www.edvantagescience.com

Edvantage Science

AP® CHEMISTRY 2

Chapter

2

Big Idea 6

Order your
copy now

COPIES OF THIS BOOK MAY BE
OBTAINED BY CONTACTING:

Edvantage Interactive

E-MAIL:
info edvantageinteractive.com

TOLL-FREE FAX:
866.275.0564

TOLL-FREE CALL:
866.422.7310

Authors

Cheri Smith
Yale Secondary
School District 34 Abbotsford

Gary Davidson
School District 22 Vernon

Megan Ryan
Walnut Grove Secondary School
District 35 Langley

Chris Toth
St. Thomas More Collegiate
Burnaby

Program Consultant
Lionel Sandner
Edvantage Interactive

EDVANTAGE
INTERACTIVE

AP Chemistry 2

Please contact publisher for ISBN information.
Reprint August 2015

Care has been taken to trace ownership of copyright material contained in this text. The publishers will gladly accept any information that will enable them to rectify any reference or credit in subsequent printings.

Vice-President of Marketing: *Don Franklin*
Director of Publishing: *Yvonne Van Ruskenveld*
Design and Production: *Donna Lindenberg, Paula Gaube*
Editorial Assistance: *Rhys Sandner*
Proofreading: *Eva van Emden*

The AP Big Ideas at the beginning of each chapter are quoted from *AP Chemistry: Course and Exam Description*, revised edition, effective Fall 2013, published by the College Board, New York, NY. Advanced Placement, AP, and College Board are registered trademarks of the College Board.

QR Code — What Is This?

The image to the right is called a QR code. It's similar to bar codes on various products and contains information that can be useful to you. Each QR code in this book provides you with online support to help you learn the course material. For example, find a question with a QR code beside it. If you scan that code, you'll see the answer to the question explained in a video created by an author of this book.

You can scan a QR code using an Internet-enabled mobile device. The program to scan QR codes is free and available at your phone's app store. Scanning the QR code above will give you a short overview of how to use the codes in the book to help you study.

Note: We recommend that you scan QR codes only when your phone is connected to a WiFi network. Depending on your mobile data plan, charges may apply if you access the information over the cellular network. If you are not sure how to do this, please contact your phone provider or us at info edvantageinteractive.com

2 Chemical Equilibrium

This chapter focuses on the following AP Big Idea from the College Board:

- Big Idea 6: Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.

By the end of this chapter, you should be able to do the following:

- Explain the concept of chemical equilibrium with reference to reacting systems
- Predict, with reference to entropy and enthalpy, whether reacting systems will reach equilibrium
- Apply Le Châtelier's principle to the shifting of equilibrium
- Apply the concept of equilibrium to a commercial or industrial process
- Draw conclusions from the equilibrium constant expression
- Perform calculations to evaluate the changes in the value of K_{eq} and in concentrations of substances within an equilibrium system

---

By the end of this chapter, you should know the meaning of these **key terms**:

- chemical equilibrium
- closed system
- dynamic equilibrium
- enthalpy
- entropy
- equilibrium concentration
- equilibrium constant expression
- equilibrium shift
- Haber process
- heterogeneous reaction
- homogeneous reaction
- ICE table
- K_{eq}
- Le Châtelier's principle
- macroscopic properties
- open system
- PE diagram

When the number of shoppers travelling between the two floors on the escalators is equal, the crowd has reached equilibrium.

2.1 Introduction to Dynamic Equilibrium

Warm Up

Every weekday from 7 a.m. to 9 a.m. a large volume of traffic flows into Vancouver as people who live in the surrounding communities (Surrey, Langley, North and West Vancouver) drive to work.

1. Are there any cars leaving Vancouver between 7 a.m. and 9 a.m.?

   ____

2. Explain how the number of cars in Vancouver remains relatively constant between 10 a.m. to 2 p.m. when cars are still entering the city.

   ____
   ____

3. The number of cars in Vancouver decreases between 3 p.m. and 7 p.m. Describe the traffic flow during this period.

   ____

Defining Chemical Equilibrium

Many chemical reactions are reversible. For example a decomposition reaction is the reverse of a synthesis reaction. This reversibility of chemical reactions facilitates an important phenomenon known as chemical equilibrium.

Chemical equilibrium exists when the forward rate of a chemical reaction equals its reverse rate.

Chemical equilibria are said to be *dynamic*, which means they are active. In chemical equilibria, the forward and reverse reactions continue to occur. This contrasts with a *static* equilibrium of forces, such as the equal and opposite forces acting on a weight hanging motionless on the end of a string. In a chemical equilibrium, each reactant is being "put back" by the reverse reaction at the same rate that it is being "used up" by the forward reaction and vice versa for each product. Note that the rate at which one chemical is being consumed and produced is not necessarily the same as the rate at which another chemical is being consumed and produced. The consumption and production ratios are provided by the coefficients in the balanced chemical equation. The example below describes the synthesis and decomposition of water. The equation shows that hydrogen is consumed and produced at twice the rate in moles per second that oxygen is.

$$2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(g)$$

Sample Problem 2.1.1 — Determining Equivalent Reaction Rates at Equilibrium

NO_2 is being consumed at a rate of 0.031 mol/s in the equilibrium below. How many moles of N_2O_4 are being consumed each second?

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

What to Think About	How to Do It
1. Recall that, at equilibrium, the rate of any chemical's consumption equals the rate of its production. Therefore, NO_2 is also being produced at 0.031 mol/s.	$0.031\,\frac{\text{mol } NO_2}{\text{s}} \times \frac{1\text{ mol } N_2O_4}{2\text{ mol } NO_2} = \frac{0.016\text{ mol } N_2O_4}{\text{s}}$
2. Look at the coefficients.	The coefficients in the balanced equation indicate that 1 mol of N_2O_4 is consumed for each 2 mol of NO_2 produced.

Practice Problems 2.1.1 — Determining Equivalent Reaction Rates at Equilibrium

SO_2 and O_2 are placed in a sealed flask where they react to produce SO_3. When equilibrium is achieved, SO_3 is being produced at a rate of 0.0082 mol/s.

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

1. How many moles of SO_3 are being consumed each second?

2. How many moles of O_2 are being produced each second?

3. How many grams of O_2 are being consumed each second?

Recognizing Chemical Equilibrium

How do chemists recognize a chemical equilibrium? There are three criteria for a system to be at chemical equilibrium. It must:

1. have constant **macroscopic** properties. Macroscopic properties are those that are large enough to be measured or observed with the unaided eye.
2. be closed.
3. shift when conditions change.

1. Constancy of Macroscopic Properties

A system at equilibrium has constant macroscopic properties such as color, pH, temperature, and pressure because the amount of each reactant and product remains constant. Each chemical is being produced (put back) at the same rate that it is being consumed (removed). There is no macroscopic activity in a system at equilibrium because the continuing forward and reverse reactions are not observable because we cannot see atoms or molecules. Minor unobservable fluctuations in rates and concentrations are presumed to occur in equilibria since reaction rates are dependent on random collisions between reactant species. Another notable characteristic of equilibria is that they are self-perpetuating because the forward and the reverse reactions continuously supply each other with reactants.

2. Closed System

A system is **closed** if no chemicals are entering or leaving the defined system. If a system's properties are constant but the system is open then it is a **steady state** rather than an equilibrium (Figure 2.1.1). In a steady state, components enter and leave the system at the same rate rather than going back and forth within an equilibrium system. A steady state exists when the water level behind Cleveland dam stays constant because water is flowing into Capilano Lake, the lake behind the dam, at the same rate that it is flowing through the dam.

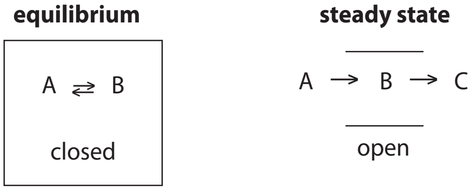


Figure 2.1.1 *Equilibrium occurs only in a closed system. In an open system, steady state can be reached, but not equilibrium.*

A reaction occurring in aqueous solution may only achieve equilibrium if all the reactant particles, product particles, and solvent water molecules remain in the solution. If an equilibrium system is temporarily disrupted by opening it and removing chemicals, the remaining chemicals will re-establish equilibrium if the system is closed again. Chemicals could be removed in a disruption, for example, if a chemical in the aqueous equilibrium is precipitated out or evaporates.

For a system to be at equilibrium, it must be closed and at a constant temperature (constancy of macroscopic properties). The intent of these conditions is to hold the amount of matter and energy constant within the system. For a system to be at a constant temperature it must be at thermal equilibrium with its surroundings, meaning that kinetic energy must be entering and leaving the system at the same rate.

3. A Shift due to Changed Conditions

The world is full of closed systems at constant temperatures in which nothing appears to be happening. In the vast majority of these, there really is nothing happening. They are just chemical mixtures. Equilibrium exists in only a small percentage of those systems that meet the first two criteria. Just as a child might poke a snake to see if it's alive, chemists "poke" chemical systems by changing their conditions. A change in temperature usually forces an equilibrium to reveal itself by causing a change or a *shift* in the amounts of reactants and products. When the solution's original temperature is restored, so are the original amounts. The equilibrium shifts back. Various shifts in response to changes of conditions will be discussed in sections 2.2 and 2.3. If the reaction is photoactivated, it will respond to a change in lighting conditions rather than a change in temperature.

Quick Check

1. Why are chemical equilibria referred to as dynamic? ____

2. List three criteria that must be satisfied for chemical equilibrium to exist.

   ______________________________________ ____

   ____

3. What is a closed chemical system? ____

4. What is a macroscopic property? ____

How Equilibrium Is Established

Recall from section 1.1 that, as a reaction proceeds, reactant concentrations fall. Hence, the forward rate of the reaction (r_f) decreases. In a closed system, the product concentrations rise at the same time as the reactant concentrations are falling. Hence, the reverse rate of the reaction (r_r) increases. This continues until $r_r = r_f$ and equilibrium is established (Figure 2.1.2).

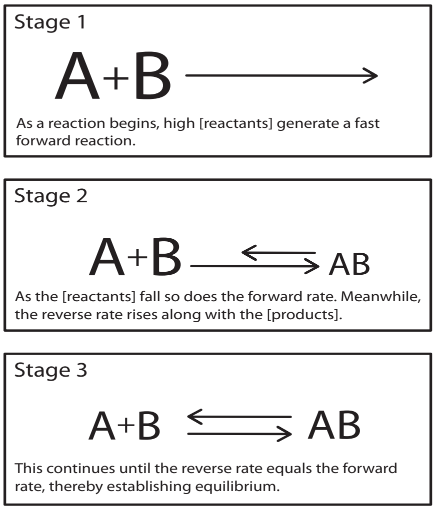


Figure 2.1.2 *Diagrammatic representation of chemical equilibrium being established*

Figure 2.1.3 shows equilibrium being achieved at about $t = 7$ s when the reactant and product concentrations become constant. It is important to note that the concentrations of reactants are not equal to the concentration of products at equilibrium. Only the forward and reverse reaction *rates* are equal.

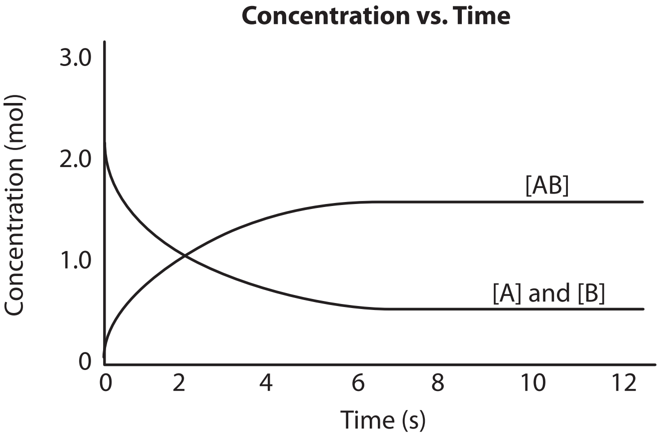


Figure 2.1.3 *This graph shows what happens with reactant and product concentrations as a function of time as equilibrium is established.*

Quick Check

Is each question below true or false? Place T or F in the places provided.

