

# Preparation for Topics in College Chemistry



## Module 24: Equilibrium

### How to Use These Modules

The objective of these lessons is to help students to **solve problems** on tests and assignments in Introductory College Chemistry.

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Additional topics and resources are available online at [www.ChemReview.net](http://www.ChemReview.net) .

Modules 20 and above are *beta* versions. They are being posted in *draft* form to provide help on as many topics as possible during this semester. If you have need for help in this topic *now*, they will be useful, but not all topics are covered, and they will have a higher than usual rate of typos and errors. Check back for updated versions at [www.ChemReview.Net](http://www.ChemReview.Net) if you have time.

## Module 24 – Equilibrium

### Introduction

Chemical reactions can be divided into three types.

1. **Reactions that go nearly 100% to completion.** Burning paper is one such reaction. Once the reaction begins, the reaction goes until one of the reactants (the paper or oxygen) is essentially used up.
2. **Reactions that don't go.** Trying to convert carbon dioxide and water into paper is very difficult to do in a chemist's laboratory (though plants are able to accomplish most steps in this reaction through the remarkable process of photosynthesis).
3. **Reactions that are reversible and go partially to completion.** In reversible reactions, as the reaction proceeds, the reactants are gradually used up. As a result, the forward reaction slows down. As product concentrations increase, they more frequently collide and react to re-form the reactants. Finally, both the forward and reverse reactions are going at the same rate. As long as no substances or energy are added to or removed from the reaction system, the two rates will remain equal and no further reaction seems to take place. The reaction is said to be at **equilibrium**.

For equilibrium to exist,

- all reactants and products must be present in at least small quantities, and
- the reaction must be in a *closed* system: no particles or energy can be entering or leaving.

At equilibrium, no reaction seems to be taking place, but this appearance is deceiving. Equilibrium is **dynamic**: the forward and reverse reactions continue to occur. However, because the rates of reaction of the products and reactants are the same, there is no *net* change.

In theory, all reactions are reversible, and all reactions go to equilibrium. In practice, many equilibria favor the products so much that the reactions go almost 100% to completion, with nearly all of the limiting reagent used up.

In the reaction calculations that we have done in previous lessons, the reactions have been those that go essentially to completion. Calculations for those reactions can be done using standard stoichiometry rules. Equilibrium requires more complex calculations, because the reactions do not go until one of the reactants is all used up. At equilibrium, all of the reactants and products are present to some extent; there is no limiting reactant that will decide how much of the products will form.

## **Lesson 24A: Le Châtelier's Principle**

**Timing:** Problems using Le Châtelier's Principle may be assigned at the beginning or end of a unit on Equilibrium. This lesson may be completed at either point. At the point when Le Châtelier's Principle is assigned in *your* class, read the introduction on the previous page and then do this lesson.

\* \* \* \* \*

### **Shifts In Equilibrium**

Equilibrium is important because many reactions, especially those in biological systems, are in practice reversible. For reversible reactions, we want to

- predict what happens when a system at equilibrium is *disrupted*, and
- *shift* an equilibrium to make as much of a wanted substance as possible.

Shifts in an equilibrium can be predicted by

#### **Le Châtelier's Principle**

If a system at equilibrium is subjected to a change, processes occur which tend to counteract that change.

Le Châtelier's Principle predicts shifts in concentration, temperature, and pressure.

#### **Changes in Concentration**

Another way of stating Le Châtelier's Principle is useful for shifts in equilibrium due to changes in *concentration* of either gases or substances dissolved in solution.

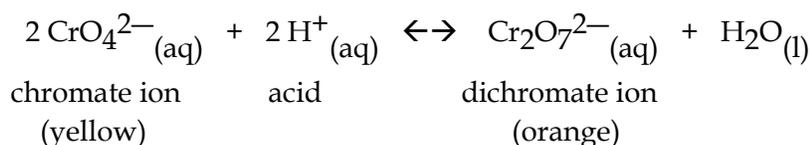
#### **To Predict Equilibrium Shifts Due to Concentration Changes**

For reversible reactions at equilibrium, write the balanced equation using a *two-way* arrow. Then,

- Increasing* a [substance] which appears on one side of a equilibrium equation shifts an equilibrium to the *other* side. The other substance concentrations on the *same* side as the [increased substance] are *decreased*, and the substance concentrations on the *other* side are *increased*.
- Decreasing* a [substance] which appears on one side of a equilibrium equation shifts the equilibrium *toward* that side. The other [substances] on the *same* side are *increased*, and the [substances] on the *other* side are *decreased*.

Memorize the rules in the two boxes above, and then apply the rules to this problem.

**Q.** Chromate ions react with acids to form dichromate ions in this reversible reaction.



Below, cover below the \* \* \* \* \* line, and answer the questions above the line.

1. If acid ( $\text{H}^+$ ) is added to a yellow chromate ion solution at equilibrium,
  - a. Which direction will the equilibrium shift (left or right)? \_\_\_\_\_
  - b. The  $[\text{CrO}_4^{2-}]$  will (increase or decrease?) \_\_\_\_\_.
  - c. The [dichromate ion] will (increase or decrease?) \_\_\_\_\_.
  - d. What visible change will occur? \_\_\_\_\_

\* \* \* \* \*

Answers

- a. The equilibrium will shift to the **right**. Increasing the concentration of  $\text{H}^+$  that reacts on the left side shifts the equilibrium to the right side.
- b. The  $[\text{CrO}_4^{2-}]$  will **decrease**. Increasing the concentration of a substance that appears on one side decreases the concentration of the other substances on that side.
- c. The [dichromate ion] will **increase**. Increasing the  $[\text{H}^+]$  that appears on the left increases the concentration of the substances on the right.
- d. Since adding acid decreases the [chromate] and increases the [dichromate], the solution color shifts from yellow to **orange**.

These shifts fit what we know about chemical reactions.

- When  $[\text{H}^+]$  increases, there will be more collisions between the acid and the chromate ions. Though the *percentage* of collisions that lead to a reaction stays the same if the temperature remains constant, more collisions means more forward reaction. Increasing the  $[\text{H}^+]$  means that the rates of the forward and reverse reaction, equal at equilibrium, are thrown out of balance. The increased forward reaction uses up chromate and forms dichromate.

In terms of Le Châtelier's Principle, when  $\text{H}^+$  is added, the system response is to decrease the  $[\text{H}^+]$  by increasing the rate at which  $\text{H}^+$  is used up.

- As more dichromate forms, its collisions with the water increase, and the speed of the reverse reaction increases. A new balance is reached, however, only after some of the yellow chromate has been used up and more orange dichromate has formed.

\* \* \* \* \*

2. If a *base* is added to the orange solution that results after adding acid,
  - a. What will happen to the acid concentration? \_\_\_\_\_

\* \* \* \* \*

- a. Bases neutralize acid (see Lesson 13A). This lowers the  $[\text{H}^+]$ .
- b. Which direction will the equilibrium shift (left or right)? \_\_\_\_\_
- c. The  $[\text{CrO}_4^{2-}]$  will (increase or decrease) \_\_\_\_\_.

- d. The  $[\text{Cr}_2\text{O}_7^{2-}]$  will (increase or decrease) \_\_\_\_\_.
- e. What visible change will occur? \_\_\_\_\_

\* \* \* \* \*

- b. Decreasing the concentration of  $\text{H}^+$ , which is in the equation on the left side, will shift the equilibrium *toward* that side.
- c. Shifting to the left means that the  $[\text{CrO}_4^{2-}]$  will **increase**.
- d. Decreasing the concentration of a term on the left decreases the concentration of the terms on the right. The  $[\text{Cr}_2\text{O}_7^{2-}]$  will **decrease**.
- e. Adding base decreases the [acid]. The equilibrium shifts to the side with the acid term, increasing the [yellow chromate] and decreasing the [orange dichromate]. The color changes from orange toward **yellow**.

In terms of what we know about chemical reactions, these shifts are logical.

- When  $[\text{H}^+]$  decreases, the balanced rates at equilibrium are upset. There will be fewer collisions between the acid and the chromate ions. Fewer collisions means that the reverse reaction is now faster than the slowed forward reaction. The reverse reaction uses up orange dichromate and forms yellow chromate until a new balanced equilibrium is reached.

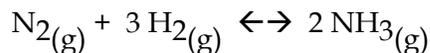
### Driving a Reversible Reaction

Given a reversible reaction at equilibrium, if the system is opened and a reactant or product is allowed to escape (such as letting a gas product escape from a solution reaction), the reversible reaction will shift toward the side that contains the escaping particle.

\* \* \* \* \*

### Practice A: Check your answer after Part a.

1. For the Haber process reaction:



- a. If the  $[\text{H}_2]$  is increased,
1. Equilibrium will shift to the (left or right?) \_\_\_\_\_.
  2.  $[\text{N}_2]$  will (increase or decrease?) \_\_\_\_\_.
  3.  $[\text{NH}_3]$  will (increase or decrease?) \_\_\_\_\_.
- b. If the  $[\text{N}_2]$  is decreased,
1. Equilibrium will shift to the (left or right?) \_\_\_\_\_.
  2.  $[\text{H}_2]$  will (increase or decrease?) \_\_\_\_\_.
  3.  $[\text{NH}_3]$  will \_\_\_\_\_.

\* \* \* \* \*

**Changes in Temperature**

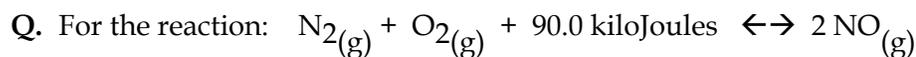
When *energy* is a term in for a reaction at equilibrium, it follows Le Châtelier's Principle in a manner similar to the rules for concentration.

- *Adding* energy shifts the equilibrium *away* from the side with the energy term, and
- *removing* energy shifts the equilibrium *toward* the side with the energy term.

Energy can be added to a system by increasing its temperature. Energy can be removed by cooling a system. When energy is produced by a shift in equilibrium, the temperature of the system goes up. When energy is used up, the system's temperature goes down.

\* \* \* \* \*

Apply those rules to the following problem. Check Part 1 answers before doing Part 2.



1. If the temperature of the reaction vessel is increased,
  - a. The equilibrium will shift to the (left or right?) \_\_\_\_\_
  - b. The  $[\text{O}_2]$  will (increase or decrease?) \_\_\_\_\_.
  - c. The  $[\text{NO}]$  will \_\_\_\_\_.
2. If the  $[\text{O}_2]$  is decreased,
  - a. The equilibrium will shift to the \_\_\_\_\_
  - b. The  $[\text{N}_2]$  will \_\_\_\_\_.
  - c. The temperature will \_\_\_\_\_.

\* \* \* \* \*

**Answers**

- 1a. The equilibrium will shift to the right. Energy is a term on the left, so if energy is added, the system uses up energy by shifting the equilibrium to the right.
- 1b. The  $[\text{O}_2]$  will decrease. Adding a term that appears on one side uses up terms on that side.
- 1c. The  $[\text{NO}]$  will increase. Increasing energy that is a term on the left causes more of substances on the right to form.

\* \* \* \* \*

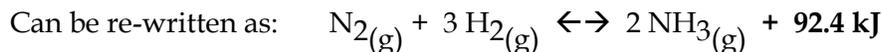
- 2a. The equilibrium will shift to the left.
- 2b. The  $[\text{N}_2]$  would increase.
- 2c. The temperature of the mixture will increase. Shifting the equilibrium to the left makes more of the terms shown on the left, including more energy.

\* \* \* \* \*

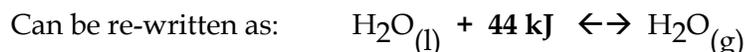
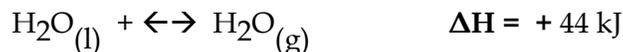
When using Le Châtelier's Principle, if an energy term is expressed in  $\Delta H$  notation, it helps to convert the energy to a term written *inside* the equation with a *positive* sign.

Examples:

For negative  $\Delta H$ , the energy term can be converted to a positive term on the *right*.



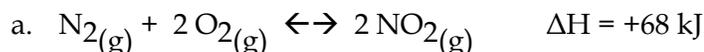
For positive  $\Delta H$ , the energy term can be converted to a positive term on the *left*.



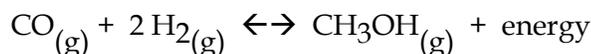
\* \* \* \* \*

**Practice B**

1. Convert these reactions to notation where the energy term is written as a positive quantity on the left or right. (For additional practice, see Lesson 19A.)



2. In the equilibrium for the synthesis of methyl alcohol,



a. If the temperature is decreased,

1. equilibrium will shift to the (left or right?) \_\_\_\_\_.

2.  $[\text{CH}_3\text{OH}]$  will (increase or decrease?) \_\_\_\_\_.

b. If the  $[\text{H}_2]$  is increased,

1. equilibrium will shift to the \_\_\_\_\_.

2.  $[\text{CH}_3\text{OH}]$  will \_\_\_\_\_.

3. The temperature in the vessel will \_\_\_\_\_.

3. For the reaction: 
$$2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{g}) \quad \Delta H = -566 \text{ kJ}$$

a. Write the reaction with energy as a positive term in the equation.

b. If the temperature is increased,

1. equilibrium will shift to the \_\_\_\_\_. 2.  $[\text{CO}_2]$  will \_\_\_\_\_.

c. If the  $[\text{O}_2]$  is increased,

1. equilibrium will shift to the \_\_\_\_\_. 2.  $[\text{CO}]$  will \_\_\_\_\_.

3. The temperature in the vessel will (inc. or dec?) \_\_\_\_\_.

\* \* \* \* \*

**Changes in Pressure**

Pressure will affect an equilibrium which has gases, but only if one side of the equation has more moles of gas than the other. For a system at equilibrium,

- Increasing the *pressure* on a gas will shift the equilibrium toward the side with *fewer total moles* of gas.
- Decreasing the pressure on a gas will shift the equilibrium toward the side with more moles of gas.

To find which side has more moles of gas, simply add the coefficients of the gas molecules on each side of the balanced equation. If the moles of gas are equal on both sides, changing pressure will not shift the equilibrium.

Usually, the volume of a reaction vessel containing gases is increased or decreased by using a tightly sealed but moveable piston attached to the reaction vessel. Pushing the piston in a distance increases the pressure on the gases and decreases the volume of the container. Pulling the piston out a distance increases the container volume and decreases the pressure on the gases.

\* \* \* \* \*

Write and recite the rules in the box above until they are committed to memory. Then apply the rules to the following problem. Check your answer after each part.

**Q.** For the reaction at equilibrium:  $2\text{NO}_2(\text{g}) \leftrightarrow \text{N}_2\text{O}_4(\text{g}) + \text{energy}$

1. If the pressure on the gases in the mixture is decreased,
  - a. The equilibrium will shift to the (left or right?) \_\_\_\_\_
  - b. The  $[\text{NO}_2]$  will (increase or decrease?) \_\_\_\_\_.
  - c. The  $[\text{N}_2\text{O}_4]$  will (increase or decrease?) \_\_\_\_\_.
  - d. The temperature in the vessel will (increase or decrease?) \_\_\_\_\_.
2. If the volume of the reaction container is decreased,
  - a. The equilibrium will shift to the (left or right?) \_\_\_\_\_
  - b. The  $[\text{NO}_2]$  will (increase or decrease?) \_\_\_\_\_.
  - c. The  $[\text{N}_2\text{O}_4]$  will (increase or decrease?) \_\_\_\_\_.
  - d. The temperature in the vessel will (increase or decrease?) \_\_\_\_\_.

\* \* \* \* \*

**Answers**

- 1a. The equilibrium will shift to the left. Decreased pressure favors the side with more gas molecules.
- 1b.  $[\text{NO}_2]$  will increase as the equilibrium shifts to the left.
- 1c.  $[\text{N}_2\text{O}_4]$  will decrease as the equilibrium shifts to the left.

- 1d. The temperature in the vessel will decrease. As a term on the right side, energy must be used up as the equilibrium shifts to the left.
- 2a. Decreasing the volume increases the pressure. The equilibrium will shift to the right. The left side has two moles of gas and the right has only one. When the pressure is increased, the system's response is to oppose the change and decrease the pressure. The way it can do that is to make fewer gas molecules.
- 2b. The  $[\text{NO}_2]$  will decrease as the equilibrium shifts to the right.
- 2c. The  $[\text{N}_2\text{O}_4]$  will increase as the equilibrium shifts to the side with fewer gas moles.
- 2d. The temperature in the vessel will increase. As a term on the right side, energy must be formed as the equilibrium shifts to the right.

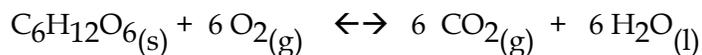
\* \* \* \* \*

### **Practice C**

1. In the equilibrium for the formation of nitrogen dioxide:

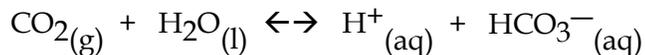


- a. Which side has fewer gas molecules?
- b. If the pressure on the gas mixture is increased,
- Equilibrium will shift to the \_\_\_\_\_.
  - $[\text{NO}_2]$  will \_\_\_\_\_.
  - The temperature in the vessel will \_\_\_\_\_.
- c. If the volume of the reaction vessel is increased,
- Equilibrium will shift to the \_\_\_\_\_.
  - $[\text{O}_2]$  will (increase or decrease?) \_\_\_\_\_.
  - The temperature in the vessel will \_\_\_\_\_.
2. In the equilibrium:



If the pressure on the reaction vessel is decreased, the equilibrium will shift to the (left or right?) \_\_\_\_\_

3. If, for an equilibrium that is found in sealed carbonated beverages,



the cap is left off the bottle,

- which way will the equilibrium shift? \_\_\_\_\_
- What will happen to the acidity of the beverage? \_\_\_\_\_.

\* \* \* \* \*

**Concentration Changes: Special Cases**

There are two special rules for concentration changes.

