

Calculations In Chemistry

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Module 28: Equilibrium

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Module 28 — Equilibrium

Pretests: In this module, if you have had a prior chemistry course, the initial lessons may be review. If you think you are familiar with the topic of a lesson, try a few problems at the end of the last problem set in the lesson. If you get those right, move to the next lesson.

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Introduction to Equilibrium

Chemical reactions can be divided into three types.

1. **Reactions that go nearly 100% to completion.** Burning paper is one such reaction. Once it begins, the reaction continues 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 by the remarkable process of photosynthesis).
3. **Reactions that are reversible and go partially to completion.** As a reversible 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 reform 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 system, the two rates will remain equal and no further reaction seems to take place. The system is said to be at **equilibrium**.

For equilibrium to exist, both of these conditions must be met:

- 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 the reaction vessel.

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

In theory, all reactions that occur are reversible, and *all* reactions go to equilibrium. In practice, many equilibria favor the products so much that nearly all of the limiting reactant is used up, and the reaction is considered to go "to completion." For those reactions, if the limiting reactant is known, the amounts of reactants used up and products formed can be calculated by conversion stoichiometry.

When reactions go only partially to completion, there is no limiting reactant that decides how much of the products form. Reactions that go to equilibrium require an accounting system to track the particles used up and formed.

Lesson 28A: Le Châtelier's Principle

Timing: Depending on the sequence in your course, problems based on Le Châtelier's principle may be assigned either at the beginning or end of a unit on Equilibrium. This lesson may be completed at either point. When Le Châtelier's principle is assigned in *your* class, read the introduction above and then complete this lesson.

Pretest: If you are familiar with Le Châtelier's principle, try Problems 3 and 4 in Practice D at the end of this lesson. If you can do those problems correctly, you may skip this lesson.

* * * * *

Shifts In Equilibrium

Equilibrium is important because many reactions, including 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 that tend to counteract that change.

Le Châtelier's principle predicts the direction that a reversible reaction will shift when a reaction mixture at equilibrium is subjected to changes in concentration, temperature, and pressure.

Changes in Concentration

To predict shifts in equilibrium due to changes in *concentration*, it is helpful to re-state Le Châtelier's principle in the following manner.

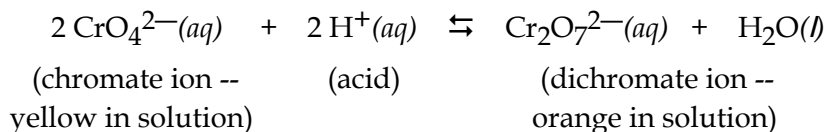
To Predict Shifts Due to Concentration Changes:

For reversible reactions at equilibrium, write the balanced reaction equation using a *two-way* (\rightleftharpoons) arrow, then apply these rules.

- Increasing* a [substance] that appears on one side of an 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] that appears on one side of an 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*.

Commit to memory the rules in the two boxes above, then apply the rules to the following problem.

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



For the above reaction,

1. If acid (H^+) is added to a yellow chromate ion solution at equilibrium,
 - a. In 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 color change will tend to occur? _____

* * * * *

Answers

- a. The equilibrium will shift to the **right**. Increasing the concentration of the H^+ found on the left side shifts the equilibrium toward 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 toward **orange**.

Le Châtelier's principle helps us to quickly predict these shifts, but to understand the logic behind the rule, we need to examine what is happening at the molecular level.

- When $[\text{H}^+]$ increases, there will be more collisions between the H^+ and the chromate ions. Though the *percentage* of collisions that result in 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 more dichromate.
- As more dichromate forms, its collisions with water increase, and the speed of the reverse reaction increases. A new balance is reached, but 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? _____

* * * * *

Answer

- a. Bases neutralize acid (see Lesson 14A). This lowers the $[\text{H}^+]$.

- b. In 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 color change will occur? _____

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- b. Decreasing the concentration of 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 shifts the equilibrium to the left and 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 toward 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 mean 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 is no longer in a closed system at equilibrium. In this case, the reaction and the mixture composition will shift toward the side that contains the escaping particle. This type of shift can be used to drive a reversible reaction toward a side with products that are wanted.

Practice A: First learn the rules, then do the problems by applying the rules from memory. Check your answers after Part a.

1. For the Haber process reaction: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
- 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 $[N_2]$ is decreased,
1. Equilibrium will shift to the (left or right?) _____.
 2. $[H_2]$ will (increase or decrease?) _____.
 3. $[NH_3]$ will _____.

Energy Changes

For a reversible reaction at equilibrium that includes an energy term, changes in *energy* follow Le Châtelier's principle in a manner similar to changes in 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.

One way to add energy to a system is to heat it. Energy can be removed by cooling a system.

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

Q. For the reaction: $N_2(g) + O_2(g) + 90.0 \text{ kilojoules} \rightleftharpoons 2 \text{ NO}(g)$

1. If the reaction vessel is heated,
 - a. The equilibrium will shift to the (left or right?) _____
 - b. The $[O_2]$ will (increase or decrease?) _____.
 - c. The $[NO]$ will _____.
2. If the $[O_2]$ is decreased,
 - a. The equilibrium will shift to the _____
 - b. The $[N_2]$ will _____.
 - c. The temperature will _____.

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Answers

1. a. The equilibrium shifts to the **right**. Energy is a term on the left, so if energy is added, the system shifts the equilibrium to the right.
- b. The $[O_2]$ **decreases**. If heat is needed to cause a reaction on one side, adding heat drives the rate of that reaction to increase, using up other substances on that side.
- c. The $[NO]$ **increases**. Adding energy (a term on the left) causes more of substances on the right to form.

2. a. The equilibrium shifts to the **left**. b. The $[N_2]$ **increases**.
- c. Shifting the equilibrium to the left makes more of the terms shown on the left, including more energy. In this system, the increased heat will be manifested as an increase in average kinetic energy: the temperature **increases**.

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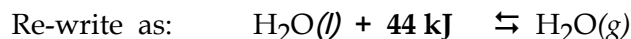
When working with Le Châtelier's principle, if an energy term is expressed in ΔH notation, it helps to re-write the equation with the energy term written *inside* the equation with a *positive* sign.

Examples: To apply Le Châtelier's principle for energy

Convert a *negative* ΔH to a positive term on the *right*.

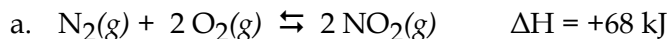


Convert a *positive* ΔH to a positive term on the *left*.



Practice B First learn the rules, then do the problems.

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 22B.)



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



- a. If the temperature is decreased,
- equilibrium will shift to the (left or right?) _____.
 - $[CH_3OH]$ will (increase or decrease?) _____.
- b. If the $[H_2]$ is increased,
- equilibrium will shift to the _____.
 - $[CH_3OH]$ will _____.
 - The temperature in the vessel will _____.
3. In a closed system, for the reaction: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad \Delta H = -93 \text{ kJ}$
- 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. $[\text{PCl}_5]$ will _____.
- c. If the $[\text{Cl}_2]$ is increased,
1. equilibrium will shift to the _____.
 2. $[\text{PCl}_3]$ will _____.
 3. The temperature in the vessel will (inc. or dec.?) _____.

Changes in Pressure

Pressure will affect an equilibrium which is composed of reacting gases, but only if one side of the equation has more moles of gas than the other. For a reversible reaction at equilibrium that includes gases that are reacting,

- Increasing the *pressure* on the system will shift the equilibrium to create *fewer total moles* of gas.
- Decreasing the pressure on the system will shift the equilibrium to create more moles of gas.
- Changing the pressure does not shift the equilibrium if the total of the gas coefficients is the same on both sides.

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 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 in the piston to decrease the volume of the container increases the pressure on the gases and the balancing pressure exerted by the gases. Pulling the piston out a distance increases the container volume and decreases the pressure on and of the gases.

For a system of reacting gases at equilibrium (which must be a closed system),

- Decreasing the volume increases the pressure, shifting the equilibrium to create fewer gas molecules.
- Increasing the volume decreases the pressure, shifting the equilibrium to create more gas molecules.

However, adding a *non*-reacting gas to a reaction mixture at constant volume will not shift the equilibrium. Such a change will not change the moles per liter of the reacting gases or the partial pressures they exert, and as a result the equilibrium will not shift.

* * * * *

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

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

1. If the pressure on the gases in the reaction vessel is decreased,
 - a. The equilibrium will shift to the (left or right?) _____

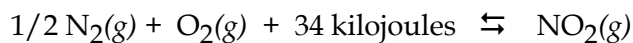
- b. The moles of NO_2 will (increase or decrease?) _____.
- c. The moles of N_2O_4 will (increase or decrease?) _____.
- d. The temperature in the vessel will (increase or decrease?) _____.
2. If the volume of the reaction container is decreased by a piston,
 - a. The equilibrium will shift to the (left or right?) _____
 - b. The moles of N_2O_4 will (increase or decrease?) _____.
 - c. The temperature in the vessel will (increase or decrease?) _____.
3. If helium gas is added to the vessel, equilibrium shifts (left or right?) _____

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- 1a. Equilibrium shifts **left**. Decreasing pressure favors the side with more gas molecules.
- 1b. Moles of NO_2 **increase** as equilibrium shifts left. 1c. Moles of N_2O_4 **decrease**.
- 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. A way it can do so is to make fewer gas molecules.
- 2b. Moles of N_2O_4 **increase** as the equilibrium shifts to the side with fewer gas moles.
- 2c. 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.
3. Helium, a noble gas, does not react with other substances. Adding non-reacting gases does not shift an equilibrium with reacting gases.

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,
 1. equilibrium will shift to the _____.
 2. Moles of NO_2 will _____.
 3. The temperature in the vessel will _____.
- c. If the volume of the reaction vessel is increased,
 1. Equilibrium will shift to the _____.
 2. Moles of O_2 will (increase or decrease?) _____.
 3. The temperature in the vessel will _____.

2. In the equilibrium: $C_6H_{12}O_6(s) + 6 O_2(g) \rightleftharpoons 6 CO_2(g) + 6 H_2O(l)$
 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,
 $CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$, the cap is left off the bottle,
- in which direction will the reaction shift? _____
 - What will happen to the acidity of the beverage? _____.

Concentration Changes: Special Cases

There are two special rules for concentration changes.

1. For a reaction at equilibrium, adding or removing a *solid* or a *liquid* does not shift the equilibrium.

Solids have a constant concentration determined by their density. Adding or removing solid does not change the concentration of the solid, and therefore 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: $NaCl(s) \rightleftharpoons NaCl(aq)$ 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 does not increase the *concentration* of the solid salt or the *dissolved* salt. Adding a solid does not shift the equilibrium concentrations.

In a solid substance, the particles are tightly packed: about as concentrated as they can be. If you hit a solid substance with a hammer, its particles may separate into pieces, but they will not permanently compress. The concentration of a solid substance is constant.

Pure liquids also have a constant concentration at a given temperature. 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 the *solvent* for a reaction is a term in the equation, adding more solvent, or using up or forming solvent in the reaction, does not shift the equilibrium, because the high concentration of a solvent is difficult to change.

By definition, a solvent is a substance present in very high concentration compared to the other substances present in a solution. This means that in reasonably dilute

solutions, the solvent concentration remains very close to constant even if it is used up or formed in the reaction occurring in the solvent.

In chemistry and in living systems, the solvent encountered most often is liquid water. Adding more water to an aqueous solution at equilibrium will not substantially shift the equilibrium. Even reactions that use up or form water will not significantly change the concentration of water if water is the solvent for the reaction.

Catalysts: No Shift

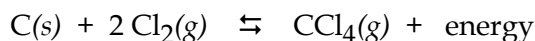
A **catalyst** is a substance that is not used up in a reaction, but when added to a reaction mixture, increases the rate of the reaction.

Adding a catalyst to a mixture at equilibrium will not shift the equilibrium.

However, adding a catalyst will cause the reaction to reach equilibrium more quickly.

Practice D. Commit the rules for Le Châtelier's principle to memory, then work these problems. Check your answers after each lettered section. Save the last problem as a review for your next study session.

1. For the reaction at equilibrium at high temperature

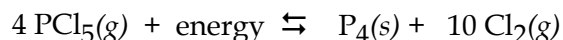


- a. If the $[\text{Cl}_2]$ is decreased,
 1. Equilibrium will shift to the (left or right?) _____.
 2. $[\text{CCl}_4]$ will (increase or decrease?) _____.
 3. $[\text{C}]$ will _____.
 4. The amount of carbon will _____.
 5. The temperature in the reaction vessel will _____.
 - b. If the pressure in the reaction vessel is decreased,
 1. Equilibrium will shift to the _____.
 2. Moles of Cl_2 will _____.
 3. The temperature in the reaction vessel will _____.
 - c. If a catalyst is added, equilibrium will shift to the _____.
2. Consider the following system at equilibrium.
- $$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)$$
- a. If liquid water is added, equilibrium will shift to the (left or right?) _____.

- b. If the $[\text{OH}^-]$ is increased:
1. Equilibrium will shift to the _____.
 2. $[\text{CH}_3\text{COOH}]$ will _____.
 3. $[\text{H}_2\text{O}]$ will _____.
- c. If H^+ is added:
1. Equilibrium will shift to the _____.
 2. $[\text{CH}_3\text{COO}^-]$ will _____.
3. For this system at equilibrium:



- a. If the $[\text{O}_2]$ is increased,
1. Equilibrium will shift to the _____.
 2. $[\text{HCl}]$ will _____.
- b. If the $[\text{HCl}]$ is decreased,
1. equilibrium will shift to the _____.
 2. $[\text{O}_2]$ will _____.
 3. $[\text{Cl}_2]$ will _____.
 4. The temperature in the reaction vessel will _____.
- c. If the temperature in the reaction vessel is decreased,
1. equilibrium will shift to the _____.
 2. $[\text{O}_2]$ will _____.
 3. $[\text{H}_2\text{O}]$ will _____.
- d. If the total pressure on the gases in the vessel is increased,
1. equilibrium will shift to the (left or right?) _____.
 2. Moles of O_2 will _____.
 3. Moles of Cl_2 will _____.
 4. The temperature in the reaction vessel will _____.
- e. If a piston is used to increase the volume of the vessel,
1. equilibrium will shift to the _____.
 2. Moles of O_2 will _____.
 3. Moles of H_2O will _____.
- f. If a catalyst is added to the reaction mixture,
1. equilibrium will shift to the _____.
 2. $[\text{O}_2]$ will _____.
4. For this system at equilibrium:



- a. If the temperature in the reaction vessel is decreased,
1. equilibrium will shift to the _____.
 2. $[\text{Cl}_2]$ will _____.
 3. $[\text{PCl}_5]$ will _____.
 4. $[\text{P}_4]$ will _____.

- b. If a piston is used to decrease the volume of the vessel,
- equilibrium will shift to the _____.
 - Moles of Cl_2 will _____. 3. Moles of PCl_5 will _____.
 - The number of gas molecules in the vessel will _____.