1. The reactant concentrations always equal the product concentrations at equilibrium. ________
2. When approaching equilibrium, [reactants] decreases while the [products] increases. ________
3. The [reactants] hold steady at equilibrium. ________
4. Before achieving equilibrium, the forward rate (r_f) is less than the reverse rate (r_r). ________

2.1 Activity: A Mathematical Model of Dynamic Equilibrium That Makes Cents

Question

Can we use a model to demonstrate how an equilibrium develops?

Background

Chemical equilibrium exists when each reactant and product is being consumed at the same rate that it is being produced. Chemical species are represented by pennies in this model with heads representing reactants and tails representing products.

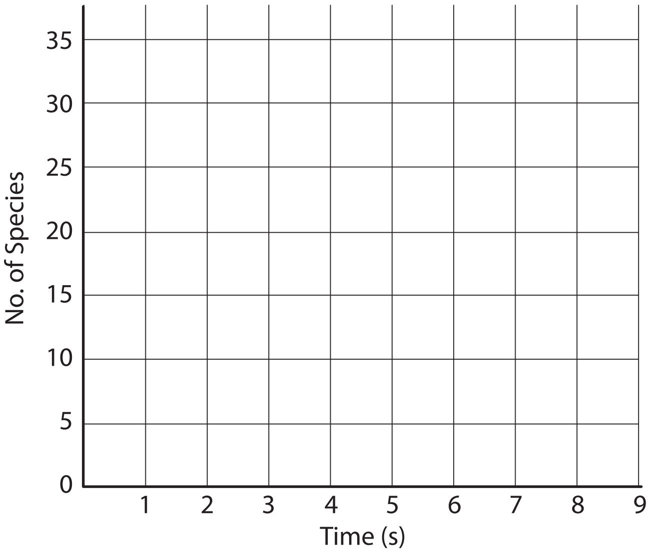
Procedure

1. Perform this activity in groups of 2 to 4 students. Each group requires 32 pennies and one six-sided die.
2. Begin by placing all 32 pennies on your desk with their head side up.
3. Each round represents 1 s of reaction time. Reactants (heads) have a 50.0% (1/2) chance of turning into products (tails) each round. Products (tails) have a 16.7% (1/6) chance of turning into reactants (heads) each round. For each round:
   (a) For each head: Simply flip the coin to see whether it remains a head or changes to a tail. This means that in round 1 you flip all 32 coins.
   (b) For each tail: Roll a die and only turn the coin over if you roll a 6.

   Note: Although the reactant and product species would actually be mixed, it is easier to keep track of your heads and tails if you put them in separate groups after each round.
4. Use the table and graph provided below to record the number of reactant and product species present after each round. Draw the reactant's and product's plots using different colored pencils.

Time (Round) (s)	No. of Reactant Species (Heads)	No. of Product Species (Tails)
0	32	0
1		
2		
3		
4		
5		
6		
7		
8		
9		

No. of Reactant and Product Species vs. Time



Results and Discussion

1. What does turning over a coin represent in this model?

2. Approximately one-half of the reactants are converted into products each second while only about one-sixth of the products are converted into reactants each second. Identify two possible reasons for the reverse reaction being more difficult to complete than the forward reaction.

3. Why should the percentage of tails that react (turn over) actually increase as the number of tails increases?

2.1 Review Questions

1. Identify each of the following as being either an *equilibrium* or a *steady state*:
   (a) As bees go back and forth from their hive to a flowerbed, the number of bees inside the hive and at the flowerbed remains constant.

   (b) Despite people checking in and out of a motel each day, the number of guests registered at the motel each night remains constant.

   (c) During a basketball game, team members are frequently being substituted in and out of the game. There are always five players on the floor and seven players on the bench.

   (d) Two new students enrol in your chemistry class each day because they hear from their friends how interesting the class is. Unfortunately two students also withdraw each day.

   (e) Shoppers at the Hotel California Mall can never leave (but it's a lovely place). Shoppers travel back and forth on escalators between the mall's two levels though the number of shoppers on each level never changes.

2. An equilibrium exists when a reaction's forward rate equals its reverse rate. Answer the questions below for the following equilibrium:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$$

   (a) Do the moles of NO consumed per second equal the moles of NO produced per second?

   (b) Do the moles of NO consumed per second equal the moles of NOCl consumed per second?

   (c) Do the moles of NOCl produced per second equal the moles of Cl_2 consumed per second?

   (d) Do the grams of NO consumed per second equal the grams of NO produced per second?

   (e) Do the grams of NO consumed per second equal the grams of NOCl consumed per second?

3. $H_2(g)$ is being consumed at a rate of 0.012 mol/s in the following equilibrium:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

(a) How many moles of N_2 are being produced and consumed each second?

(b) How many grams of NH_3 are being produced and consumed each second?

4. Melting and evaporating are physical changes, not chemical changes, but changes of physical state can also form dynamic equilibria.

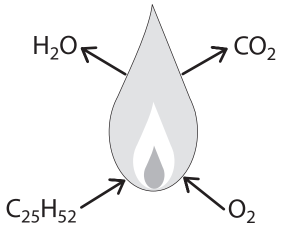
(a) An ice cube floats in a water bath held at 0°C. The size of the ice cube remains constant because the ice is melting at the same rate as the water is freezing. Describe and explain what you would observe if the temperature of the water bath was increased slightly.

(b) The water level in a flask drops as water evaporates from it. The flask is then closed using a rubber stopper. The water level continues to drop for a while but eventually holds steady. Explain why the water level is no longer falling. (Has the evaporation stopped?)

5. A chemist observes a closed system at a constant temperature in which no macroscopic changes are occurring. To determine whether or not the system is at equilibrium, the chemist increases its temperature and notes a change in the properties of the system. Can you be sure that this system is at equilibrium? Explain your answer.

6. Nobel laureate (prize winner) Ilya Prigogine coined the term *dissipative structures* for systems such as candle flames that are in steady state. The chemical reaction for burning one type of wax is:

$$C_{25}H_{52}(g) + 38\,O_2(g) \rightarrow 25\,CO_2(g) + 26\,H_2O(g)$$



A continuous reaction occurs in a flame. The amount of each reactant and product in the flame remains relatively constant as reactants are continuously drawn in to replace those consumed and the products continuously dissipate into the surrounding air.

(a) How is this situation like an equilibrium?

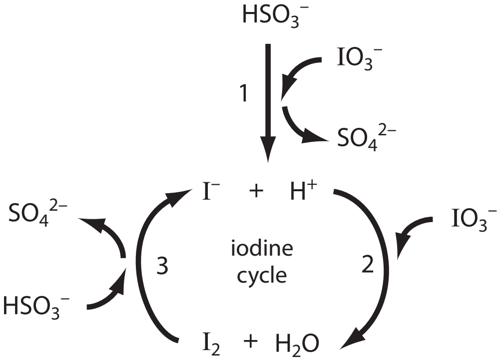
(b) How is this situation different from an equilibrium?

Fascinate your friends by blowing out a candle flame and then re-igniting the evaporating paraffin gas by placing a lit match a couple centimeters above the wick. Try it!

7. Clock reactions are often used to demonstrate the effect of concentration and temperature on reaction rates. The distinctive aspect of clock reactions is a long delay followed by a sudden appearance of product. This peculiar behavior frequently results from a cyclic mechanism. Consider the mechanism of the iodine clock reaction below:

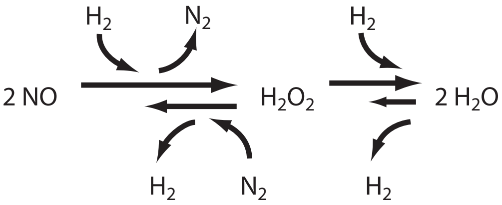
Step 1 $3\ HSO_3^- + IO_3^- \rightarrow I^- + 3\ H^+ + 3\ SO_4^{2-}$
Step 2 $10\ I^- + 12\ H^+ + 2\ IO_3^- \rightarrow 6\ I_2 + 6\ H_2O$
Step 3 $I_2 + H_2O + HSO_3^- \rightarrow 2\ I^- + 3\ H^+ + SO_4^{2-}$

Why is the two-step iodine cycle at the end of this mechanism not an equilibrium even when the two steps are proceeding at the same rate?



8. When considering equilibria, chemists sometimes forget that the forward and reverse reactions may occur through a series of steps. Consider the following reaction mechanism approaching equilibrium:

Step 1: $2\ NO + H_2 \rightarrow N_2 + H_2O_2$
Step 2: $H_2O_2 + H_2 \rightarrow 2\ H_2O$
Overall: $2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$



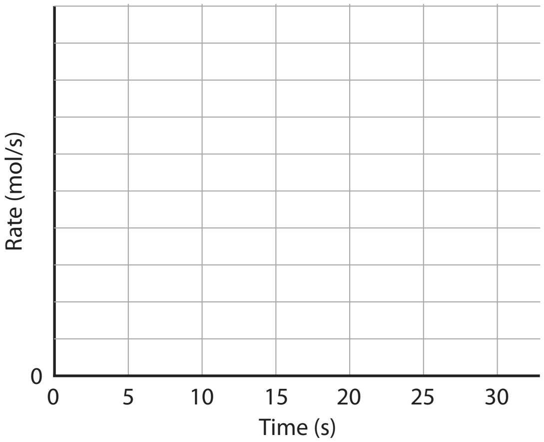
If a reaction is at equilibrium, every step in its mechanism must be at equilibrium. When the above reaction establishes equilibrium, how do you know that:

(a) step 1 must be at equilibrium?

(b) step 2 must be at equilibrium?

9. A chemical reaction achieves equilibrium 20 s after it is initiated. Plot and label the forward reaction rate and the reverse reaction rate as a function of time from *t* = 0 s (initiation) until *t* = 30 s. (Caution: This is **not** the same kind of plot as in Figure 2.1.3. Here you are plotting the rate as a function of time whereas in Figure 2.1.3, we plotted the concentration of reactants and products as a function of time.)

Rate (forward and reverse) vs. Time for a Reaction Achieving Equilibrium



10. Nitrogen dioxide gas is placed in a sealed flask.

$2\,NO_2(g) \rightarrow N_2O_4(g)$

orange colorless

(a) What would you see as the reaction approaches equilibrium?

(b) Describe the change in the concentrations of reactants and products as the reaction approaches equilibrium.

(c) Describe the change in the forward and reverse rates as the reaction approaches equilibrium.

11. A system at equilibrium has all of its reactants suddenly removed. Describe how the system would restore equilibrium in terms of its forward and reverse reaction rates and its reactant and product concentrations.

2.2 Le Châtelier's Principle

Warm Up

Consider the following equilibrium: $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

1. What is equal at equilibrium?

____

2. What would happen to the forward rate if some O_2 were removed from this equilibrium?

____

3. Explain why, in terms of collision theory.

____

4. Would the reaction still be at equilibrium at this point?

____

Equilibria Response to Adding or Removing Chemicals

In 1888, the French chemist Henry Le Châtelier wrote, "Every change of one of the factors of an equilibrium occasions a rearrangement of the system in such a direction that the factor in question experiences a change in a sense opposite to the original change." Le Châtelier's principle has since been expressed in many different ways that are fortunately easier to understand than Le Châtelier's own wording.

Le Châtelier's principle: An equilibrium system subjected to a stress will shift to partially alleviate the stress and restore equilibrium.

In other words, when an equilibrium system is disrupted, it will shift its reactant and product concentrations, changing one into the other, to reduce the disruption and re-establish equilibrium. Le Châtelier's principle allows chemists to predict what will happen to an equilibrium's reactant and product concentrations when its conditions change.

When a quantity of reactant or product is added to an equilibrium system, the system will shift to remove *some* of the added chemical.

When a quantity of reactant or product is removed from an equilibrium system, the system will shift to replace *some* of the removed chemical.

An **equilibrium system** is a reacting system that is at or approaching equilibrium. When we change the concentration of a reactant or a product, we "stress" the equilibrium system by temporarily destroying the equilibrium condition. When a system responds by changing some reactants into products, the response is referred to as a "**shift right**" because the products are on the right side of a chemical equation. When a system responds by changing some products into reactants, the response is called a "**shift left**."

Sample Problem 2.2.1(a) — Predicting How an Equilibrium System Will Respond to the Addition of Reactant or Product

Some HI is added to the system below. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the concentration of each substance compare to its concentration before the HI was added?