1. Adding or removing a *solid* or a *liquid* from a reaction at equilibrium does not shift the equilibrium.

Solids have a constant concentration determined by their density. Adding or removing solid does not change the solid's concentration and does not shift an equilibrium.

Example. If solid table salt (NaCl) is added to a glass of water, initially all of the salt dissolves. However, if enough salt is added and stirred, the solution becomes **saturated**: at a given temperature it reaches the limit of dissolved salt it can hold.

This result is in agreement with Le Châtelier's Principle. The equilibrium for this reaction:  $\text{NaCl(s)} \leftrightarrow \text{NaCl(aq)}$  cannot not be reached until some solid remains after stirring, since equilibrium requires that all reactants and products be present. However, once equilibrium is reached, adding more salt crystals increases the *amount* of solid salt on the bottom, but it does not increase the *concentration* of dissolved salt. Adding solid does not shift an equilibrium.

In a solid, the particles are packed tightly, usually as concentrated as they can get. To shift an equilibrium we must change concentration, and the concentration of a solid is constant.

For a pure liquid, the rule is the same as for solids. A liquid has a constant concentration. Adding or removing a pure liquid from a system at equilibrium will not change the concentration of the liquid, and therefore will not shift the equilibrium.

2. If a *liquid solvent* for the reaction is a term in the equation, adding or removing solvent does not shift the equilibrium. Shifting the equilibrium will not change the concentration of the solvent.

A solvent is a liquid, but it is not a pure liquid. In theory, if material is dissolved in a solvent, the concentration the liquid solvent can change as the particles of the solvent are displaced by the dissolved substance.

In practice, for most reactions in chemistry, if a solvent is used it will be in the reaction mixture at much higher concentrations than the other reaction components. At high solvent concentrations, changes caused by adding, forming, or using up the solvent will nearly always be negligible.

The most common solvent in chemistry is water. Adding water to an aqueous system at equilibrium will rarely shift the equilibrium. Reactions in aqueous solutions that use up or form water will not significantly change the concentration of the water.

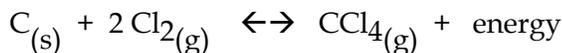
**The Effect of a Catalyst**

Including a catalyst in a mixture at equilibrium will not shift the equilibrium. However, the catalyst will cause the reaction equilibrium to be reached more quickly.

\* \* \* \* \*

**Practice D.** Be certain that you have first memorized the rules for Le Châtelier's Principle so that these problems serve as a practice test. However, if you are unsure of an answer, check your answers after each numbered question.

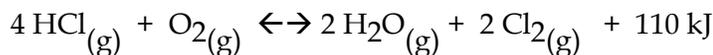
1. For the reaction at equilibrium at high temperature



- a. If the  $[\text{Cl}_2]$  is decreased,
- Equilibrium will shift to the (left or right?) \_\_\_\_\_.
  - $[\text{CCl}_4]$  will (increase or decrease?) \_\_\_\_\_.
  - $[\text{C}]$  will \_\_\_\_\_.
  - The amount of carbon will \_\_\_\_\_.
  - The temperature in the reaction vessel will \_\_\_\_\_.
- b. If the pressure in the reaction vessel is decreased,
- Equilibrium will shift to the \_\_\_\_\_.
  - $[\text{Cl}_2]$  will \_\_\_\_\_.
  - The temperature in the reaction vessel will \_\_\_\_\_.
2. Consider this reaction at equilibrium.

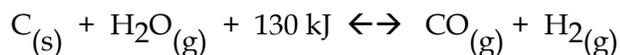


- a. If water is added,
- equilibrium will shift to the (left or right?) \_\_\_\_\_.
- b. If the  $[\text{OH}^-]$  is increased,
- equilibrium will shift to the \_\_\_\_\_.
  - $[\text{HCOOH}]$  will \_\_\_\_\_.
  - $[\text{H}_2\text{O}]$  will \_\_\_\_\_.
- c. If  $\text{H}^+$  is added,
- equilibrium will shift to the \_\_\_\_\_.
  - $[\text{HCOO}^-]$  will \_\_\_\_\_.
- d. If a catalyst is added,
- equilibrium will shift to the \_\_\_\_\_.
3. For the reaction at equilibrium,



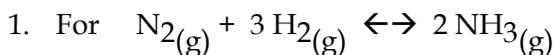
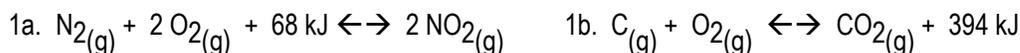
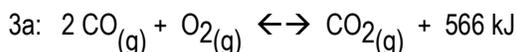
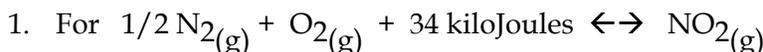
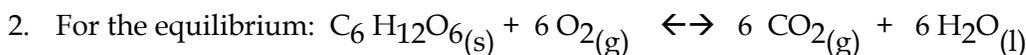
- a. if the  $[\text{O}_2]$  is increased,
- equilibrium will shift to the \_\_\_\_\_.
  - $[\text{HCl}]$  will \_\_\_\_\_.
- b. If the  $[\text{HCl}]$  is decreased,
- equilibrium will shift to the \_\_\_\_\_.

2.  $[O_2]$  will \_\_\_\_\_. 3.  $[Cl_2]$  will \_\_\_\_\_.
4. The temperature in the reaction vessel will \_\_\_\_\_.
- c. If the temperature in the reaction vessel is decreased,
- equilibrium will shift to the \_\_\_\_\_.
  - $[O_2]$  will \_\_\_\_\_. 3.  $[H_2O]$  will \_\_\_\_\_.
- d. If the total pressure on the gases in the vessel is increased,
- equilibrium will shift to the (left or right?) \_\_\_\_\_.
  - $[O_2]$  will \_\_\_\_\_. 3.  $[Cl_2]$  will \_\_\_\_\_.
  - The temperature in the reaction vessel will \_\_\_\_\_.
- e. If a piston is used to increase the volume of the vessel,
- equilibrium will shift to the \_\_\_\_\_.
  - $[O_2]$  will \_\_\_\_\_. 3.  $[H_2O]$  will \_\_\_\_\_.
- f. If a catalyst is added to the reaction mixture,
- equilibrium will shift to the \_\_\_\_\_.
  - $[O_2]$  will \_\_\_\_\_.
- g. What conditions of temperature and pressure will favor the production of the highest  $[Cl_2]$  at equilibrium?
- (High or low for each) \_\_\_\_\_ Pressure and \_\_\_\_\_ Temperature.
4. For the reaction at equilibrium:

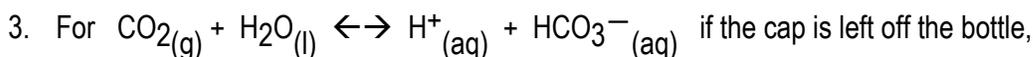
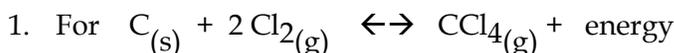


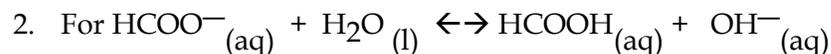
- a. If the temperature in the reaction vessel is decreased,
- equilibrium will shift to the \_\_\_\_\_.
  - $[H_2]$  will \_\_\_\_\_.
  - $[H_2O]$  will \_\_\_\_\_.
  - $[C]$  will \_\_\_\_\_.
- b. If a piston is used to decrease the volume of the vessel,
- equilibrium will shift to the \_\_\_\_\_.
  - $[H_2]$  will \_\_\_\_\_. 3.  $[H_2O]$  will \_\_\_\_\_.
  - The number of gas molecules in the vessel will \_\_\_\_\_.
- c. What conditions of temperature and pressure will favor the production of the highest  $[H_2]$  at equilibrium?
- (High or low for each) \_\_\_\_\_ pressure and \_\_\_\_\_ temperature.

\* \* \* \* \*

**ANSWERS****Practice A**a. If  $[\text{H}_2]$  is increased: 1. Equilibrium shifts **right**. 2.  $[\text{N}_2]$  will **decrease**. 3.  $[\text{NH}_3]$  will **increase**.b. If  $[\text{N}_2]$  is decreased: 1. Equilibrium shifts **left**. 2.  $[\text{H}_2]$  will **increase**. 3.  $[\text{NH}_3]$  will **decrease**.**Practice B**2a. If the temperature is decreased: 1. Equilibrium shifts **right**. 2.  $[\text{CH}_3\text{OH}]$  will **increase**.2b. If  $[\text{H}_2]$  increases: 1. Equilibrium shifts **right**. 2.  $[\text{CH}_3\text{OH}]$  **increases**. 3. Energy is on the right, so the temperature **increases**.3b. If temperature is increased: 1. Equilibrium shifts **left**. 2.  $[\text{CO}_2]$  will **decrease**.3c. If  $[\text{O}_2]$  is increased: 1. Equilibrium shifts **right**. 2.  $[\text{CO}]$  will **decrease**. 3. Temp. **increases**.**Practice C**1a. Which side has fewer gas molecules? Left has 1.5 moles, **right** has 1 mole.1b. If pressure is increased: 1. Equilibrium shifts **right**. 2.  $[\text{NO}_2]$  will **increase**. 3. Temp. **decreases**.1C1. If volume is increased, pressure is decreased; equilibrium shifts to **left** side which has more gas moles.1C2.  $[\text{O}_2]$  will increase. 1C3. The temperature will **increase**.

Pressure will not shift the equilibrium, since both sides have the same moles of gas.

a. As the  $\text{CO}_2$  escapes, the equilibrium shifts **left**.b. Carbonated beverages are mildly acidic. As the  $\text{CO}_2$  escapes, the  $[\text{H}^+]$ , which determines the level of the acidity, will decrease, and the taste of the beverage will change.**Practice D**1a.. If the  $[\text{Cl}_2]$  is decreased: 1. Equilibrium shifts **left**. 1a2.  $[\text{CCl}_4]$  will **decrease**.1a3.  $[\text{C}]$  will **not change**, because C is solid. 1a4. Amount of carbon **increases**. 1a5. Temp. **decreases**.1b. If pressure is decreased: 1b1. Equilibrium shifts **left** because left has 2 gas moles and right has one. Decreasing pressure favors side with more gas moles. 1b2.  $[\text{Cl}_2]$  **increases**. 1b3. Temp. **decreases**.



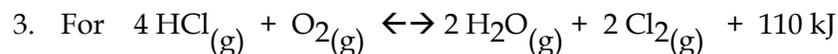
2a. If water is added: 2a1. The equilibrium **does not shift**. In an aqueous reaction, water is the solvent, and adding solvent does not shift an equilibrium.

2b. If  $[\text{OH}^-]$  is increased: 2b1. Equilibrium shifts **left**. 2b2.  $[\text{HCOOH}]$  will **decrease**.

2b3.  $[\text{H}_2\text{O}]$  will **not change**. Adding solvent does not shift an equilibrium.

2c1 If  $\text{H}^+$  is added:  $\text{H}^+$  neutralizes  $\text{OH}^-$ , lowering  $[\text{OH}^-]$ . Equilibrium shifts **right**.

2c2.  $[\text{HCOO}^-]$  **decreases**. 2d. Catalysts **do not shift** the position of an equilibrium.



3a. If  $[\text{O}_2]$  is increased: 3a1. Equilibrium shifts **right**. 3a2.  $[\text{HCl}]$  will **decrease**.

3b. If  $[\text{HCl}]$  is decreased: 3b1. Equilib. shifts **left**. 3b2.  $[\text{O}_2]$  will **increase**. 3b3.  $[\text{Cl}_2]$  will **decrease**.

3b4. Energy is used up when the reaction goes left, so temperature will **decrease**.

3c. If temperature is decreased: 3c1. Equilibrium shifts **right**. 3c2.  $[\text{O}_2]$  will **decrease**.

3c3.  $[\text{H}_2\text{O}]$  will **increase**. If water is in the gas state, as steam, its concentration can change.

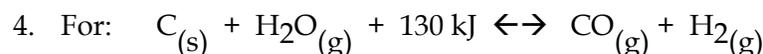
3d. If the total pressure on the gases is increased: 3d1. The left has 5 gas moles, the right has 4; lowering pressure favors the **right** side which has fewer gas moles.

3d2.  $[\text{O}_2]$  will **decrease**. 3d3.  $[\text{Cl}_2]$  will **increase**. 3d4. Temperature will **increase**.

3e. If V increases: 3e1. P decreases; equilib. shifts **left**. 3e2.  $[\text{O}_2]$  **increases**. 3e3.  $[\text{H}_2\text{O}]$  **decreases**.

3f. If catalyst is added: 3f1. Equilibrium **will not shift** 3f2.  $[\text{O}_2]$  will **not change**.

3g. For highest  $[\text{Cl}_2]$  at equilibrium: **High pressure** and **low temperature** favor the right side.



4a. If temp. is decreased: 4a1. Equilib. shifts left. 4a2.  $[\text{H}_2]$  will decrease. 4a3.  $[\text{H}_2\text{O}]$  gas increases.

4a4.  $[\text{C}]$  solid will not change.

4b. If V: 4b1. P increases, and equilibrium shifts to **left** side with one mole gas.

4b2.  $[\text{H}_2]$  **decreases**. 4b3.  $[\text{H}_2\text{O}]$  gas **increases**. 4b4. Number of gas molecules **decreases**.

4c. What conditions favor highest  $[\text{H}_2]$ ? **Low pressure** and **high temperature**.

\* \* \* \* \*

## Lesson 24B: Powers and Roots of Exponential Notation

**Timing:** Do this lesson before you begin *calculations* involving  $K$  (the equilibrium constant).

**Prerequisites:** Review Module 1 on Scientific Notation if needed.

\* \* \* \* \*

**Pretest:** If you solve these problems correctly, you may skip to Lesson 24C. Express your final answers in scientific notation. Answers are at the end of this lesson.

- Do this problem without a calculator.  $(3.0 \times 10^3)^3 =$
- Use a calculator.  $(4.5 \times 10^{-4})^2 =$
- Do not use a calculator. Write the cube root of  $8.0 \times 10^{24}$ .
- Use a calculator for all or part of this problem.  $(2.5 \times 10^5)^{1/3} =$

\* \* \* \* \*

### Taking Numbers to a Power

Many calculators have an  $\boxed{x^2}$  key. To calculate both squares and higher powers, most calculators also have power functions labeled  $\boxed{x^y}$  or  $\boxed{y^x}$  or  $\boxed{(y)^x}$  or  $\boxed{\wedge}$ .

To learn to use the power keys, you may check your calculator manual, or experiment using simple examples for which you know the answer, or (preferably) do both.

Cover the answer below the \* \* \* \* \*, then do this calculation in your head.

$$2^3 = \underline{\hspace{2cm}}$$

\* \* \* \* \*

$$2^3 = 2 \times 2 \times 2 = 8.$$

Now, by entering **2** and using the keys noted above, see what *key sequence* will give the *same* answer on your calculator.

Write your key sequence: \_\_\_\_\_.

To test your power key sequence, first solve in your head, then use your key sequence on the following problems. Make sure that you get the same answers in your head and on the calculator.

a.  $2^4 = \underline{\hspace{2cm}}$       b.  $3^4 = \underline{\hspace{2cm}}$       c. Do *two* ways on keys:  $12^2 = \underline{\hspace{2cm}}$ .

\* \* \* \* \*

**Answers:** a. 16      b. 81      c.  $12 \times 12 = 144$

On each problem below, use your power-key sequence to do the calculation. Then use the calculator to multiply each base number by the number of times indicated by the power (as in  $2^3 = 2 \times 2 \times 2$ ). Write the answer. Compare your answers.

d.  $16^3 = \underline{\hspace{2cm}}$     e.  $2.5^4 = \underline{\hspace{2cm}}$     f. Do two ways on keys:  $0.50^2 = \underline{\hspace{2cm}}$  .

\* \* \* \* \*

**Answers:** d. 4096    e. 39.0625    f. 0.25

Note that all of the calculations above can be done at least two ways. Always do calculator calculations two different ways to check your work.

### Taking Exponential Notation to a Power Without a Calculator

1. Memorize this rule: To take *exponential terms* to a power, *multiply the exponents*. (As used here, *power* and *exponent* have the same meaning.)

Examples:  $(10^3)^2 = 10^6$                        $(10^5)^{-2} = 10^{-10}$

$(10^{-3})^{-4} = 10^{+12}$  (Recite: “a minus times a minus is a plus.”)

Without a calculator, write answers to these, then check below.

a.  $(10^6)^2 =$                       b.  $(10^5)^{-5} =$                       c.  $(10^{-12})^{-3} =$

\* \* \* \* \*

**Answers:** a.  $10^{12}$     b.  $10^{-25}$     c.  $10^{36}$

2. When taking exponential notation to a power, the fundamental rules apply:

Do numbers by number rules and exponents by exponential rules.

Example:  $(2.0 \times 10^4)^3 = 8.0 \times 10^{12}$

Treat numbers as numbers. 2 cubed is 8.

Treat exponents as exponents.  $(10^4)^3$  is  $10^{12}$ .

Without a calculator, write answers to these, then check below.

a.  $(3 \times 10^3)^2 =$                       b.  $(2 \times 10^{-5})^3 =$

\* \* \* \* \*

**Answers:** a.  $9 \times 10^6$     b.  $8 \times 10^{-15}$

On the two problems below, without a calculator, write answers, then re-write the answers converted to scientific notation.

c.  $(5 \times 10^4)^2 =$                       d.  $(2 \times 10^{-3})^4 =$

\* \* \* \* \*

**Answers:** c.  $25 \times 10^8 = 2.5 \times 10^9$                       d.  $16 \times 10^{-12} = 1.6 \times 10^{-11}$

### Taking Exponential Notation to a Power With a Calculator

To take exponential notation to a power, most calculators use the same keys that you used above to take numbers to a power. However, you should also know how to take exponential notation to a power

- without entering the powers of 10, and
- by estimating an answer without using the calculator at all.