ANSWERS

Practice A

- For $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$
 - If $[\text{H}_2]$ is increased: 1. Equilibrium shifts **right**. 2. $[\text{N}_2]$ will **decrease**. 3. $[\text{NH}_3]$ will **increase**.
 - If $[\text{N}_2]$ is decreased: 1. Equilibrium shifts **left**. 2. $[\text{H}_2]$ will **increase**. 3. $[\text{NH}_3]$ will **decrease**.

Practice B

- 1a. $\text{N}_2(g) + 2 \text{O}_2(g) + 68 \text{ kJ} \rightleftharpoons 2 \text{NO}_2(g)$ 1b. $\text{C}(g) + \text{O}_2(g) \rightleftharpoons \text{CO}_2(g) + 394 \text{ kJ}$
- For $\text{CO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g) + \text{energy}$
 - If the temperature is decreased: 1. Equilibrium shifts **right**. 2. $[\text{CH}_3\text{OH}]$ will **increase**.
 - 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**.
- $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g) + 93 \text{ kJ}$
 - If temperature is increased: 1. Equilibrium shifts **left**. 2. $[\text{PCl}_5]$ will **decrease**.
 - If $[\text{Cl}_2]$ is increased: 1. Equilibrium shifts **right**. 2. $[\text{PCl}_3]$ will **decrease**. 3. Temp. **increases**.

Practice C

- For $1/2 \text{N}_2(g) + \text{O}_2(g) + 34 \text{ kilojoules} \rightleftharpoons \text{NO}_2(g)$
 - Which side has fewer gas molecules? Left has 1.5 moles, **right** has 1 mole.
 - If pressure is increased: 1. Equilibrium shifts **right**. 2. Moles of NO_2 **increase**. 3. Temp. **decreases**.
 - If volume is increased, pressure is decreased; equilibrium shifts to **left** side which has more gas moles.
 - Moles of O_2 will **increase**. c3. The temperature will **increase**.
- For the equilibrium: $\text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{O}_2(g) \rightleftharpoons 6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l)$
Pressure will not shift the equilibrium, since both sides have the same 6 moles of gas.
- For $\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^-(aq)$ if the cap is left off the bottle,
 - As the CO_2 escapes, the forward rate slows, and the net reaction shifts **left**.
 - As the CO_2 escapes, the $[\text{H}^+]$, which determines the level of acidity, will **decrease**.

Practice D

1. For $C(s) + 2 Cl_2(g) \rightleftharpoons CCl_4(g) + \text{energy}$
 - a. If the $[Cl_2]$ is decreased: 1. Equilibrium shifts **left**. 2. $[CCl_4]$ will **decrease**. 3. $[C]$ will **not change**, because C is solid. 4. Amount of carbon **increases**. 5. Temp. **decreases**.
 - b. If pressure is decreased: 1. Equilibrium shifts **left** because left has 2 gas moles and right has one. Decreasing pressure favors side with more gas moles. 2. Moles of Cl_2 **increase**. 3. Temp. **decreases**.
 - c. Catalysts do not shift the position of an equilibrium.

2. For $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
 - a. If water is added, the equilibrium **does not shift**. In an aqueous reaction, water is the solvent, and adding solvent does not shift an equilibrium.
 - b. If $[OH^-]$ is increased: 1. Equilibrium shifts **left**. 2. $[CH_3COOH]$ will **decrease**.
3. $[H_2O]$ will **not change**. Adding solvent does not shift an equilibrium.
 - c. If H^+ is added: 1. H^+ neutralizes OH^- , lowering $[OH^-]$, so equilibrium shifts **right**.
2. $[CH_3COO^-]$ **decreases**.

3. For $2 H_2O(g) + 2 Cl_2(g) + \text{energy} \rightleftharpoons 4 HCl(g) + O_2(g)$
 - a. If $[O_2]$ is increased: 1. Equilibrium shifts **left**. 2. $[HCl]$ will **decrease**.
 - b. If $[HCl]$ is decreased: 1. Equilib. shifts **right**. 2. $[O_2]$ will **increase**. 3. $[Cl_2]$ will **decrease**.
4. Energy is used up when the reaction goes left, so temperature will **decrease**.
 - c. If temperature is decreased: 1. Equilibrium shifts **left**. 2. $[O_2]$ will **decrease**.
3. $[H_2O]$ will **increase**. If water is in the gas state as steam, its concentration can change.
 - d. If the total P is increased: 1. The right has 5 gas moles, the left has 4; lowering pressure favors the **left** side. 2. Moles of O_2 **decrease**. 3. Moles of Cl_2 **increases**. 4. Temperature **increases**.
 - e. If V increases: 1. P decreases; equilib. shifts **right**. 2. Moles O_2 **increase**. 3. Moles H_2O **decrease**.
 - f. If catalyst is added: 1. Equilibrium **will not shift** 2. $[O_2]$ will **not change**.

4. For: $4 PCl_5(g) + \text{energy} \rightleftharpoons P_4(s) + 10 Cl_2(g)$
 - a. If temp. is decreased: 1. Equilib. shifts **left**. 2. $[Cl_2]$ will **decrease**. 3. $[PCl_5]$ gas **increases**.
4. $[P_4]$, since it is a solid, will **not change**.
 - b. If V decreases: 1. P increases, and equilibrium shifts to **left** side with fewer moles of gas.
2. Moles of Cl_2 **decreases**. 3. Moles of PCl_5 gas **increases**.
4. Number of gas molecules **decreases**.

* * * * *

Lesson 28B: Powers and Roots of Exponential Notation

Timing: Complete this lesson *before* calculations involving K (the equilibrium constant).

Prerequisites: Review Module 1 on Scientific Notation if needed.

Pretest: If you can solve these problems correctly, skip to Lesson 28C. Express your final answers in scientific notation. Answers are at the end of this lesson.

- Without using a calculator, write the answer to: $(3.0 \times 10^3)^3 =$
- Use a calculator. $(4.5 \times 10^{-4})^2 =$
- Do not use a calculator. 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 x^2 key. To calculate both squares and higher powers, most calculators also have power functions labeled x^y or y^x or $(y)^x$ or \wedge .

To learn to use the power keys, you may check your calculator manual, 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.

$$2^3 =$$

* * * * *

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

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

Write your key sequence: _____.

To test your key sequence, first solve in your head, then apply your sequence on the following problems. Make sure that you get the same answers in your head and on the calculator. [In this lesson, assume whole numbers (those without a decimal) are *exact* numbers for purposes of significant figures.]

a. $2^4 =$

b. $3^4 =$

c. Do *two* ways on keys: $12^2 =$

* * * * *

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

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

d. $16^3 =$

e. $2.500^4 =$

f. $0.50^2 =$

* * * * *

Answers: d. 4096 e. 39.06 f. 0.25

Note that each of the calculations above can be done in at least two ways. Complex calculator operations should always be done in two different ways as a check on your calculator use.

Taking Exponential Notation to a Power Without a Calculator

- Recall the 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}

- 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.

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

* * * * *

Answers: a. 9×10^6 b. 8×10^{-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 used above to take fixed decimal 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 the answer without using a calculator at all.

Let's learn with an example.

- a. Using a calculator as needed and any method you prefer, write an answer in scientific notation to:

$$(3.5 \times 10^{-4})^3 =$$

Now let's check the answer. Write your answers to *parts b* and *c* below *without* converting to scientific notation at the end and *without* a calculator.

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

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

* * * * *

For 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 the (b) and (c) answers,

write an *estimate* of what $(3.5 \times 10^{-4})^3$ should be: _____.

* * * * *

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

- e. Calculate $(3.5)^3$ using a y^x -type calculator function: _____

- f. Calculate $(3.5)^3$ on the calculator *without* the y^x or \wedge -type keys.

* * * * *

Multiply: $3.5 \times 3.5 \times 3.5 =$ _____. 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

and apply *sf*: _____

* * * * *

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

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

- A "standard TI-type" calculator *may* use 3.5 $\boxed{\text{E or EE}}$ 4 $\boxed{+/-}$ $\boxed{y^x}$ 3 $\boxed{=}$
- A graphing calculator *might* use 3.5 $\boxed{\text{EE}}$ $\boxed{(-)}$ 4 $\boxed{\text{enter}}$ $\boxed{\wedge}$ 3 $\boxed{\text{enter}}$
- On an RPN calculator, try 3.5 $\boxed{\text{E or EE or EXP}}$ 4 $\boxed{+/-}$ $\boxed{\text{enter}}$ 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. Then practice the calculation until you can repeat it without looking at hints or directions.

Write the calculator answer, rounded to proper *sf*: _____.

- i. 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 on the calculator? Which method is easier to remember?

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 should be done two *different ways* as a check on your calculator use. Estimating the math “in your head” is a good way to check a calculator answer.

Practice A:

1. Do *not* use a calculator on these.

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

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

2. Write answers without a calculator, then convert to the final answers to scientific notation.

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

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

On problems below,

- First write an *estimated* answer, then re-write the estimate in scientific notation;
- Then use the calculator for whatever parts you wish and write a *final* answer in scientific notation.

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

3. $(2.1 \times 10^6)^2$ Est =

Sci Note =

Calc =

4. $(3.9 \times 10^{-2})^3$ Est =

Sci Note =

Calc =

5. $(7.70 \times 10^4)^4$ Est =

Sci Note =

Calc =

6. $(5.5 \times 10^{-2})^3$ Est =

Sci Note =

Calc =

Roots

To calculate a *square* root, some calculators have a square root button: \sqrt{x} or $x^{1/2}$.

Other calculators use this two-key sequence: $2^{\text{nd or INV}} x^2$.

However, to take a *cube* root or higher, you will need to use a different key sequence. You will also need to know multiple ways to take roots in order to check your calculations. One way to do this is to treat taking a root of a term as taking the term to a fractional power.

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 *cube* root of x can be written as $x^{1/3}$. $16^{1/4}$ means the fourth *root* of 16.
- In general, $\sqrt[y]{x} = x^{1/y}$.

Taking Higher Roots

On many calculators, both square and higher *roots* may be calculated using the 2nd or INV key followed by the keys used to calculate *powers*, such as y^x or $(y)^x$ or ^.

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

Knowing at least two ways to calculate a root 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 ways to calculate a root.

Once you determine two key sequences that work, it is important to practice and test those sequences by entering sample calculations that are easy to check. Do the following calculation in your head.

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

* * * * *

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

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

Write one and if possible *two* key sequences that work and make sense to you.

To take a root: _____

Then, on the problems below, *check* your key sequence. First try the problem “in your head” and write your answer. Then solve two different ways using the calculator.

- | | |
|-----------------------------------|---------------------|
| a. $16^{1/4}$ in your head = | On the calculator = |
| b. $125^{1/3}$ in your head = | On the calculator = |
| c. $(0.001)^{1/3}$ in your head = | On the calculator = |
| d. $(0.008)^{1/3}$ in your head = | On the calculator = |

★ ★ ★ ★ ★

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 _____.
- For problems c and d above, start from the answer, reverse the process using your power key sequences, and see whether the result is the original number.

Practice B:

Take these roots by entering the numbers into a calculator. Try each two ways.

- | | |
|-------------------------------|-------------------------|
| 1. The square root of 9,025 = | 2. $(0.004096)^{1/3} =$ |
|-------------------------------|-------------------------|

Roots of Divisible Powers of 10

When estimating roots for numbers in exponential notation, it is important to be able to take a root of 10^x without a calculator. In some cases, this is easy.

- 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 calculate the root of an evenly divisible exponential term, use these steps.

1. Write the *root* as a *fractional* exponent.

Example:

Write the *square* root of 10^x as $(10^x)^{1/2}$, and the *fourth* root of 10^x as $(10^x)^{1/4}$.

2. 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 C

- Do not use a calculator. Write answers to these as powers of 10.
 - The square root of $10^{12} =$
 - $(10^6)^{1/2} =$
 - The cube root of $10^{-6} =$
 - $(10^{-12})^{1/4} =$
 - Which root is this equivalent to: $x^{0.125}$? 3. Without a calculator: $81^{0.25} =$
-
-

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, solve: $(8.0 \times 10^{15})^{1/3} =$

* * * * *

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

Treat exponentials as exponentials. $(10^{15})^{1/3} = 10^5$

$$(8.0 \times 10^{15})^{1/3} = 2.0 \times 10^5$$

For roots that cannot be solved by inspection, use these steps.

- If the exponential term is *not* evenly divisible by the root, make the exponent *smaller* (and significant larger) until the exponent times the fractional power results in a whole number.

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

* * * * *

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

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

- Without a calculator, write a rough *estimate* of the root of the significant in front of the *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, you might guess ≈ 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 value that has 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**.

$(10^{-6})^{1/3}$ without the calculator is **10^{-2}** .

Combine those two parts. Answer = **4.32×10^{-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 calculator, try **8.04** EE 5 +/- 2nd or INV y^x 3 =

and/or try **8.04** E or EE or EXP 5 +/- y^x (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^x

The calculator answer should match the step 3 answer.

Circle or write one or two key sequences that work: _____

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 to an evenly divisible root. However, using that conversion to estimate the root is a good way to *check* the calculator result. Complex calculations must be done in *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 this answer *without* a calculator: The cube root of $10^{16} =$ _____

* * * * *

To find the root without a calculator, the power of 10 must be divisible by 3. Try changing the exponent to 15, to make it smaller and divisible.

If the exponent is changed from 16 to 15, how must the value be written?

* * * * *

$$(10^{16})^{1/3} = (10 \times 10^{15})^{1/3} =$$

* * * * *

Finish estimating the answer.

Estimate: $(10^{16})^{1/3} = (10 \times 10^{15})^{1/3} = (10^{1/3} \times 10^5) \approx 2.2 \times 10^5$

Now try taking the cube root of 10^{16} on the calculator.

* * * * *

You *may* need to enter 1×10^{16} to take the root.

* * * * *

Answer: 2.15×10^5 Compare this to your estimate.

Summary: Roots and Powers

- If you are not certain that you are using calculator keys correctly, do a *simple* similar calculation, first on *paper* and then on the calculator.
- For complex operations on a calculator, do each calculation a *second* time. Use estimates on paper with rounded numbers *or* use different steps or keys.
- When working with exponential notation, it is often easier to do the numbers on the calculator but the exponents on paper.
- In calculations using exponential notation, handle numbers and exponential terms separately. Do numbers by number rules and exponents by exponential rules.
 - When you multiply exponentials, you add the exponents.
 - When you divide exponentials, you subtract the exponents.
 - To take an exponential to a power, multiply the exponentials.
- To take roots of exponential notation without a calculator:
 - Convert roots to fractional exponents, then
 - Adjust the exponential to be smaller and the significand to be larger to make the exponent evenly divisible by the root.