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

What to Think About	How to Do It
1. Using Le Châtelier's principle, determine that the system will shift to remove some of the added HI.	The system must *shift left* (toward reactants) to consume some of the added HI.
2. Infer from Le Châtelier's principle that the shift left produces H_2 and I_2. Note that Le Châtelier's principle doesn't explicitly state what happens to the concentrations of H_2 and I_2, but you can infer what happens from your understanding of the principle	Since not all of the added HI will be removed, the [HI] will increase. The $[H_2]$ and $[I_2]$ will also increase

How does a chemist remove chemicals from an equilibrium system? Obviously you can't simply reach in and pick some ions or molecules out. Chemists usually remove one chemical by reacting it with another. The reaction that removes the chemical might also arrive at equilibrium. We'll discuss this situation in later chapters.

Students often state that a stressed equilibrium system "*tries to* restore equilibrium" or "*tries to* remove some of the added chemical." As Yoda of *Star Wars* says, "Do or do not. There is no try." A stressed system doesn't *try to* restore equilibrium; it *does* restore equilibrium. When a reactant or product is added to an equilibrium system, it doesn't *try to* remove some of the added chemical; it *does* remove some of the added chemical.

Sample Problem 2.2.1(b) — Predicting How an Equilibrium System Will Respond to the Removal of Reactant or Product

Some solid calcium hydroxide is in equilibrium with a saturated solution of its ions.

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ OH^-(aq)$$

This is a solubility equilibrium. The rate of dissolving equals the rate of recrystallizing. Some OH^- is removed by adding some hydrochloric acid to the solution. (The H^+ in the acid neutralizes some OH^- to produce H_2O.) In what direction will the equilibrium shift? When equilibrium is restored, how will the calcium ion and the hydroxide ion concentrations compare to their concentrations before the acid was added?

What to Think About	How to Do It
1. Using Le Châtelier's principle, determine that the system will shift to replace some of the removed OH^-.	The system must shift right (towards products) to replace some of the removed OH^-.
2. Determine the effect of the shift right. The shift right also produces some Ca^{2+} and causes more of the $Ca(OH)_2(s)$ to dissolve.	Since not all of the removed OH^- is replaced, the $[OH^-]$ will decrease. The $[Ca^{2+}]$ will increase.

Practice Problems 2.2.1 — Predicting How an Equilibrium System Will Respond to the Addition or Removal of Reactant or Product

Use the following system for questions 1 and 2:

$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$

1. (a) What does Le Châtelier's principle say will occur if some $Fe(NO_3)_3$ is added to the system? ($Fe(NO_3)_3$ dissociates into independent Fe^{3+} and NO_3^{-} ions in solution.)

   (b) In what direction will the system shift?

   (c) When equilibrium is restored, how will the concentration of each substance compare to its concentration before the $Fe(NO_3)_3$ was added?

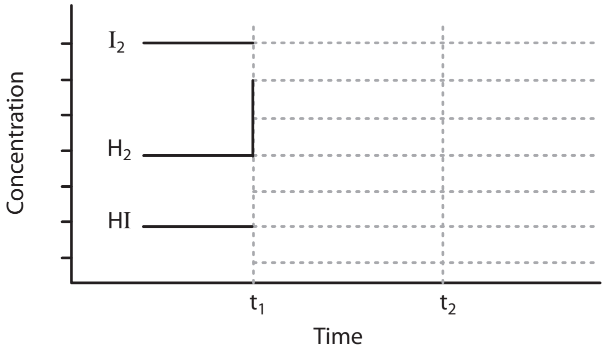
2. (a) What does Le Châtelier's principle say will occur if some sodium biphosphate is added to the system? (The HPO_4^{2-} ion reacts with the Fe^{3+} ion to produce $FeHPO_4^{+}$.)

   (b) In what direction will the system shift?

   (c) When equilibrium is restored, how will the concentration of each substance compare to its concentration before the sodium biphosphate was added?

3. Look at the graph below. At t_1 more H_2 was suddenly added to the closed system as shown. Equilibrium was re-established at t_2. Complete the plots to show how the system would respond.

Concentration vs. Time for $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$



The Shift Mechanism: Effects of Stress on Forward and Reverse Reaction Rates

Le Châtelier's principle describes how an equilibrium system responds to a stress without offering any explanation of the response. The explanation is related to the effect of the stress on the equilibrium's forward and reverse reaction rates. To an equilibrium system, a **stress** is any action that has a different effect on the forward reaction rate than it does on the reverse reaction rate, thus disrupting the equilibrium. In other words, a disrupted or stressed equilibrium system is no longer at equilibrium because its forward and reverse reaction rates are not equal.

Sample Problem 2.2.2(a) — Describing the Shift Mechanism

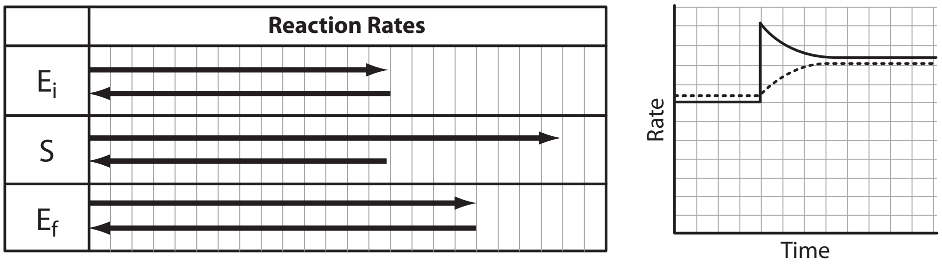
Explain in terms of forward and reverse reaction rates how the following equilibrium system would respond to adding some iron(III) chloride. ($FeCl_3$ dissociates into independent Fe^{3+} and Cl^- ions in solution.)

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

What to Think About	How to Do It
1. Determine the immediate effect of the stress on the forward and/or reverse reaction rates	Adding some Fe^{3+} increases the forward reaction rate (r_f).
2. Decide if this results in a net forward or net reverse reaction.	This results in a net forward reaction, also known as a shift right.

The system in Sample Problem 2.2.2(a) would re-equilibrate in the same manner that it established equilibrium in the first place. Figure 2.2.1(a) shows the rates when the system is initially at equilibrium (E_i), when the system is stressed (S), and when the system restores equilibrium (E_f). The net forward reaction would cause the reactant concentrations and the forward rate (r_f) to decrease, while the product concentrations and the reverse rate (r_r) increase, until r_f once again equals r_r.

The graph in Figure 2.2.1(b) is the more traditional way of depicting the same information shown in the arrow diagram in (a). In (b), the solid line represents the forward rate and the dotted line represents the reverse rate.



(a) (b)

Figure 2.2.1 *Two different ways of representing a reaction in a diagram*

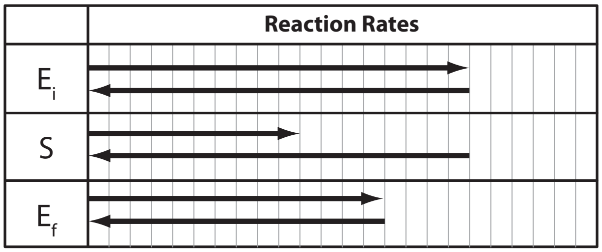
Sample Problem 2.2.2(b) — Describing the Shift Mechanism

Explain in terms of forward and reverse reaction rates how the following reaction would respond to removing some SO_2.

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

What to Think About	How to Do It
1. Determine the immediate effect of the stress on the forward and/or reverse reaction rates.	Removing some SO_2 decreases the forward reaction rate (r_f).
2. Decide if this results in a net forward or net reverse reaction.	This results in a net reverse reaction, also known as a shift left.

The kinetics diagram on the right illustrates the rates at the initial equilibrium, at the time of the stress, and when equilibrium is restored. Note that the rates are lower when equilibrium is restored than they were at the initial equilibrium. This is logical since some chemical was removed from the system.



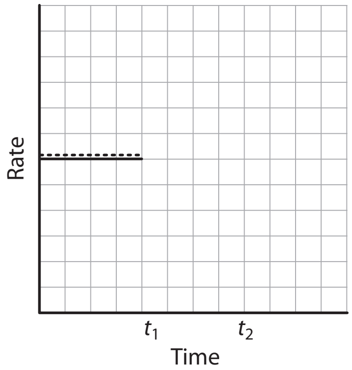
Practice Problems 2.2.2 — Describing the Shift Mechanism

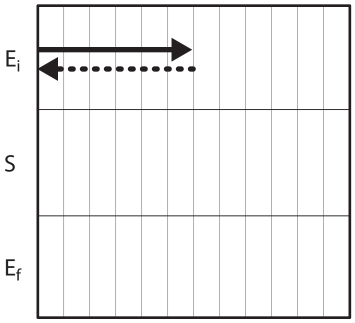
Consider the following equilibrium system:

$$2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$$

1. Explain in terms of forward and reverse reaction rates how the equilibrium would respond to each of the following changes.
   - (a) adding some NO
   - (b) removing some Cl_2
   - (c) removing some NOCl

2. Show how the forward and the reverse reaction rates respond to a sudden addition of NO to the system at t_1. Use a solid line for the forward rate and a dotted line for the reverse rate. The system re-equilibrates at t_2. The arrow diagram on the right of the graph is another way of depicting the same information. You may use it to do your rough work.





Changing Surface Area and Adding Catalysts

In heterogeneous reactions, an increase in surface area increases the forward and reverse rates equally since both forward and reverse reactions occur at the same surface. Adding more solid or crushing the solid present at equilibrium therefore has no effect on the equilibrium concentrations of the reactants and products in solution. When the initial reactants have a greater surface area, the system reaches equilibrium sooner. Likewise, adding a catalyst increases the forward and reverse rates equally and therefore has no effect on the position of the equilibrium. When a catalyst is added to the initial reactants, the system reaches equilibrium sooner.

The Equilibrium Position

The phrase **equilibrium position** refers to the relative concentrations of reactants and products at equilibrium and is usually expressed as percent yield. In Chemistry 11, you learned that percent yield is the amount of a product formed or recovered as a percentage of what the complete reaction will theoretically produce.

$$\textbf{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

An equilibrium system with an increased percent yield is said to have an equilibrium position farther to the right. "The equilibrium *position* shifted right" translates to: "the system has a greater percent yield than it had at the previous equilibrium." It is important to make a distinction between the equilibrium system shifting in response to a stress (as described by Le Châtelier's principle) and the equilibrium position shifting as a possible result. When you lose your balance snowboarding, you shift your weight to regain your balance. Sometimes you also shift your balance farther forward or backward on your board. Likewise, when an equilibrium system shifts to remove some of an added chemical or to replace some of a removed chemical, the system may "overshoot" or "undershoot" the original equilibrium position, depending on the circumstance. Consider the following equilibrium:

$$\underset{\text{yellow}}{HP(aq)} \rightleftharpoons H^+(aq) + \underset{\text{blue}}{P^-(aq)}$$

A green solution indicates equal concentrations of HP and P^- and therefore a 50% yield. If some yellow HP is added to a green equilibrium mixture, the *system will shift right* to remove some of the added HP. However, when equilibrium is restored, the solution is still yellow so we know that *the equilibrium position has shifted left*.

The expression "products are favored" is sometimes used to describe an equilibrium system. Be careful making inferences from this expression. Let's examine what the phrase does and, perhaps more importantly, does not mean. Products are *favored* when the equilibrium has a greater than 50 percent yield. This means that more than half of the limiting reactant has been converted into product.

Without knowing which reactant is limiting, you cannot infer that any one reactant or product has a higher or lower concentration than any other reactant or product solely from the products being favored. For example:

$$H_3BO_3(aq) + CN^-(aq) \rightleftharpoons H_2BO_3^-(aq) + HCN(aq)$$

Even though products are favored in the above equilibrium, the [HCN] may be less than the $[CN^-]$ if the CN^- is in excess. Likewise, the [HCN] may be less than the $[H_3BO_3]$ if the H_3BO_3 is in excess. Furthermore, a reasonable excess of either reactant ensures that the total [reactants] will be greater than the total [products] even though the products are favored.