Try these steps in your notebook.

a. Write  $(3.5 \times 10^{-4})^3 = ?$

Do parts b and c *without* converting to scientific notation at the end.

- b. Write an answer to  $(3 \times 10^{-4})^3$ . Try it without the calculator.  
 c. Write an answer to  $(4 \times 10^{-4})^3$ . Try it without the calculator.

\* \* \* \* \*

Both:  $(10^{-4})^3 = 10^{-12}$ ; (b)  $3 \times 3 \times 3 = 27 \times 10^{-12}$  (c)  $4 \times 4 \times 4 = 64 \times 10^{-12}$

d. Based on (b) and (c), write an *estimate* of what  $(3.5 \times 10^{-4})^3$  should be.

\* \* \* \* \*

3.5 is half way between 3 and 4, so you might estimate that half way between  $3^3 = 27$  and  $4^3 = 64$  ... is *about*  $45 \times 10^{-12}$ .

- e. Calculate  $(3.5)^3$  using a  $\boxed{y^x}$ -type calculator function. Write the answer.  
 f. Calculate  $(3.5)^3$  on the calculator *without* the  $\boxed{y^x}$  or  $\boxed{\wedge}$ -type keys.

\* \* \* \* \*

$3.5 \times 3.5 \times 3.5 = \underline{\hspace{2cm}}$ . Does this match your part (e) answer?

g. Based on (e) and (f), write a precise answer to  $(3.5 \times 10^{-4})^3$ . Compare your answer to your estimate in (d) above. Then convert your answer to scientific notation, round to two digits, and check below.

\* \* \* \* \*

$42.9 \times 10^{-12} = \boxed{4.3 \times 10^{-11}}$  in scientific notation.

h. Now try  $(3.5 \times 10^{-4})^3$  by plugging everything into the calculator. You will probably need keys labeled  $\boxed{x^y}$  or  $\boxed{y^x}$  or  $\boxed{\wedge}$  or  $\boxed{(y)^x}$ .

- A “standard TI-type” calculator *may* use  $3.5 \boxed{\text{E or EE}} \boxed{4} \boxed{+/-} \boxed{y^x} \boxed{3} \boxed{=}$
- A graphing calculator *might* use  $3.5 \boxed{\text{EE}} \boxed{(-)} \boxed{4} \boxed{\text{enter}} \boxed{\wedge} \boxed{3} \boxed{\text{enter}}$
- On an RPN calculator, *try*  $3.5 \boxed{\text{E or EE or EXP}} \boxed{4} \boxed{+/-} \boxed{\text{enter}} \boxed{3} \boxed{y^x}$

An online search with your calculator name and model number and “exponential notation” may offer a better approach. Try to work through the *logic* for key

sequences that you use. Then practice the calculation until you can do it from memory, without looking at hints or directions.

Write the calculator answer, rounding the significand to two digits.

- h. Compare answers in steps (g) and (h). They should agree. They should also be close to the value of your estimate in step (d).

Which method is easier: Numbers on the calculator but exponents in your head, or all of the numbers and exponents on the calculator? Which method is easier to remember how to do?

You may do calculations using any method you choose, but doing numbers on the calculator and exponents by mental arithmetic can speed and simplify your work.

In addition, every calculation on a calculator should be done two *different ways* as a check on your calculator use. Estimating the number math “in your head” is one way to check a calculator answer.

\* \* \* \* \*

**Practice A:** Convert final answers to scientific notation. Check answers at the end of the lesson.

Do *not* use a calculator on these first four.

1.  $(10^{-3})^2 =$

2.  $(10^{-5})^{-2} =$

3.  $(2.0 \times 10^4)^4 =$

4.  $(3.0 \times 10^{-1})^3 =$

On 5-8 below,

- first write down an *estimated* answer, then re-write it in scientific notation;
- then use the calculator for whatever parts you wish and get a *final* answer in scientific notation.

Try any two. Need more practice? Do more. Check answers as you go.

5.  $(2.1 \times 10^6)^2 =$

6.  $(3.9 \times 10^{-2})^3 =$

7.  $(7.7 \times 10^4)^4 =$

8.  $(5.5 \times 10^{-2})^3 =$

\* \* \* \* \*

## Roots

Once you learn how to use a calculator take roots of numbers in exponential notation, doing the entire calculation on the calculator is often the fastest way to calculate a root. However, roots can also be found without entering the power of 10 into the calculator; a method that can be used to both calculate and check roots.

In this lesson you will learn to take roots of exponential notation by performing both *some* steps and *all* steps on the calculator.

## Roots as Exponents

“Taking the root” of a quantity is the same as assigning the quantity the **fractional exponent** (or **reciprocal exponent**) of the root.

- The *square* root of 4.7 can be written as  $4.7^{1/2}$ .
- The *cube* root of  $x$  can be written as  $x^{1/3}$ .
- $10^{1/2}$  means the *square root* of 10.  $16^{1/4}$  means the fourth *root* of 16.

## Taking Roots of Numbers

To calculate a *square* root, many calculators use this two-key sequence:

$\boxed{2\text{nd or INV}} \boxed{x^2}$ . Both square and higher roots may be calculated using the  $\boxed{2\text{nd or INV}}$  key followed by the keys used to calculate *powers*, such as  $\boxed{x^y}$  or  $\boxed{y^x}$  or  $\boxed{(y)^x}$  or  $\boxed{\wedge}$ .

It may also be possible to calculate roots using the reciprocal key  $\boxed{1/x \text{ or } x^{-1}}$  or the division operation ( $1/x = 1 \boxed{\div} x$ ) to enter *fractional* exponents as powers.

Knowing at least two ways to calculate roots is necessary in order to check your calculator answers.

A web search with the name and model number of your calculator, plus the word *root*, may help in learning one or more ways to calculate a root. Once you determine key sequences that work, it is important to practice and test those sequences by doing sample calculations with answers that are easy to check.

Do the following calculation in your head.

The cube root of 8 =  $8^{1/3} =$  \_\_\_\_\_

\* \* \* \* \*

$8 = 2 \times 2 \times 2$ , so  $8^{1/3} = 2$

Now, by entering 8 and using the inverse, or reciprocal, or division, and/or power keys, see what key sequences give the same *answer* for the root on your calculator.

\* \* \* \* \*

One or more of these sequences *may* work. Others may work as well.

- On a standard TI-type, try  $8 \boxed{2\text{nd or INV}} \boxed{y^x} 3 \boxed{=}$   
and/or try  $8 \boxed{y^x} \boxed{(} 1 \boxed{\div} 3 \boxed{)} \boxed{=}$
- On a graphing calculator (if allowed), try  $8 \boxed{\wedge} \boxed{(} 1 \boxed{\div} 3 \boxed{)} \boxed{\text{enter}}$   
and/or try  $8 \boxed{\wedge} 3 \boxed{1/x \text{ or } x^{-1}} \boxed{\text{enter}}$
- On an RPN calculator, try  $8 \boxed{\text{enter}} 3 \boxed{1/x} \boxed{y^x}$   
and/or try  $8 \boxed{\text{enter}} 0.33333333 \boxed{y^x}$

Try to understand the logic of two or more successful key sequences.

Write one and, if possible, *two* key sequences that both work and make sense to you. Then, on the problems below, *check* your key sequence. First try the problem “in your head” and write your answer. Then try the calculation using the calculator.

a.  $16^{1/4} =$

b.  $125^{1/3} =$

c.  $(0.001)^{1/3} =$

d.  $(0.008)^{1/3} =$

\* \* \* \* \*

**Answers:** a. 2    b. 3    c. 0.1    d. 0.2

One way to *check* a root calculation is to reverse the process: Take the *answer* to the *power* of the root. This should result in the original number. For example,

- If the cube root of  $125 = 125^{1/3} = 5$ , then  $5^3$  should equal \_\_\_\_\_.
- Now take the root, and then reverse the process, using your root and power key sequences.

### Roots of Divisible Powers of 10

To take a roots of  $10^x$ , a calculator is *not* needed *if* the exponent, when divided by the root, results in a whole number. To calculate such roots, use these steps.

1. Convert all *roots* to *fractional exponents*.

The *square* root of  $x$  is written  $x^{1/2}$ , the *fourth* root of  $x$  is converted to  $x^{1/4}$ .

2. Roots of exponential terms can be taken *without* a calculator if the power of 10, when multiplied by the fractional exponent, results in a *whole number*.

Another way to say this: the root of  $10^x$  can be found without the calculator if  $x$  is *evenly divisible* by **2** to find a *square* root, and by **3** to find a *cube* root, etc.

To find these evenly divisible roots, apply the rule: to take an exponential term to a power, multiply the exponents.

Examples:    The square root of  $10^4 = (10^4)^{1/2} = 10^2$

                  The cube root of  $10^{-9} = (10^{-9})^{1/3} = 10^{-3}$

\* \* \* \* \*

**Practice B:** Answers are at the end of the lesson.

1. The square root of 9,025 =

2.  $(0.004096)^{1/3} =$

3. Write answers to these as powers of 10.

a. The square root of  $10^{12} =$

b.  $(10^6)^{1/2} =$

c. The cube root of  $10^{-6} =$

d.  $(10^{-12})^{1/4} =$

\* \* \* \* \*

## Roots of Exponential Notation

To find a root of numbers written in exponential notation, apply the fundamental rule: Treat numbers as numbers, and exponents as exponents.

Cover the answer below and, *without* a calculator, try:  $(8.0 \times 10^{12})^{1/3} =$

\* \* \* \* \*

Answer: Treat numbers as numbers. The cube root of 8 is 2.

Treat exponentials as exponentials.  $(10^{12})^{1/3} = 10^4$

$$(8.0 \times 10^{12})^{1/3} = \mathbf{2.0 \times 10^4}$$

For more difficult roots, use these steps.

1. If the exponential term is *not* evenly divisible by the root, make the exponent *smaller* until the exponent times the fractional power results in a whole number.

Try that step on  $(8.04 \times 10^{-5})^{1/3} =$

\* \* \* \* \*

$$(8.04 \times 10^{-5})^{1/3} = (80.4 \times 10^{-6})^{1/3}$$

To make the exponent divisible by 3, it is lowered from  $10^{-5}$  to  $10^{-6}$ . When you make the exponent smaller, make the significant larger.

2. Write a rough *estimate* of the root of the significant of this evenly divisible exponent. Find the exact root of the exponential term. Combine these two parts and write the estimate for the root.

Apply step 2 to the step 1 answer:  $(80.4 \times 10^{-6})^{1/3} \approx$  \_\_\_\_\_

\* \* \* \* \*

$$(80.4 \times 10^{-6})^{1/3} = (80.4)^{1/3} \times (10^{-6})^{1/3}$$

To estimate a cube root of 80, since  $4 \times 4 \times 4 = 64$ , and 80 is a *little* higher than 64, guess  $\approx 4.2$ . ( $\approx$  means approximately equals.)

Handle exponents as exponents.  $(10^{-6})^{1/3} = 10^{-2}$

Combine the two parts. Estimate  $\approx 4.2 \times 10^{-2}$

3. To get a precise answer,
  - Write the number with the *evenly divisible* exponent.
  - Find the *precise* root of the significant on the calculator.
  - Take the root of the exponential term *without* the calculator.

Try those steps on the above problem.

\* \* \* \* \*

$(8.04 \times 10^{-5})^{1/3} = (80.4 \times 10^{-6})^{1/3}$  The calculator cube root of 80.4 is **4.32**.

$(10^{-6})^{1/3}$  is  **$10^{-2}$** . Answer =  **$4.32 \times 10^{-2}$**

4. Compare the step 3 calculator answer to the estimate. They should be close.
5. Now take the root by entering the *original* number in the problem into the calculator.

\* \* \* \* \*

One or more of these key sequences (and others) *may* work.

- On a standard TI-type, try **8.04** EE **5** +/- 2nd or INV y<sup>x</sup> **3** =

and/or try **8.04** E or EE or EXP **5** +/- y<sup>x</sup> ( **1** ÷ **3** ) =

- On a graphing calculator, try **8.04** EE (-) **5** enter ^ ( **1** ÷ **3** ) enter

- On an RPN calculator, try **8.04** E or EE or EXP **5** +/- enter **3** 1/x y<sup>x</sup>

The calculator answer should match the step 3 answer.

Write and learn a key sequence that works: \_\_\_\_\_

Whatever sequence you use, work through the logic of *why* it works. Without the *why*, it will be difficult to remember the correct sequence.

Once you have debugged and *practiced* a key sequence to calculate roots, doing the entire calculation on the calculator may be faster than converting the exponential to an evenly divisible root. However, using that conversion to estimate the root is a way to *check* the calculator result. Complex calculations must be done *two* ways.

### **Roots of Non-Divisible Powers of 10**

Changing an exponent to make it divisible by the root can put a *number* in front of the exponential term that was not there before. Try this example.

First, estimate the answer *without* a calculator.  $(10^7)^{1/2} =$  \_\_\_\_\_

\* \* \* \* \*

Answer:  $(10^7)^{1/2} = (10 \times 10^6)^{1/2} = (10^{1/2} \times 10^3) \approx 3.2 \times 10^3$

To find the root without a calculator, the power of 10 must be divisible by 2. Changing the exponent to 6, to make it smaller and divisible, puts the number 10 in front of the exponential term.

Now try taking the root on the calculator.

\* \* \* \* \*

**$3.16 \times 10^3$** . You *may* need to enter ( **$1 \times 10^7$** ) to take the root on the calculator.

\* \* \* \* \*

**Summary: Roots and Powers**

1. If you are not certain that you are using the calculator keys correctly, do a *simple* similar calculation, first on *paper* and then on the calculator.
2. For complex operations on a calculator, do each calculation a *second* time using rounded numbers and/or different steps or keys.
3. On complex calculations, it is often easier to do the numbers on the calculator but the exponents on paper.
4. In calculations using scientific or exponential notation, handle numbers and exponential terms separately. Do numbers by number rules and exponents by exponential rules.
  - When multiplying exponentials, add the exponents.
  - When you dividing exponentials, subtract the exponents.
  - To take an exponential to a power, multiply the exponentials.
5. To take roots of exponential terms without a calculator,
  - convert roots to fractional exponents, then
  - adjust the significand and exponential to make the exponent evenly divisible by the root.

\* \* \* \* \*

**Practice C**

1. Fill in the blanks.
  - a.  $4 \times 4 \times 4 = \underline{\hspace{2cm}}$ , so  $(\underline{\hspace{2cm}})^{1/3} = 4$ .
  - b. Using your calculator, find the cube root of 64.
  - c.  $64 = 6.4 \times 10^1$ , so  $(6.4 \times 10^1)^{1/3}$  should equal  $\underline{\hspace{2cm}}$ .  
What answer to  $(6.4 \times 10^1)^{1/3}$  does the calculator show?  $\underline{\hspace{2cm}}$
  - d.  $0.4 \times 0.4 \times 0.4 = 0.064 = 6.4 \times 10^{-2}$ , so  $(6.4 \times 10^{-2})^{1/3}$  in your head =  $\underline{\hspace{2cm}}$   
See if you get the same answer to  $(6.4 \times 10^{-2})^{1/3}$  on the calculator.
2. Do the problems below in your notebook using these steps.
  - A. First convert to an exponent with a divisible root.
  - B. Write an estimated answer for the root.
  - C. Starting from the divisible root, use the calculator for the root of the number, do the root of the exponential in your head, write the answer, then convert the answer to scientific notation. Round the significand to two digits.
  - D. Take the root of the original exponential notation on the calculator.
  - E. Compare your answers in steps B, C and D.

Do as many as you need to feel confident. Check your answer after each part.

a. The square root of  $8.1 \times 10^5 =$

b.  $(6.0 \times 10^{23})^{1/3} =$

c.  $(10^{15})^{1/4} =$

d. The cube root of  $1.25 \times 10^{-7} =$

e.  $(7.0 \times 10^{-12})^{1/2} =$

f.  $(1.6 \times 10^{-11})^{1/4} =$

g.  $(9.0 \times 10^{12})^{1/2} =$

h.  $(1.25 \times 10^{-13})^{1/3} =$

\* \* \* \* \*

**Practice D**

If you would like additional practice and review, try some of these.