Practice D

- Fill in the blanks.
 - $4 \times 4 \times 4 = \underline{\hspace{2cm}}$, so $(\underline{\hspace{2cm}})^{1/3} = 4$.
 - Using your calculator, find the cube root of 64: $\underline{\hspace{2cm}}$
 - $64 = 6.4 \times 10^1$, so $(6.4 \times 10^1)^{1/3}$ should equal $\underline{\hspace{2cm}}$.
Find this root using the calculator: $(6.4 \times 10^1)^{1/3} =$
 - $0.4 \times 0.4 \times 0.4 = 0.064 = 6.4 \times 10^{-2}$, 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. Complete the problems below using the following steps. Do as many as you need to feel confident. Check your answer after each part.
- First convert the given amount to have an exponent with a divisible root.
 - Write an *estimated* answer for the root.
 - Starting from the divisible root, use the calculator for the root of the number, take the root of the exponential in your head, write the answer, then convert the answer to scientific notation. Round the significand to two digits.
 - Take the root of the original exponential notation on the calculator.
 - Compare your answers in steps B, C, and D.
- $(6.0 \times 10^{23})^{1/3}$ Divisible = _____ Root Est. = _____
 Estimate in SciNote = _____ Calculator = _____
 - $(10^{15})^{1/4}$ Divisible = _____ Root Est = _____
 Estimate in SciNote = _____ Calculator = _____
 - The cube root of 1.25×10^{-7} Divisible = _____ Est = _____
 Estimate in SciNote = _____ Calculator = _____
 - $(1.6 \times 10^{-11})^{1/4}$ Divisible = _____ Root Est = _____
 Estimate in SciNote = _____ Calculator = _____

Practice E: Use a calculator as needed.

- $2^4 =$
- $(0.25)^4 =$
- $(4.5 \times 10^3)^5 =$
- $(2.0 \times 10^5)^6 =$
- $(3.3 \times 10^{-3})^8 =$
- $(4.7 \times 10^{-4})^4 =$
- $(81)^{1/4} =$
- $\sqrt[5]{0.01024} =$
- $(6.20 \times 10^4)^{1/8} =$
- The sixth root of $9.5 \times 10^{15} =$
- $(3.3 \times 10^{-3})^{1/9} =$
- $(6.5 \times 10^{-3})^7 =$

ANSWERS

Pretest: 1. 2.7×10^{10} 2. 2.0×10^{-7} 3. 2.0×10^8 4. 6.3×10^1

Practice A

- $(10^{-3})^2 = 10^{-6}$
- $(10^{-5})^{-2} = 10^{+10}$
- $(2.0 \times 10^4)^4 = 16 \times 10^{16} = 1.6 \times 10^{17}$
- $(3.0 \times 10^{-1})^3 = 27 \times 10^{-3} = 2.7 \times 10^{-2}$

3. $(2.1 \times 10^6)^2 = 4.4 \times 10^{12}$

4. $(3.9 \times 10^{-2})^3 = 59 \times 10^{-6} = 5.9 \times 10^{-5}$

5. $(7.70 \times 10^4)^4 = 3,515 \times 10^{16} = 3.52 \times 10^{19}$

6. $(5.5 \times 10^{-2})^3 = 166 \times 10^{-6} = 1.7 \times 10^{-4}$

Practice B

1a. 95 1b. 0.16

Practice C1a. 10^6 1b. 10^3 1c. 10^{-2} 1d. 10^{-3}

2. $x^{0.125} = x^{1/8} =$ the **eighth root** 3. $81^{0.25} = 81^{1/4} = (81^{1/2})^{1/2} = (9)^{1/2} = 3.0$

Practice D1a. 64 1b. 4 1c. 4 1d. 0.40 or 4.0×10^{-1}

2a. $(6.0 \times 10^{23})^{1/3} = (600 \times 10^{21})^{1/3} = (600^{1/3} \times 10^7) = 8.4 \times 10^7$

2b. $(10^{15})^{1/4} = (10^3 \times 10^{12})^{1/4} = (1000 \times 10^{12})^{1/4} = (1000^{1/4} \times 10^3) = 5.6 \times 10^3$

2c. $(1.25 \times 10^{-7})^{1/3} = (125 \times 10^{-9})^{1/3} = (125^{1/3} \times 10^{-3}) = 5.00 \times 10^{-3}$

2d. $(1.6 \times 10^{-11})^{1/4} = (16 \times 10^{-12})^{1/4} = (16^{1/4}) \times (10^{-12})^{1/4} = 2.0 \times 10^{-3}$

Practice E1. 16 2. 3.9×10^{-3} 3. 1.8×10^{18} 4. 6.4×10^{31} 5. 1.4×10^{-20} 6. 3.7×10^{-14} 7. 3.0 8. 0.4000 9. 3.97 10. 4.60×10^2 11. 0.53 12. 4.9×10^{-16}

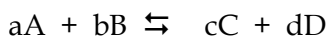
* * * * *

Lesson 28C: Equilibrium Constant Expressions**Prerequisites:** Read the introduction to Module 28 and complete Lesson 28B before starting this lesson.**Pretest:** If you are familiar with equilibrium constants, try Problems 2 and 3 in Practice C at the end of this lesson. If you can do those problems correctly, you may skip this lesson.

* * * * *

The Law of Mass Action

At a fixed temperature, for the general reversible reaction

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

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

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

- The *concentrations* of the particles in the *products* are *multiplied on top*.

- The concentrations of particles on the left side (reactants) are multiplied on the bottom.
- The *coefficient* for each substance becomes the *power* of its concentration.

Example:

For the reaction
$$\text{S}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{S}(\text{g})$$

The equilibrium constant *expression* is
$$K = \frac{[\text{H}_2\text{S}]^2}{[\text{S}_2][\text{H}_2]^2}$$

An equilibrium constant **equation** has two parts:

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

A **K equation** is the combination of the expression and value.

Example:

For the reaction
$$\text{S}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{S}(\text{g})$$

The equilibrium constant *value* is 1.1×10^7 at 973 K.

The equilibrium constant *equation* at 973 K is
$$K = \frac{[\text{H}_2\text{S}]^2}{[\text{S}_2][\text{H}_2]^2} = 1.1 \times 10^7$$

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

Note these conventions:

- We abbreviate kelvins as K and the equilibrium constant as an italicized *K*.
- If a concentration is written in a *K* expression, it must be a concentration measured at equilibrium: $[X]_{\text{at equilibrium}}$ or $[X]_{\text{at eq}}$. As a simplification, the label *at equilibrium* is often left off, but you should assume that all terms in a *K* expression are values *at equilibrium*.

Equilibrium Constant Expressions

To write a *K* expression, all that is needed is a balanced equation for a reaction. Try this problem.

- Q. For the Haber process reaction:
$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$$

write the equilibrium constant expression.

★ ★ ★ ★ ★

Answer

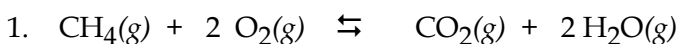
$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad \text{with all concentrations measured at equilibrium.}$$

The law of mass action 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,

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

Practice A: Write the equilibrium constant expression for these reactions.



Concentrations That Are Constant

The correlation between a balanced equation and its equilibrium constant expression is simple, but there is one important exception.

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

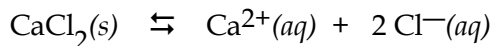
- *Solids, pure liquids, and solvents* have concentrations that do not change substantially during reactions.
- In place of terms for the concentration of *solids, pure liquids, and solvents* (including *liquid water*), a **1** is substituted in the *K* expression.

By convention, if the concentration of a particle involved in a reaction is essentially constant, that constant value is included in the *value* of the equilibrium constant. Mathematically, in the *K* expression, this is equivalent to substituting a 1 for the term.

The concentrations that are assigned a value of **1** in a *K* expression are the same as those that do not shift an equilibrium when applying Le Châtelier's principle.

Using the rules above, try the following example.

Q1. Write the equilibrium constant expression for this reaction.



* * * * *

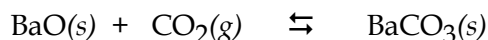
$$K = [\text{Ca}^{2+}] [\text{Cl}^{-}]^2$$

The reaction equation shows that the ions on the right are aqueous, meaning that the solvent for the reaction is water. When dissolved in a solvent, the concentration of ions can vary. Terms for concentrations that can vary are included in *K* expressions.

Because the reactant on the left is a solid, its concentration is assigned a value of 1.

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**. The **1** must be written if it is alone in the numerator (on top), but it is generally omitted when writing a K expression.

Try another. **Q2.** Write the equilibrium constant expression for this reaction.



* * * * *

Answer

$$K = \frac{1}{[\text{CO}_2]}$$

Both sides of the equation have solids, and in the place of the terms for the concentration of a solid, we write a **1**. Because the concentration of a gas can vary, the term for the gas concentration must be included in the K expression. A **1** must be included if it is in the numerator, but the 1 in the denominator is omitted as understood

Substance States

The *phase* or *state* (solid, liquid, gas, or aqueous) of a substance must be known in a K expression. However, if the balanced equation is also written and includes states, the states can be omitted as understood in the accompanying K expression.

Water: The “constant concentration terms = 1” rule means that a $[\text{H}_2\text{O}]$ term will be represented by a 1 in K expressions when the water is a solid (ice), a pure liquid, or a solvent. However, if water is a reactant or product in its *gas* phase (as vapor or steam), since all gases are compressible, its concentration can *vary*, and the term for $[\text{H}_2\text{O}(g)]$ must be included in the K expression.

In addition, when liquids are mixed with other liquids, they may dissolve in each other, as occurs with many alcohols and water. In such cases, if the concentrations are relatively close in value, the liquid concentrations *can* vary, and neither liquid is considered as the solvent. Concentrations that can *vary* are *included* in K expressions. The general rule is:

For H_2O , $[\text{H}_2\text{O}(g)]$ is included in K expressions; but $[\text{H}_2\text{O}(s)]$ and $[\text{H}_2\text{O}(l)]$ if pure or the solvent] are replaced by a **1**.

Vapor Pressure: Most solids and liquids release gas particles into a system at equilibrium, creating a measurable vapor pressure. However, because vapor pressure depends only on temperature, vapor pressure creates a constant pressure and gas concentration at each temperature. Because it is constant, the vapor pressure of solids and liquids is omitted as a factor in K expressions (but is a factor in the value of K).

Flashcards

In your notebook, make a list of the key rules covered so far in this module. Compare your list to the Summary at the end of the module for the topics covered so far. Then, as needed, design flashcards to help in moving the rules to long-term memory.

Practice B: Write the equilibrium constant expression for these reactions.

- $2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightleftharpoons 4 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$
 - $\text{BaO}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{BaCO}_3(\text{s})$
 - $\text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3 \text{Ca}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq})$
-

ANSWERS

Practice A

$$1. K = \frac{[\text{CO}_2][\text{H}_2\text{O}]^2}{[\text{CH}_4][\text{O}_2]^2} \qquad 2. K = \frac{[\text{CO}_2]^8[\text{H}_2\text{O}]^{10}}{[\text{C}_4\text{H}_{10}]^2[\text{O}_2]^{13}}$$

Practice B

$$1. K = \frac{[\text{CO}_2]^4}{[\text{C}_2\text{H}_6]^2[\text{O}_2]^7} \qquad 2. K = \frac{1}{[\text{CO}_2]} \qquad 3. K = \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{OH}^-]} \qquad 4. K = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

* * * * *

Lesson 28D: Equilibrium Constant Values

Why K Values Do Not Have Units

K values are *numbers without units*. This is in part because the K expression is a “shortcut” equation: a convenient simplification derived from more complex relationships in thermodynamics that are based on a unitless quantity called activity.

Concentrations and gas partial pressures are related to activity but are easier to measure directly, so we use their values in most calculations involving K . For “real” relationships in science, units must cancel properly, but in “shortcut” simplified equations, units may not.

For now, it is important to remember the following.

When solving calculations based on a K equation,

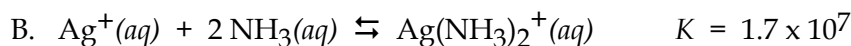
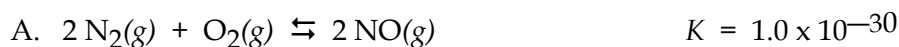
- K values are not assigned units.
- Units of concentration or pressure data must be made *consistent* before calculating.
- When solving for a concentration using K values, the unit M (mol/L) must be added to the answer.

K Values And The Favored Side

Equilibrium constant values are always positive numbers, and the values are 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 10 to a negative power).
- The more a reaction favors the products (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 that is positive, but is much less than one. At equilibrium, the substances on the left side (the reactants) will be favored.

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

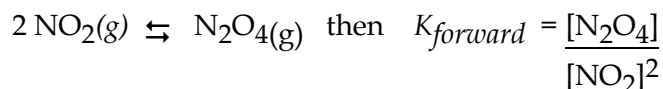
For K values much larger than one, the reactions go close to completion. For K values much smaller than one, the reaction goes only slightly.

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 more balanced mixture of reactants and products than in Reaction A or B.

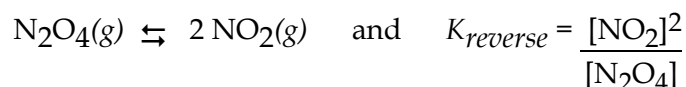
K Values For Reversed Reactions

Equilibrium is the result of a reversible reaction. Reversible reactions can be written in either direction. For this reason, in every K problem, the reaction equation must be written in order to define the forward direction.

Example: The conversion of nitrogen dioxide to dinitrogen tetroxide is reversible. If we designate this as the forward reaction:



By that designation, this means that the reverse reaction is



In the above example, the two equilibrium constant expressions are different, but related:

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

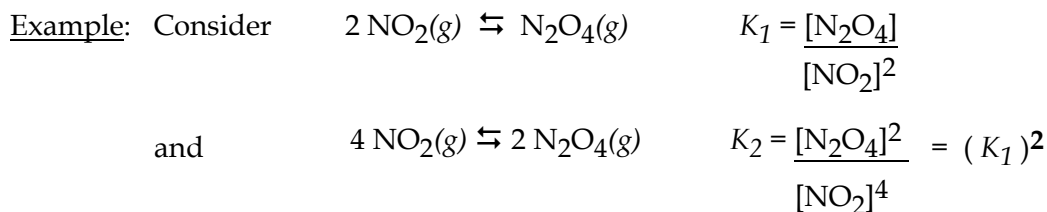
The relationship $K_f = 1/K_r$ will be true for all reactions. Stated in words:

If a reaction equation is reversed, the new K value is 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, and only one set of ratios will balance an equation, but different coefficients can be used to balance the equation so long as the coefficients 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 different coefficients can easily be determined.

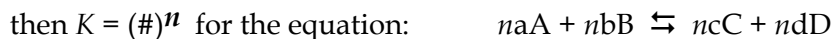


The coefficients of the second equation are double the first. The ratios are the same, and both equations are balanced. The K values will be different, but related. If the coefficients are *doubled*, the new K value for the K expression based on those doubled coefficients is the original K value *squared*.