Quick Check

1. State Le Châtelier's principle in your own words.

   ____

   ____

2. According to Le Châtelier's principle, how will an equilibrium respond when a quantity of product is removed?

   ____

3. How is a stress to an equilibrium system defined?

   ____

4. How does adding a catalyst affect an equilibrium's forward and reverse reaction rates?

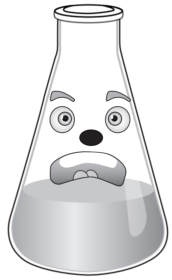
   ____

5. A chemist dissolves $NaHSO_3$ in a solution of HNO_2. The following equilibrium is established with reactants being favored:

   $HSO_3^-(aq) + HNO_2(aq) \rightleftharpoons H_2SO_3(aq) + NO_2^-(aq)$

   True or False? We can infer from this that $[HNO_2] > [H_2SO_3]$. ____________

2.2 Activity: How an Equilibrium System "Copes" With Stress



Question

Can we use our mathematical model to demonstrate how an equilibrium system "copes" with having some reactant added?

Background

Le Châtelier's principle states that any equilibrium system subjected to a stress will restore equilibrium by partially counteracting the stress. Let's test this principle by adding some reactant to the equilibrium we established in the 2.1 Activity.

Procedure

1. Perform this activity in groups of two to four students. Each group requires 48 pennies.
2. Begin by recreating the equilibrium you achieved in the 2.1 Activity by placing 32 pennies on your desk, 8 with their "head" side up and 24 with their "tail" side up.
3. Each round represents 1 s of reaction time. Reactants (heads) have a 50.0% (1/2) chance of turning into products (tails) each round. Products (tails) have a 16.7% (1/6) chance of turning into reactants (heads) each round. For each round:
   (i) For each head: Simply flip the coin to see whether it remains a head or changes to a tail.
   (ii) For each tail: Roll a die and only turn the coin over if you roll a 6.
4. After two rounds, add 16 heads to the reacting mixture and then continue the activity as before until equilibrium has been restored.

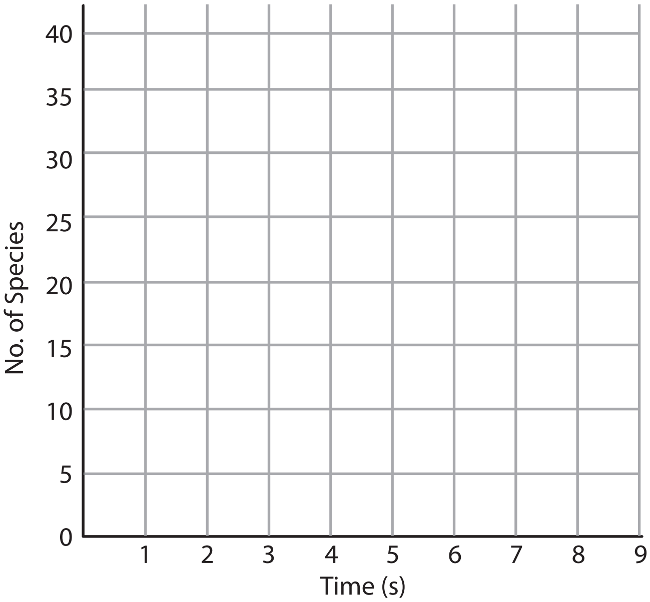
Continued opposite

2.2 Activity: *Continued*

5. Use the table and graph provided below to record the number of reactant and product species present after each round. Draw the reactant's plot and the product's plot with different-colored pencils.

Time (Round) (s)	No. of Reactant Species (Heads)	No. of Product Species (Tails)
0	8	24
1		
2	+ 16 =	
3		
4		
5		
6		
7		
8		
9		

No. of Reactant and Product Species vs. Time



Results and Discussion

1. According to Le Châtelier's principle, the number of heads present when equilibrium is restored could be as few as _________ or as many as __________. Explain.

2. How many heads were present when equilibrium was re-established? _________

2.2 Review Questions

1. Consider the following equilibrium system: $2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$

   (a) What does Le Châtelier's principle say will occur if some NO is added to the system?

   (b) In which direction will this system shift in response to the stress?

   (c) Compare the $[Cl_2]$ when equilibrium is reestablished to its concentration before the NO was added.

2. Consider the following equilibrium system: $2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g)$

   (a) Explain in terms of forward and reverse reaction rates how the system responds to removing some O_2.

   (b) Compare the rates of the forward and reverse reactions when equilibrium is reestablished with the rates before some O_2 was removed.

3. Silver nitrate is added to the equilibrium system:
   $Ag(S_2O_3)_2^{3-}(aq) \rightleftharpoons Ag^+(aq) + 2\ S_2O_3^{2-}(aq)$

   When equilibrium is restored, how will each ion's concentration compare with its concentration before the silver nitrate was added? Explain how you arrived at your answer.

4. Cholesterol is a component of cell membranes and a building block for hormones such as estrogen and testosterone. About 80% of the body's cholesterol is produced by the liver, while the rest comes directly from our diet. There are two forms of cholesterol: a "good" form (HDL) that helps lubricate blood vessels and a "bad" form (LDL) that deposits on the inside of artery walls where it can restrict blood flow. Suppose these two forms could be converted from one to the other via the following "equilibrium" reaction:
   $LDL + X \rightleftharpoons HDL + Y$

   (a) Briefly explain why a drug that removes the bad cholesterol (LDL) would not be completely effective (i.e., it would have a bad side-effect).

   (b) Referring to the above equilibrium, how could a drug company effectively treat people with too high an LDL:HDL ratio?

5. Sulphur dioxide is an important compound in wines, where it acts as an antimicrobial and antioxidant to protect the wine from spoiling. The following equilibrium exists in wines:
$SO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$
State whether a winemaker should increase the wine's pH (by removing H^+) or decrease the wine's pH (by adding H^+) to shift the equilibrium toward the active SO_2?

6. Complete the following table using the words "decrease," "same," or "increase" to indicate how the equilibrium concentrations are affected by the stated stress. "Increase" means that when equilibrium is restored, the chemical's concentration is greater than it was before the stress.

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$$

		Add NH_3	**Remove some H_2**	**Add N_2**
Equilibrium Concentration	N_2			
	H_2			
	NH_3			

7. $\underset{\text{red}}{HP} \rightleftharpoons H^+ + \underset{\text{yellow}}{P^-}$

The above equilibrium system appears orange due to equal concentrations of HP and P^-.
(a) What action will shift the equilibrium so the solution turns red?

(b) What could be done to shift the equilibrium so the solution turns yellow?

8. Hemoglobin is the protein in red blood cells that transports oxygen to cells throughout your body. Each hemoglobin (Hb) molecule attaches to four oxygen molecules:
$Hb(aq) + 4\,O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$

In which direction does the above equilibrium shift in each of the following situations:
(a) At high elevations the air pressure is lowered reducing the $[O_2]$ in the blood.

(b) At high altitude, climbers sometimes breathe pressurized oxygen from a tank to increase the $[O_2]$ in the blood.

(c) People who live at higher altitudes produce more hemoglobin.

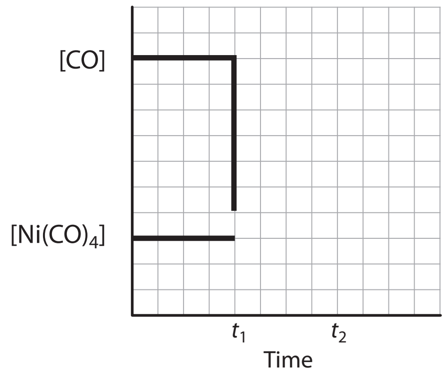
(d) Carbon monoxide poisoning occurs when carbon monoxide molecules bind to hemoglobin instead of oxygen molecules. Carboxyhemoglobin is even redder than oxyhemoglobin; therefore, one symptom of carbon monoxide poisoning is a flushed face.

9. Explain why neither adding a catalyst nor increasing the surface area of S(*s*) stresses the following equilibrium, even though each of these actions increases the forward reaction rate.
$2\ S(s) + 3\ O_2(g) \rightleftharpoons 2\ SO_3(g)$

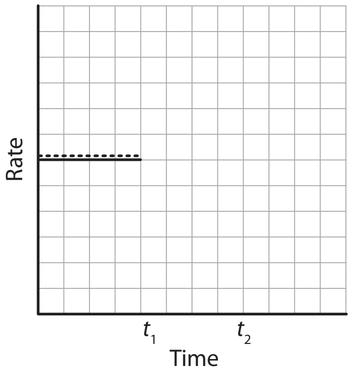
10. The following equilibrium exists in an aqueous solution of copper(II) chloride:
$CuCl_4^{2-}(aq) + 4\ H_2O(l) \rightleftharpoons Cu(H_2O)_4^{2+}(aq) + 4\ Cl^-(aq)$
green blue
    (a) Some Cl^- is removed by adding some silver nitrate to the solution. The Ag^+ in the silver nitrate precipitates with the Cl^- to produce AgCl(*s*). In what direction will the equilibrium shift?

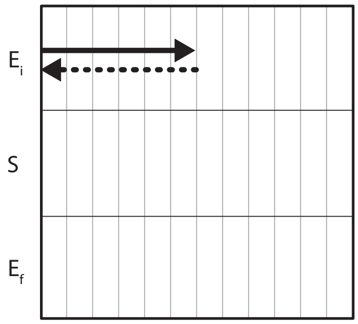
    (b) If the initial equilibrium mixture was blue, what would you observe as a sodium chloride solution was added dropwise to the equilibrium mixture?

11. At t_1 some CO was suddenly removed from the closed system shown below. Equilibrium was reestablished at t_2. Complete the plots to show how the system would respond.
$Ni(s) + 4\ CO(g) \rightleftharpoons Ni(CO)_4(g)$

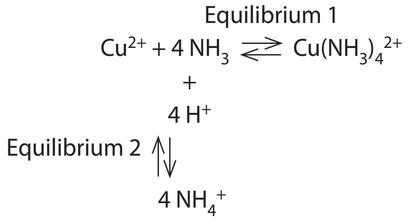


12. Show how the forward and reverse reaction rates respond to having some HOCl suddenly removed from the following system at t_1.
$H_2O(g) + Cl_2O(g) \rightleftharpoons 2\ HOCl(g)$
Use a solid line for the forward rate and a dotted line for the reverse rate. The system re-equilibrates at t_2. The arrow diagram on the right is another way of displaying the same information. You may use it to do your rough work.





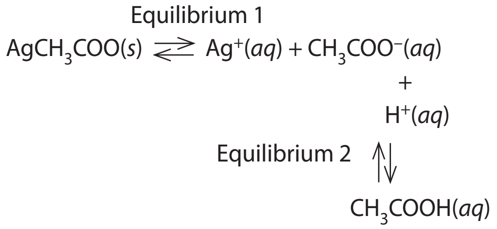
13. Equilibria are often linked through one chemical common to both. Even two equilibria coupled together present an interesting dynamic.



$$\begin{array}{c} \text{Equilibrium 1} \\ Cu^{2+} + 4\,NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} \\ + \\ 4\,H^+ \\ \text{Equilibrium 2}\ \Updownarrow \\ 4\,NH_4^+ \end{array}$$

How would the $[Cu^{2+}]$ be affected by adding some H^+ to this coupled system? Briefly explain using Le Châtelier's principle.

14. Silver acetate has a low solubility in water. A small amount of solid silver acetate is in equilibrium with a saturated solution of its ions.



$$\begin{array}{c} \text{Equilibrium 1} \\ AgCH_3COO(s) \rightleftharpoons Ag^+(aq) + CH_3COO^-(aq) \\ + \\ H^+(aq) \\ \text{Equilibrium 2}\ \Updownarrow \\ CH_3COOH(aq) \end{array}$$

What would you observe occurring in the beaker as $H^+(aq)$ is added dropwise to the solution? Briefly explain using Le Châtelier's principle.

15. Consider the following equilibrium:

$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$

Describe how [NO] could be greater than the $[NO_2]$ despite the products being favored at equilibrium.

16. Because few natural systems are closed, many of nature's reversible reactions are perpetually "chasing after" equilibrium. In *At Home in the Universe*, the author, Stuart Kauffman, describes living systems as "persistently displaced from chemical equilibrium." Describe one way to ensure that a reversible reaction never achieves equilibrium.

2.3 How Equilibria Respond to Volume and Temperature Changes

Warm Up

1. What is the scientific meaning of *pressure*?

   ____

2. To increase gas pressure, we _______________ the gas into less space.

3. What is temperature a measure of?

   ____

4. An increase in temperature increases the rate of reactions because the molecules collide more ________________ and ____.