1.  $2^4 =$

2.  $(0.25)^4 =$

3.  $(4.5 \times 10^3)^5 =$

4.  $(2.0 \times 10^5)^6 =$

5.  $(3.3 \times 10^{-3})^8 =$

6.  $(4.7 \times 10^{-4})^4 =$

7.  $(81)^{1/4} =$

8. The fifth root of 0.01024 =

9.  $(6.20 \times 10^4)^{1/8} =$

10. The sixth root of  $9.5 \times 10^{15} =$

11.  $(3.3 \times 10^{-3})^{1/9} =$

12.  $(6.5 \times 10^{-3})^7 =$

\* \* \* \* \*

**ANSWERS**

**Pretest:** 1.  $(3.0 \times 10^3)^3 = 2.7 \times 10^{10}$       2.  $(4.5 \times 10^{-4})^2 = 2.0 \times 10^{-7}$   
 3.  $(8.0 \times 10^{24})^{1/3} = 2.0 \times 10^8$       4.  $(2.5 \times 10^5)^{1/3} = 6.3 \times 10^1$

**Practice A**

1.  $(10^{-3})^2 = 10^{-6}$       2.  $(10^{-5})^{-2} = 10^{+10}$   
 3.  $(2.0 \times 10^4)^4 = 16 \times 10^{16} = 1.6 \times 10^{17}$       4.  $(3.0 \times 10^{-1})^3 = 27 \times 10^{-3} = 2.7 \times 10^{-2}$   
 5.  $(2.1 \times 10^6)^2 = 4.4 \times 10^{12}$       6.  $(3.9 \times 10^{-2})^3 = 59 \times 10^{-6} = 5.9 \times 10^{-5}$   
 7.  $(7.7 \times 10^4)^4 = 3,515 \times 10^{16} = 3.5 \times 10^{19}$       8.  $(5.5 \times 10^{-2})^3 = 166 \times 10^{-6} = 1.7 \times 10^{-4}$

**Practice B**

1. 95      2. 0.16      3a.  $10^6$       3b.  $10^3$       3c.  $10^{-2}$       3d.  $10^{-3}$

**Practice C**

1a. 64      1b. 4      1c. 4      1d. 0.40 or  $4.0 \times 10^{-1}$   
 2a.  $(8.1 \times 10^5)^{1/2} = (81 \times 10^4)^{1/2} = (81^{1/2} \times 10^2) = 9.0 \times 10^2$   
 2b.  $(6.0 \times 10^{23})^{1/3} = (600 \times 10^{21})^{1/3} = (600^{1/3} \times 10^7) = 8.4 \times 10^7$   
 2c.  $(10^{15})^{1/4} = (10^3 \times 10^{12})^{1/4} = (1000 \times 10^{12})^{1/4} = (1000^{1/4} \times 10^3) = 5.6 \times 10^3$   
 2d.  $(1.25 \times 10^{-7})^{1/3} = (125 \times 10^{-9})^{1/3} = (125^{1/3} \times 10^{-3}) = 5.0 \times 10^{-3}$   
 2e.  $(7.0 \times 10^{-12})^{1/2} = (7.0^{1/2} \times 10^{-6}) = 2.6 \times 10^{-6}$   
 2f.  $(1.6 \times 10^{-11})^{1/4} = (16 \times 10^{-12})^{1/4} = (16^{1/4}) \times (10^{-12})^{1/4} = 2.0 \times 10^{-3}$   
 2g.  $(9.0 \times 10^{12})^{1/2} = 3.0 \times 10^6$   
 2h.  $(1.25 \times 10^{-13})^{1/3} = (125 \times 10^{-15})^{1/3} = (125^{1/3}) \times (10^{-15})^{1/3} = 5.0 \times 10^{-5}$

**Practice D**

1. 16      2.  $3.9 \times 10^{-3}$       3.  $1.8 \times 10^{18}$       4.  $6.4 \times 10^{31}$       5.  $1.4 \times 10^{-20}$       6.  $3.7 \times 10^{-14}$   
 7. 3.0      8. 0.4000      9. 3.97      10.  $4.60 \times 10^2$       11. 0.53      12.  $4.9 \times 10^{-16}$

\* \* \* \* \*

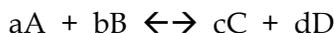
## Lesson 24C: Equilibrium Constants

**Prerequisites:** Read the introduction to Module 21 and complete Lesson 24B before starting this lesson.

\* \* \* \* \*

### The Law of Mass Action

At a given temperature, for the general reaction



the **Law of Mass Action** states that for a reaction at equilibrium, the ratio

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{\text{product of the [Products]}}{\text{product of the [Reactants]}}$$
 will be constant.

This ratio is called the **equilibrium constant**, symbol *K*. In an equilibrium constant,

- The *concentrations* of the substances on the *right* side of the reaction equation are *multiplied on top*,
- The concentrations of substances on the left side are multiplied are on the bottom.
- The *coefficient* for each substance becomes the *power* of its concentration.

An equilibrium constant equation has two parts:

- The equilibrium constant **expression** is the ratio which shows the *symbols* for the substance concentrations and their powers.
- The equilibrium constant **value** is the number that is the value of the ratio.

As temperature changes, *K* values change, but the *K* expression stays the same.

### Equilibrium Constant Expressions

To write a *K* expression, all that is needed is a balanced equation for a reaction. Cover below the \* \* \* \* \* line below and then try this problem.

**Q.** For the Haber process reaction:  $N_{2(g)} + 3 H_{2(g)} \leftrightarrow 2 NH_{3(g)}$

write the equilibrium constant expression.

\* \* \* \* \*

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
 with all concentrations measured at equilibrium.

This equation means that at a given temperature, if a reaction is run until equilibrium is reached,

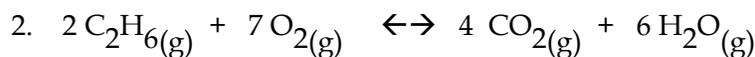
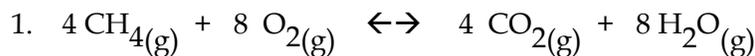
- whether starting with all of the substances written on the left side of the equation, or all substances on the right, or any mixture of those substances,
- no matter how much of each substance is present at the beginning, nor how much an equilibrium is subsequently shifted by adding or removing substances,

when equilibrium is reached, the concentrations of the substances can differ, but the *ratio* calculated by this equilibrium constant will always have the same numeric value.

\* \* \* \* \*

### **Practice A**

Write the equilibrium constant expression for these reactions.



\* \* \* \* \*

### **Omitting Concentrations That Are Constant**

There is one exception to the simple correlation between a balanced equation and its equilibrium constant expression.

Only concentrations that can *change* are included in *K* expressions.

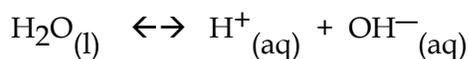
Terms for *solids*, *pure liquids*, and *solvents* (including *liquid water*) are omitted from *K* expressions, because the concentrations of those substances do not change during chemical reactions.

By convention, if a concentration involved in a reaction is essentially constant, its value is included in the value of the equilibrium constant, rather than in the variables of the *K* expression.

The concentrations left out of a *K* expression are the same as those that are omitted when applying Le Châtelier's Principle.

Using the rules above, try the following example.

**Q.** Write the equilibrium constant expression for this reaction.



\* \* \* \* \*

$$K = [\text{H}^+][\text{OH}^-]$$

The reaction equation shows that the two ions on the right are aqueous, meaning that the solvent for the reaction is water. Solvent concentrations for most reactions are high enough that they are not significantly changed by shifts in an equilibrium. Since its concentration remains essentially constant during equilibrium shifts, [liquid water] is not included as a term in *K* equations.

Substance states (solid, liquid, gas, or aqueous) must be shown in either the balanced equation or the *K* expression. However, if the balanced equation is written with the *K* calculations and includes the states, the states can be omitted in the *K* expression.

Most *K* expressions will be fractions with a numerator and a denominator. For some reactions, however, including the one above, the numerator or denominator of *K* will be **1**. A one in the denominator is usually omitted when writing a *K* expression.

Water: The “omit solids and liquids” rule means that  $[\text{H}_2\text{O}]$  will be omitted from  $K$  expressions when the water is a solid (ice), a pure liquid, or a solvent at high concentration. However, if the water is present in a reaction in its *gas* phase, as vapor or steam, since all gases are compressible, its concentration can vary. Concentrations that can vary are included in  $K$  expressions. The general rule is:

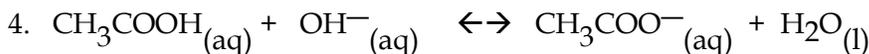
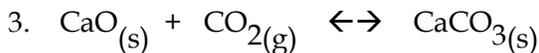
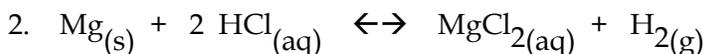
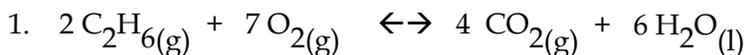
For  $\text{H}_2\text{O}$ ,  $[\text{H}_2\text{O}_{(g)}]$  is included in  $K$  expressions; but  $[\text{H}_2\text{O}_{(s)}]$  and  $[\text{H}_2\text{O}_{(l)}]$  (if the liquid has a concentration is essentially constant during the reaction) are omitted.

Vapor Pressure: All solids and liquids have a vapor pressure: they will release gas particles into a system at equilibrium. However, because vapor pressure depends only on temperature, vapor pressure creates a constant pressure and concentration at each temperature. Because it is constant, the vapor pressure of solids and liquids is omitted as a factor in  $K$  expressions. It is, however, one of the factors that determines the numeric value of the equilibrium constant.

\* \* \* \* \*

### **Practice B**

Write the equilibrium constant expression for these reactions.



\* \* \* \* \*

### **Equilibrium Constant Calculations**

Equilibrium calculations can be solved in a systematic fashion by adding a step or two to our standard *equation* solving methods. To help in remembering this method, the rule will be, “For calculations using  $K$  and multiple concentrations, write the **WREK** steps.”

1. **W (WANTED):** First write the **WANTED** unit.
2. **R (Reaction):** Write a balanced equation for the *reaction*.
3. **E (Extent):** Add the *extent* of the reaction: “goes partially” or “goes 100%.”

If the reaction goes 100%, essentially to completion, use standard stoichiometry to solve.

If the reaction goes to equilibrium (only partially to completion), use the equilibrium equation to solve.

4. **K:** If the reaction goes to equilibrium, write the  $K$  expression.

5. Make a DATA table that includes each symbol in the  $K$  expression. Indicate the WANTED symbol with a ?. Solve for the WANTED symbol in symbols before plugging in numbers.
6. If a *concentration* is calculated using an equilibrium equation, its units, moles/liter, should be added to the answer.

$K$  values have units based on the  $K$  expression. However, because the units are complex to write, by convention in nearly all cases,  $K$  values are written as numbers without units. When a concentration is solved using the  $K$  equation, the concentration is labeled with units consistent with the other data in the problem.

Because  $K$  values do not include units, unit cancellation will not catch mistakes.  $K$  calculations must therefore be solved with special care.

Try the above 6-step method on the following problem. If you get stuck, read a bit of the answer until you are unstuck, and then complete your work.

**Q.** For the reversible reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ , if the equilibrium concentrations are  $[\text{H}_2] = 0.20 \text{ M}$  and  $[\text{I}_2] = 0.12 \text{ M}$ , and  $K = 25$ , find  $[\text{HI}]_{\text{at eq.}}$ .

\* \* \* \* \*

**Answer**

For calculations using  $K$  and multiple concentrations, write the WREK steps.

1. **W** (WANTED): ? =  $[\text{HI}]_{\text{eq.}}$  in mol/L
2. **R** (Balanced Reaction Equation):  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$
3. **E** (Extent): goes to equilibrium; only partially to completion.

4. **K**: 
$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad \text{at equilibrium.}$$

DATA:  $K = 25$

$$[\text{HI}]_{\text{eq.}} = ([\text{HI}]^2)^{1/2} = ? \text{ (WANTED)}$$

$$[\text{H}_2]_{\text{eq.}} = 0.20 \text{ M}$$

$$[\text{I}_2]_{\text{eq.}} = 0.12 \text{ M}$$

Since the WANTED symbol is in the  $K$  equation, but it is squared, it will simplify the calculation to solve in steps.

First solve for the term in the equation that *contains* the WANTED symbol, and then solve for the WANTED symbol itself.

In this problem, first solve the  $K$  equation in symbols for  $[\text{HI}]^2$ .

(Do that step, and then check your answer below.)

\* \* \* \* \*

$$[\text{HI}]^2 = K \cdot [\text{H}_2] \cdot [\text{I}_2] = (25) (0.20) (0.12) = 0.600$$

(Carry an extra sig fig until the final step.) Then solve for the WANTED symbol.

$$[\text{HI}]_{\text{eq.}} = \text{square root of } [\text{HI}]^2 = ([\text{HI}]^2)^{1/2} = (0.600)^{1/2} = \boxed{0.77 \text{ Mol/L}}$$

When solving  $K$  for a concentration, **M** or **mol/L** must be added to the answer.

\* \* \* \* \*

### **Practice C**

1. Given the reaction:  $4 \text{NH}_3 + 5 \text{O}_2 \leftrightarrow 4 \text{NO} + 6 \text{H}_2\text{O}$  (all gases)

At a certain temperature the equilibrium concentrations are:

$$[\text{NH}_3] = 0.0010 \text{ M}, [\text{O}_2] = 0.0020 \text{ M}, [\text{NO}] = 0.10 \text{ M}, [\text{H}_2\text{O}] = 0.20 \text{ M}.$$

What is the value of  $K$  at this temperature?

2. Given the reaction:  $2\text{A} + \text{B} \leftrightarrow 4\text{C}$  (all gases), concentrations at equilibrium are  $[\text{B}] = 2.0 \text{ M}$  and  $[\text{C}] = 0.50 \text{ M}$ . If  $K = 12.5$ , find  $[\text{A}]$ .
3. For the reaction at equilibrium:  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$

in a 2.0 liter container is found 0.40 mol  $\text{CO}_2$ , 0.60 mol  $\text{H}_2\text{O}$ , and 0.90 mol  $\text{H}_2$ . If the value of the equilibrium constant is 1.6, how many moles of  $\text{CO}$  are in the mixture?

\* \* \* \* \*

## **ANSWERS**

### **Practice A**

$$1. K = \frac{[\text{CO}_2]^4 [\text{H}_2\text{O}]^8}{[\text{CH}_4]^4 [\text{O}_2]^8} \quad 2. K = \frac{[\text{CO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{C}_2\text{H}_6]^2 [\text{O}_2]^7}$$

### **Practice B**

$$1. K = \frac{[\text{CO}_2]^4}{[\text{C}_2\text{H}_6]^2 [\text{O}_2]^7} \quad 2. K = \frac{[\text{MgCl}_2] [\text{H}_2]}{[\text{HCl}]^2} \quad 3. K = \frac{1}{[\text{CO}_2]}$$

$$4. K = \frac{[\text{CH}_3 \text{COO}^-]}{[\text{CH}_3\text{COOH}] [\text{OH}^-]} \quad 5. K = [\text{Ca}^{2+}] [\text{Cl}^-]^2$$

### **Practice C**

1. For calculations using  $K$  and multiple concentrations, write the WREK steps.

**WANT:**  $? = K$

**Rxn:**  $4 \text{NH}_3 + 5 \text{O}_2 \leftrightarrow 4 \text{NO} + 6 \text{H}_2\text{O}$  (all gases)

**Extent:** Goes to equilibrium, use  $K$  equation.

**K:**  $K = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$  (Since  $\text{H}_2\text{O}$  is a gas, it is included in the  $K$  equation.)

DATA: See list in problem.

SOLVE: The equation as written solves for the WANTED symbol. Plugging in numbers:

$$\begin{aligned} ? = K &= \frac{[0.10]^4 [0.20]^6}{[0.0010]^4 [0.0020]^5} = \frac{[1.0 \times 10^{-1}]^4 [2.0 \times 10^{-1}]^6}{[1.0 \times 10^{-3}]^4 [2.0 \times 10^{-3}]^5} = \frac{(1.0 \times 10^{-4})(2.0)^6 \times 10^{-6}}{(1.0 \times 10^{-12})(2.0)^5 \times 10^{-15}} \\ &= \frac{(2.0)^6 \times 10^{-10}}{(2.0)^5 \times 10^{-27}} = \boxed{2.0 \times 10^{+17}} \quad (\text{K values are not written with units.}) \end{aligned}$$

The arithmetic may be done in any way that results in the right answer.

(If you need practice at these exponential calculations, review Lesson 1C.)

2. For calculations using  $K$  and multiple concentrations, write the WREK steps.

WANT:  $? = [A]$

Rxn:  $2A + B \leftrightarrow 4C$  (all gases)

Extent: Goes to equilibrium, use  $K$ .

$$K = \frac{[C]^4}{[A]^2 [B]}$$

SOLVE: First solve  $K$  for the term that includes the WANTED symbol.

$$[A]^2 = \frac{[C]^4}{K [B]} = \frac{(0.50)^4}{(12.5)(2.0)} = \frac{0.0625}{25} = 0.0025 \quad \text{The solve for the WANTED symbol.}$$

$$? = [A] = ([A]^2)^{1/2} = (0.0025)^{1/2} = \boxed{0.050 \text{ M}} \quad (\text{When solving } K \text{ for concentration, add M})$$

3. For calculations using  $K$  and multiple concentrations, write the WREK steps.

WANT:  $? = \text{mol CO}$

R+E:  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$  (Goes to equilibrium, use  $K$ .)

$$K = \frac{[\text{CO}]}{[\text{CO}_2][\text{H}_2]} \quad (\text{Liquids are left out of } K \text{ expressions.})$$

DATA:  $K = 1.6$

$[\text{CO}] = ?$

$[\text{CO}_2] = ?$

Data is given in moles, but the  $K$  equation requires concentration (mol/L). All of the gases are in a 2.0 liter container.

If you needed that hint, adjust your work and continue.

\* \* \* \* \*

To find mol/L, divide mol by L.

$[\text{CO}_2] = 0.40 \text{ mol in } 2.0 \text{ liters} = 0.20 \text{ mol/L}$

$[\text{H}_2] = 0.90 \text{ mol}/2.0 \text{ L} = 0.45 \text{ M}$

SOLVE: First solve the  $K$  equation for the WANTED symbol, then plug in the numbers.

$$[\text{CO}] = K \cdot [\text{CO}_2] \cdot [\text{H}_2] = (1.6)(0.20)(0.45) = 0.144 \text{ M}$$

Done? Always check your WANTED *unit* (especially after a long calculation).

$$? = \text{mol CO} = 2.0 \text{ L} \cdot \frac{0.144 \text{ mol CO}}{\text{L}} = \boxed{0.29 \text{ mol CO}}$$

A good habit at the end of each calculation may be to (a) box your final answers, but (b) each time you make the box, look back at the WANTED unit or symbol at the start of your answer, to make sure that you found the unit WANTED.