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,

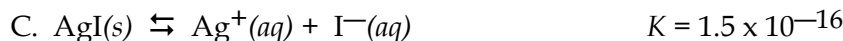
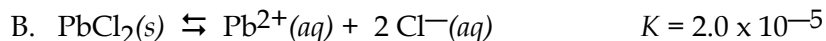
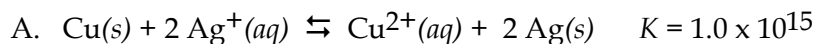


The factor n can be any positive number: an integer, decimal, or fraction.

This rule illustrates why, when you write a K value, the reaction coefficients on which it is based must also be shown by writing either the K expression or the balanced equation.

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

$$\text{Cu}^{2+}(aq) + 2 \text{Ag}(s) \rightleftharpoons \text{Cu}(s) + 2 \text{Ag}^+(aq)$$
- What will be the K expression and K value for the equation

$$1/2 \text{PbCl}_2(s) \rightleftharpoons 1/2 \text{Pb}^{2+}(aq) + \text{Cl}^-(aq)$$
- What will be the K expression and K value for the equation

$$1/2 \text{Cu}^{2+}(aq) + \text{Ag}(s) \rightleftharpoons 1/2 \text{Cu}(s) + \text{Ag}^+(aq)$$

ANSWERS

1A. $K = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$ 1B. $K = [\text{Pb}^{2+}][\text{Cl}^-]^2$ 1C. $K = [\text{Ag}^+][\text{I}^-]$

- Reaction A, with the largest K value, most favors the right side (products).
- Reaction C, with the K value much smaller than the others, will most favor the left side (reactants), and will form the smallest concentrations of products.
- This is reaction A written *backwards*. Both the K expression and K value will be the reciprocals of reaction 1.

$$K \text{ expression} = \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]} \quad K \text{ value} = K_r = \frac{1}{K_f} = \frac{1}{1.0 \times 10^{15}} = 1.0 \times 10^{-15}$$

- This is reaction B with all coefficients multiplied by 1/2. The K value will be the reaction B K value to the 1/2 power: the square root of the K in reaction B.

$$K \text{ expression} = [\text{Pb}^{2+}]^{1/2} [\text{Cl}^-] \quad K \text{ value} = (2.0 \times 10^{-5})^{1/2} = (20 \times 10^{-6})^{1/2} = 4.5 \times 10^{-3}$$

- This is reaction A written backwards and multiplied by 1/2. When writing the reaction backwards, invert the K value. When multiplying coefficients by 1/2, take the K value to the 1/2 power.

$$K \text{ expression} = \frac{[\text{Ag}^+]}{[\text{Cu}^{2+}]^{1/2}} \quad K \text{ value} = \text{square root of } \frac{1}{K_f} = (1.0 \times 10^{15})^{-1/2} = (10 \times 10^{-16})^{1/2} = 3.2 \times 10^{-8}$$

* * * * *

Lesson 28E: Equilibrium Constant Calculations

Equilibrium Constant Calculations

To solve equilibrium calculations in a systematic fashion, we add a step or two to our standard *equation* solving methods. Our rule will be,

For calculations involving K and concentrations, write the **WRECK** steps.

The **WRECK** steps are

1. **W (WANTED):** Write the **WANTED** unit and/or symbol.
2. **R (Reaction):** Write a balanced equation for the **Reaction**.
3. **E (Extent):** After the reaction, add the **Extent** of the reaction, such as: “(goes partially)” or “(goes ~100%).”
4. **Concentration@Eq:** List or calculate the concentrations at equilibrium for each of the particles in the reaction equation.
5. **K:** If the reaction goes to equilibrium, write the K equation.
6. Substitute numbers into the K equation, then SOLVE the K equation for the **WANTED** symbol.
7. If a *concentration* is calculated using an equilibrium equation, the unit moles/liter (M) must be added to the answer.

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

Apply the above 7-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 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, the concentrations at equilibrium are $[\text{H}_2] = 0.020 \text{ M}$ and $[\text{I}_2] = 0.32 \text{ M}$ and $K = 25$. Find $[\text{HI}]_{\text{at eq.}}$

* * * * *

Answer

For calculations involving K and concentrations, write the **WRECK** steps.

1. **W (WANTED):** ? = $[\text{HI}]_{\text{eq.}}$ in mol/L
2. **R (Balanced Reaction Equation):** $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$ (goes partially)
3. **E (Extent):** If a reaction goes to equilibrium; assume unless otherwise noted that it *goes partially* to completion.
4. **C:**

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

$$[\text{H}_2]_{\text{eq.}} = 0.020 \text{ M}$$

$$[\text{I}_2]_{\text{eq.}} = 0.32 \text{ M}$$

5. K :
$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 25 \quad \text{at equilibrium.}$$
6. Substitute numbers into the K equation, then SOLVE the K equation for the WANTED symbol.

Until this point, our rules have been:

- Always include units when you solve, and
- Solve in symbols before substituting numbers, because symbols move more quickly than numbers with their units.

For the special case of K calculations,

- Units are omitted from values substituted into K equations (since concentrations and gas pressures are a stand-in for the unitless quantity of activity); and
- You *may* plug numbers into the original equation, and move the numbers to solve, since numbers without units will likely move as quickly and accurately as symbols.

However, because unit cancellation will not catch mistakes, in K calculations you must carefully check your substitution and algebra.

Substitute the data numbers directly into the K equation above, solve, then check below.

* * * * *

$$\frac{[\text{HI}]^2}{(0.020)(0.32)} = 25 \quad \text{at equilibrium.}$$

$$[\text{HI}]^2 = (25)(0.020)(0.32) = 0.160 \quad (\text{Carrying an extra } sf \text{ until the final step.})$$

$$[\text{HI}]_{\text{eq.}} = \text{square root of } [\text{HI}]^2 = ([\text{HI}]^2)^{1/2} = (0.160)^{1/2} = \boxed{0.40 \text{ mol/L}}$$

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

Significant figures in K calculations: All numbers in the original data had 2 *sf*, so the answer is rounded to 2 *sf*. Coefficients are exact, and in terms such as $[\text{HI}]^2$ above, since the 2 is based on coefficients, the 2 is exact. All numbers based on coefficients have infinite *sf* and do not restrict the *sf* in an answer.

Practice

Update the list in your notebook of the key rules covered so far in this module. Make new flashcards as needed, and practice until you can answer them from memory. Then try the problems below.

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

at a certain temperature the equilibrium concentrations are:

$$[\text{NH}_3] = 0.050 \text{ M}, [\text{O}_2] = 0.0020 \text{ M}, [\text{NO}] = 0.50 \text{ M}, [\text{H}_2\text{O}] = 0.20 \text{ M.}$$

What is the value of K at this temperature?

2. Given the reaction: $2A + B \rightleftharpoons 4C$ (all gases), concentrations at equilibrium are $[A] = 0.050 \text{ M}$ and $[B] = 0.125 \text{ M}$. If $K = 0.020$, find $[C]$.
3. For this system in a 20. liter sealed container: $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{l})$ at equilibrium is found 0.40 mol CO_2 , 0.60 mol H_2O , and 0.90 mol H_2 . If the value of the equilibrium constant is 4.8, how many moles of CO are in the mixture?
4. For problems 2 and 3 above, in which problem are the products favored at equilibrium?

ANSWERS

1. For calculations involving K and concentrations, write the *WRECK* steps.

WANT: $? = K$

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

Extent: Goes to equilibrium, use K equation.

Conc@Eq. (See list in problem)

K: $K = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$ (Since this H_2O is a gas, it is included in the K equation.)

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

$$\begin{aligned} ? = K &= \frac{[0.50]^4 [0.20]^6}{[0.050]^4 [0.0020]^5} = \frac{[5.0 \times 10^{-1}]^4 [2.0 \times 10^{-1}]^6}{[5.0 \times 10^{-2}]^4 [2.0 \times 10^{-3}]^5} = \frac{(625 \times 10^{-4})(2.0)^6 \times 10^{-6}}{(625 \times 10^{-8})(2.0)^5 \times 10^{-15}} \\ &= \frac{(2.0)^6 \times 10^{-10}}{(2.0)^5 \times 10^{-23}} = \boxed{2.0 \times 10^{+13}} \quad (K \text{ values are written without units.}) \end{aligned}$$

The arithmetic may be done in any way that results in a correct answer.

If you need practice at exponential notation calculations, review Lessons 1C and 28B.

2. For calculations involving K and concentrations, write the *WRECK* steps.

WANT: $? = [A]$

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

Extent: Goes to equilibrium, use K .

Conc@Eq. (See list in problem)

K: $K = \frac{[C]^4}{[A]^2 [B]} = 0.020$

$$[C]^4 = K \cdot [A]^2 \cdot [B] = (0.020) (0.050)^2 (0.125) = 6.25 \times 10^{-6}$$

Then solve for the WANTED symbol.

$$[C] = (6.25 \times 10^{-6})^{1/4} = (625 \times 10^{-8})^{1/4} = \mathbf{5.0 \times 10^{-2} \text{ M} = 0.050 \text{ M}}$$

3. For calculations involving K and concentrations, write the *WRECK* steps.

WANT: ? = mol CO

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

Conc@Eq. $[\text{CO}] = ?$ $[\text{CO}_2] = ?$

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.

$$[\text{CO}_2] = 0.40 \text{ mol in } 20. \text{ liters} = \mathbf{0.020 \text{ mol/L}}$$

$$[\text{H}_2] = 0.90 \text{ mol}/20. \text{ L} = \mathbf{0.045 \text{ M}}$$

$$K: \quad K = \frac{[\text{CO}]}{[\text{CO}_2][\text{H}_2]} = \mathbf{4.8} \quad ([\text{Liquids}] = 1 \text{ in } K \text{ expressions.})$$

$$\text{SOLVE:} \quad [\text{CO}] = K \cdot [\text{CO}_2] \cdot [\text{H}_2] = (4.8)(0.020)(0.045) = \mathbf{0.00432 \text{ M CO}} \quad (\text{carrying extra } sf)$$

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

$$? = \text{mol CO} = 20. \text{ L} \cdot \frac{0.00432 \text{ mol CO}}{\text{L}} = \mathbf{0.086 \text{ mol CO}}$$

A good habit at the end of each long calculation is 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.

4. Problem 3 has a K value above 1. When products are favored, K values are greater than one.

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Lesson 28F: K_p Calculations

Prerequisites: Gas lessons 17A, 17D, 18D, and the prior lessons in Module 28.

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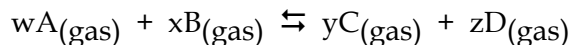
K_c Versus K_p

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

To distinguish between these two kinds of equilibrium constants,

- K_c is written instead of K for equilibrium constants based on concentration, and
- K_p is written for equilibrium constants based on pressures.

At a given temperature, for the general reaction



at equilibrium these ratios will be constant:

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

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 are not assigned units.
- Terms for pressures of solids and pure liquids are written as **1** in K_P expressions.

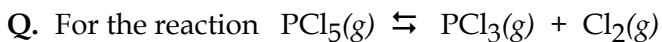
The differences between K_C and K_P include

- 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 K is written without a subscript, it is assumed to be 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 are solved using the same steps. Use the rule: "For calculations using K and concentrations *or* pressures, write the WRECK steps."

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



at 250°C , $K_P = 1.78$. If at equilibrium the partial pressures are 0.820 atm. for Cl_2 and standard pressure for PCl_5 , calculate the partial pressure of PCl_3 .

* * * * *

Answer

For calculations using K and concentrations *or* pressures, write the WRECK steps.

1. **W** (WANTED): $? = P_{PCl_3}$ in atm.
2. **R** (Balanced Reaction Equation): $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
3. **E** (Extent): This reaction goes to equilibrium (only partially to completion).
4. **Conc@Eq.** (In K_P calculations, use partial pressures in place of concentrations.)

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

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

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

5. K (Write the K equation):
$$K_p = \frac{P_{\text{PCl}_3} \cdot P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = 1.78$$

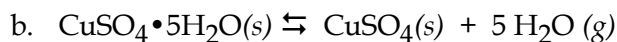
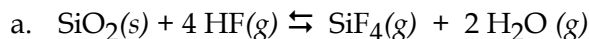
You may either plug the numbers into the equation above and solve or solve in symbols then numbers.

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

When using K_p to find a partial pressure, all pressure units in the DATA must be converted to atmospheres. If a pressure is WANTED, the unit atm. must be added to the answer.

Practice A

1. Write the K_p expression for each of these reactions.



2. For the reaction $\text{CH}_4(\text{g}) + 2 \text{ H}_2\text{S}(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 4 \text{ H}_2(\text{g})$ at 700°C ,

$K_p = 8.9 \times 10^{-4}$. If the partial pressures at equilibrium are 0.32 atm. for H_2 , standard pressure for CH_4 , and 50.5 kPa for CS_2 , calculate the partial pressure of H_2S .

Converting Between K_c and K_p

When all of the variable terms in a K expression are gases, either K_c or K_p equations can be applied to solve calculations, but the numeric *values* of K_c and K_p may or may not be the same. The rules are:

1. If the two sides of a balanced equation have the same number of total moles of gas (based on adding the coefficients of the gas terms), the K_c and K_p values are the same.
2. 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.
3. If either the K_c or K_p value is known at a given temperature, the other value can be calculated using

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

- **R** is the Gas Constant using atmospheres ($R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$)

- T is absolute temperature in kelvins, and
- Δn = (the sum of the coefficients of the gases in the *products*) MINUS (the sum of the coefficients of the gases in the *reactants*)

The number for Δn may be positive or negative, and it may be a fraction.

This conversion equation, including the Δn definition, must be memorized. As always when using K equations, the coefficients and reaction direction must be indicated in the calculation. In this K_p equation, the units for R and T must be as specified above, but units do not cancel in the calculation.

To learn to use the K_p to K_c conversion equation, write it and the Δn definition until it is in memory, then try the following problems.

Q1. Solve the conversion equation for the case in which the sum of the coefficients for the gases on both sides of the reaction equation are equal.

* * * * *

$$\boxed{K_p = K_c (RT)^{\Delta n}} \quad \text{If the moles of gas on both sides are the same,}$$

$$\Delta n = 0, K_p = K_c (RT)^0 = K_c (1) = K_c \quad \text{This matches rule 1 above:}$$

$$\boxed{\text{If the gas coefficient totals are equal on both sides, } K_p = K_c}$$

Q2. For the Haber Process reaction: $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$
if $K_c = 9.5$ at $300.^{\circ}C$, find K_p .

* * * * *

WANTED: K_p

DATA: $K_c = 9.5$

The fundamental equation that relates K_p and K_c is $\boxed{K_p = K_c (RT)^{\Delta n}}$.

$R = 0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$ (K_p calculations solve in liters and atm.)

$T = 300^{\circ}C + 273 = 573 \text{ K}$ (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.