How Equilibria Respond to Volume Changes

We've described and explained how equilibria respond to changing the concentration of a single reactant or product. The concentrations of all the reactants and products can be changed simultaneously by changing the volume of the reacting system. The volume of a gaseous system can be changed by compressing or decompressing it. The volume of an aqueous system can be changed by evaporating water from it or by diluting it. A change in volume changes all the reactants' and products' concentrations.

It isn't possible for a shift to partially restore all the chemicals' concentrations but some equilibria can shift to partially restore the total or combined concentration of the chemicals. For example, if an aqueous equilibrium is diluted then all the chemical concentrations are decreased. A shift can't increase the concentrations of chemicals on both sides of the equation but some equilibria can increase the total chemical concentration by shifting to the side of the equation with the greater number of particles. Le Châtelier views this situation from the perspective of pressure.

> Equilibria respond to volume changes by shifting to relieve some of the added pressure or to replace some of the lost pressure.

You are probably familiar with the concept of gas pressure, but you may not be familiar with the concept of solute (osmotic) pressure. A detailed discussion of osmosis and osmotic pressure is not required here. You need only know that osmotic pressure is to dissolved particles what gas pressure is to gas particles. In 1901, the Dutch chemist Jacobus van't Hoff discovered that dissolved particles in an aqueous solution behave just like gas particles in a container. The relationship between the concentration, temperature, and pressure is the same for gas particles and dissolved particles. Van't Hoff won the first Nobel Prize in chemistry for his work on osmotic pressure and chemical equilibrium. Just as a gas's pressure is proportional to its concentration of gas particles, an aqueous solution's osmotic pressure is proportional to its concentration of solute particles. Decompressing a gas lowers its gas pressure. Diluting a solute lowers its osmotic pressure.

Chemists sometimes refer to the partial pressure of a gas. **Partial pressure** is the gas's part of the total gas pressure or the pressure exerted by this gas alone in a mixture of gases. The sum of the partial pressures equals the total pressure of the gas mixture. A gas's partial pressure is proportional to its concentration. The same concepts and principles apply to solutes and their partial osmotic pressures.

Consider the following equilibrium:
$H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)$

This equilibrium doesn't respond to a volume change. It cannot partially restore the pressure by shifting in either direction since there are the same number of gas particles on each side of the equation.

Quick Check

1. According to Le Châtelier's principle, how will an equilibrium respond to being compressed?

   ____

2. What is *partial pressure*?

   ____

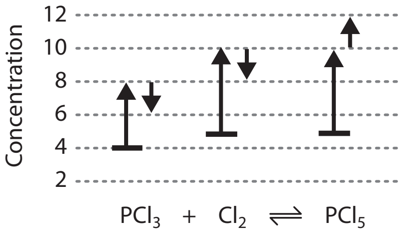
3. According to Le Châtelier's principle, how will an aqueous equilibrium respond to being diluted?

   ____

Sample Problem 2.3.1(a) — Predicting How an Equilibrium Will Respond to a Decrease in Volume

The system described by the equation below is compressed. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the number of each type of molecule and the concentration of each substance compare to those before the system was compressed?

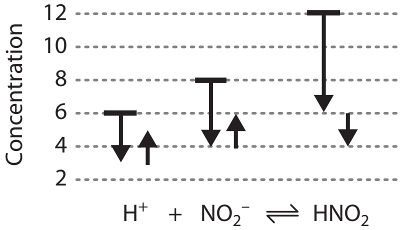
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

What to Think About	**How to Do It**
1. Recall that Le Châtelier's principle says the system will shift to relieve *some* of the added pressure.	The system must shift right to reduce the pressure.
2. Consider the effect the stress has on the system to determine the number of each type of molecule. The stress changed the amount of space that the particles move around in, not the number of particles. Only the system's response to the stress changes the number of particles. The forward reaction converts two molecules into one molecule. Thus a shift right reduces the total number of particles and the pressure of the system.	The number of PCl_5 molecules will increase, while the number of PCl_3 and Cl_2 molecules will decrease.
3. Determine the effect of compression on the concentrations of the substances in the system. The situation regarding concentration is illustrated below:  In this diagram, all the original concentrations are doubled by the compression so the volume must have been halved.	Because the system was compressed, every substance has a higher concentration or partial pressure at the new equilibrium than it did at the initial equilibrium. (Although the shift can't reduce all the chemicals' concentrations or partial pressures, it is reducing most of them (2/3) by shifting to the right. The result is that some of the added pressure is relieved.)

Sample Problem 2.3.1(b) — Predicting How an Equilibrium Will Respond to an Increase in Volume

The system below is diluted. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the number of each type of particle and the concentration of each species compare to those before the system was diluted?

$$H^+(aq) + NO_2^-(aq) \rightleftharpoons HNO_2(aq)$$

What to Think About	How to Do It
1. Recall that Le Châtelier's principle says that equilibrium will be restored by replacing *some* of the lost osmotic pressure.	The system must shift left to increase the pressure.
2. Consider the effect the stress has on the system to determine the number of each type of molecule. Only the system's response to the stress, not the stress itself, changes the number of particles. The reverse reaction converts one particle into two particles thus a shift left increases the total number of particles and the osmotic pressure of the system.	The number of HNO_2 molecules will decrease while the number of H^+ and NO_2^- ions will increase.
3. Determine the effect of dilution on the concentrations of the substances in the system. The situation regarding concentration is illustrated below:  In this diagram, all the original concentrations are halved by the dilution so the volume must have been doubled.	Because the system was diluted, every substance has a lower concentration at the new equilibrium than it did at the initial equilibrium.

Practice Problems 2.3.1 — Predicting How an Equilibrium Will Respond to a Volume Change

1. The system below is compressed:

   $2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$

   In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the number of each type of molecule and the concentration of each substance compare to those before the system was compressed?

2. The system below is diluted:

   $Ag(S_2O_3)_2^{3-}(aq) \rightleftharpoons Ag^+(aq) + 2\ S_2O_3^{2-}(aq)$

   In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the number of each type of particle and the concentration of each species compare to those before the system was diluted?

Continued opposite

Practice Problems 2.3.1 — *Continued*

3. The volume of the system below is decreased:
   $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
   Will the equilibrium system respond? Explain.

The Shift Mechanism: The Effect of Volume Change on Forward and/or Reverse Reaction Rates

For an explanation of what causes this shift, we must once again turn to chemical kinetics. When the volume of an equilibrium system changes, all the reactant and product concentrations change proportionately. Nevertheless, the forward and reverse reaction rates may change by different amounts. In doing so, they become unequal. From Le Châtelier's predictions, we can infer the following:

> The direction (forward or reverse) that has the greater sum of gaseous or aqueous reactant coefficients is the more sensitive of the two directions to volume changes.

By "more sensitive," we mean that a volume change will decrease or increase the rate of that direction more than that of the opposite direction. At equilibrium, the relationship between concentration and the reaction rate depends only on the coefficients in the balanced equation. For example, consider the following system:

$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$

Diluting this aqueous system decreases its forward rate more than its reverse rate because the sum of the reactant coefficients for the forward reaction is 2 whereas the lone reactant coefficient for the reverse reaction is only 1. If the sum of gaseous or aqueous reactant coefficients equals the sum of the gaseous or aqueous product coefficients then the equilibrium is not stressed by volume changes. This is because any volume change will have the same effect on the forward and reverse rates. For example, consider the following system:

$H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)$

Compressing this gaseous system increases its forward and reverse rates equally and therefore does not disrupt the equilibrium.

The only external factors that affect reaction rates are the reactant concentrations and temperature. A pressure change only stresses an equilibrium if the pressure change reflects a change in the reactant and product concentrations. The pressure of an equilibrium system can be changed without changing its concentrations by, for example, adding an inert gas to the system. Since this pressure change does not reflect any change of reactant or product concentrations, it does not affect the equilibrium.

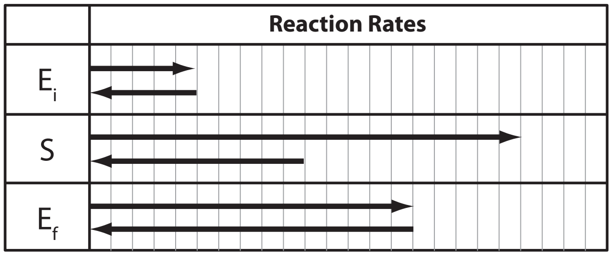
Sample Problem 2.3.2(a) — Describing the Shift Mechanism for a Decrease in Volume

Explain in terms of forward and reverse reaction rates how the equilibrium system below would respond to a decrease in volume.

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

What to Think About	How to Do It
1. Determine the immediate effect of the stress on the forward and/or reverse reaction rates.	Compressing the system increases the forward rate (r_f) more than the reverse rate (r_r).
2. Decide if this would result in a net forward or net reverse reaction.	This results in a net forward reaction, also known as a shift right.

The arrow diagram on the right illustrates the rates at the initial equilibrium, at the time of the stress, and when equilibrium is restored.



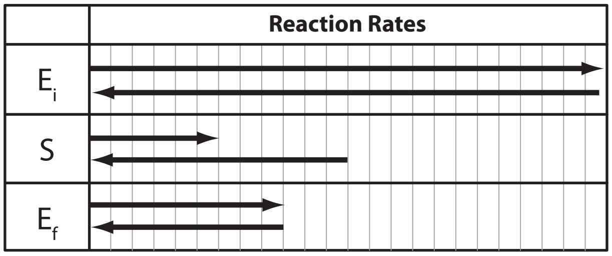
Sample Problem 2.3.2(b) — Describing the Shift Mechanism for a Volume Change

Explain in terms of forward and reverse reaction rates how the equilibrium system below would respond to being diluted.

$$H^+(aq) + SO_4^{2-}(aq) \rightleftharpoons HSO_4^-(aq)$$

What to Think About	How to Do It
1. Determine the immediate effect of the stress on the forward and/or reverse reaction rates.	Diluting the system decreases the forward rate (r_f) more than the reverse rate (r_r).
2. Decide if this would result in a net forward or net reverse reaction.	This results in a net reverse reaction, also known as a shift left.

The arrow diagram on the right illustrates the rates at the initial equilibrium, at the time of the stress, and when equilibrium is restored.

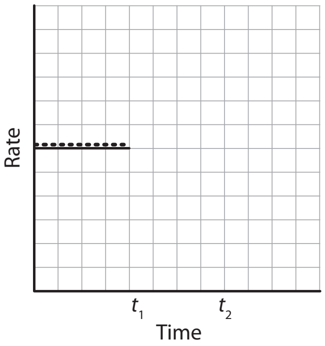


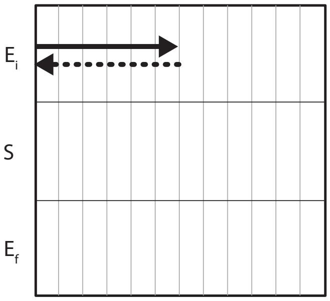
Practice Problems 2.3.2 — Describing the Shift Mechanism for Changes in Volume

1. Explain in terms of forward and reverse reaction rates how the equilibrium system below would respond to a decrease in volume. $2\ \mathrm{NOCl}(g) \rightleftharpoons 2\ \mathrm{NO}(g) + \mathrm{Cl_2}(g)$

2. Explain in terms of forward and reverse reaction rates how the equilibrium system below would respond to being diluted.
   $\mathrm{Ag(S_2O_3)_2^{3-}}(aq) \rightleftharpoons \mathrm{Ag^+}(aq) + 2\ \mathrm{S_2O_3^{2-}}(aq)$

3. Show how the forward and reverse reaction rates respond to a sudden compression of the system at t_1. Use a solid line for the forward rate and a dotted line for the reverse rate. The system restores equilibrium at t_2. The arrow diagram on the right is another way of depicting the same information. You may use it to do your rough work.
   $2\ \mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{SO_3}(g)$





How Equilibria Respond to Temperature Changes

Le Châtelier's principle states the following:

> Equilibria respond to changing temperatures by shifting to remove some of the added kinetic energy or to replace some of the removed kinetic energy.

Sample Problem 2.3.3(a) — Predicting How an Equilibrium Will Respond to an Increase in Temperature

The system below is heated. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the concentration of each species compare to its concentration before the system was heated?

$$\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{NO}(g) \qquad \Delta H = 181\ \mathrm{kJ/mol}$$

What to Think About	How to Do It
1. Recall that Le Châtelier's principle says the system will shift to remove *some* of the added kinetic energy and cool itself.	The system must shift right (in the endothermic direction) to convert some of the added KE into PE.
2. Determine the effect of heating on the concentrations of the substances in the system. Note that 2 NO molecules are formed for each $\mathrm{N_2}$ and $\mathrm{O_2}$ molecule that react.	The $[\mathrm{N_2}]$ and $[\mathrm{O_2}]$ will decrease and the [NO] will increase.