\* \* \* \* \*

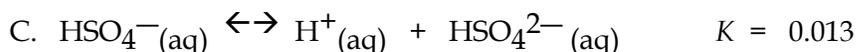
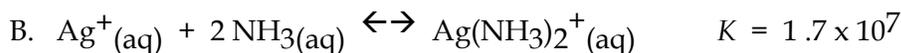
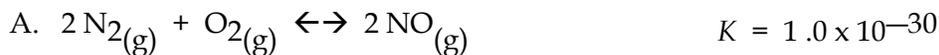
## Lesson 24D: Equilibrium Constant Values

### K Values And The Favored Side

An equilibrium constant value is a number greater than zero. It is most often written in scientific notation. At equilibrium

- If the substances on the right side of an equation have higher concentrations than the substances on the left, the products are said to be **favored**, and the value of  $K$  will be a number *greater than one*.
- If the substances on the left have higher concentrations than those on the right, the reactants are favored, and the value of  $K$  will be a number between zero and one (in scientific notation, a positive number times a negative power of 10).
- The more a reaction goes to the right, the higher will be the value of its equilibrium constant.

Examples: For these reactions at 25°C,



Reaction A has a  $K$  value less than one. At equilibrium, the substances on the left side (the reactants) will be favored.

Reaction B has a  $K$  value that is greater than one. At equilibrium, the substances on the right side (the products) will be favored.

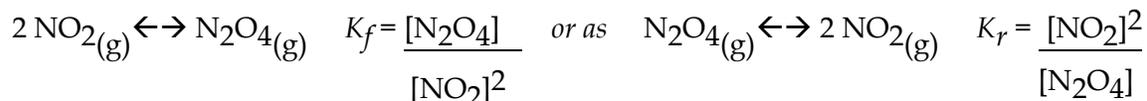
For  $K$  values much larger than one, the reactions go close to completion. For  $K$  values much smaller than one, the reaction goes only slightly.

Reaction C has a  $K$  value that is smaller than one, favoring the left side, but compared to most  $K$  values,  $K$  is not far from one. At equilibrium in Reaction C, you would expect to find a relatively balanced mixture of reactants and products.

### K Values For Reversed Reactions

Equilibrium is the result of a reversible reaction. Reversible reactions can be written in either direction.

For example, the conversion of nitrogen dioxide to dinitrogen tetroxide is reversible. It can be written as either



The two equilibrium constants are different, but related:

$$K_f = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}} = \frac{1}{K_r} \quad \text{or} \quad \boxed{K_f = 1/K_r}$$

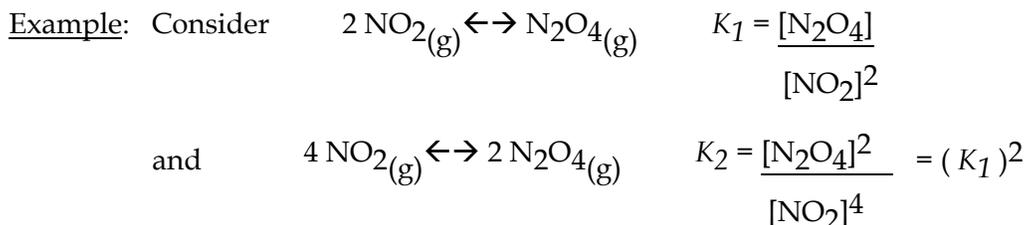
The relationship  $K_f = 1/K_r$  will be true for all reactions. Stated in words:

If a value of  $K$  is known for a reaction written in one direction, the value of  $K$  for the reaction written in the reverse direction will be the reciprocal of the original  $K$ .

### K Values When Coefficients Are Multiplied

When writing a  $K$  value, *either* the balanced equation *or* the  $K$  expression must also be written to indicate the coefficients used to balance the equation. Coefficients are ratios, so any numbers can be used to balance the equation so long as the numbers are in the same ratio. The value of  $K$  will depend on the coefficients used to balance the equation, but if the  $K$  value is known for any one set of coefficients, the value for  $K$  for a different coefficients can easily be determined.

If all of the coefficients of a balanced equation are multiplied by the same positive number, the coefficient numbers change, but the coefficient ratios remain the same, and the equation remains balanced.

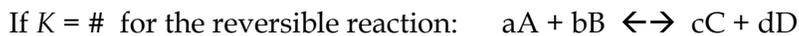


The second equation is simply double the first. The ratios are the same, and both equations are balanced. The  $K$  values will be different, but related. If the coefficients are *doubled*, the new  $K$  value is the original  $K$  value *squared*.

This relationship will be true for all  $K$  values:

If a value of  $K$  is known for a reaction with one set of coefficients, those coefficients can be multiplied by any positive number, and the new value of  $K$  will be the original  $K$  to the power of the multiplier.

In equation form, this rule can be written,



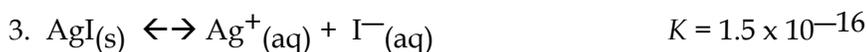
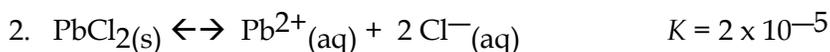
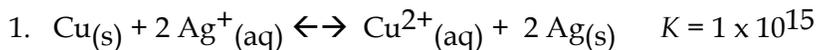
The factor  $n$  can be any positive number: an integer, decimal, or fraction.

This rule illustrates why, whenever you write a  $K$  expression or value, the reaction coefficients on which it is based must also be shown.

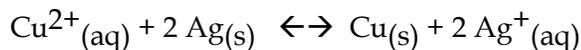
\* \* \* \* \*

### **Practice**

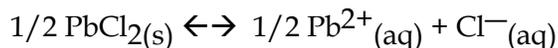
For the following reactions at 25°C:



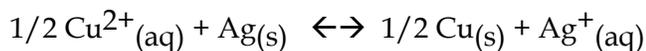
- Write the  $K$  expression for each reaction.
- Which equilibrium most favors the substances on the right side of the equation?
- Which reaction will form the least amount of product?
- What will be the  $K$  expression and  $K$  value for the equation



- What will be the  $K$  expression and  $K$  value for the equation



- What will be the  $K$  expression and  $K$  value for the equation



\* \* \* \* \*

### **ANSWERS**

$$1a. K = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad 2. K = [\text{Pb}^{2+}][\text{Cl}^-]^2 \quad 3. K = [\text{Ag}^+][\text{I}^-]$$

- Reaction 1, with the largest  $K$  value, most favors the right side (products).
- Reaction 3, with the  $K$  value much smaller than the others, will most favor the left side (reactants), and will form the smallest concentrations of products.
- The Part d equation is equation 2 written backwards. Both the  $K$  expression and  $K$  value will be the reciprocals of equation 1.

$$K \text{ expression} = \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]} \quad K \text{ value} = \frac{1}{K_f} = \frac{1}{1 \times 10^{15}} = 1 \times 10^{-15}$$

- 1e. The Part e equation is equation 2 with all coefficients multiplied by 1/2. In the  $K$  expression, the new coefficients become the powers of the concentrations. The  $K$  value for Part e will be the equation 2  $K$  value to the 1/2 power: the square root of the  $K$  in equation 2.

$$K \text{ expression} = [\text{Pb}^{2+}]^{1/2} [\text{Cl}^-] \quad K \text{ value} = (2 \times 10^{-5})^{1/2} = (20 \times 10^{-6})^{1/2} = 4.5 \times 10^{-3}$$

- 1f. Part f has equation 1 written backwards and multiplied by 1/2. When writing the equation backwards, invert the  $K$  value. When multiplying coefficients by 1/2, take the  $K$  value to the 1/2 power.

$$K \text{ expression} = \frac{[\text{Ag}^+]}{[\text{Cu}^{2+}]^{1/2}} \quad K \text{ value} = \text{square root of } \frac{1}{K_f} = ((1 \times 10^{15})^{-1})^{1/2} = (10 \times 10^{-16})^{1/2} = 3.2 \times 10^{-8}$$

\* \* \* \* \*

## Lesson 24E: $K_p$ Calculations

**Prerequisites:** Gas lessons 16A, 16C, 17D, and the prior lessons in Module 21.

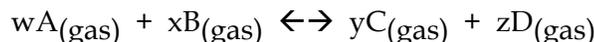
\* \* \* \* \*

For the special case of reactions that include gases but do not include substances dissolved in a solvent, an equilibrium constant can be calculated based on either the gas concentrations or the partial pressures of the gases present.

To distinguish between these two kinds of equilibrium constants,

- $K_c$  may be used instead of  $K$  for equilibrium constants based on concentration, and
- $K_p$  is used for equilibrium constants based on pressures.

At a given temperature, for the general reaction



at equilibrium these ratios will be constant:

$$K_c = \frac{[\text{C}]^y [\text{D}]^z}{[\text{A}]^w [\text{B}]^x} \quad \text{and} \quad K_p = \frac{(P_C)^y \cdot (P_D)^z}{(P_A)^w \cdot (P_B)^x} \quad \text{where } P \text{ represents partial pressure.}$$

In most respects, the rules for  $K_c$  and  $K_p$  are the same.

- Coefficients of the balanced equation become powers in the  $K_p$  expression.
- If a  $K_p$  value is listed, the coefficients and direction of the reaction must be shown.
- If an equation is reversed, the  $K_p$  value will be the reciprocal of the original.
- If coefficients are multiplied by a positive number,  $K_p$  will have a value of the original  $K_p$  value to the power of the number.
- $K_p$  values have units, but the units are usually omitted.
- Terms for solids and pure liquids are omitted from  $K_p$  expressions.

The differences between  $K_c$  and  $K_p$  include

- By convention,  $K_p$  is calculated based on atmospheres as the pressure unit. In calculations that use  $K_p$ , all pressures must be converted to atmospheres.
- When calculating a partial pressure using  $K_p$  values, atmospheres must be added as the unit of the answer.
- If the two sides of the balanced equation have the same number of total moles of gases, the values for  $K_c$  and  $K_p$  will be the same. If the two sides of the equation have a different total number of moles of gas,  $K_c$  and  $K_p$  will have different values.

If  $K$  is written without a subscript, it is assumed to represent a  $K_c$ . Because  $K_c$  can be used for reactions that include both gases and substances dissolved in a solvent, and  $K_p$  cannot,  $K_c$  is encountered more frequently.

$K_p$  and  $K_c$  calculations should be solved using the same steps. "For calculations using  $K$  and multiple concentrations *or pressures*, write the WREK steps."

Try the following problem. If you get stuck, read the answer until unstuck and try again.

**Q.** For the reaction  $\text{PCl}_5(\text{g}) \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

at  $250^\circ\text{C}$ ,  $K_p = 1.78$ . If at equilibrium the partial pressures are 0.820 atm. for  $\text{Cl}_2$  and standard pressure for  $\text{PCl}_5$ , calculate the partial pressure of  $\text{PCl}_3$ .

★ ★ ★ ★ ★

### Answer

For calculations using  $K$  and multiple concentrations *or pressures*, write the WREK steps.

1. **W** (WANTED):  $? = P_{\text{PCl}_3}$  in atm.
2. **R** (Balanced Reaction Equation):  $\text{PCl}_5(\text{g}) \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
3. **E** (Extent): This reaction goes to equilibrium (only partially to completion).
4. **K** (Write the  $K$  expression): 
$$K_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

DATA:  $K_p = 1.78$

$P_{\text{PCl}_3} = ?$

$P_{\text{Cl}_2} = 0.820 \text{ atm.}$

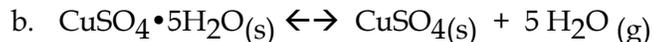
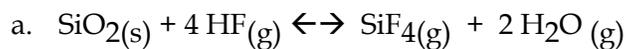
$P_{\text{PCl}_5} = \text{standard pressure} = 1 \text{ atm. (exact)}$

Solve the fundamental equation for the WANTED symbol, then substitute data.

$$P_{\text{PCl}_3} = \frac{K_p \cdot P_{\text{PCl}_5}}{P_{\text{Cl}_2}} = \frac{1.78 \cdot 1 \text{ atm.}}{0.820 \text{ atm.}} = \boxed{2.17 \text{ atm.}}$$

When using  $K_p$  to find a partial pressure, all pressure units must be converted to atmospheres, and atm. as a unit must be added to the answer.

\* \* \* \* \*

**Practice A**1. Write the  $K_p$  expressions for these reactions.2. For the reaction  $\text{CH}_4(\text{g}) + 2 \text{H}_2\text{S}(\text{g}) \leftrightarrow \text{CS}_2(\text{g}) + 4 \text{H}_2(\text{g})$  at  $700^\circ\text{C}$ , $K_p = 8.9 \times 10^{-4}$ . If the partial pressures at equilibrium are 0.32 atm. for  $\text{H}_2$ , standard pressure for  $\text{CH}_4$ , and 55 kPa for  $\text{CS}_2$ , calculate the partial pressure of  $\text{H}_2\text{S}$ .

\* \* \* \* \*

**Converting Between  $K_c$  and  $K_p$** 

When all of the terms in a  $K$  expression are gases, both  $K_c$  and  $K_p$  equations can be applied to reactions at equilibrium. If either a  $K_c$  or a  $K_p$  value is known at a given temperature, the other value can be calculated using

$$K_p = K_c (RT)^{\Delta n} \quad \text{where}$$

- **R** is the Gas Constant using liters and atmospheres ( $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ )
- **T** is absolute temperature in kelvins, and
- **$\Delta n$**  = (the sum of the coefficients of the gases on the right side) MINUS (the sum of the coefficients of the gases on the left side)

This equation, including the  $\Delta n$  definition, must be memorized. As always when using  $K$  equations, the coefficients and reaction direction must be indicated with the calculation.

The number for  $\Delta n$  may be positive or negative, and it may be a fraction.

If the *totals* for the gaseous coefficients on the two sides of the reaction equation are *equal*, the change in **n** is zero, and  $K_p = K_c$ .

The logic is

$$K_p = K_c (RT)^{\Delta n} \quad \text{For } \Delta n = 0, K_p = K_c (RT)^0 = K_c (1) = K_c$$

\* \* \* \* \*

Write the  $K_p$  to  $K_c$  conversion equation and  $\Delta n$  definition until they are memorized.

Then try the following problem.

**Q.** For the Haber Process reaction:  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$

if  $K_c = 9.5$  at  $300.^\circ\text{C}$ , find  $K_p$ .

\* \* \* \* \*

WANTED:  $K_p$ DATA:  $K_c = 9.5$ The fundamental equation that relates  $K_p$  and  $K_c$  is  $K_p = K_c (RT)^{\Delta n}$ . $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$  ( $K_p$  calculations solve in liters and atm.) $T = 300^\circ\text{C} + 273 = 573 \text{ K}$  (T must be in kelvins) $\Delta n = (\text{right side total gas coefficients MINUS left}) = 2 - 4 = -2$  (exact)

If needed, adjust your work and finish from here.

\* \* \* \* \*

$$\begin{aligned} \text{SOLVE: } K_p &= K_c (RT)^{\Delta n} = 9.5 \cdot \{ (0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(573 \text{ K}) \}^{-2} \\ &= 9.5 \cdot (47.04)^{-2} = 9.5 \cdot 4.52 \times 10^{-4} = 4.3 \times 10^{-3} \end{aligned}$$

The units are not included when writing  $K$  values.

\* \* \* \* \*

### Non-Ideal Behavior

The  $K$  rules we have been using are based on *ideal* gas and solution behavior, including the assumption that particles in gases or solutions do not attract when they collide. In practice, all particles attract to some extent. This causes the **effective** pressure and concentration to be less than predicted by ideal behavior.

Effective concentrations and pressures should be used in  $K$  calculations, and corrections can be made to reflect the real activity of particles. In most cases, however, the consequences of non-ideal behavior are small in comparison to other sources of experimental error in determining  $K$  values.

\* \* \* \* \*

### Practice B

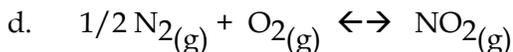
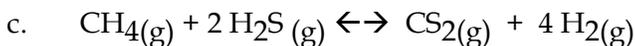
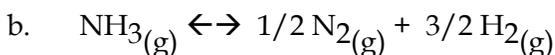
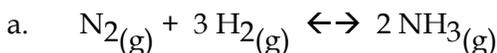
1. Convert these to scientific notation. Use a calculator as needed. Try to do each calculation two different ways.

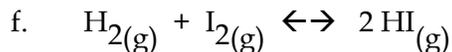
a.  $(3.33)^{-1} =$                       b.  $(3.5 \times 10^3)^{-2} =$                       c.  $(4.8 \times 10^{-3})^{-2}$

2. If  $K_p = K_c (RT)^{\Delta n}$  and  $\Delta n = +2$ , which of these could be used to solve for  $K_c$ ?

a.  $K_c = K_p \cdot R^2 \cdot T^2$     b.  $K_c = K_p \cdot R^{-2} \cdot T^{-2}$     c.  $K_c = \frac{K_p}{R^2 T^2}$     d.  $K_c = \frac{K_p}{(RT)^2}$

3. Calculate  $\Delta n$  for these reactions.





4. For which reactions in Problem 3 will  $K_p = K_c$  ?

5. If, for the reaction  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3(\text{g})$  at  $27^\circ\text{C}$ ,  $K_c = 1.3$ , calculate  $K_p$ .

6. If the Haber Process reaction is written as  $\text{NH}_3(\text{g}) \leftrightarrow 1/2 \text{N}_2(\text{g}) + 3/2 \text{H}_2(\text{g})$

with a  $K_p$  of 670 at  $600.^\circ\text{C}$ ,

a. What would be the value of  $K_p$  for  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$  at  $600.^\circ\text{C}$ ?

b. What would be the value of  $K_c$  for  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$  at  $600.^\circ\text{C}$ ?

\* \* \* \* \*

## **ANSWERS**

### **Practice A**

$$1a. \quad K_p = \frac{P_{\text{SiF}_4} \cdot (P_{\text{H}_2\text{O}})^2}{(P_{\text{HF}})^4} \qquad 1b. \quad K_p = (P_{\text{H}_2\text{O}})^5$$

2. "For calculations using  $K$  expressions, write the *WREK* steps."