* * * * *

$$\text{SOLVE: } \boxed{K_p = K_c (RT)^{\Delta n}} = 9.5 \cdot \{ (0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(573 \text{ K}) \}^{-2}$$

$$= 9.5 \cdot (47.04)^{-2} = 9.5 \cdot 4.52 \times 10^{-4} = \boxed{4.3 \times 10^{-3}}$$

In K calculations, units often do not cancel properly, and K values are not assigned units.

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 **effective** pressures and concentrations to be less than predicted based on 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 K calculations.

Flashcards

Update the list in your notebook of the key rules covered so far in this chapter. Make new flashcards as needed, and practice until you can do them from memory. Then try the problems below.

Practice B

- Convert these to scientific notation. Use a calculator as needed. Try to do each calculation two different ways.
 - $(3.33)^{-1} =$
 - $(3.5 \times 10^3)^{-2} =$
 - $(4.8 \times 10^{-3})^{-2} =$
- If $K_p = K_c (RT)^{\Delta n}$ and $\Delta n = +2$, which of these could be used to solve for K_c ?
 - $K_c = K_p \cdot R^2 \cdot T^2$
 - $K_c = K_p \cdot R^{-2} \cdot T^{-2}$
 - $K_c = \frac{K_p}{R^2 T^2}$
 - $K_c = \frac{K_p}{(RT)^2}$
- Calculate Δn for these reactions.
 - $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$
 - $NH_3(g) \rightleftharpoons 1/2 N_2(g) + 3/2 H_2(g)$
 - $CH_4(g) + 2 H_2S(g) \rightleftharpoons CS_2(g) + 4 H_2(g)$
 - $1/2 N_2(g) + O_2(g) \rightleftharpoons NO_2(g)$
 - $2 C_2H_6(g) + 7 O_2(g) \rightleftharpoons 4 CO_2(g) + 6 H_2O(g)$
 - $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$
- For which reactions in Problem 3 will $K = K_c$?
- If, for the reaction $2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$ at $27^\circ C$, $K_c = 1.3$, calculate K_p .
- If the Haber Process reaction is written as $NH_3(g) \rightleftharpoons 1/2 N_2(g) + 3/2 H_2(g)$ with a K_p of 670 at $600.^\circ C$,
 - What is the value of K_p for $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ at $600.^\circ C$?
 - What is the value of K_c for $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ at $600.^\circ C$?

ANSWERS**Practice A**

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

2. For calculations involving K and concentrations or pressures, write the *WRECK* steps.

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

R + E: $\text{CH}_4(g) + 2 \text{H}_2\text{S}(g) \rightleftharpoons \text{CS}_2(g) + 4 \text{H}_2(g)$ (goes to equilibrium)

C: $P_{\text{CS}_2} = 50.5 \text{ kPa} \cdot \frac{1 \text{ atm.}}{101 \text{ kPa}} = 0.500 \text{ atm.}$

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

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

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

In calculations using a K_p value, all pressures must be converted to atmospheres.

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

$$(P_{\text{H}_2\text{S}})^2 = \frac{P_{\text{CS}_2} \cdot (P_{\text{H}_2})^4}{P_{\text{CH}_4} \cdot K_p} = \frac{(0.500) \cdot (0.32)^4}{1.0 \cdot 8.9 \times 10^{-4}} = 5.89$$

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

Practice B

1a. 3.00×10^{-1} b. 8.2×10^{-8} c. 4.3×10^4

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.

3a. $2 - 4 = -2$ 3b. $2 - 1 = +1$ 3c. $5 - 3 = +2$ 3d. $1 - 1.5 = -0.5$ or $-1/2$

3e. $10 - 9 = +1$ 3f. $2 - 2 = 0$ 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 $K_p = K_c (RT)^{\Delta n}$.

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

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

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

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

$$= (1.3) \cdot (24.63)^{-1} = (1.3) \cdot (4.06 \times 10^{-2}) = \boxed{0.053}$$

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 .

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

6b. K_p was found in *part a*. K_c is WANTED. The equation relating K_p and K_c is $\boxed{K_p = K_c (RT)^{\Delta n}}$.

WANTED: K_c

DATA: $K_p = 2.2 \times 10^{-6}$

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

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

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

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

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

$$= (2.2 \times 10^{-6}) \cdot (5.14 \times 10^3) = \boxed{0.011}$$

* * * * *

Lesson 28G: K and RICE Moles Tables

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

To solve equilibrium calculations, we need a “chemistry accounting system.” For complex reactions, our rule has been to make a **RICE moles** table: **RICE** for the labels of the rows:

Reaction, Initial, Change, End/Equilibrium,

and **moles** for the *numbers* that go into the table.

We have previously used **RICE** tables to calculate mixture amounts at the end of a reaction (Lesson 10H). For reactions that go to *equilibrium*, a **RICE** table also is the preferred method to track changes in reactant and product amounts.

Our rule will be:

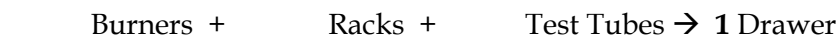
RICE Tables: In calculations for reactions that go to *equilibrium* (or for any reaction that is complex), to find moles, concentrations, or gas pressures, use a **RICE** table.

When using *RICE* tables for that go to *completion*, the limiting reactant has a count of zero in the *End* row. For reactions that go to equilibrium, all reactants and products must be present at equilibrium, so none of the reactant or product counts go to zero. Otherwise, the rules for *RICE* tables are the same.

Let's illustrate this method with a variation on our previous "lab drawer" problem.

- Q.** The morning chemistry lab assistant is filling lab drawers. The initial inventory contains 95 burners, 220 racks, and 2,500 test tubes. Into each top drawer is placed one Bunsen burner, two test tube racks, and 20 test tubes. When the afternoon assistant arrives, 60 racks remain in the inventory. How many drawers were filled? How many burners and test tubes remain in the inventory at the end of the process?

First balance this "equation" for the process:



Then, to solve, complete the following table.

Reaction/Process	___ Burner	___ Racks	__ Test Tubes	___ Drawer
Initial Count				
Change (use + and -)				
At Equilibrium (End)				

* * * * *

The initial data:

Reaction/Process	1 Burner	2 Racks	20 Test Tubes	1 Drawer
Initial Count	95	220	2,500	0
Change (use + and -)				
At Equilibrium (End)		60		

Adjust your work if needed then fill-in all of the boxes in the table.

* * * * *

Calculate the one change for which there is sufficient 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, when the mixture is at equilibrium.

* * * * *

Reaction/Process	1 Burner	2 Racks	20 Test Tubes	1 Drawer
Initial Count	95	220	2,500	0
Change (use + and -)	- 80	- 160	- 1,600	+ 80
At Equilibrium (End)	15	60	900	80

Note a key to the table: the *ratios* in Row 1 (Reaction) must match the ratios in Row 3 (Change). The coefficients determine the *Change* ratios.

This same method can be used to find values for moles for chemical substances at equilibrium. Construct a *RICE moles* table to solve this problem.

- Q.** A reaction that occurs at high temperatures (and can cause air pollution from car engines) is: $\text{N}_2 + \text{O}_2 \rightleftharpoons 2 \text{NO}$ (all gases). If 1.00 moles of N_2 , 2.00 moles of O_2 , and no NO are initially mixed, and at equilibrium, 1.80 moles of O_2 remains, how many moles of N_2 and NO are present at equilibrium?

* * * * *

WANT: moles of N_2 and NO at equilibrium.

Strategy: To solve for values at equilibrium, construct a *RICE moles* table.

Reaction	1 N_2	1 O_2	2 NO
Initial	1.00 mol	2.00 mol	0 mol
Change (use + and −)			
At Equilibrium		1.80 mol	

- Calculate the *change* that you can.
- Use the coefficients to complete the *Change* row. Coefficients show the *ratios* in which the moles of reactants are used up and moles of products form.
- Calculate the **Equilibrium** row: the moles present after the change.

* * * * *

The one change that can be calculated is below. Finish from here.

Reaction	1 N_2	1 O_2	2 NO
Initial	1.00 mol	2.00 mol	0 mol
Change (use + and −)		− 0.20 mol	
At Equilibrium		1.80 mol	

* * * * *

From the O_2 moles change and the ratios of reaction (the coefficients), the other changes can be calculated. Be sure to include the + and − signs. Complete the *Equilibrium* row.

Reaction	1 N_2	1 O_2	2 NO
Initial	1.00 mol	2.00 mol	0 mol
Change (use + and −)	− 0.20 mol	− 0.20 mol	+ 0.40 mol
At End/Equilibrium		1.80 mol	

* * * * *

Using the row labels, the WANTED moles at equilibrium can be found.

Reaction	1 N ₂	1 O ₂	2 NO
Initial	1.00 mol	2.00 mol	0 mol
Change (use + and -)	- 0.20 mol	- 0.20 mol	+ 0.40 mol
At End/Equilibrium	0.80 mol N ₂	1.80 mol O ₂	+ 0.40 mol NO

Practice A

- For the reaction $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$, the initial gas mixture is composed of 2.00 moles of H_2 and 1.00 moles of CO_2 . At equilibrium, 0.30 moles of CO gas is found. Calculate the moles of the other substances present at equilibrium.

RICE Tables Using Concentration and Pressure

Which *units* can be entered into a *RICE* table?

- Moles can always be used. *RICE* calculations are based on coefficients, and coefficients can always be read as moles.
- Concentrations (molarity) and gas pressures can also be used in *RICE* 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 of the moles are contained in the same volume, dividing each of the moles by that same volume will not change the ratios. The mole and the mol/L *ratios* will be the same, and the *RICE* table can be used to calculate either the *moles* or the *mol/L* used up and formed.

Pressure ratios will also be the same as mole ratios if volume is 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 18A) if V and T are constant. T must be constant for the system to be at equilibrium. Since coefficients are mole *ratios*, they will also hold for any ratios that are directly proportional to moles (n), which P is in this case.

- If gases or solutions are *added together* as part of a problem, measurements of the *initial* moles per liter and gas pressures cannot be substituted directly into a *RICE* table, because the volume that the moles are in varies during the process.

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. Using concentrations before mixing as concentrations that apply to a reaction that occurs after mixing would cause an error.

- If substances are mixed but all initial amounts are converted to *moles*, a *RICE* table can be used to solve. Dilution does not change the moles of substance present. From moles, the mol/L at equilibrium can be calculated if the total volume is known.

Bottom line?

- *RICE* tables can always be solved in moles.
- *RICE* tables can use values for *molarity* or *gas pressure* IF the *volume* in which the reactants and products are measured is the same in *all parts* of the problem.
- In *RICE* tables, units must be shown and must all be the same.

Practice B: Check your answers after each part.

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 with temperature held constant, the initial gas mixture contains $[\text{SO}_2] = 0.0100 \text{ M}$, $[\text{O}_2] = 0.0030 \text{ M}$, and no SO_3 . At equilibrium, $[\text{SO}_3] = 0.0040 \text{ M}$.
 - a. Calculate the concentrations of all reactants and products at equilibrium.
 - b. Use your *part a* answer to calculate a value for the equilibrium constant under these conditions.
 - c. Using your *part b* answer, calculate K for the reverse reaction.

Using *RICE* Tables with K Calculations

The values calculated in a *RICE* table can be used in K calculations, as was done in Part 2 of the Practice B problem above. However, care must be taken to write the *units* in a *RICE* table. Why?

- *RICE moles* tables can always be solved in *moles*, and moles are often supplied in problem data. K equations, however, require consistent units of either *mol/L* for solutions or gases or *atmospheres* for gases. K equations *cannot* be solved in moles.
- If data in a K calculation is supplied in moles, as is often the case, at some point the data must be converted to moles *per liter at equilibrium* before it is used in a K_C equation.

This means that in both the *RICE* table and the DATA table that is used with K calculations, it is important to distinguish measurements in moles (*mol*) from moles/liter (*M*).

When data is supplied in moles, it is often easiest to solve the *RICE* table in moles, *then* to convert the moles at equilibrium found in the table to moles *per liter*, then to substitute those values into K calculations.

Using those hints, try the following problem, then check your answer below.

- Q. For the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ (all gases), initial amounts are 0.100 moles of H_2 , 0.090 moles of I_2 , and no HI . At equilibrium, 0.020 moles of H_2 are present.
- a. Calculate the moles of all of the substances present at equilibrium.
 - b. If the reaction takes place in a 2.0 liter vessel, calculate the value of K .

★ ★ ★ ★ ★

a. WANT: Moles of H_2 , I_2 , and HI at equilibrium.

Strategy: To solve for values at equilibrium, use a RICE table.

★ ★ ★ ★ ★

Reaction	1 H_2	1 I_2	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 RICE tables, the units must be stated and must all be the same.

The bottom row answers Part A.

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

★ ★ ★ ★ ★

b. Part B involves a K value and concentrations. A K equation relates those terms.

The rule is: for calculations using K equations, write the WRECK steps.

1. WANTED unit or symbol. If the type of K is not specified, assume K means K_C .
2. Reaction: $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ (all gases)
3. Extent: The reaction goes to equilibrium. Use a K equation to solve.
4. Conc@Eq. The important rule is:

To find Concentrations at equilibrium (step C in the WRECK steps), calculate the values in the bottom row of a RICE table. Convert to moles/liter if needed to solve using K .

In the RICE moles table for this problem, we know moles at equilibrium, but a K_C equation requires mol/L. If needed, adjust your work.

★ ★ ★ ★ ★

All of these moles are in 2.0 L. In the DATA table, convert moles to the unit that measures the symbol: mol/L at equilibrium.

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

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

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

5. K (Write the K equation): $K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$ all measured at equilibrium

$$6. \text{ SOLVE: } K = \frac{(0.080)^2}{(0.010)(0.0050)} = \frac{64 \times 10^{-4}}{5.0 \times 10^{-5}} = \boxed{130}$$

If a K value is calculated, it is not assigned units. At the point when values are substituted into a K equation, the units are omitted. However, until that step, the units must be included with all DATA. The values for moles and moles per liter will often not be the same, so careful *labeling* of DATA with units and symbols is essential in order to keep track of which data to use at each step.

Practice C

If you find that you need to look back at the lesson when solving Practice problems, try to write and box in your notebook a summary of the rule that is needed. If possible, design a flashcard to help with remembering the rule.

- For the reaction $2 \text{NO} + \text{Cl}_2 \rightleftharpoons 2 \text{NOCl}$ (all gases), 0.40 mol NO and 0.60 mol Cl_2 are originally mixed in a 4.0 L sealed glass vessel. At equilibrium, 0.20 moles of NO gas remains.
 - Calculate the moles of Cl_2 and NOCl present at equilibrium.
 - Calculate the value for K under the above conditions.
 - Calculate the K value for this reaction: $\text{NO} + 1/2 \text{Cl}_2 \rightleftharpoons \text{NOCl}$ (all gases)

ANSWERS

Practice A

- WANTED: moles of H_2 , CO_2 , and H_2O at equilibrium.

Strategy: To find values at equilibrium when some of the data is *not* at equilibrium, use a RICE table.