Note that ΔH can be included as part of a thermochemical equation:

$N_2(g) + O_2(g) + 181\ \text{kJ} \rightleftharpoons 2\ NO(g)$

In that case, the kinetic energy can be treated just as though it were a chemical. Adding O_2 would cause a shift to the right to remove some of the added O_2. Likewise, adding kinetic energy causes a shift to the right to remove some of the added kinetic energy.

Sample Problem 2.3.3(b) — Predicting How an Equilibrium Will Respond to a Decrease in Temperature

The system below is cooled. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the concentration of each species compare to its concentration before the system was cooled?

$$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g) \qquad \Delta H = 181\ \text{kJ/mol}$$

What to Think About	How to Do It
1. Recall that Le Châtelier's principle says the system will shift to replace *some* of the lost kinetic energy and warm itself.	The system must shift left (in the exothermic direction) to convert some PE into KE.
2. Determine the effect of cooling on the concentrations of the substances in the system. Note that 2 NO molecules are consumed for each N_2 and O_2 molecule formed.	The [NO] will decrease. The $[N_2]$ and $[O_2]$ will increase.

Practice Problems 2.3.3 — Predicting How an Equilibrium Will Respond to a Temperature Change

1. The system below is heated. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the concentration of each species compare to its concentration before the system was heated?

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \qquad \Delta H = -198\ \text{kJ/mol}$$

2. The system below is cooled. In what direction will the system shift to restore equilibrium? When equilibrium is restored, how will the concentration of each species compare to its concentration before the system was cooled?

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g) + 17\ \text{kJ/mol}$$

Effects of Volume and Temperature Changes

Figure 2.3.1 depicts the situation described in Sample Problem 2.3.3(b) above. When the stress is a sudden concentration or volume change it appears as a spike(s) on plots of concentrations versus time. Temperature changes do not appear on these plots so the system responds to an invisible stress. Another difference is that concentration changes, both individual and those resulting from volume changes, can be very sudden. However, the temperature of a system, particularly an aqueous system, cannot change rapidly. This means that chemical systems begin responding while the temperature is still changing. In other words, the response begins before the stress is complete.

Neither volume nor temperature change itself changes the percent yield so a system's response to these stresses shifts its equilibrium position in the same direction that the system shifted in response to the stress.

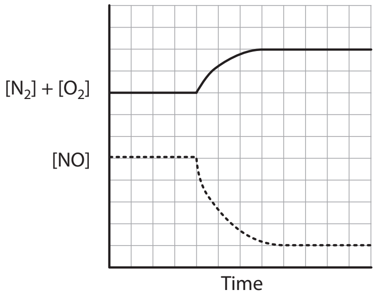


Figure 2.3.1 *Changes in concentration show up in the graph but the temperature change doesn't.*

Pressure-Temperature Relationships

Increasing the temperature of gases in a closed container increases their pressure. The temperature change itself affects the equilibrium. However, the resulting pressure change is irrelevant to the equilibrium because it does not reflect a change of concentrations. The same cannot be said for the reverse.

When a gas is compressed, its temperature rises because some of the particles' potential energy converts to kinetic energy as the particles are forced closer together. The temperature change resulting from compressing or decompressing a gas mixture does affect its equilibrium. In questions where a gaseous equilibrium is compressed or decompressed, assume that its temperature was held constant unless otherwise stated. Such a stipulation allows you to deal with only one variable at a time.

The Shift Mechanism: The Effect of Temperature Change on Forward and Reverse Reaction Rates

If the collision geometry requirements are the same for the forward and reverse reactions, then their rates depend solely on the frequency of collisions possessing the activation energy. The forward and reverse reaction rates are equal at equilibrium. Therefore the frequency of collisions possessing the activation energy must be the same for the forward and reverse reactions. The percentage of the area under a collision energy distribution curve that is at or beyond the activation energy (E_a) represents the percentage of collisions having enough energy to react.

For an endothermic reaction, like that represented in Figures 2.3.2 and 2.3.3, the forward reaction has a lower percentage of collisions with the activation energy needed than the reverse reaction does. The forward reaction must therefore have a greater frequency of collisions to achieve the same frequency of successful collisions as the reverse reaction. For example, 4% of the forward reaction's 800 collisions per second and 20% of the reverse reaction's 160 collisions per second would both equal 32 successful collisions per second. For an endothermic reaction, a higher concentration of reactants is therefore required to generate the same rate as a lower concentration of products because a lower percentage of the reactant collisions are successful.

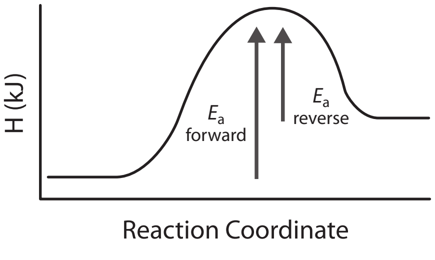


Figure 2.3.2 *Potential energy diagram.*

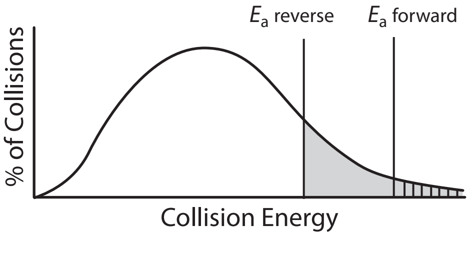


Figure 2.3.3 *Collision energy diagram*

Increases in temperature cause a shift in the endothermic direction because they increase the rate of the endothermic direction more than they increase the rate of the exothermic direction. The endothermic direction has the harder task due to its higher activation energy so it benefits more from the assistance provided by the increased temperature. Likewise, decreases in temperature cause a shift in the exothermic direction because they decrease the rate of the endothermic direction more than they decrease the rate of the exothermic direction. The endothermic direction is hindered more than the exothermic direction by the decreased temperature.

An equilibrium’s endothermic direction is more sensitive to temperature changes than its exothermic direction due to the endothermic direction’s greater activation energy.

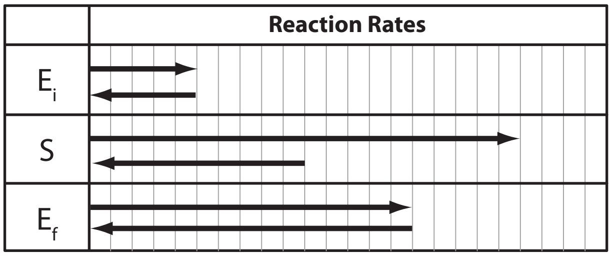
Sample Problem 2.3.4(a) — Describing the Shift Mechanism for an Increase in Temperature

Explain in terms of forward and reverse reaction rates how the system below would respond to being heated.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad \Delta H = 181 \text{ kJ/mol}$$

What to Think About	How to Do It
1. Determine the immediate effect of the stress on the forward and/or reverse reaction rates.	Heating the system increases the forward rate (r_f) more than the reverse rate (r_r).
2. Decide if this would result in a net forward or net reverse reaction.	This results in a net forward reaction, also known as a shift right.

The arrow diagram on the right illustrates the rates at the initial equilibrium, at the time of the stress, and when equilibrium is restored.



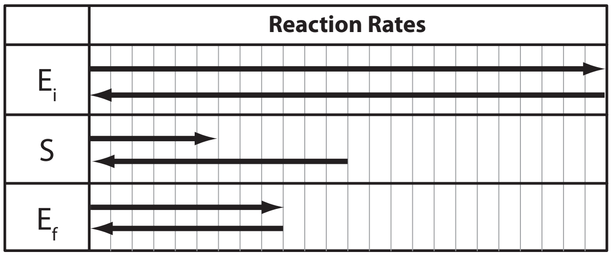
Sample Problem 2.3.4(b) — Describing the Shift Mechanism for a Decrease in Temperature

Explain in terms of forward and reverse reaction rates how the system below would respond to being cooled.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad \Delta H = 181 \text{ kJ/mol}$$

What to Think About	How to Do It
1. Determine the immediate effect of the stress on the forward and/or reverse reaction rates?	Cooling the system decreases the forward rate (r_f) more than the reverse rate (r_r).
2. Decide if this would result in a net forward or net reverse reaction.	This results in a net reverse reaction, also known as a shift left.

The arrow diagram on the right illustrates the rates at the initial equilibrium, at the time of the stress, and when equilibrium is restored.



Practice Problems 2.3.4 — Describing the Shift Mechanism for Changes in Temperature

1. Explain in terms of forward and reverse reaction rates how the system below would respond to being heated.

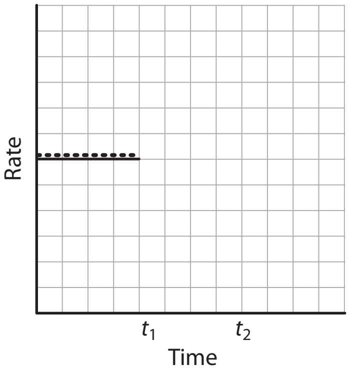
$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \qquad \Delta H = -198\text{ kJ/mol}$$

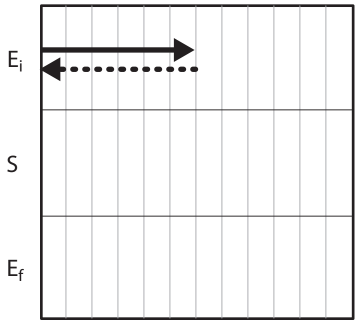
2. Explain in terms of forward and reverse reaction rates how the system below would respond to being cooled.

$$2\,Cl_2(g) + 2\,H_2O(g) + 113\text{ kJ/mol} \rightleftharpoons 4\,HCl(g) + O_2(g)$$

3. Show how the forward and reverse reaction rates in the system below would respond to a temperature increase at t_1. Use a solid line for the forward rate and a dotted line for the reverse rate. The system restores equilibrium at t_2. The arrow diagram on the right is another way of depicting the same information. You may use it to do your rough work.

$$2\,NCl_3(g) \rightleftharpoons N_2(g) + 3\,Cl_2(g) \qquad \Delta H = -460\text{ kJ/mol}$$





The Haber-Bosch Process

Almost all of the world's ammonia is produced via the Haber-Bosch process and almost all of our inorganic nitrogen compounds are produced from this ammonia. More than 100 million tonnes of ammonia with a value in excess of $600 million are produced annually. About 80% of the world's ammonia is used to produce fertilizers. Other products include explosives, plastics, fibres, and dyes.

German chemist Fritz Haber developed the equipment and procedures for producing ammonia (NH_3) from its constituent elements (N_2 and H_2) in 1910. In 1918, he received the Nobel Prize in chemistry for this accomplishment. In 1931, another German chemist, Carl Bosch, won the Nobel Prize in chemistry, in part for transforming the process to an industrial scale. The balanced equation and enthalpy for the reaction are:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -92.4\text{ kJ/mol}$$

Process Production Rate and Temperature Considerations

Consider the plight of a chemist who wants to produce NH_3 in his or her laboratory by allowing a single set of reactants to achieve equilibrium within a closed container. The percent yield and the reaction rate both need to be considered in choosing the optimal temperature. Lower temperatures produce higher percent yields of NH_3 at equilibrium since lower temperatures shift this equilibrium toward products. However, at lower temperatures the reaction proceeds at slower rates in both forward and reverse directions. Therefore it takes longer to produce any given amount of product. In other words, a higher temperature generates a faster forward rate but sustains it for a much shorter time period, both because the reaction rate is faster and the percent yield is less. To use a racing analogy, at higher temperatures the reaction runs faster toward a closer finish line (lower % yield).

Reactions proceeding at lower temperatures will eventually produce the amount produced at higher temperatures and then just keep rumbling along. This is the chemical version of the familiar tale of the tortoise versus the hare. Maximum productivity might be achieved by initially establishing equilibrium at a high temperature and then shifting the equilibrium toward products by lowering the temperature. Using a catalyst allows chemists to increase the reaction rate at a lower temperature that produces a higher percent yield.

For the Haber-Bosch process, lower temperatures produce a higher percent yield but at a lower rate.