**WANT** ? =  $P_{\text{H}_2\text{S}}$  in atm.

**R + E:**  $\text{CH}_4(\text{g}) + 2 \text{H}_2\text{S}(\text{g}) \leftrightarrow \text{CS}_2(\text{g}) + 4 \text{H}_2(\text{g})$  (goes to equilib.)

$$\mathbf{K:} \quad K_p = \frac{P_{\text{CS}_2} \cdot (P_{\text{H}_2})^4}{P_{\text{CH}_4} \cdot (P_{\text{H}_2\text{S}})^2}$$

$$\mathbf{DATA:} \quad K_p = 8.9 \times 10^{-4}$$

$$P_{\text{CS}_2} = 55 \text{ kPa} \cdot \frac{1 \text{ atm.}}{101 \text{ kPa}} = 0.50 \text{ atm.}$$

$$P_{\text{H}_2} = 0.32 \text{ atm.}$$

$$P_{\text{CH}_4} = \text{standard pressure} = 1 \text{ atm. (exact)}$$

$$P_{\text{H}_2\text{S}} = ?$$

All pressures must be converted to atmospheres.

$$(P_{\text{H}_2\text{S}})^2 = \frac{P_{\text{CS}_2} \cdot (P_{\text{H}_2})^4}{P_{\text{CH}_4} \cdot K_p} = \frac{(0.50) \cdot (0.32)^4}{1.0 \cdot 8.9 \times 10^{-4}} = 5.89$$

$$P_{\text{H}_2\text{S}} = ((P_{\text{H}_2\text{S}})^2)^{1/2} = (5.89)^{1/2} = \boxed{2.4 \text{ atm.}} \quad (\text{solving } K \text{ for } P, \text{ add atm.})$$

**Practice B**

1a.  $3.00 \times 10^{-1}$       b.  $8.2 \times 10^{-8}$       c.  $4.3 \times 10^4$

2.  $K_p = K_c (RT)^2 = K_c R^2 T^2$  ;  $K_c = \frac{K_p}{(RT)^2} = \frac{K_p}{R^2 T^2} = K_p R^{-2} T^{-2}$

Answers **b**, **c**, and **d** are equivalent to the given equation, answer **a** is not.

3. a.  $2 - 4 = -2$       b.  $2 - 1 = +1$       c.  $5 - 3 = +2$   
d.  $1 - 1.5 = -0.5$  or  $-1/2$       e.  $10 - 9 = +1$       f.  $2 - 2 = 0$

4. Only 3f.  $K_p = K_c$  only if  $\Delta n = 0$ .5. WANT:  $K_p$ DATA:  $K_c = 1.3$ The fundamental equation that relates  $K_p$  and  $K_c$  is  $K_p = K_c (RT)^{\Delta n}$ .

$R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$

$T = 27^\circ\text{C} + 273 = 300. \text{ K}$

$\Delta n = (\text{right side total gas coefficients MINUS left}) = 2 - 3 = -1$

SOLVE:  $K_p = K_c (RT)^{\Delta n} = K_c (RT)^{-1} = (1.3) \cdot \{ (0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(300. \text{ K}) \}^{-1}$   
 $= (1.3) \cdot (24.63)^{-1} = (1.3) \cdot (4.06 \times 10^{-2}) = 0.053$

6a. The part a reaction is the Question 4 reaction reversed and doubled. The new  $K_p$  value will be the reciprocal, squared, of the original  $K_p$ .

$K_p \text{ new} = ((670)^{-1})^2 = (670)^{-2} = 2.2 \times 10^{-6}$

6b.  $K_p$  was found in part a.  $K_c$  is WANTED. The equation relating  $K_p$  and  $K_c$  is  $K_p = K_c (RT)^{\Delta n}$ .WANTED:  $K_c$ DATA:  $K_p = 2.2 \times 10^{-6}$ 

$R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$

$T = 600.^\circ\text{C} + 273 = 873 \text{ K}$

$\Delta n = (\text{right side total gas coefficients MINUS left}) = 2 - 4 = -2$

SOLVE:  $K_p = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = K_p$

$K_c = K_p (RT)^2 = (2.2 \times 10^{-6}) \cdot \{ (0.0821)(873) \}^2 = (2.2 \times 10^{-6}) \cdot (71.67)^2$   
 $= (2.2 \times 10^{-6}) \cdot (5.14 \times 10^3) = 0.011$

\* \* \* \* \*

## Lesson 24F: The Rice Moles Table

So far in our  $K$  calculations, concentrations or pressures at *equilibrium* have been known. However, if pressures or concentrations are known for an initial mixture of *reactants* (with no products), *as well as* for any *one* reactant or product after the reaction has reached equilibrium, pressures and concentrations at equilibrium for all substances at equilibrium, and a value for  $K$ , can be calculated.

To solve this equilibrium stoichiometry, we will use a **rice moles** table. To illustrate the method, let's do a simple problem.

**Q.** Perfect Pamphlet Publications is producing spiral-bound graph paper notebooks. Each notebook has one spiral binder, two identical covers, and 40 sheets of graph paper. The initial inventory contains 95 spirals, 220 covers, and 4,250 sheets of graph paper. After the night shift produces and ships a set of notebooks, the day shift finds 60 covers remaining. How many notebooks were shipped? How much of each booklet component remains?

To solve, do the following steps in your notebook.

1. Balance this equation to find the ratios for the production process.



2. Complete the following table, then check your answer below.

Reaction	___ Spiral	___ Covers	___ Pages	___ Booklet
Initial				
Change (use + and –)				
At Equilibrium (End)				

\* \* \* \* \*

The initial data:

Reaction	1 Spiral	2 Covers	40 Pages	1 Booklet
Initial	95	220	4,250	0
Change (use + and –)				
At Equilibrium (End)		60		

Adjust your work if needed, and then complete all of the boxes in the table.

\* \* \* \* \*

Calculate the one change for which there is data. From that number, use the ratios of the process to complete the *change* row. Include a *– sign* for components used up and a *+ sign* for those formed. Then calculate the amount of each component present at the end.

\* \* \* \* \*

Reaction	1 Spiral	2 Covers	40 Pages	1 Booklet
Initial	95	220	4,250	0
Change (use + and –)	– 80	– 160	– 3,200	+ 80
At Equilibrium (End)	15	60	1,050	80

\* \* \* \* \*

Calculations using *K* values require concentrations and pressures measured at equilibrium, when the changes in the amounts present have ended. The table method above can be used to find concentrations and pressures at equilibrium. We will call this a **rice moles** table: **rice** for the labels for the rows:

Reaction, Initial, Change, Equilibrium,

and **moles** for the *numbers* that go into the table. The rule will be,

***Rice Moles.*** To find measurements at equilibrium from those *not* at equilibrium, use a *rice moles* table.

Cover the answer below, use a *rice moles* table to solve this problem.

**Q2.** For the reaction  $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$  (all gases), initial amounts are 0.100 moles of  $\text{H}_2$ , 0.090 moles of  $\text{I}_2$ , and no HI. At equilibrium, 0.020 moles of  $\text{H}_2$  are present.

- Calculate the moles of all of the substances that will be present at equilibrium.
- If the reaction takes place in a 2.0 liter vessel, calculate the value of the equilibrium constant.

\* \* \* \* \*

- WANT: moles of  $\text{H}_2$ ,  $\text{I}_2$ , and HI at equilibrium.

Strategy: Since most moles in the data are not at equilibrium, enter the data into a *rice moles* table to solve.

Reaction	1 $\text{H}_2$	1 $\text{I}_2$	2 HI
Initial	0.100 mol	0.090 mol	0 mol
Change (use + and –)			
At Equilibrium	0.020 mol		

Calculate the one *change* that you can. Then use the coefficients to complete the *change* row, and then calculate the *equilibrium* row.

\* \* \* \* \*

Reaction	1 H <sub>2</sub>	1 I <sub>2</sub>	2 HI
Initial	0.100 mol	0.090 mol	0 mol
Change (use + and –)	– 0.080 mol	– 0.080 mol	+ 0.16 mol
At Equilibrium	0.020 mol	0.010 mol	0.16 mol

In the *change* row, be sure that all of the numbers have signs.

The bottom row answers Part A.

If you have not already done so, complete Part B.

\* \* \* \* \*

- b. Part B involves  $K$  and concentrations at equilibrium. A  $K$  expression relates those terms. For calculations using  $K$  expressions, write the WREK steps.
1. **WANTED** unit or symbol. If the type of  $K$  is not specified, assume  $K$  means  $K_c$ .
  2. **R** (Reaction).  $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$  (all gases)
  3. **E**xtent: goes to equilibrium. Use  $K$  to solve.
  4. **K** (Write the  $K$  expression):  $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$  all measured at equilibrium

DATA:  $K_c = ?$  Do a data table with the  $K$  expression symbols.

In the *rice* table are moles. A  $K_c$  equation requires *mol/L* at equilibrium. All of these moles are in 2.0 L. Convert moles to mol/L.

$$[\text{HI}]_{\text{eq.}} = 0.16 \text{ mol at eq.} / 2.0 \text{ L} = 0.080 \text{ M at eq.}$$

$$[\text{H}_2]_{\text{eq.}} = 0.020 \text{ mol} / 2.0 \text{ L} = 0.010 \text{ M}$$

$$[\text{I}_2]_{\text{eq.}} = 0.010 \text{ mol} / 2.0 \text{ L} = 0.0050 \text{ M}$$

$$\text{Solve: } K = \frac{[\text{HI}]_{\text{eq.}}^2}{[\text{H}_2]_{\text{eq.}}[\text{I}_2]_{\text{eq.}}} = \frac{(0.080)^2}{(0.010)(0.0050)} = \frac{64 \times 10^{-4}}{5 \times 10^{-5}} = \boxed{130}$$

$K$  calculations can have many numbers and steps. Careful labeling of numbers with units and symbols takes time, but it is necessary to determine which data to use in solving the multiple steps of complex problems.

\* \* \* \* \*

### List DATA Before Or After the WREK Steps?

Should you list the DATA before or after the WREK steps? In most  $K$  calculations, you will need to list and analyze the WANTED and DATA first, to decide which sequence, tables, and equations to use. You will often need to re-write the DATA in later parts of the problem.

Take the time and paper you need to solve these multi-step problems methodically.

\* \* \* \* \*

**Rice Calculations and Units**

Which *units* can be use in a *rice moles* table?

1. Moles can always be used. *Rice* calculations are based on coefficients, and coefficients can always be read as moles.
2. Concentrations (molarity) and gas pressures can also be used in *rice moles* tables if all of the moles and pressures in a problem are measured in the same volume.

Why? Coefficients are mole ratios. However, if all moles are in the same volume, the mole and the mol/L *ratios* will be the same. The *rice mole* table can be used to calculate either the moles or the mol/L used up and formed.

Partial pressures will also be proportional to moles if volumes are held constant.

The logic: since  $PV = nRT$ ,  $P = n$  (constant  $1/V$ )(gas constant  $R$ )(constant  $T$ ). This simplifies to  $P = (\text{constant}) n$ , so  $P$  and  $n$  are directly proportional (Lesson 17A) if  $V$  and  $T$  are constant.

However, if volumes are *mixed* in a problem, measurements of moles per liter and gas pressures will not work in coefficient calculations.

For example, if 10 mL of 0.50 M Reactant A is *mixed* with 20 mL of 0.50 M Reactant B to conduct a reaction, both A and B are diluted as the solutions are mixed. Substituting the 0.50 M concentrations before mixing as concentrations for a reaction that occurs after mixing would cause an error. However, if all initial amounts are converted to *moles*, the *rice moles* table will work. Dilution does not change the moles of substance present.

Bottom line?

- *Rice moles* calculations always work in moles.
  - *Rice* tables can use molarity and gas pressure values if the volume remains the same in all parts of the problem.
  - If volumes change during a problem, solve the *rice* calculation in moles.
3. If a *rice* calculation is done in moles, the moles calculated in the equilibrium row must be converted to moles per liter for  $K_c$  calculations, and to atmospheres for  $K_p$  calculations.  $K$  equations work with mol/L or atmospheres as units, but not moles.

Including units with numbers in the *rice* table is necessary to identify which numbers to enter into equations in later steps of complex problems.

\* \* \* \* \*

**Practice**

1. For the reaction  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$ , in a sealed glass vessel, the initial gas mixture contains  $[\text{SO}_2] = 1.00 \text{ M}$ ,  $[\text{O}_2] = 0.60 \text{ M}$ , and no  $\text{SO}_3$ . At equilibrium,  $[\text{SO}_3] = 0.40 \text{ M}$ . Calculate the equilibrium constant.

\* \* \* \* \*

## **ANSWERS**

1. WANTED:  $K_c$

DATA: some measurements are not at equilibrium, so a *rice moles* table is needed.

Since this reaction involves gases in a container with a fixed volume, moles, mol/L or gas pressures can be used in the *rice moles* table.

Enter the initial data. Calculate the *change* row using the coefficients, and then the equilibrium row.

Reaction	2 SO <sub>2</sub>	1 O <sub>2</sub>	2 SO <sub>3</sub>
Initial	1.00 M	0.60 M	0 M
Change (use + and -)	- 0.40 M	- 0.20 M	+ 0.40 M
At Equilibrium	0.60 M	0.40 M	0.40 M

If needed, adjust your work.

\* \* \* \* \*

To find a  $K_c$  value, substitute *equilibrium* concentrations into the  $K$  expression.

$$\text{WANTED} = K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(0.40)^2}{(0.60)^2 (0.40)} = \frac{(0.16)}{(0.36)(0.40)} = \boxed{1.1}$$

\* \* \* \* \*

## **Lesson 24G: Q: The Reaction Quotient**

**Timing:** Do this lesson when you are asked to calculate values for  $Q$ .

\* \* \* \* \*

The **reaction quotient ( $Q$ )** is the number that results when concentration or pressure values for a reaction *mixture* that may *not* be at equilibrium are substituted into the  $K$  expression.

If  $K$  is known,  $Q$  will determine which way a given reaction mixture for a reversible reaction will need to shift to reach equilibrium.

During a reaction in a closed system, reactants and products that are not at equilibrium will continue to react in a *direction* that takes them toward equilibrium. (The *speed* at which a reaction proceeds is determined by reaction kinetics, but the *direction* of a reaction is determined by  $K$ .)

To determine

- whether a mixture for a given reversible reaction is at equilibrium, or
- the direction a reaction mixture must shift to reach equilibrium,

the concentrations or pressures in the reaction mixture are substituted into the  $K$  expression to calculate a value for  $Q$ . Then,

- If  $Q = K$ , the mixture is at equilibrium.
- If  $Q > K$ , the mixture is shifting left, toward the reactants, to reach equilibrium.

- If  $Q < K$ , the mixture is shifting right, toward products, to reach equilibrium.

Those three cases must be memorized, or you may derive them when you need them, because the direction of these shifts makes sense. Since

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{\text{product of the [products]}}{\text{product of the [reactants]}} = K \text{ if measured at equilibrium,}$$

- If  $Q$  is a larger number than  $K$ , for the  $Q$  ratio to reach  $K$ , as it must at equilibrium, product concentrations must go down, and reactant concentrations must go up.
- If  $Q < K$ , the [products] must go up, and the [reactants] down.

Note that the expression for  $K$  and  $Q$  are the same.

To calculate both  $K$  and  $Q$ , concentrations or pressures are substituted into the equilibrium constant expression, but  $Q$  can be calculated from measurements in any mixture. A  $K$  value only applies to measurements at equilibrium.

As with  $K$  values,  $Q$  has units, but  $Q$  is nearly always written as a number without units.

To summarize, this rule must be memorized.

### The Q Rule

To determine which direction a mixture will shift to get to equilibrium, compare the numeric values of  $Q$  and  $K$ .

If  $Q$  is less than  $K$ , the mixture will shift to the *right*, toward the *products*, to reach equilibrium.

If the rule for a shift in one direction is memorized or constructed by logic, the cases for  $Q = K$  and  $Q > K$  can easily be written.

Using the  $Q$  rule, try the following problem.

**Q.** For the reaction in a closed system  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$  at  $400.^\circ\text{C}$ ,

$K_c = 3.8 \times 10^4$ . The gas mixture not yet at equilibrium is found to contain  $[\text{N}_2] = 0.12 \text{ M}$ ,  $[\text{H}_2] = 0.030 \text{ M}$ , and  $[\text{NH}_3] = 0.60 \text{ M}$ .

- Calculate the reaction quotient.
- As the mixture continues to react, will  $[\text{NH}_3]$  increase or decrease?

★ ★ ★ ★ ★

### Answer

a. WANTED:  $Q$  = number found by substituting the current concentrations or pressures into the  $K$  expression.

DATA: *initial* concentrations:  $[\text{N}_2] = 0.12 \text{ M}$ ,  $[\text{H}_2] = 0.030 \text{ M}$ ,  $[\text{NH}_3] = 0.60 \text{ M}$ .

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.60)^2}{(0.12)(0.030)^3} = \frac{(0.36)}{(0.12)(2.7 \times 10^{-5})} = \boxed{1.1 \times 10^5}$$

- b. To find the direction a mixture will shift to reach equilibrium, compare  $Q$  to  $K$ .

Since  $Q = 1.1 \times 10^5$  and  $K_c = 3.8 \times 10^4$ ,  $Q$  is larger than  $K_c$ , and the  $[\text{NH}_3]$  product in the current mixture is higher than it will be at equilibrium. The  $[\text{NH}_3]$  in the products must therefore *decrease* as the reaction continues, because the  $Q$  value using the  $K$  expression must shift toward a final value of  $K_c$ .