Initial data:

Reaction	1 H_2	1 CO_2	1 H_2O	1 CO
Initial	2.00 mol	1.00 mol	0	0
Change				+ 0.30 mol
At Equilibrium				0.30 mol

Calculate the change row based on coefficients, then find the moles at equilibrium WANTED.

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Reaction	1 H_2	1 CO_2	1 H_2O	1 CO
Initial	2.00 mol	1.00 mol	0	0
Change	— 0.30 mol	— 0.30 mol	+ 0.30 mol	+ 0.30 mol
At Equilibrium	1.70 mol	0.70 mol	0.30 mol	0.30 mol

Practice B

1. WANTED: $[]_{\text{eq}}$ for all 3 substances, in mol/L .

DATA: measurements at equilibrium are WANTED, 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. Since the data is in mol/L, and you want mol/L, use mol/L as the units in the *RICE* table.

Reaction	2 SO ₂	1 O ₂	2 SO ₃
Initial	0.0100 M	0.0030 M	0 M
Change (use + and -)	- 0.0040 M	- 0.0020 M	+ 0.0040 M
At Equilibrium	0.0060 M	0.0010 M	0.0040 M

1b. For K calculations, write the *WRECK* steps.

WANTED = K

Reaction and Extent: $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$ (goes to *equilibrium* mixture)

Conc@Eq. Use the values in the *bottom row* of the *RICE* table.

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

These values substituted to find K must be concentrations at equilibrium, the values in the *bottom* row of the *RICE* table.

$$\text{SOLVE: } K = \frac{(4.0 \times 10^{-3})^2}{(6.0 \times 10^{-3})^2 (1.0 \times 10^{-3})} = \frac{16 \times 10^{-6}}{36 \times 10^{-9}} = 0.444 \times 10^3 = \boxed{440} \text{ (no units)}$$

1c. $K_{\text{reverse}} = \frac{1}{K_{\text{forward}}} = \frac{1}{440} = 2.3 \times 10^{-3}$ (K values do not have units)

Practice C

1a. WANTED: moles of reactants and products at equilibrium.

DATA: To find measurements at equilibrium when some supplied data is not, use a *RICE* table.

Since the WANTED unit is moles, solve the *RICE* table in *moles*.

Reaction	2 NO	1 Cl ₂	2 NOCl
Initial	0.40 mol	0.60 mol	0
Change (use + and -)	- 0.20 mol	- 0.10 mol	+ 0.20 mol
At Equilibrium	0.20 mol	0.50 mol	0.20 mol

1b. For calculations using K , write the *WRECK* steps.

WANTED: $K_{\text{c}} = ?$

Reaction and Extent: $2 \text{NO} + \text{Cl}_2 \rightleftharpoons 2 \text{NOCl}$ (all gases) (goes to an *equilibrium* mixture)

Conc@Eq. To find concentrations at equilibrium, use the bottom row of the *RICE moles* table.

In the above *RICE* table are *moles*. A K_C equation requires *mol/L* at equilibrium. All of these moles in the table are in **4.0 L**. In the data table, convert moles to the unit of each symbol: mol/L, then solve the K equation.

$$[\text{NOCl}]_{\text{eq.}} = 0.20 \text{ mol at eq.}/4.0 \text{ L} = \mathbf{0.0500 \text{ M at eq.}}$$
 (carry extra *sf* until end)

$$[\text{NO}]_{\text{eq.}} = 0.20 \text{ mol}/4.0 \text{ L} = \mathbf{0.0500 \text{ M}}$$

$$[\text{Cl}_2]_{\text{eq.}} = 0.50 \text{ mol}/4.0 \text{ L} = \mathbf{0.125 \text{ M}}$$

$$K_C = \frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]}$$

$$\text{Solve: } K = \frac{\cancel{(0.0500)^2}}{\cancel{(0.0500)^2}(0.125)} = \frac{1}{0.125} = \boxed{8.0}$$

1c. This is the original reaction with all coefficients multiplied by 1/2.

The new value of K is the value for original K taken to the power of the multiplier. $K = (\#)^n$

For this reaction, this is the K value for the original reaction taken to the 1/2 power: the square root of the original K .

$$K \text{ value with coefficients halved} = (8.0)^{1/2} = \mathbf{2.8}$$

* * * * *

Lesson 28H: K Calculations From Initial Concentrations

In K equations, concentrations or gas pressures must be measured at equilibrium.

In some cases, knowing *only* concentrations or pressures in the *initial* mixture before the reaction begins, the concentrations or pressures at equilibrium can be calculated with the help of algebra. Let's learn this method using an example.

Q. The reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ (all gases) is carried out in a closed system with constant volume, at a temperature where $K_C = 144$. In the initial mixture before the reaction begins, $[\text{H}_2] = [\text{I}_2] = 0.500 \text{ M}$. What will be the concentration of each substance at equilibrium?

K calculations are solved using the *WRECK* steps. Complete the following steps for the problem above.

Steps 1-3: WRE. Write the *WANTED* unit, balanced *Reaction* equation, and *Extent* to which the reaction goes to completion.

Step 4. Conc@Eq. In finding the concentrations or pressures in a reaction mixture at equilibrium, there are several variations in K calculations. Let's compare.

a. When concentrations at equilibrium are supplied in a problem, the answers to this step are supplied, and a *RICE* table is not needed (Lesson 28C).

- b. When concentrations or gas pressures at equilibrium are not known, we use a *RICE* table to find them.
- If the *initial* moles, mol/L or gas pressures are known for reactants, and any *one* value is known at equilibrium, the bottom row of the *RICE* table (values at equilibrium) can be solved using arithmetic (Lesson 28F).
 - If moles, mol/L or gas pressures are known for all of the initial reactants, the bottom row of the *RICE* table can often be solved using algebra. A key step is assigning *signs* to *x values* in the *Change* row of the *RICE* table.

For the problem above, make a *RICE* table. In the *Change* row, represent the change that will take place to reach equilibrium using terms such as $+x$, $-x$, $+2x$, $-3x$, etc.

Fill in the *Equilibrium* row using terms that include x .

Complete Steps 1-4 above, and then check your answer below.

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Answer

- WANT:** $[H_2]$, $[I_2]$, and $[HI]$ at equilibrium.
- Reaction:** $H_2 + I_2 \leftrightarrow 2 HI$ (all gases)
- Extent:** Since the reaction has a K value, it goes to equilibrium.
- Conc@Eq.**

The concentrations are supplied for the initial reactants only, with no products yet formed. As the reaction begins, some of the $[H_2]$ and $[I_2]$ reactants are used up, and some products form. In the *Change* row, the signs for all of the reactant terms must therefore be *negative*, and the signs for all of the product terms must be positive.

If needed, use that hint to fill in the *Change* row, then complete the table.

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According to the coefficients, if $[H_2]$ changes by $-x$, $[I_2]$ must also change by $-x$ as it reacts with H_2 , and $[HI]$ must increase by $+2x$.

Reaction	1 H_2	1 I_2	2 HI
Initial	0.500 M	0.500 M	0 M
Change	$-x$ M	$-x$ M	$+2x$ M
At Equilibrium			

Complete the bottom row using terms with numbers and x 's.

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Reaction	1 H ₂	1 I ₂	2 HI
Initial	0.500 M	0.500 M	0 M
Change	- x M	- x M	+ 2x M
At Equilibrium	(0.500 - x) M	(0.500 - x) M	2x M

As a check, use this rule: The *numbers* in front of *x*'s in rows 3 and 4 must be the same as the *coefficients* in row 1. Coefficients determine the Change ratios.

Step 5. K: Write the K equation and solve for x. Substitute the Equilibrium row terms into the K equation.

* * * * *

Hint: you will need to take a square root.

* * * * *

K:
$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 144$$
 using mol/L measured at equilibrium.

$$K = \frac{(2x)^2}{(0.500 - x)^2} = 144$$
 Take the square root of both sides, then solve for x.

* * * * *

$$\frac{(2x)}{(0.500 - x)} = (144)^{1/2} = 12.0$$
 Finish solving for x.

* * * * *

$$2x = 12(0.500 - x)$$

$$2x = 6 - 12x$$

$$14x = 6; \quad x = 6/14 = 0.429$$

Step 6. Solve for the WANTED unit. Substitute x into the equilibrium row to find the WANTED values for each equilibrium concentration.

* * * * *

	H ₂	I ₂	HI
At Equilibrium	0.500 - 0.429 = 0.071 M	0.071 M	+ 2(0.429) = 0.858 M

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.

* * * * *

7. Check:
$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.858)^2}{(0.071)^2 \cdot 0.00504} = \frac{0.736}{0.00504} = 146$$
 versus $K = 144$ in the data.

When your check K agrees with the K supplied in the problem, allowing for the doubtful digit, your answer is likely correct.

Summary: Solving K Calculations - The WRECK Steps

- 1-3: WRE.** Write the *WANTED* unit, balanced *Reaction* equation, and *Extent* to which the reaction goes to completion.
- 4. Concentrations@Equilibrium.**
- If concentrations at equilibrium are given in a problem, use them. A *RICE* table is not needed.
 - When concentrations or gas pressures at equilibrium are not known, make a *RICE* table. The bottom row values are the concentrations at equilibrium, or can be used to calculate those concentrations, that are needed in the *K* equation.
 - If *initial* moles, mol/L or gas pressures are known for reactants, and any *one* value is known at equilibrium, the bottom row of the *RICE* table can be solved using *arithmetic*.
 - If moles, mol/L or gas pressures are known for all of the initial reactants, the *Equilibrium* row of the *RICE* table can often be solved using *algebra*.

A key step is assigning *signs* and *x values* to the *Change* row of the *RICE* table. The *Change* row will have terms such as $-x$, $+2x$, etc.
- 5. K: Write the K equation.** Substitute the *Equilibrium* row terms into the *K* equation, then solve for *x* if needed.
- 6. Solve** for the *WANTED* unit. If needed, substitute *x* into the *Equilibrium* row to find the values for each equilibrium concentration.
- 7. Check.** Substitute the equilibrium concentrations into the *K* expression. Calculate a value for *K*. Compare to the *K* value supplied in the problem.

Practice: If you get stuck, read a part of the answer below, then try again.

- Try solving without a calculator:
$$\frac{(2x)^2}{(0.200 - x)^2} = 64$$
- Use a calculator as needed:
$$\frac{(2x)^2}{(0.600 - x)^2} = 81$$
- Based on the following *RICE* table,

Reaction	1 CO	1 H ₂ O	1 CO ₂	1 H ₂
Initial	0.200 M	0.200 M	0 M	0 M
Change				
At Equilibrium				

- Complete the *Change* row using terms with *x*'s.
- Write the concentrations at equilibrium using terms with numbers and *x*'s.

- c. Write the equilibrium constant expression for the reaction.
- d. If $K = 0.49$, calculate the value of x .
- e. Calculate values for the concentrations at equilibrium.
- f. Check your answers by using them to calculate a value for K .
4. In a closed system with constant volume, for the reaction $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2 \text{HCl}$ (all gases) at 3050 K, $K_p = 225$. In the initial mixture before the reaction begins, $P_{\text{H}_2} = P_{\text{Cl}_2} = 0.750$ atm. What will be the partial pressure of each substance at equilibrium?

ANSWERS

1. $\frac{(2x)^2}{(0.200 - x)^2} = 64$ Taking the square root of both sides: $\frac{2x}{0.200 - x} = 8.0$
- $$2x = 8.0(0.200 - x)$$
- $$2x = 1.6 - 8x$$
- $$10x = 1.6, \quad \boxed{x = 0.16}$$
2. $\frac{(2x)^2}{(0.600 - x)^2} = 81$ Taking the square root of both sides: $\frac{2x}{0.600 - x} = 9.0$
- $$2x = 9.0(0.600 - x)$$
- $$2x = 5.4 - 9x$$
- $$11x = 5.4, \quad \boxed{x = 0.49}$$

3. a. The numbers in front of x must match the coefficients of the balance equation.

Since the table shows reactants but no products in the initial mixture, to reach equilibrium, some of the reactants must be used up. The reactants must therefore have negative signs in the **Change** row.

Some products must be formed, so the signs in the **Change** row for the products must be positive.

- b. See table below.

Reaction	1 CO	1 H ₂ O	1 CO ₂	1 H ₂
Initial	0.200 M	0.200 M	0 M	0 M
Change	- x M	- x M	+ x M	+ x M
At Equilibrium	0.200 - x M	0.200 - x M	+ x M	+ x M

c. $K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$

d. $K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(x)^2}{(0.200 - x)^2} = 0.49$

Taking the square root of both sides: $\frac{x}{0.200 - x} = 0.70$

$$x = 0.70(0.200 - x)$$

$$x = 0.14 - 0.70x$$

$$1.7x = 0.14, \quad x = 0.0824$$

e.

	1 CO	1 H ₂ O	1 CO ₂	1 H ₂
At Equilibrium	0.200 - 0.0824 = 0.118 M	0.118 M	0.0824 M	0.0824 M

f. $K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0824)^2}{(0.118)^2} = \frac{0.006790}{0.01392} = 0.49$ Matches K . Check.

4. Calculations using K_p values and gas partial pressures in atmospheres solve in the same manner as K calculations using concentration. To solve K calculations, write the *WRECK* steps, solve, and check.

WANT: P_{H_2} and P_{Cl_2} and P_{HCl} at equilibrium.

R and E: $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2 \text{HCl}$ (goes to equilibrium)

Conc@Eq. If pressures at equilibrium are not known, a *RICE* table is needed.

RICE tables can be solved in partial pressures if volume is held constant.

Reaction	1 H ₂	1 Cl ₂	2 HCl
Initial	0.750 atm	0.750 atm	0 atm
Change	- x atm	- x atm	+ 2x atm
At Equilibrium	(0.750 - x) atm	(0.750 - x) atm	2x atm

In the change row, the coefficient of x must match the coefficient for that term in the balanced equation, and the reactant and product terms must have *opposite* signs.

If only the initial concentrations or pressures are known, the reactant concentrations or pressures must decrease in going to equilibrium, and products must be formed. This means that the signs in the **Change** row must be negative for the reactants and positive for the products.

K: Use the K equation to solve for x .

$$K = \frac{(P_{\text{HCl}})^2}{P_{\text{H}_2} \cdot P_{\text{Cl}_2}} = 225 \quad \text{using partial pressures at equilibrium.}$$

$$K = \frac{(2x)^2}{(0.75 - x)^2} = 225$$

Take the square root of both sides, then solve for x .

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$$\frac{(2x)}{(0.75 - x)} = (225)^{1/2} = 15.0 \quad \text{Finish solving for } x.$$

* * * * *

$$2x = 15(0.75 - x)$$

$$2x = 11.25 - 15x$$

$$17x = 11.25; \quad x = 11.25/17 = \mathbf{0.662}$$

Step 6. Solve for the WANTED unit. Substitute x into the equilibrium row to find the WANTED values for each equilibrium concentration.