The chemical industry does not produce ammonia by allowing single sets of reactants to establish equilibria within closed containers. As the reacting mixture is cycled and recycled through a Haber reactor, N_2 and H_2 are continuously fed in at one location while NH_3 is continuously liquefied and removed at another. The ammonia can be selectively removed because hydrogen bonding between NH_3 molecules causes them to condense at a higher temperature than hydrogen and nitrogen. The temperatures in the reactor are adjusted to maximize the concentration of NH_3, when and where it is extracted. The forward rate is kept high by replacing the consumed reactants while the reverse rate is kept low by removing product. Percent yield ceases to be a consideration if the system doesn't achieve equilibrium.

An industrial chemist must strike a compromise between the increased rate provided by a greater temperature and the increased cost to produce it. The reaction rate is also increased by using a catalyst. The "bottom line" for industry is its annual profit, not its annual production of ammonia. A plant strives to generate the greatest possible amount of ammonia for the lowest possible cost. The industry is obviously influenced by a tremendous number of commercial and economic factors as well as chemical factors.

Process Production Rate and Pressure Considerations

Higher pressures generate faster rates and push the reaction toward a higher percent yield.

According to Le Châtelier's principle, the system partially relieves the increased pressure by shifting right as the forward reaction converts four molecules into two. Compressing the gases also raises their temperature. High compression systems are expensive to build and to operate. Most Haber reactors operate at about 3.5×10^4 kPa. The increased yield at this pressure more than compensates for the higher construction and operation costs.

Quick Check

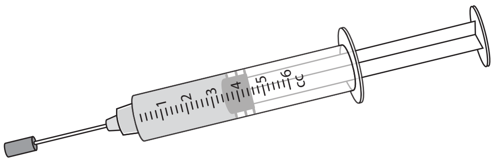
1. Name the chemical produced by the Haber-Bosch process.

   ____

2. What increases the rate of the Haber-Bosch process without decreasing its percent yield?

   ____

2.3 Activity: Dealing With Pressure



Question

What will a gaseous equilibrium mixture look like at the molecular level as it responds to being compressed?

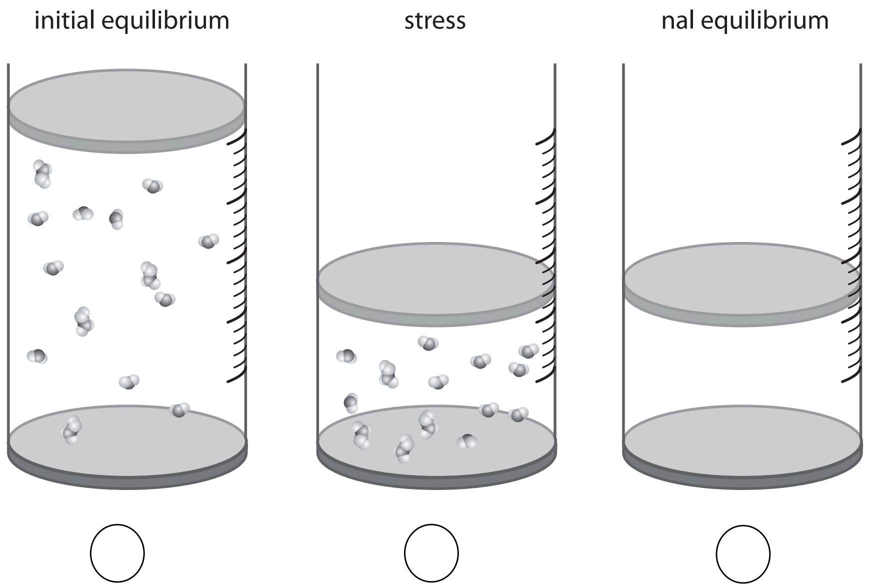
Background

An equilibrium mixture of colorless dinitrogen tetroxide, $N_2O_4(g)$, and orange nitrogen dioxide, $NO_2(g)$, forms when nitric acid is poured over copper. When this equilibrium mixture is compressed in a plugged syringe, the mixture becomes darker orange as a result of concentrating the NO_2 molecules. Within seconds the mixture's color changes slightly, yet unmistakeably, as the equilibrium shifts in response to the stress.

$$\underset{\text{colorless}}{N_2O_4(g)} + \text{energy} \rightleftharpoons \underset{\text{orange}}{2\ NO_2(g)}$$

Procedure

1. The three diagrams below represent the tube in a syringe. Complete the third diagram by drawing in a possible number of NO_2 and N_2O_4 molecules after the system has responded to the stress and restored equilibrium.
2. Color in the circle underneath each syringe to indicate how pale or dark orange the gas would appear.



Results and Discussion

1. In response to the compression, the number of NO_2 molecules ______________ and the number of N_2O_4 molecules ___________ _____.

2. Describe the molecules' behavior when the reaction in the syringe is at equilibrium.

3. How would the color of the equilibrium mixture change when the syringe is plunged into an ice bath? Explain.

2.3 Review Questions

1. Consider the following equilibrium: $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$
   (a) In which direction will the system shift if it is diluted? Explain your answer in terms of Le Châtelier's principle.

   (b) Compare the number and the concentration of SCN^{-} ions when equilibrium is restored to their number and concentration before the system was diluted.

2. Explain *in terms of forward and reverse reaction rates* how this system responds to an increase in volume.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

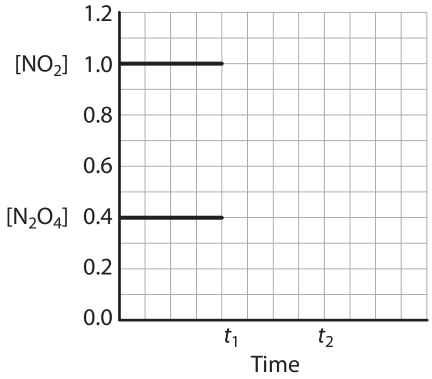
3. In which direction does the following equilibrium shift when the gas mixture is compressed? Explain using Le Châtelier's principle *and* in terms of forward and reverse reaction rates.

$$2\ C(s) + O_2(g) \rightleftharpoons 2\ CO(g)$$

4. Describe a situation when equilibrium concentrations change but no stress occurs.

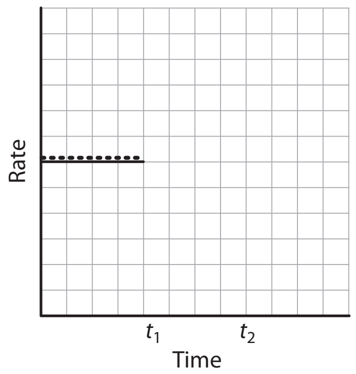
5. Complete the following plots. The system is at equilibrium prior to t_1. At t_1 the volume of the system is suddenly doubled. The system responds to this stress between t_1 and t_2 until it re-equilibrates at t_2.

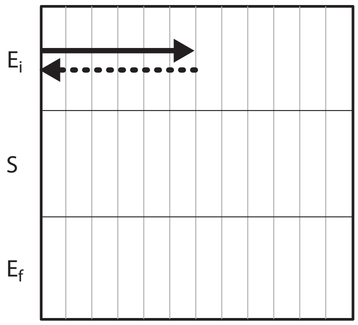
$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$



6. Show how the forward and reverse reaction rates respond to a sudden increase in the volume of the system at t_1. Use a solid line for the forward rate and a dotted line for the reverse rate. The system restores equilibrium at t_2. The arrow diagram on the right is another way of depicting the same information. You may use it to do your rough work.

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$





7. The solubility of a substance is its highest possible concentration at a given temperature. Any further solid added to the solution will remain undissolved in equilibrium with the dissolved state. Dissolving sodium sulphate in water is exothermic.

$$Na_2SO_4(s) \rightleftharpoons 2\ Na^+(aq) + SO_4^{2-}(aq) + \text{heat}$$

State whether sodium sulphate will be less soluble or more soluble when the temperature of the solution is increased. Explain.

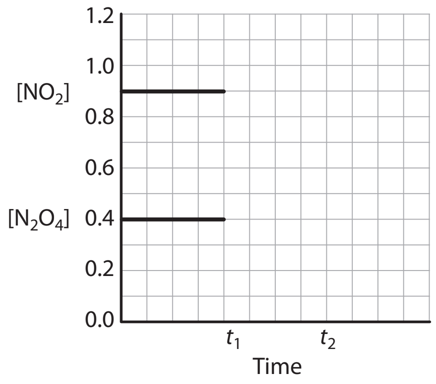
8. In which direction will the following equilibrium system shift when it is heated?

$$2\ SO_3(g) + 192\ \text{kJ/mol} \rightleftharpoons 2\ SO_2(g) + O_2(g)$$

Provide two ways to arrive at this answer.

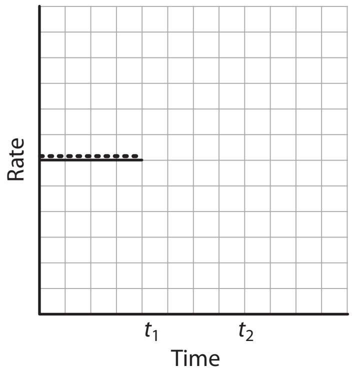
9. Complete the following plots. The system below is at equilibrium prior to t_1. The system is suddenly cooled at t_1. The system responds to this stress between t_1 and t_2 until it re-equilibrates at t_2.

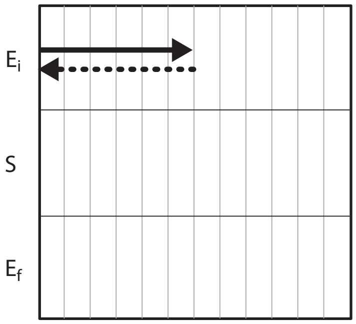
$$N_2O_4(g) + 57\ \text{kJ} \rightleftharpoons 2\ NO_2(g)$$



10. Show how the forward and reverse reaction rates respond to a sudden increase in the temperature of the system below at t_1. Use a solid line for the forward rate and a dotted line for the reverse rate. The system restores equilibrium at t_2. The arrow diagram on the right is another way of depicting the same information. You may use it to do your rough work.

$$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g) \qquad \Delta H = -603 \text{ kJ/mol}$$

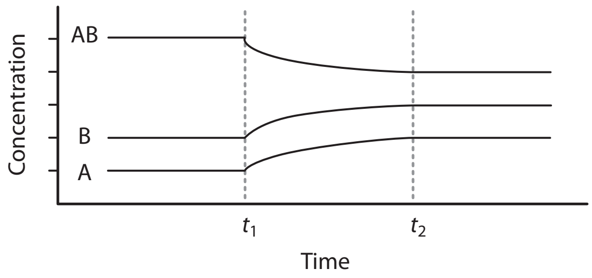




11. $Co(H_2O)_6^{2+}(aq) + 2\,Cl^-(aq) \rightleftharpoons Co(H_2O)_4Cl_2(aq) + 2\,H_2O(l)$
pink purple

A flask containing the above equilibrium turns from purple to pink when cooled. State whether the forward reaction is endothermic or exothermic. Explain how you arrived at your answer.

12. $A + B \rightleftharpoons AB + 16.8$ kJ/mol



(a) In which direction is the equilibrium system shifting?

(b) What specifically was done to this system at t_1?

13. Explain *in terms of forward and reverse reaction rates* how the equilibrium below responds to a decrease in temperature:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -92.4 \text{ kJ/mol}$$

14. Why is an equilibrium's endothermic direction more sensitive to temperature changes than its exothermic direction?

15. What conditions of temperature and pressure favor products in the following reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H = 238 \text{ kJ/mol}$$

16. Briefly describe the conflicting factors that chemists face when choosing a temperature to perform the Haber-Bosch process.

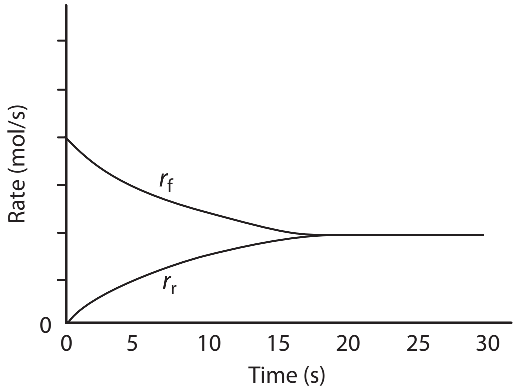
17. Consider the system below. When equilibrium is restored, how will the number of each type of molecule and the concentration of each substance compare to those before the stress was introduced? Complete the following table using the words "decrease," "same," or "increase."