\* \* \* \* \*

### **Practice**

- For a given reversible reaction, what is the difference between
  - the  $K$  expression and the  $Q$  expression?
  - A  $K$  value and a  $Q$  value?
- For a given mixture in a reversible reaction,  $Q = 2.0 \times 10^4$  and  $K_c = 4.0 \times 10^3$ . To reach equilibrium from this mixture, will the reaction shift toward the left or the right?
- For the reaction  $\text{PCl}_5(\text{g}) \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ,  $K_c = 0.56$ , a gas mixture in a closed system is found to contain  $[\text{PCl}_5] = 0.50 \text{ M}$ ,  $[\text{PCl}_3] = 0.20 \text{ M}$ , and  $[\text{Cl}_2] = 0.40 \text{ M}$ . As the mixture continues to react, will the reaction shift to the left or right?

\* \* \* \* \*

### **ANSWERS**

- The  $K$  and  $Q$  expressions are the same.
  - The  $K$  value for a given reaction at a given temperature is always the same, but it only applies to a reaction mixture at equilibrium. The  $Q$  value will vary.  $Q$  can be measured for any mixture of reactants and products, at any point in the reaction.
- $Q$  is larger than  $K_c$ . Based on the  $K$  and  $Q$  expression, to reach  $K$  the [products] must decrease, so the reaction must shift to the left. Anytime  $Q > K$ , the reaction must shift left to reach equilibrium.
  - WANT: Which direction the reaction will shift.

To find which way a mixture must shift to reach equilibrium, compare  $Q$  to  $K$ .

DATA: Current, not at equilibrium:

$$[\text{PCl}_5] = 0.50 \text{ M}, [\text{PCl}_3] = 0.20 \text{ M}, \text{ and } [\text{Cl}_2] = 0.40 \text{ M},$$

$$K_c = 0.56$$

The  $K_c$  value is known. To calculate  $Q$ , substitute the current concentrations into the  $K_c$  expression.

$$Q = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.20)(0.40)}{(0.50)} = \mathbf{0.16}$$

, which is less than  $K_c = 0.56$  in the data.

Since  $Q$  is less than  $K$ , the [products] on top must increase to reach  $K$ . To get to equilibrium from the current mixture, the reaction must shift to the **right**.

\* \* \* \* \*

## **Lesson 24H: Calculations Using $K$ and $Q$**

**Timing:** Do this lesson when you are asked to do calculate concentrations or gas pressures at equilibrium starting from mixtures of reactants and products that are not at equilibrium.

\* \* \* \* \*

So far, for reversible reactions, we have studied  $K$  calculations in three situations.

- If concentrations or gas pressures *at equilibrium* are known,  $K$  calculations are done by substituting those values into the  $K$  expression.
- If concentrations or gas pressures are known for an initial mixture that is *all reactants* (with no products), *as well as* for any *one* reactant or product after the reaction has reached equilibrium, values at equilibrium can be found using a *rice moles* table and *arithmetic*.
- For any *mixture* of reactants and products for a known reversible reaction, the *direction* that the reaction will shift to reach equilibrium can be determined by comparing  $K$  and  $Q$ .

In our fourth type of  $K$  calculation, we want to be able to calculate concentrations or gas pressures for a known reaction at equilibrium, starting from non-equilibrium concentrations or pressures for a *mixture* of the reactants and products, plus a value for  $K$ . In these cases, concentrations and gas pressures at equilibrium can often be calculated using a *rice* table,  $Q$  and  $K$  values, and *algebra*.

### **Equilibrium Calculations Based on Mixtures of Reactants and Products**

For reversible reaction calculations that begin with *all reactants* at the start, in the *rice moles* table, the change row will always have a *negative* sign for the *reactants*, because if at the beginning of a reaction there are only reactants, some of the reactants must be used up. The change row for the products will always have a positive sign, because if the reaction goes at all, some products will be formed.

However, if a closed system has a *mixture* of reactants and products, and the reaction is not yet at equilibrium, the mixture will need to shift to the right toward the products, or shift to the left toward reactants, to reach equilibrium. A comparison of values for  $K$  and  $Q$  will predict whether the reaction equation will shift left or right to reach equilibrium.

If a reaction mixture must shift to the right to reach equilibrium, the *signs* in the change row of the *rice moles* table will be *negative* for the reactants, and positive for the products. Reactants will be used up, and products will form.

If a reaction mixture must shift left to reach equilibrium, the signs for the terms in the change row will be *positive* for the reactants, and negative for the products, since in shifting left, the products will be used up and reactants will form.

This means that for  $K$  calculations involving mixtures of reactants and products, the signs in the change row of the *rice moles* table must be assigned carefully.

Let's learn the method to solve reaction mixture  $K$  calculations by example.

- Q.** In the reaction  $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$  (all gases) with a  $K_c = 46$ , in a closed system with a constant volume, if 1.00 M concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  are mixed, what will be the concentrations of each substance at equilibrium?

When concentrations or pressures are known for a mixture not at equilibrium, but are not known for any of the substances at equilibrium, do these seven steps.

**Step 1: WREK.** Complete the WREK steps.

**Step 2. Direction.** Find the direction the reaction is shifting by comparing  $Q$  to  $K$ .

Complete those steps, and then check your answer below.

\* \* \* \* \*

1. **WANT:**  $[\text{H}_2]$ ,  $[\text{I}_2]$ , and  $[\text{HI}]$  at equilibrium.

**R+E:**  $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$  (all gases) (goes to equilibrium. Use  $K$ ).

**K:**  $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$  measured at equilibrium.

2. To determine which way a mixture is shifting, use the  $Q$  rule.

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.00)^2}{(1.00)^2} = 1.00$$

Since  $Q = 1.00 < K = 46$ , the reaction must shift to the *right*, toward the products, to get to equilibrium.

**Step 3: Rice.** Write the *rice* table with the initial concentrations or pressures.

In the *change* row, represent the change that will take place to reach equilibrium using terms like  $+x$ ,  $-x$ ,  $+2x$ ,  $-3x$ , etc.

Finish Step 3, and then check your answer below.

\* \* \* \* \*

As the reaction shifts toward products to reach equilibrium, some of the  $[\text{H}_2]$  and  $[\text{I}_2]$  reactants are used up.

Since the reaction must shift to the *right* to reach equilibrium, in the *change* row, the signs for all of the reactant terms must be negative, and the signs for all of the product terms must be positive.

\* \* \* \* \*

According to the coefficients, if  $[\text{H}_2]$  changes by  $-x$ ,  $[\text{I}_2]$  must change by  $-x$  as it reacts with  $\text{H}_2$ , and  $[\text{HI}]$  must increase by  $+2x$ .

Reaction	1 $\text{H}_2$	1 $\text{I}_2$	2 $\text{HI}$
Initial	1.00 M	1.00 M	1.00 M
Change	$-x$ M	$-x$ M	$+2x$ M
At Equilibrium			

**Step 4. Equilibrium row.** Complete the equilibrium row using terms that include  $x$ .

\* \* \* \* \*

Reaction	1 H <sub>2</sub>	1 I <sub>2</sub>	2 HI
Initial	1.00 M	1.00 M	1.00 M
Change	- $x$ M	- $x$ M	+ $2x$ M
At Equilibrium	(1.00 - $x$ ) M	(1.00 - $x$ ) M	(1.00 + $2x$ ) M

**Step 5. Solve  $K$  for  $x$ .** Substitute the equilibrium row terms into the  $K$  equation and solve for  $x$ .

\* \* \* \* \*

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.00 + 2x)^2}{(1.00 - x)^2} = 46$$

Taking the square root of both sides,

$$\frac{(1.00 + 2x)}{(1.00 - x)} = (46)^{1/2} = 6.78$$

Solve for  $x$ .

\* \* \* \* \*

$$1.00 + 2x = 6.78(1.00 - x)$$

$$1.00 + 2x = 6.78 - 6.78x$$

$$8.78x = 5.78 ; x = 5.78/8.78 = 0.658$$

**Step 6. Find the equilibrium values.** Substitute the value for  $x$  into the equilibrium row to find the WANTED values for each equilibrium concentration.

**Step 7. Check.** substitute those equilibrium concentrations into the  $K$  expression. Calculate a value of  $K$ . Compare to the  $K$  value given in the problem.

Try those steps, and then check your answer below.

\* \* \* \* \*

	H <sub>2</sub>	I <sub>2</sub>	HI
At Equilibrium	1.00 - 0.658 = <b>0.34 M</b>	<b>0.34 M</b>	1.00 + 2(0.658) = <b>2.32 M</b>

7. Check:  $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2.32)^2}{(0.34)^2} = 47$  versus 46 in the data .

When the check  $K$  agrees with the given  $K$ , allowing for the doubtful digit, the answer is likely correct.

\* \* \* \* \*

**Summary**

To calculate  $K$  when concentrations or pressures are known only for values not at equilibrium, use these 7 steps.

1. **WREK.** Complete the WREK steps.
2. **Direction.** Find the reaction direction using  $Q$ .
3. **Rice Change.** Write the *rice* table using  $+ \#x$  and  $- \#x$  in the *change* row.
4. **Equilibrium row.** Write the *equilibrium* row in terms of  $x$ .
5. **Solve  $K$  for  $x$ .**
6. **Solve equilibrium values.**
7. **Check:** Calculate  $K$  using the equilibrium values. Compare to  $K$  in the data.

\* \* \* \* \*

**Practice:** For hints, read a part of the answer.

1. When solving for an equilibrium concentration using a rice moles table, if  $K = 25$  and  $Q = 55$ ,
  - a. will the reaction shift to the right or left to reach equilibrium?
  - b. will the sign of the reactant terms in the change row of the rice moles table be positive or negative?
2. A mixture for a reversible reaction has the following *rice* table.

Reaction	1 A	1 B	2 C
Initial	0.50 M	0.50 M	2.0 M
Change	+ x M	+ x M	- 2x M
At Equilibrium			

- a. Write an expression for the equilibrium constant  $K_C$ .
  - b. Calculate a  $Q$  value for the initial mixture.
  - c. Will the mixture shift toward reactants or products to reach equilibrium?
  - d. In the table, complete the concentrations at equilibrium in terms of  $x$ .
  - e. If the value for the equilibrium constant is 4.0, calculate the value of  $x$  in the table.
  - f. Calculate the concentrations of A, B, and C at equilibrium.
  - g. Check your answer by using the part f answers to calculate  $K$ .
3. In the reaction  $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$  all gases in a closed system, if  $K_p = 0.36$  and the initial concentrations are 0.50 M for each reactant and 1.00 M for each product,
    - a. What will be the value of  $K_C$ ?
    - b. What will be concentration of each substance at equilibrium?

\* \* \* \* \*

**ANSWERS**

- 1a. Since  $Q$  is higher than  $K$ , to reach equilibrium, the reaction mixture must shift to the left, toward the reactants, to reach equilibrium.
- 1b. When the reaction must shift to the left to reach equilibrium, the reactant terms in the change row of the *rice* moles table will have positive signs, because their concentration will increase during the shift.

2a. Since the reaction is  $A + B \leftrightarrow 2C$ ,  $K = \frac{[C]^2}{[A][B]}$

2b. To calculate  $Q$ , substitute the initial concentrations into the  $K$  expression.

$$Q = \frac{[C]^2}{[A][B]} = \frac{[2.0]^2}{[0.50][0.50]} = \frac{4.0}{0.25} = 16$$

2b. To calculate  $Q$ , substitute the initial concentrations into the  $K$  expression.

2c. Since the signs for the reactants in the change row are positive, the *reactant* concentrations will be *increasing* as the mixture shifts toward equilibrium. The reaction is shifting to the left toward reactants.

2d. 

At Equilibrium	<b>0.50 M + x</b>	<b>0.50 M + x</b>	<b>2.0 M - 2x</b>
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2e. To calculate  $x$ , substitute the equilibrium concentrations into the  $K$  equation.

$$K = 4.0 = \frac{[C]^2}{[A][B]} = \frac{[2.0 \text{ M} - 2x]^2}{[0.50 \text{ M} + x]^2} = 4.0$$

To find  $x$ , begin by taking the square root of both sides.

$$\frac{[2.0 \text{ M} - 2x]}{[0.50 \text{ M} + x]} = 2.0$$

$$2.0 \text{ M} - 2x = 2.0(0.50 \text{ M} + x)$$

$$2.0 \text{ M} - 2x = 1.0 \text{ M} + 2x$$

$$4x = 1.0 \text{ M}$$

$$x = 0.25 \text{ M}$$

2f. Substitute for  $x$  in the bottom row of the *rice* table.

$$[A] = 0.50 \text{ M} + 0.25 \text{ M} = 0.75 \text{ M} = [B]; [C] = 2.0 \text{ M} - 2(0.25 \text{ M}) = 1.5 \text{ M}$$

2g.  $K = \frac{[C]^2}{[A][B]} = \frac{[1.5]^2}{[0.75][0.75]} = \frac{2.25}{0.5625} = 4.0$  This agrees with the  $K$  given in part e.

3a. Since the moles of gas are the same on both sides,  $K_p = K_c$ .

3b. **WANT:** The four *equilibrium* concentrations.

**DATA:** In the given *non-equilibrium* mixture, [reactants] =  $[CO] = [H_2O] = 0.50 \text{ M}$

[products] =  $[CO_2] = [H_2] = 1.00 \text{ M}$

$$K_p = K_c = 0.36$$

To calculate equilibrium measures from *non-equilibrium* measures, do the seven steps.

1. **WREK.** Complete the WREK steps.

**WANT:** See above.

**R+E:**  $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$  (all gases) (goes to equilibrium, use  $K$  to solve).

$$K: \quad K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

2. **Direction.** Compare  $Q$  and  $K$ .  $Q = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.00)(1.00)}{(0.50)(0.50)} = \frac{1}{0.25} = 4.0$

Since  $4.0 = Q > 0.36 = K$ , the mixture is shifting toward *reactants* to get to equilibrium.

3. **Rice Change.** Write the *rice* table using a simple  $+x$  or  $-x$  in the *change* row. If reaction is shifting toward reactants, reactants must get a  $+$  sign, and products a  $-$ .
4. **Solve Eq. row.** In terms of  $x$ .

Reaction	1 CO	1 H <sub>2</sub> O	1 CO <sub>2</sub>	1 H <sub>2</sub>
Initial	0.50 M	0.50 M	1.00 M	1.00 M
Change	$+x$ M	$+x$ M	$-x$ M	$-x$ M
At Equilibrium	$0.50 + x$ M	$0.50 + x$ M	$1.00 - x$ M	$1.00 - x$ M

5. **Solve  $K$  for  $x$ .** Solve the  $K$  equation for  $x$ , using the equilibrium row terms.

$$K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.00 - x)^2}{(0.50 + x)^2} = 0.36$$

Taking the square root of both sides:  $\frac{(1.00 - x)}{(0.50 + x)} = (0.36)^{1/2} = 0.60$

Solving for  $x$ :  $(1.00 - x) = 0.60(0.50 + x)$

$$1.00 - x = 0.30 + 0.60x$$

$$0.70 = 1.60x$$

$$x = 0.438 \quad (\text{carry an extra sig fig until the end})$$

6. **Solve the equilibrium values.**

WANTED:  $[\text{reactants}] = [\text{CO}] = [\text{H}_2\text{O}] = 0.50 \text{ M} + x = 0.50 \text{ M} + 0.438 = \boxed{0.94 \text{ M}}$

$[\text{products}] = [\text{CO}_2] = [\text{H}_2] = 1.00 \text{ M} - x = 1.00 \text{ M} - 0.438 = \boxed{0.56 \text{ M}}$

(Hundredths has doubt in both. Adding and subtracting, the place decides the doubtful digit.)

7. **Check:**  $K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.56)^2}{(0.94)^2} = 0.35 \text{ calculated} \approx 0.36 \text{ in original data. Check!}$

\* \* \* \* \*

## Lesson 24I: Solving Quadratic Equations

**Timing:** Do this lesson *if* you are asked to solve quadratic equations as part of *K* or other calculations. Even if you feel confident about the math of quadratic equations, this lesson may contain information on the use of quadratics in science problems that will be helpful to review.

\* \* \* \* \*

### Quadratic Equations

In the calculations in the prior lesson, the numbers and formulas were chosen to allow solving for *K* values by simply taking a square root. In other problems, you may need to solve a **quadratic equation** or a higher order equation for *x*.

The **general format** for a quadratic equation is  $ax^2 + bx + c = 0$ , where *a*, *b*, and *c* are numbers. A quadratic equation has  $x^2$  terms, but no *x* powers higher than 2.

For the quadratic equations most often encountered in chemistry, the steps to solve are:

1. Move all terms to one line and eliminate parentheses.
2. Group the terms into the *general quadratic format*:  $ax^2 + bx + c = 0$
3. Substitute the values for *a*, *b*, and *c* into the **quadratic formula**:

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

4. Substitute the two resulting *x* values into the data and see which one *makes sense*.

The quadratic formula will find two values for *x*, but in science problems one of them will usually result in a quantity that cannot work in the problem, such as resulting in negative values for quantities that can only be positive. The other root will be a solution that does make sense and should be used to answer the problem.

The *general quadratic format* and the *quadratic formula* must be memorized. The quadratic formula may be best memorized by repeated recitation: “*x* equals minus *b* plus or minus the square root of *b* squared minus 4*ac*, all over 2*a*.”

Some calculators and tools available online (search *quadratic formula calculator*) will solve a quadratic equation for *x* once you have values for *a*, *b*, and *c*. However, you may not always be allowed to use these tools on quizzes and tests. This lesson will review how to solve quadratic formulas with minimal calculator use.

\* \* \* \* \*

Use the four steps above to solve the following problem. If you get stuck, read the below answer until unstuck, adjust your work, and finish from that point.

**Q.** For the reaction in a closed system:  $A + B \leftrightarrow C$

$K = 10.$ ,  $[C] = (1.4 + x)$  M,  $[B] = (0.40 - x)$  M, and  $[A] = (1.00 - x)$  M. Solve for *x*.

