]2[M]

 [L][M]2 [N]4[O]3 [L]2[M] 4[N]3[O]

1. The value of an equilibrium constant

 a. changes with concentration b. changes with time

 c. changes with temperature d. is the same under all conditions

1. At equilibrium

 a. nothing occurs b. only the forward reaction continues

 c. only the reverse reaction continues d. both the forward and reverse reactions continue.

1. According to Le Chatelier's principle, an equilibrium system subjected to stress

 a. is not affected by the stress. b. shifts in the direction that increases the stress.

 c. shifts in the forward direction. d. shifts in the direction that relieves the stress.

1. A very high value of Keq indicates that

 a. equilibrium is reached slowly. b. products are favored.

 c. reactants are favored. d. equilibrium has been reached.

1. What is the effect on the quantities of substances present if the pressure on the equilibrium system

**N2(g) + O2(g) ⇌ 2NO(g)** is decreased?

a. the quantity of N2(g) decreases b. the quantity of NO(g) decreases

c. the quantity of NO(g) increases d. there is no effect

1. What is the effect on the quantities of substances present if the pressure on the equilibrium system

**2CO(g) + O2(g) ⇌ 2CO2(g)** is increased?

 a. the quantity of CO(g) increases b. the quantity of CO2(g) increases

 c. the quantity of CO2(g) decreases d. there is no effect

1. What is the effect on Keq if more CO(g) is added to the system in question 26?

 a. Keq increases b. Keq decreases

 c. Keq may either increase or decrease d. Keq remains the same

1. The chemical equilibrium expression for the equation 2 A2B + 3 CD ⇌ A4D + C3B2 is

 a. K = 2[A2B]3[CD] b. K = [A4D][C3B2] c. K = [A2B]2[CD] d. K = [A4D][C3B2]

 [A4D][C3B2] 2[A2B]3[CD] [A4D][C3B2] [A2B]2[CD]3

1. A very low value of Keq indicates that

 a. equilibrium is reached very slowly. b. products are favored.

 c. reactants are favored. d. equilibrium has been reached.

1. A change in which of the following is a stress on equilibrium systems?

 a. pressure only. b. concentration only. c. temperature only. d. pressure, conc., and temp.

1. At equilibrium, the amount of product

 a. is always equal to the amount of reactant. b. is always greater than the amount of reactant.

 c. is never equal to the amount of reactant. d. may be = , > , or < the amount of reactant.

1. What is the effect on concentrations if more CO(g) is added to the following equilibrium system:

 **2 CO (g) + 02 (g) ⇌ 2 CO2 (g)**

 a. [CO2] increases and [O2] decreases b. [CO2] increases and [O2] increases

 c. [CO2] decreases and [O2] decreases d. both [CO2] and [O2] remain the same

*How to review these concepts for an Exam: A checklist*

\_\_\_Is your homework complete?

\_\_\_Did you complete the review if one was given?

\_\_\_Did you seek out and get help on the review if you did not understand a concept?

\_\_\_Have you reworked any problems you struggled with from this unit?

\_\_\_Did you complete any/all labs associated with this unit?

­­­\_\_\_Did you correct your quizzes from this unit?

\_\_\_Did you seek out and get help if you struggled with any part of this unit?

­­­\_\_\_Have you come to tutorials?

\_\_\_Have you read your hand-written notes and created questions about your notes?

\_\_\_Can you explain to someone else how to answer the big questions from this unit? Have you done that?

\_\_\_Have you participated in a study group for this unit?

Although this list is not exhaustive, if you can honestly answer yes to the first 7 questions, then you have a high chance of doing well on the equilibrium portion of the exam. If you can honestly answer yes to all questions, then you have a much higher chance of doing extremely well on the exam.

Do not expect to accomplish a thorough review for an exam the night before the exam date. Pace yourself and work with study groups during the days leading up to the exam. This is a skill that must be developed. You must practice being a student, then practice some more!