* * * * *

	H ₂	Cl ₂	HCl
At Equilibrium	0.750 - 0.662 = 0.088 atm	0.088 atm	+ 2(0.662) = 1.32 atm

Step 7. Check: $K = \frac{(P_{\text{HCl}})^2}{P_{\text{H}_2} \cdot P_{\text{Cl}_2}} = \frac{(1.32)^2}{(0.088)^2} = \frac{1.742}{0.007744} = \mathbf{225}$ versus $K = 225$ in the data.

If the check K agrees with the supplied K , allowing for the doubtful digit, your answer is likely correct.

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Lesson 28! Q: The Reaction Quotient

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

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

For a reversible reaction, if K is known, Q will identify the *direction* in which a reaction mixture will need to shift (toward products or reactants) to reach equilibrium.

In a closed system, if a mixture of reactants and products is *not* at equilibrium, the reaction will continue in the direction that takes the mixture *toward* equilibrium. The Q value will shift continuously to get closer to K . When $Q = K$, net change stops.

The *speed* at which a reaction proceeds is determined by reaction kinetics, but the *direction* that the reaction will shift is determined by Q and 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,

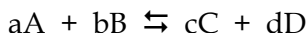
the concentrations or pressures in the reaction mixture are substituted into the K expression. This calculates a value for Q .

Then,

- If $Q < K$, the mixture must shift right, toward products, to reach equilibrium.
- If $Q > K$, the mixture must shift left, toward the reactants, to reach equilibrium.
- If $Q = K$, the mixture is at equilibrium.

Those three cases must either be memorized or be derived when you need them.

The logic of these shifts makes sense. For the general reaction



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

- 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. That means the reaction mixture must “shift toward reactants” to reach K .
- If $Q < K$, the [products] must go up, and the [reactants] down. The mixture must shift toward the products.

The equation for the expression for K and Q is the same, but the numeric values for K and Q will often differ. Q can be calculated from measurements in any reaction mixture. A K value must be based on measurements at equilibrium.

As with K values, Q is written as a number without units.

To summarize, this rule must be memorized.

The Q Rule: As a reaction proceeds, Q values shift to get closer to K .

To determine which direction a mixture will shift in order to reach equilibrium,

- substitute the mixture concentrations or pressures into the K expression to calculate Q , then
- compare the numeric values of Q and K .

If $Q < K$, the mixture will shift to the *right*, toward the *products*.

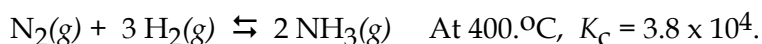
If $Q > K$, the mixture will shift to the *left*, toward the *reactants*.

If $Q = K$, the mixture is at equilibrium and net changes do not occur.

If the $Q < K$ rule for a shift in *one* direction is memorized, the cases for $Q = K$ and $Q > K$ should be easy to write as needed.

Using the Q rule, try the following problem.

Q. For the reaction in a closed system:



A mixture of those gases not yet at equilibrium contains $[N_2] = 0.12 \text{ M}$, $[H_2] = 0.030 \text{ M}$, and $[NH_3] = 0.60 \text{ M}$.

- Calculate the reaction quotient.
- As the mixture continues to react, will the equilibrium shift left or right?
- As the mixture continues to react, will $[NH_3]$ increase or decrease?

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Answer

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

DATA: *mixture* 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 $K_C = 3.8 \times 10^4 = 0.38 \times 10^5$, and Q is larger than K_C . This means that the reaction direction must shift to the *left* to reach equilibrium.

c. The $[\text{NH}_3]$ in the products must *decrease* as the reaction continues and shifts left. The Q value must shift toward a final value of K_C .

Practice

- Circle the largest numeric value of the three in the series.
 - 2.0×10^6 or 32.5×10^4 or 0.026×10^7
 - 2.0×10^{-6} or 32.5×10^{-4} or 0.026×10^{-7}
- 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 mixture, if $Q = 0.0010$, does the mixture have more reactants or more products?
- For a given mixture in a reversible reaction, $Q = 2.0 \times 10^4$ and $K_C = 4.0 \times 10^5$. To reach equilibrium from this mixture, will the reaction shift toward the left or the right?
- For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, $K_C = 0.56$, 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

- To compare values, change to a *consistent* power of 10. Below we convert to the *largest* power in the series. When the exponential terms are the same, the significand will determine which value is higher.
 - 0.20×10^7 or 0.0325×10^7 or 0.026×10^7
 - 0.020×10^{-4} or 32.5×10^{-4} or $0.000\ 026 \times 10^{-4}$
- 2a. 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 can vary. Q can be measured for any mixture of reactants and products, at any point in the reaction.
 - $Q = (\text{product of [products]})/(\text{product of [reactants]})$. If Q is less than one, the bottom term of the ratio must be larger. This mixture must have higher concentrations of reactants than products.
 - Q is less than K_c . Based on the K and Q expression, to reach K , the [products] must increase, so the reaction must shift to the right. Anytime $Q < K$, the reaction must shift right to reach equilibrium.
5. WANT: Which direction the reaction will shift.

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

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**.

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Lesson 28]: Calculations Using K and Q

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

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So far, we have solved calculations involving equilibrium concentrations or gas pressures in four 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* table and arithmetic.

- If concentrations or gas pressures are known for an initial mixture that is *all reactants* (with no products), values at equilibrium may be able to be found using a *RICE* table and algebra.
- In a *mixture* of reactants and products, the *direction* that a reaction will shift to reach equilibrium can be determined by comparing K and Q .

In our fifth type of calculation, we will calculate concentrations or gas pressures in a reaction at equilibrium, starting from a *non-equilibrium mixture* of the reactants and products. 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

In all of our K calculations to this point, our initial mixtures have been reactants only, with no products. This has meant that the *sign* of the terms in the change row in the *RICE* table has always been *negative* for the reactants and *positive* for the products. This is logical: if there are only reactants, the reaction has not yet started. If the reaction goes at all, some reactants must be used up and some products formed.

However, if a closed system has a *mixture* of reactants *and* products, and the reaction is not yet at equilibrium, whether the mixture will need to shift to the right toward the products or left toward reactants to reach equilibrium is not obvious. To calculate which way the equilibrium will shift, we must compare K and Q .

- If a reaction mixture must shift to the *right* to reach equilibrium, the *signs* in the Change row of the *RICE* table will be *negative* for the reactants, and positive for the products. As a reaction shifts to the right, reactants are used up and products 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, because in shifting left, products are used up and reactants form.

The above means that for K calculations involving *mixtures* of reactants and products, the *signs* in the Change row of a *RICE* table must be assigned carefully, based on K versus Q .

For K calculations based on an initial mixture of reactants and products, let's learn to apply these rules using an example.

- Q.** For the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$ (all gases), at a temperature where $K_c = 16$, in a closed system with constant volume, if in the mixture $[\text{H}_2] = [\text{I}_2] = 0.100 \text{ M}$ and $[\text{HI}] = 0.500 \text{ M}$, what will be the concentrations of each substance at equilibrium?

K calculations are solved using the *WRECK* steps. Complete the following steps for the problem above.

Steps 1-3: WRE. Write the **WANTED** unit, balanced **R** reaction equation, and **E**xtent to which the reaction goes to completion.

Step 4. Conc@Eq. This step is where K calculations *differ*.

If the concentrations at equilibrium are *not* known, make a RICE table.

If the data in the problem is for a *mixture* of reactants and products, Q is compared to K to determine in which direction the mixture must shift to reach equilibrium. The direction of the shift determines the signs in the Change row.

- If the reaction mixture must shift to the left to reach equilibrium, the Change row for *reactants* will have + # x terms, and the products – # x .
- If the mixture must shift to the right, the Change row for *products* will have + # x terms, and the reactants – # x .

In the Change row of a RICE table, all of the *reactant* terms must have the *same* sign, and all of the *product* terms must have the *opposite* sign.

Complete those steps, and then check your answer below.

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1. WANT: $[H_2]$, $[I_2]$, and $[HI]$ at equilibrium.
- 2,3. R+E: $H_2 + I_2 \rightleftharpoons 2 HI$ (all gases) (goes to equilibrium. Use K).
4. Conc@Eq. Since the concentrations at equilibrium are not given, a RICE table is needed.

For a *mixture* of reactants and products, to decide the *signs* in the Change row, compare Q to K to determine the direction the mixture must shift.

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.500)^2}{(0.100)^2} = 25.0$$

Since $Q = 25.00 > K = 16$, the reaction must shift to the *left*, toward the reactants, to get to equilibrium.

Now write the RICE table. In the Change row, represent the change that will take place to reach equilibrium using terms like + x , – x , +2 x , –3 x , etc.

Complete the *Equilibrium* row using terms that include x .

Finish Step 4, and then check your answer below.

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As the reaction shifts toward *reactants* to reach equilibrium, some of the $[H_2]$ and $[I_2]$ reactants are formed. In the *change* row, the signs for all reactant terms must therefore be *positive*, and the signs for all product terms must be *negative*.

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According to the coefficients, if $[H_2]$ changes by + x , $[I_2]$ must change by + x , and the change in $[HI]$ must be –2 x . For x terms, the *coefficients* in the top row and the *numbers* in front of the x 's in the Change row must be the same.

Reaction	1 H ₂	1 I ₂	2 HI
Initial	0.100 M	0.100 M	0.500 M
Change	+ x M	+ x M	- 2x M
At Equilibrium			

Complete the bottom row.

* * * * *

Reaction	1 H ₂	1 I ₂	2 HI
Initial	0.100 M	0.100 M	0.500 M
Change	+ x M	+ x M	- 2x M
At Equilibrium	(0.100 + x) M	(0.100 + x) M	(0.500 - 2x) M

Step 5. K: Write the K equation, then solve for x. Substitute the equilibrium row terms into the K equation.

* * * * *

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.500 - 2x)^2}{(0.100 + x)^2} = 16 \quad \text{Take the square root of both sides, then solve for } x.$$

* * * * *

$$\frac{(0.500 - 2x)}{(0.100 + x)} = (16)^{1/2} = 4.0 \quad \text{Finish solving for } x.$$

* * * * *

$$\begin{aligned} 0.500 - 2x &= 4.0 (0.100 + x) \\ 0.500 - 2x &= 0.400 + 4x \quad (\text{Don't round to } sf \text{ until the end of the calculation}) \\ 6x &= 0.100 ; \quad x = 0.100/6 = 0.0167 \end{aligned}$$

Step 6. Solve for the WANTED units and symbols. Substitute the x values into equilibrium row terms.

* * * * *

	H ₂	I ₂	HI
At Equilibrium	0.100 + 0.017 = 0.117 M	0.117 M	0.500 - 2(0.017) = 0.466 M

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.

* * * * *

$$7. \text{ Check: } K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.466)^2}{(0.117)^2} = 15.9 \text{ versus } K = 16 \text{ in the data.}$$

The check K agrees with the given K , allowing for the doubtful digit.

Summary: Solving K Calculations

To calculate concentrations or pressures at equilibrium from those that are not at equilibrium, write the *WRECK* steps, solve, and check.

- 1,2,3. **WRE.** Write the **WANTED** symbol or unit, balanced **R** reaction equation, and **E**xtent of the reaction.
4. **Conc@Eq.** Find all concentrations or partial pressures at equilibrium.
If values at equilibrium are not known, make a *RICE* table.
If all known values are *initial* reactants, **C**hange row reactant signs are all negative.
For a *mixture* of reactants *and* products not at equilibrium, the mixture will shift to reach equilibrium. Find the reaction direction using Q . The direction of the shift decides **C**hange row *signs* (+ # x or - # x).
5. **K:** Solve K for x .
6. **Find the WANTED unit** using the x values.
7. **Check.** Calculate K using 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 $Q = 15$,
 - 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 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 .

- f. Calculate the concentrations of A, B, and C at equilibrium.
- g. Check your answer by using the *part f* answers to calculate a K value.
3. In the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ 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,
- What will be the value of K_c ?
 - What will be concentration of each substance at equilibrium?

ANSWERS

- 1a. Since Q is lower than K , to reach equilibrium, Q must increase. The reaction mixture must shift to the right, toward higher product concentrations, to reach equilibrium.
- 1b. When the reaction must shift to the right to reach equilibrium, the product terms in the **Change** row of the *RICE* table will have *positive* signs, because their concentration will increase during the shift.
- 2a. The *RICE* table coefficients show that the reaction is $\text{A} + \text{B} \rightleftharpoons 2\text{C}$, so $K = \frac{[\text{C}]^2}{[\text{A}][\text{B}]}$
- 2b. To calculate Q , substitute the initial concentrations into the K expression.

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

- 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	0.50 M + x	0.50 M + x	2.0 M - 2x
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- 2e. To calculate x , substitute the equilibrium concentrations into the K equation.

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

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

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

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

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

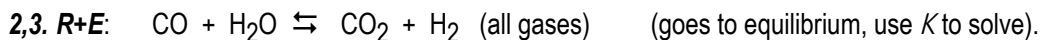
$$4x = 1.0 \text{ M}; \quad \boxed{x = 0.25 \text{ M}}$$

- 2f. Substitute for x in the bottom row of the *RICE* table.

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

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

- 3a. Because the total moles of gas are the same on both sides, $K_p = K_c = 0.36$
- 3b. To calculate equilibrium measures from *non*-equilibrium measures, do the 7 steps: *WRECK*, solve, check.
1. **WANT:** The four concentrations at equilibrium.



4. **Conc@Eq.** If concentrations at equilibrium are not known, a *RICE* table is needed.

For a *mixture* of reactants and products, to determine the *signs* in the **Change** row, determine the *direction* the equilibrium must shift by comparing 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 reach equilibrium.

In the **Change** row, if the reaction is shifting toward reactants, reactants must get a **+** sign, and products a **-**. All reactant terms must have the same sign, and all product terms must have the opposite sign. Write **Equilibrium** row in terms of x .

Reaction	1 CO	1 H ₂ O	1 CO ₂	1 H ₂
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

4. **K:** 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 : $(1.00 - x) = 0.60(0.50 + x)$

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

$$0.70 = 1.60x$$

$$x = 0.438 \text{ M} \quad (\text{carry an extra } sf \text{ until the last step})$$

6. **Solve** for the WANTED units.

WANTED: [reactants] = [CO] = [H₂O] = 0.50 M + x = 0.50 M + 0.438 = **0.94 M**

[products] = [CO₂] = [H₂] = 1.00 M - x = 1.00 M - 0.438 = **0.56 M**

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

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

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Lesson 28K: 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 *K* calculations, you may need to solve a **quadratic equation** for *x*.

The **general format** for a quadratic equation is $ax^2 + bx + c = 0$. A quadratic equation has x^2 an term, but no *x* powers higher than 2. In a quadratic equation, the terms **a**, **b**, and **c** will be numbers and *x* is the unknown.

Once a quadratic equation is in the general format, the numbers *a*, *b*, and *c* are known, and *x* can be solved using **quadratic formula**:

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

The quadratic formula will result in *two* values for *x*, both of which solve the quadratic equation.