\* \* \* \* \*

**Answer**

WANT:  $x$ . Write the  $K$  expression, then substitute the terms containing  $x$  to solve.

$$K = \frac{[C]}{[A][B]} ; \text{ so: } 10. = \frac{(1.4 + x)}{(1.00 - x)(0.40 - x)}$$

The arithmetic shown below can be done in a different way, but the four general steps above should be followed.

1. Move all terms to one line.  $10(0.40 - x)(1.00 - x) = (1.4 + x)$

Eliminate parentheses.  $10(0.40 - 1.4x + x^2) = 1.4 + x$

$$4 - 14x + 10x^2 = 1.4 + x$$

2. Group terms into the general quadratic format. On the left side, write a single  $x^2$  term, a single  $x$  term, and a single number term. On the right side must be *zero*.

\* \* \* \* \*

General:  $ax^2 + bx + c = 0$       In this problem:  $10x^2 - 15x + 2.6 = 0$

3. To solve for  $x$ , substitute the values for  $a$ ,  $b$ , and  $c$  into the quadratic formula.

Fill in these blanks:  $a = \underline{\hspace{2cm}}$ ,  $b = \underline{\hspace{2cm}}$ ,  $c = \underline{\hspace{2cm}}$

\* \* \* \* \*

$a = 10$ ,  $b = -15$ ,  $c = 2.6$ . Substituting these values:

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(-15) \pm \{(-15)^2 - 4(10)(2.6)\}^{1/2}}{2(10)} =$$

$$= \frac{+15 \pm (225 - 104)^{1/2}}{20} = \frac{+15 \pm (121)^{1/2}}{20} = \frac{15 \pm 11}{20} = \frac{26}{20} \text{ and } \frac{4}{20} = \boxed{1.3 \text{ and } 0.2}$$

4. Only *one*  $x$  value will *work* in the problem. Substitute the two resulting answers for  $x$  into the problem data and see which one makes sense.

\* \* \* \* \*

Since  $[B] = (0.40 - x)$ , if  $x = 1.3$ ,  $[B]$  would equal  $-0.90$  Molar. Concentrations in chemistry cannot be negative. The  $x$  value that gives a *positive* number for every concentration is  $\boxed{x = 0.2}$ . That's the answer.

Check: Using the original equation, calculate  $[A]$ ,  $[B]$ , and  $[C]$ . Then calculate a  $K$  from those values, and compare this calculated  $K$  to the given  $K$ .

\* \* \* \* \*

$$[A] = (1.4 + x) = (1.4 + 0.2) = 1.6$$

$$[B] = (0.4 - x) = (0.40 - 0.2) = 0.20$$

$$[C] = (1.0 - x) = (1.00 - 0.2) = 0.80$$

Using  $K = \frac{[A]}{[B][C]} = \frac{1.6}{(0.20)(0.80)} = \frac{1.6}{0.16} = 10.$  This matches the original  $K$  value.  
The value  $x = 0.2$  works.

\* \* \* \* \*



Then group terms into the general format:  $ax^2 + bx + c = 0$

$$2x^2 + 12x - 6.5 = 0 \quad ; \quad a = 2, \quad b = +12, \quad c = -6.5.$$

Substitute a, b, and c into the quadratic formula and solve for the two  $x$  values.

$$\begin{aligned} x &= \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(12) \pm \{(12)^2 - 4(2)(-6.5)\}^{1/2}}{2(2)} = \frac{-12 \pm (144 + 52)^{1/2}}{4} = \\ &= \frac{-12 \pm (196)^{1/2}}{4} = \frac{-12 \pm 14}{4} = \frac{2}{4} \quad \text{and} \quad \frac{-26}{4} = \boxed{+0.5 \quad \text{and} \quad -6.5} \end{aligned}$$

3. For the reaction  $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$  (all gases) at a temperature where  $K_c = 2.0$ , for a reaction in a container with a fixed volume that initially contains  $[\text{H}_2] = 2.5 \text{ M}$ ,  $[\text{I}_2] = 1.5 \text{ M}$ , and  $[\text{HI}] = 1.0 \text{ M}$ , what will be the concentrations of each substance at equilibrium?

Given concentrations or pressures not at equilibrium, to find concentrations or pressures at equilibrium, do these seven steps.

**Step 1: WREK.** Complete the WREK steps.

1. **WANT:**  $[\text{H}_2]$ ,  $[\text{I}_2]$ , and  $[\text{HI}]$  at equilibrium.

**R+E:**  $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$  (all gases) (goes to equilibrium. Use  $K$  to solve.)

**K:**  $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$  measured at equilibrium.

**Step 2. Direction.** Find the direction the reaction is shifting by comparing  $Q$  to  $K$ .

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0)^2}{(2.5)(1.5)} = \frac{1.0}{3.75} = 0.27$$

Since  $Q = 0.27 < K = 2.0$ , the reaction must shift to the **right** to get to equilibrium.

**Step 3: Rice.** Write the *rice* table with *change* row terms like  $+x$ ,  $-x$ ,  $+2x$ ,  $-3x$ , etc.

Reaction	1 $\text{H}_2$	1 $\text{I}_2$	2 $\text{HI}$
Initial	2.5 M	1.5 M	1.0 M
Change	$-x \text{ M}$	$-x \text{ M}$	$+2x \text{ M}$
At Equilibrium			

Each *change* box has an  $x$ . The number in front of  $x$  is the coefficient in that column. Signs must all be positive on the side the reaction is shifting *to*, and all negative on the other side.

**Step 4. Eq. row.** Complete the equilibrium row using terms that include  $x$ .

Reaction	1 $\text{H}_2$	1 $\text{I}_2$	2 $\text{HI}$
Initial	2.5 M	1.5 M	1.0 M
Change	$-x \text{ M}$	$-x \text{ M}$	$+2x \text{ M}$
At Equilibrium	$(2.5 - x) \text{ M}$	$(1.5 - x) \text{ M}$	$(1.0 + 2x) \text{ M}$

**Step 5. Solve K for x.** Substitute the equilibrium row terms into the  $K$  equation. Solve for  $x$ .

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0 + 2x)^2}{(2.5 - x)(1.5 - x)} = 2$$

This quadratic equation is the pretest problem, solved in Problem 2 above.

The answers are  $x = +0.5$  and  $x = -6.5$

**Step 6. Eq. values.** Substitute the value of  $x$  to find the WANTED eq. row values.

$$[\text{H}_2]_{\text{eq.}} = 2.5 - x. \quad \text{Either } 2.5 - 0.5 = \mathbf{2.0 \text{ M}} \quad \text{or } 2.5 - 6.5 = \mathbf{-4.0 \text{ M}}$$

Since real concentrations cannot be negative, the useable  $x = 0.5$ .

$$[\text{I}_2]_{\text{eq.}} = 1.5 - x = 1.5 - 0.5 = \mathbf{1.0 \text{ M}}$$

$$[\text{HI}]_{\text{eq.}} = 1.0 + 2x = 1.0 + 2(0.5) = \mathbf{2.0 \text{ M}}$$

**Step 7. Check:** substitute those  $[\ ]_{\text{eq.}}$  into the  $K$  expression. Calculate a  $K$ . Compare to data.

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2.0)^2}{(2.0)(1.0)} = \frac{4.0}{2.0} = \mathbf{2.0} \quad \text{versus } 2.0 \text{ in the problem. Check.}$$

4. For the reaction  $\text{PCl}_3 + \text{Cl}_2 \leftrightarrow \text{PCl}_5$  (all gases) in a container with a fixed volume, at a temperature where  $K_p = 20.$ , a reaction initially contains partial pressures of 0.20 atm. for  $\text{PCl}_3$ , 0.040 atm. for  $\text{Cl}_2$ , and 0.58 atm for  $\text{PCl}_5$ . What will be the partial pressure of each substance at equilibrium?

Given concentrations or pressures not at equilibrium, to find concentrations or pressures at equilibrium, do the seven steps.

**Step 1: WREK.** Complete the WREK steps.

1. WANT:  $? = P_{\text{PCl}_3}$  in atm.
2. **Rxn+ Extent**  $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \leftrightarrow \text{PCl}_5(\text{g})$  (goes to equilibrium, use  $K$ ).
4. **K:**  $K_p = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}$

**Step 2. Direction.** Find the direction the reaction is shifting by comparing  $Q$  to  $K$ .

$$Q = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}} = \frac{0.58 \text{ atm.}}{(0.20 \text{ atm.})(0.040 \text{ atm.})} = \mathbf{72}$$

Since  $Q = 72 > K = 20.$ , the reaction must shift to the **left** to reach equilibrium.

**Step 3: Rice.** Write *rice* table with *change* row terms like  $+x$ ,  $-x$ ,  $+2x$ ,  $-3x$ , etc.

**Step 4. Eq. row.** Complete the equilibrium row using terms that include  $x$ .

\* \* \* \* \*

Reaction	1 PCl <sub>3</sub>	1 Cl <sub>2</sub>	1 PCl <sub>5</sub>
Initial	0.20 atm	0.040 atm	0.58 atm.
Change	+ x	+ x	- x
At Equilibrium	(0.20 + x) atm.	(0.040 + x) atm.	(0.58 - x) atm.

Each *change* box has an **x**. The number in front of **x** is the coefficient in that column. Signs must all be positive on the side the reaction is shifting to (left), and all negative on the other side.

**Step 5. Solve K for x.** Substitute the equilibrium row terms into the *K* equation. Solve for **x**.

$$K_p = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}} = \frac{(0.58 - x)}{(0.20 + x)(0.040 + x)} = 20$$

Group all of terms on one line and eliminate parentheses.

$$20(0.20 + x)(0.040 + x) = (0.58 - x)$$

$$20(0.0080 + 0.24x + x^2) = 0.58 - x$$

$$0.16 + 4.8x + 20x^2 = 0.58 - x$$

Then group the terms into the general format:  $ax^2 + bx + c = 0$

$$20x^2 + 5.8x - 0.42 = 0$$

Substitute a, b, and c into the quadratic formula and solve for the two **x** values.

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-5.8 \pm \{(5.8)^2 - 4(20)(-0.42)\}^{1/2}}{2(20)} = \frac{-5.8 \pm (33.64 + 33.6)^{1/2}}{40}$$

$$= \frac{-5.8 \pm (67.24)^{1/2}}{40} = \frac{-5.8 \pm 8.2}{40} = \frac{2.4}{40} \text{ and } \frac{-14}{40} = \boxed{+0.060 \text{ and } -0.35}$$

**Step 6. Eq. values.** Substitute the value for **x** to find the WANTED eq. row values.

$$P_{\text{PCl}_3} = 0.20 + x = 0.20 + 0.060 = \boxed{0.26 \text{ atm.}} \text{ or } 0.20 - 0.35 = -0.15 \text{ atm.}$$

Since pressure cannot be negative, the valid value of **x** = **0.060**.

$$P_{\text{Cl}_2} = 0.040 + x = 0.040 + 0.060 = \boxed{0.100 \text{ atm.}}$$

$$P_{\text{PCl}_5} = 0.58 - x = 0.58 - 0.060 = \boxed{0.52 \text{ atm.}}$$

**Step 7. Check:** substitute those atm. into the *K* expression. Calculate a *K*. Compare to data.

$$K_p = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}} = \frac{0.52}{(0.26)(0.100)} = 20. \text{ and the } K_p \text{ value in the problem is 20. Check!}$$

\* \* \* \* \*

## **Summary – Module 24: Equilibrium**

1. Reactions can be divided into three types: those that go nearly 100% to completion, those that don't go, and reactions that are reversible and go partially to completion. Reversible reactions continue until both the forward and reverse reactions are going at the same rate, no further reaction seems to take place. The reaction is said to be at **equilibrium**.

For equilibrium to exist:

- All reactants and products must be present in at least small quantities, and
  - The reaction must be in a *closed* system: no particles or energy can be entering or leaving.
2. **Le Châtelier's Principle:** If a system at equilibrium is subjected to a change, processes occur which tend to counteract that change.

Le Châtelier's Principle *predicts* shifts in concentration, temperature, and pressure.

To apply Le Châtelier's Principle, write the reactants and products of the reversible reaction with "two-way arrows" in-between. Then,

- a. *Increasing* a [substance] which appears on one side of a equilibrium equation shifts an equilibrium to the *other* side. The other substance concentrations *on* the same side as the [increased] are *decreased*, and the substance concentrations on the *other* side are *increased*.
- b. *Decreasing* a [substance] which appears on one side of a equilibrium equation shifts the equilibrium *toward* that side. The other [substances] *on* the same side are *increased*, and the [substances] on the *other* side are *decreased*.
- c. Adding energy shifts the equilibrium away from the side with the energy term, and removing energy shifts the equilibrium toward the side with the energy term.
- e. Energy can be added to a system by increasing its temperature. Energy can be removed by cooling. When energy is produced by a shift in equilibrium, the temperature of the system goes up. When energy is used up, the system's temperature goes down.
- f. *Increasing* the *pressure* on a gas, such as by reducing the volume of the container, will shift the equilibrium toward the side with *fewer total moles* of gas.
- g. *Decreasing* the pressure on a gas, such as by increasing the volume of the container, will shift the equilibrium toward the side with more moles of gas.
- h. If gas moles are equal on both sides, pressure changes will not shift an equilibrium.
- i. Adding or removing a solid, pure liquid, or solvent does not shift an equilibrium. Shifting an equilibrium will not change the concentration of a solid, pure liquid, or solvent.

### 3. The Equilibrium Constant

- a. For the general reaction  $aA + bB \leftrightarrow cC + dD$  at any given temperature, using concentrations at equilibrium, the ratio  $\frac{[C]^c[D]^d}{[A]^a[B]^b} = K$  will be constant.
- b. The ratio which shows the *symbols* for the substance concentrations and powers is called the equilibrium constant ( $K$ ) **expression**.

The equilibrium constant **value** is the number that is the ratio.

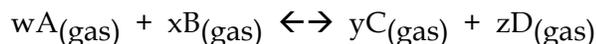
- c. Only concentrations that can *change* are included in  $K$  expressions. Terms for solids, pure liquids, and solvents (including *liquid* water) are omitted from  $K$  expressions.

### 4. K Values

- a. An equilibrium constant value is a number greater than zero. At equilibrium,
- If the substances on the right side of an equation have higher concentrations than those on the left, the value of  $K$  will be greater than one.
  - If the substances on the right side of an equation have lower concentrations than those on the left, the value of  $K$  will be a number between zero and one (in scientific notation, a number with a negative power of 10).
  - The more a reaction goes to the right, the higher will be the value of its equilibrium constant.
- b. If a value of  $K$  is known for a reaction written in one direction, the value of  $K$  for the reverse reaction will be the reciprocal of the original  $K$ .
- c. If a value of  $K$  is known for a reaction with one set of coefficients, those coefficients can be multiplied by any positive number, and the new value of  $K$  will be the original  $K$  to the power of the multiplier.

### 5. K<sub>p</sub> Equations

At a given temperature, for a reaction in which all substances are gases



at equilibrium these ratios will be constant:

$$K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x} \quad \text{and} \quad K_p = \frac{(P_C)^y \cdot (P_D)^z}{(P_A)^w \cdot (P_B)^x} \quad \text{where } P \text{ represents partial pressure.}$$

$K_c$  and  $K_p$  calculations are done in the same manner, except

- The values of  $K_c$  and  $K_p$  will not be the same *if* the two sides of the balanced equation have a different number of total moles of gases.
- In  $K_p$  calculations, partial pressures are measured in atmospheres. Pressures must be converted to atmospheres before calculations using  $K_p$ .
- When calculating a partial pressure using  $K_p$  values, atmospheres must be added as the unit of the answer.

6. For calculations using  $K_C$  or  $K_p$  expressions, write the WREK steps.

**W (WANTED):** First write the WANTED unit.

**R (Reaction):** Write the balanced equation for the reaction.

**E (Extent):** Indicate the extent of the reaction. If the reaction goes

- essentially to completion, use standard stoichiometry to solve.
- to equilibrium (only partially to completion), use  $K$  to solve.

**K:** Write the  $K$  expression.

### 7. Converting Between $K_C$ and $K_p$

When all terms in a  $K$  expression are gases, if either a  $K_C$  or a  $K_p$  value is known at a given temperature, the other value can be calculated using

$$K_p = K_C (RT)^{\Delta n} \quad \text{where}$$

- **R** is the Gas Constant, using  $R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$
- **T** is absolute temperature in kelvins, and
- **$\Delta n$**  = (the sum of the coefficients of the gases on the right side) MINUS (the sum of the coefficients of the gases on the left side)

The number for  $\Delta n$  may be positive or negative, and it may be a fraction.

If the total for the gaseous coefficients on the two sides of the reaction equation are equal,  $\Delta n = \text{zero}$ , and  $K_p = K_C$ .

8. **Rice Moles.** To find measurements at equilibrium from those not at equilibrium, use a *rice moles* table. Rice tables can always be solved in moles, and can also be solve in concentration or pressure units if the volume is the same for all measurements.
9. **The reaction quotient (Q)** is the number that results when concentration or pressure values for a reaction mixture that may *not* be at equilibrium are substituted into the  $K$  expression.
10. **The Q Rule:** To determine which direction a mixture will shift to get to equilibrium, compare  $Q$  to  $K$ . (If  $Q > K$ , the mixture will shift toward reactants).
11. Given concentrations or pressures not at equilibrium, to find concentrations or pressures at equilibrium, do these seven steps.
1. WREK. Complete the WREK steps.
  2. Direction. Find the reaction direction using  $Q$ .
  3. Rice Change. Write the *rice* table using  $+ \#x$  and  $- \#x$  in the *change* row.
  4. Eq. row. Write the *equilibrium* row in terms of  $x$ .
  5. Solve  $K$  for  $x$ .
  6. Eq. value. Calculate equilibrium row values using the  $x$  value.
  7. Check: Calculate  $K$  using equilibrium values. Compare to  $K$  in the data.

# # # # #