Both the *general 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*.”

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

The following steps will solve the type of quadratic equations most often encountered in first-year chemistry. Let’s begin with a simple example.

Q. $4x^2 + (x - 2) = 3$

Solve for *x* using the steps below.

Steps To Solve Quadratic Equations

1. Move all terms to one line and eliminate parentheses.
2. Group the terms into the *general quadratic format*: $ax^2 + bx + c = 0$

Write the numeric values for **a**, **b**, and **c**.

Complete those steps, then check below.

* * * * *

1. All terms are on one line. Removing parentheses:

$$4x^2 + (x - 2) = 3$$

$$4x^2 + x - 2 = 3$$

2. Move the terms into the general format: $ax^2 + bx + c = 0$

by rearranging the terms to get a zero on the right side.

$$4x^2 + x - 5 = 0$$

Write the values: $a = 4$, $b = 1$, $c = -5$.

Now try step 3, then check your answer below.

3. Substitute the values for a , b , and c into the **quadratic formula** and solve:

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

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3. Substituting a , b , and c into the quadratic formula:

$$\begin{aligned} x &= \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(1) \pm \{(1)^2 - 4(4)(-5)\}^{1/2}}{2(4)} = \frac{-1 \pm (1 + 80)^{1/2}}{8} = \\ &= \frac{-1 \pm (81)^{1/2}}{8} = \frac{-1 \pm 9}{8} = \frac{8}{8} \text{ and } \frac{-10}{8} = \boxed{+1 \text{ and } -1.25} \end{aligned}$$

When solving a quadratic, the result will be *two* values for x .

Now, if using a calculator is permitted in your class when solving quadratics, use the values of a , b , and c found above to solve. See if you get the same two values for x .

4. Check the two values by substituting them into the original equation.

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$$4(1)^2 + (1 - 2) = 4 - 1 = 3 \text{ and } 4(-1.25)^2 + (-1.25 - 2) = 6.25 - 3.25 = 3$$

Both values are solutions to the original equation.

Practice A. Solve for x , then substitute your answers into the original equation to check them. The second problem is more challenging.

1. $x^2 - 3x - 28 = 0$

2. $2 = \frac{(1 + 2x)^2}{(2.5 - x)(1.5 - x)}$

Solving Quadratic Equations in Science Problems

The above four steps will solve quadratic equations. The result is nearly always *two* values for x . In science problems, however, one of those x values will usually result in an “unreal” quantity. An example would be an x that results a negative value for mass or volume: quantities that must be positive in real measurements. The *other* x will be a number that, when plugged into the values in the problem, does result in measurements that are real. The x value that makes sense is the one that is used to complete the problem.

$$a = 10, b = -15, c = 2.6$$

At this point, if during tests you are allowed to use a calculator that will solve quadratic equations, use the manual for the calculator to determine which steps to use, then solve the quadratic above.

If calculator quadratic solving is not allowed, solve by substituting a , b , and c into the quadratic formula.

* * * * *

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

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

If you have computer access, search online for *quadratic formula calculator*. Use it to check the answers calculated above. You may want to compare several different online tools.

4. Check: both values work to solve the K equation, but
5. Only *one* x value will work to solve the science 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. The concentration of a substance cannot be negative. The x value that gives a *positive* number for every concentration is $x = 0.20$. Use that x value to calculate the concentrations and finish the problem.

This answers Part a of the problem. Complete part b.

* * * * *

$$\begin{aligned} \text{b. } [A] &= (1.40 + x) = (1.40 + 0.20) = \mathbf{1.60 \text{ M}} \quad (\text{when adding, track the place with doubt}) \\ [B] &= (0.40 - x) = (0.40 - 0.20) = \mathbf{0.20 \text{ M}} \\ [C] &= (1.00 - x) = (1.00 - 0.20) = \mathbf{0.80 \text{ M}} \end{aligned}$$

In problems that calculate a value for K , you can check your work by substituting the calculated answers back into the K expression, then comparing the calculated K to the K given in the problem. Let's add this to our quadratic solving process as Step

6. **Check:** If K was given in the problem, substitute your answers into the K equation and calculate K . The result should be the K given in the problem.

Do step 6, then check your answer below.

* * * * *

Check: $K = \frac{[A]}{[B][C]} = \frac{1.60}{(0.20)(0.80)} = \frac{1.60}{0.16} = \mathbf{10}$. This matches the original K value.
The value $x = \mathbf{0.20 \text{ M}}$ works.

* * * * *

SUMMARY: Solving Quadratic Equations In Science Calculations

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**. Find two values for x .
4. **Check**: Substitute your two answers into the original equation.
5. Substitute the *two x* values into the data one at a time, and see which one *makes sense*. Use that value to complete solving the science calculation.

Practice B

1. For this reaction in a closed glass cylinder $H_2 + I_2 \rightleftharpoons 2 HI$ (all gases) at a temperature where $K_c = 2.0$, initial concentrations are $[H_2] = 2.5 M$, $[I_2] = 1.5 M$, and $[HI] = 1.0 M$. What will be the concentration of each substance at equilibrium?
2. For the reaction $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ (all gases) in a container with a fixed volume, at an equilibrium temperature where $K_p = 20.$, initial partial pressures are 0.20 atm. for PCl_3 , 0.040 atm. for Cl_2 , and 0.58 atm for PCl_5 . What will be the partial pressure of each gas at equilibrium?

ANSWERS**Practice A**

1. a. $x^2 - 3x - 28 = 0$

This equation is already in the general format of a quadratic equation: $a = 1$, $b = -3$, $c = -28$. Substitute into the quadratic formula.

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(-3) \pm \{(-3)^2 - 4(1)(-28)\}^{1/2}}{2(1)} = \frac{+3 \pm (9 + 112)^{1/2}}{2}$$

$$= \frac{+3 \pm (121)^{1/2}}{2} = \frac{+3 \pm 11}{2} = \frac{14}{2} \text{ and } \frac{-8}{2} = \boxed{+7 \text{ and } -4}$$

Check: $(7)^2 - 3(7) - 28 = 49 - 21 - 28 = 0$

$(-4)^2 - 3(-4) - 28 = 16 + 12 - 28 = 0$

2. $2 = \frac{(1 + 2x)^2}{(2.5 - x)(1.5 - x)}$ Group terms on one line and eliminate parentheses.

$$2(2.5 - x)(1.5 - x) = (1 + 2x)^2$$

$$2(3.75 - 4x + x^2) = (1 + 4x + 4x^2)$$

$$7.5 - 8x + 2x^2 = 1 + 4x + 4x^2$$

Move 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.

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(12) \pm \{(12)^2 - 4(2)(-6.5)\}^{1/2}}{2(2)} = \frac{-12 \pm (144 + 52)^{1/2}}{4} =$$

$$= \frac{-12 \pm (196)^{1/2}}{4} = \frac{-12 \pm 14}{4} = \frac{2}{4} \text{ and } \frac{-26}{4} = \boxed{+0.5 \text{ and } -6.5 = x}$$

Check: $\frac{(1+2x)^2}{(2.5-x)(1.5-x)} = \frac{(1+2(0.5))^2}{(2.5-0.5)(1.5-0.5)} = \frac{4}{(2)(1)} = 2$

$$\frac{(1+2x)^2}{(2.5-x)(1.5-x)} = \frac{(1+2(-6.5))^2}{(2.5-(-6.5))(1.5-(-6.5))} = \frac{(-12)^2}{(8)(9)} = \frac{144}{72} = 2$$

Practice B

1. For K calculations, do the *WRECK* steps, solve, and check.

1. **WANTED:** $[H_2]$, $[I_2]$, and $[HI]$ at equilibrium.

2,3. **R+E:** $H_2 + I_2 \rightleftharpoons 2 HI$ (all gases) (goes to equilibrium. Use K to solve.)

4. **Conc@Eq.** If concentrations at equilibrium are not known, a *RICE* table is needed.

For a *mixture* of reactants and products, to determine the *signs* in the change row, determine the *direction* the equilibrium will shift by comparing Q and K .

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0)^2}{(2.5)(1.5)} = \frac{1.0}{3.75} = 0.27$$

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

This means that the changes in the [products] must be positive ($+ \# x$ terms).

Reaction	1 H_2	1 I_2	2 HI
Initial	2.5 M	1.5 M	1.0 M
Change	$-x$ M	$-x$ M	$+2x$ M
At Equilibrium			

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

Complete the equilibrium row using terms that include x .

* * * * *

Reaction	1 H_2	1 I_2	2 HI
Initial	2.5 M	1.5 M	1.0 M
Change	$-x$ M	$-x$ M	$+2x$ M
At Equilibrium	$(2.5 - x)$ M	$(1.5 - x)$ M	$(1.0 + 2x)$ M

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

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

This cannot be solved by a square root. Since the top and bottom when multiplied out have x^2 terms, try the quadratic steps to solve.

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This quadratic equation is solved in Problem 1c above.

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

6. **Solve.** Substitute the value of x to find the WANTED eq. row values.

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

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

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

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

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

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

2. For K calculations, do the *WRECK* steps, solve, and check.

1. **WANT:** $? = P_{\text{PCl}_3}$, P_{PCl_5} , and P_{Cl_2} , in atm at equilibrium

- 2,3. **R+E:** $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ (goes to equilibrium, use K).

4. **Conc@Eq.** If pressures at equilibrium are not known, a *RICE* table is needed.

For a *mixture* of reactants and products, to determine the *signs* in the **Change** row, determine the *direction* the equilibrium will shift by comparing Q and K .

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

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

The means the *reactants* in the **Change** row will have *positive* signs.

Write *RICE* table with **Change** row terms such as $+x$, $-x$, $+2x$, $-3x$, etc.

Complete the **Equilibrium** row using those x terms.

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Reaction	1 PCl_3	1 Cl_2	1 PCl_5
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.

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

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

The problems you are assigned will be solved either by taking a square root or solving the quadratic. This equation cannot be solved by taking the square root, but it does have x^2 terms if the denominator parentheses are removed. Arrange the terms to fit the general quadratic format.

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Group all terms on one line and eliminate parentheses.

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

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

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

Group 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.

$$\begin{aligned} x &= \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-(5.8) \pm \{(5.8)^2 - 4(20)(-0.42)\}^{1/2}}{2(20)} = \frac{-5.8 \pm (33.64 + 33.6)^{1/2}}{40} = \\ &= \frac{-5.8 \pm (67.24)^{1/2}}{40} = \frac{-5.8 \pm 8.2}{40} = \frac{2.4}{40} \text{ and } \frac{-14}{40} = \boxed{+0.060 \text{ and } -0.35} \end{aligned}$$

Which x value makes sense?

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

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

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

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

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

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

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

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Summary – Equilibrium

If you have not already done so, you may want to organize this summary into charts, numbered lists, and flashcards.

1. Reactions can be divided into three types: those that go nearly 100% to completion, those that don't go, and reactions that are in practice reversible and go partially to

completion. Reversible reactions continue until both the forward and reverse reactions are going at the same rate, and no further change seems to take place. The reaction is then 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 the system.

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 variables including 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,

- 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*.
 - 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*.
 - 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.
 - One way to add energy to a system by increasing its temperature. Energy can be removed by cooling.
 - Increasing* the *pressure* on a gas, such as by reducing the volume of the container, will shift the equilibrium to create *fewer total moles* of gas, based on adding the gas coefficients on each side of the balanced equation.
 - Decreasing* the pressure on a gas, such as by increasing the volume of the container, will shift the equilibrium to create more moles of gas.
 - If gas moles are equal on both sides, pressure changes will not shift an equilibrium.
 - Adding or removing a solid, pure liquid, or solvent does not shift an equilibrium. because shifting an equilibrium does not change the *concentration* of a solid, pure liquid, or solvent (though it may change the *amounts* present).
3. **The Equilibrium Constant**
- For the general reaction $aA + bB \rightleftharpoons cC + dD$ at a given temperature,

at equilibrium, the ratio

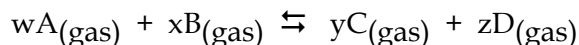
$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K$$

will be constant.

(Remember: "In K , products are on top.")

- b. The ratio with powers and *symbols* for concentrations is called the equilibrium constant (K) **expression**. The K **value** is the number that is the ratio. If the temperature changes, the K value will change, but the K expression does not.
- c. Generally, only concentrations that can *change* are included in K expressions. Terms for solids, pure liquids, and solvents (including *liquid* water) are written as **1** in K expressions. This moves the constant value of those terms into the value of K .
4. An equilibrium constant **value** is a positive number without units.
- When K values are calculated, the units are dropped.
 - When a concentration is calculated based on a K equation that includes concentrations, the unit mol/L (M) must be added to the answer.
5. 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 positive number with a negative power of 10).
 - The more a reaction goes to the right, the higher will be the value of K .
6. 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 . $K_f = 1/K_r$
7. 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 equal the original K to the *power* of the multiplier. $K = (\#)^n$
8. **K_p 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 calculations using K_p , gas pressures must be measured in *atmospheres*.
- When calculating a gas pressure using K_p values, atmospheres must be added as the unit of the answer.

9. 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 in the products) MINUS (the sum of the coefficients of the gases in the reactants).

The number for Δn may be positive or negative and may be a fraction.

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

10. RICE Moles Tables. In reaction calculations, we can track the counts of particles before, during, and at the end of a reaction with a *RICE moles* table. *RICE* tables have 4 rows: balanced Reaction equation, Initial, Change, and End/Equilibrium. *RICE* tables can always be solved in moles, and can also be solved in concentration units if the volume is the same during all measurements.
11. The reaction quotient (Q) is the number that results when concentration or pressure values for a *mixture* that may *not* be at equilibrium are substituted into the K expression.
12. To determine the direction a *mixture* will shift to reach equilibrium, compare Q to K . If $Q > K$, the mixture will shift toward reactants. At equilibrium, $Q = K$.
13. For calculations involving K values and concentrations or gas pressures,
- write the *WRECK* steps, solve, and check.
- 1,2,3. **WRE**. Write the Wanted unit or symbol, balanced Reaction equation, and reaction Extent.
4. **Conc@Eq**. Find all concentrations or partial pressures *at equilibrium*.
 If values at equilibrium are not known, solve with a *RICE* table.
 If all known values are for *initial* reactants, Change row *reactant* signs are negative.
 If known values are for a *mixture* of reactants *and* products not at equilibrium, find the reaction direction using Q . Direction decides Change row *signs* ($-#x$ or $+#x$).
 If the reaction must shift right to reach equilibrium, Change row signs for products will be positive. If reaction must shift left, reactant Change row signs are positive.
 In the Change row, all of the *reactant* terms must have the *same* sign, and all of the *product* terms must have the *opposite* sign.
5. **K**: Write the K equation.
6. **Solve** the K equation for the term WANTED.
7. **Check**. Calculate K using the solved values. Compare to the K in the data.

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