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \qquad \Delta H = 92.4 \text{ kJ/mol}$$

		Decrease Volume	**Decrease Temperature**
Equilibrium concentration	N_2		
	H_2		
	NH_3		
Equilibrium number	N_2		
	H_2		
	NH_3		

18. The graph below shows how forward and reverse reaction rates change as an exothermic reaction goes from initiation to equilibrium. Plot the forward and reverse reaction rates for the same reaction at a higher temperature.

Rate (forward and reverse) vs. Time for a Reaction as It Approaches and Achieves Equilibrium



19. Nitric acid is produced commercially by the Ostwald process. The first step of the Ostwald process is:

$$4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g) + \text{energy}$$

In which direction will the above system shift in the following situations:

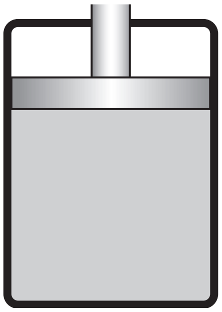
(a) Some NO is added.

(b) Some NH_3 is removed.

(c) The pressure of the system is decreased by increasing the volume.

(d) The temperature of the system is decreased.

20. A piston supported by gas trapped in a cylinder is a fixed pressure apparatus. As long as the gas in the cylinder is supporting the same piston then its pressure must be constant because it is exerting the same force over the same bottom surface of the piston. If the piston weighs more, then the fixed pressure is greater. Consider the following equilibrium system trapped in a cylinder:



$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(a) In which direction will the system shift when some weight is added to the piston?

(b) How would this shift affect the apparatus?

21. Complete the following review table.

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H = -92.4$ kJ/mol

Stress	Le Châtelier Predicts		Chemical Kinetics Explains	
	Response	**Shift**	**Effect**	**Net Rx**
Add H_2	some of the added H_2 removed			
Add NH_3		left		
Remove N_2			r_f decreases	
Decrease volume (compress)				net forward rx
Decrease temperature			r_r decreases more than r_f	

Extension

22. Holding the temperature and pressure constant when a reactant or product is added to an equilibrium system is easier said than done. Some SO_3 is added to the following system. Its temperature and pressure are *not* fixed.

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) + 198\text{ kJ/mol}$$

(a) In which direction will the system shift in response to the added SO_3?

(b) In which direction will the system shift in response to the small change in pressure resulting from the added SO_3?

(c) In which direction will the system shift in response to the small change in temperature resulting from the increased pressure?

(d) In which direction will the system shift in response to the change in temperature resulting from the system's shift to the added SO_3?

2.4 Entropy Change versus Enthalpy Change

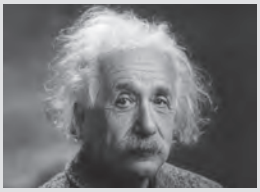
Warm Up

Everything around you can be perceived as being in a relative state of organization or disorganization. For each picture below, check the box that applies.

☐ organized
☐ disorganized

☐ organized
☐ disorganized

☐ organized
☐ disorganized



☐ organized
☐ disorganized

☐ organized
☐ disorganized

☐ organized
☐ disorganized

☐ organized
☐ disorganized

☐ organized
☐ disorganized

What Is Entropy?

Entropy is the amount of thermal energy in a closed system that is not available to do work. The entropy of a substance or a system correlates with its state of disorganization or randomness. This has become most chemists' working definition of the term. Chemists think of **entropy** as a substance's or system's state of disorganization or randomness. Every form of matter and every particle, except a fundamental particle, is a relationship of its components and thus has an entropy or degree of disorder that can be measured. Scientists use the letter *S* as the symbol for entropy. Standard molar entropies are expressed in joules per mole per kelvin (J/K·mol).

Scientists view a more organized — lower entropy — system as one with fewer available variations or fewer *degrees of freedom*. In other words, a more organized state is a more "fixed" state. Simpler things have lower entropies because they have fewer possible configurations or **microstates**. Likewise, more systematic or patterned arrangements have lower entropies because they are more distinctive. There are many more ways your clothes can be strewn around your room than there are ways they can be hung in your closet.

Chemical Systems and Entropy

Atoms are organizations of subatomic particles; molecules are organizations of atoms; and molecular substances are organizations of molecules. A molecular substance's entropy is a function of its intramolecular (within molecules) relationships and its intermolecular (between molecules) relationships. The third law of thermodynamics states that a perfect crystal at 0 kelvin has 0 entropy.

For elements of the same state within a family, the higher the element's atomic number is, the greater its entropy. More electrons provide more variability in positions. For example, the entropies of the noble gases increase as you move down the periodic table (Table 2.4.1).

Table 2.4.1 *Standard Entropies (S°) of the Noble Gases*

Noble Gas	He	Ne	Ar	Kr	Xe
S° (J/mol·K)	126	147	155	164	170

Likewise, the heavier and more complex a molecule is, the greater its compound's entropy. As well as having more atoms (each with its own variability), more complex molecules have more possible rotational and vibrational orientations. This is exemplified by the entropies of nitrogen oxides (Table 2.4.2).

Table 2.4.2 *Standard Entropies (S°) of Some Nitrogen Oxides*

Substance	$NO(g)$	$N_2O(g)$	$N_2O_4(g)$	$N_2O_5(g)$
S° (J/mol·K)	211	220	304	356

The entropy of a substance is strongly dependent on its temperature. As particles gain kinetic energy, their motion becomes increasingly chaotic. The physical state or phase of a substance affects its entropy as illustrated by the standard entropies of different phases of molecular iodine shown in Table 2.4.3. Entropy increases from solid to liquid to gas. Particle motion (whether individual atoms or molecules) in the gas state is almost completely random. Particle motion in the liquid state is limited to within the body of the liquid but the particles can still slip past one another thereby allowing many different permutations (orders) of the same particles. The order of the particles is fixed in the solid state, thereby leaving only vibrational motion to provide for different possible inter-particle configurations.

Table 2.4.3 *Standard Entropies (S°) of Different Phases of Molecular Iodine*

Substance	$I_2(s)$	$I_2(aq)$	$I_2(g)$
S° (J/mol·K)	116	137	261

Quick Check

1. How do chemists define "entropy"?

____

2. State the third law of thermodynamics.

____

3. Which of these two elements has greater entropy: Ag(*s*) or Cu(*s*)? Explain.

____

4. Which of these two compounds has greater entropy: water, $H_2O(l)$, or hydrogen peroxide, $H_2O_2(l)$? Explain.

____

Chemical Reactions and Entropy Change

A chemical equation alone does not contain enough information for you to reliably determine whether entropy increases or decreases during the reaction. This can only be determined with certainty by comparing the standard entropies of the reactants and products. The standard entropies are included in the examples below to verify each example's claim regarding entropy change. Standard entropies are commonly available in chemical handbooks but are not found in this course's data booklet. Entropy problems in this course are therefore restricted to reactions having entropy changes that conform to the general characteristics described here.

1. Entropy Changes in Reactions Involving Gases

Combining particles reduces their number but increases their complexity. The reduced number of particles usually decreases entropy more than the increased complexity increases it.

Entropy usually decreases when gas particles combine into fewer particles.

The entropy of gases is considerably greater than the entropy of solids or liquids. For this reason, the entropy change in reactions involving gases is usually dominated by the increasing or decreasing moles of gas.

In the synthesis of water from its elements, entropy decreases as three gas molecules are organized into two.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$
$$2(131) + 205 > 2(189) \quad \text{J/K·mol}$$

Solids typically decompose by releasing a gas. Entropy increases in the following example as zero gas molecules are converted into one. The standard entropies show that entropy increases mainly because a gas is produced.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
$$93 < 40 + 214 \quad \text{J/K·mol}$$

Despite the following reaction being a synthesis reaction, entropy increases because one gas molecule becomes two.

$$2\,C(s) + O_2(g) \rightarrow 2\,CO(g)$$
$$2(5.7) + 205 < 2(197.6) \quad \text{J/K·mol}$$

Recall the caution given in the opening paragraph. The standard entropies show that entropy increases in the following synthesis reaction despite six gas molecules combining into four. The phosphorus atoms changing from the solid state to the gas state in a compound with hydrogen has a greater influence on the entropy than the reduced number of gas particles.

$$P_4(s) + 6\,H_2(g) \rightarrow 4\,PH_3(g)$$
$$44 + 6(131) < 4(210) \quad \text{J/K·mol}$$

2. The Reorganization of Atoms of the Same Element

What if a reaction doesn't involve any gas molecules, or the number of product gas molecules equals the number of reactant gas molecules? In such cases, it may be evident whether entropy is decreasing or increasing by examining whether atoms of the same element are becoming less or more disordered. Organizationally, the difference between clothes strewn about your room and clothes hung up in your closet is considerably greater than the difference between various ways of arranging your clothes within your closet. Likewise, changing the phase of the substance(s) containing a substance's atoms generally has a greater impact on the entropy than changing the formula of the substance(s).

(a) Phase Changes

Entropy decreases in the reaction below as three of the oxygen atoms go from being part of a gaseous compound (CO_2) to being part of a solid compound (Fe_2O_3). All the other atoms go from reactants to products of the same phase.

$$2\,Fe(s) + 3\,CO_2(g) \rightarrow Fe_2O_3(s) + 3\,CO(g)$$
$$2(27.3) + 3(213.6) > 87.4 + 3(197.6) \quad \text{J/K·mol}$$

(b) Chemical Changes

A group of items has less entropy when the common items are grouped together. Hanging your white shirts separately from your colored shirts is more organized than any arrangement that combines the

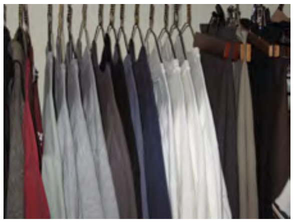


Figure 2.4.1 *A lower-entropy arrangement of shirts*

two together (Figure 2.4.1). In the example below, nitrogen and oxygen atoms have less entropy when the "like" atoms are combined together than when the "unlike" atoms are combined.

$$N_2(g) + O_2(g) \rightarrow 2\,NO(g)$$
$$191.5 + 205 \quad < \quad 2(210.7) \quad J/K\cdot mol$$

Recall that a state's entropy increases with the number of ways it can be achieved or expressed. There is only one way to combine two nitrogen atoms ($^aN^bN$) where the superscripts "a" and "b" tag or distinguish the two atoms. Likewise, there is also only one way to combine two oxygen atoms ($^aO^bO$). On the other hand, there are two ways of combining the two nitrogen atoms with the two oxygen atoms to form NO ($^aN^aO$ & $^bN^bO$ or $^aN^bO$ & $^bN^aO$). Since the product condition has more variations (more microstates), it represents the less ordered system and therefore the one with greater entropy.

Entropy increases when common items split up to form or be part of more groups. In the example below, entropy increases as the oxygen atoms go from being in the same molecule (CO_2) to being in two molecules (CO and H_2O).

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$
$$213.6 + 130.6 < 97.6 + 188.7 \quad J/K\cdot mol$$

Sample Problems 2.4.1 — Predicting by Inspection Whether Entropy Increases or Decreases

Predict whether entropy increases or decreases in each of the following and provide your reasoning:

(a) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ (b) $Fe_2O_3(s) + 3\,H_2(g) \rightarrow 2\,Fe(s) + 3\,H_2O(g)$

What to Think About	How to Do It
For both problems, consider (in usual order of importance) the following: 1. Changes in the number of gas particles	(a) Entropy decreases because two gas molecules combine into one.
2. Reorganization of atoms of the same element related to: (i) phase changes (ii) chemical changes	(b) Entropy increases because three oxygen atoms in a solid compound are relocated into a gaseous one.

Practice Problems 2.4.1 — Predicting by Inspection Whether Entropy Increases or Decreases

Predict whether entropy increases or decreases in each of the following and provide your reasoning

1. $2\,FeO(s) \rightarrow 2\,Fe(s) + O_2(g)$

2. $S_8(s) + 8\,O_2(g) \rightarrow 8\,SO_2(g)$

3. $H_2O(s) \rightarrow H_2O(l)$

Natural Thermodynamic Drives

Two thermodynamic "drives" influence an equilibrium's position:

1. the drive toward decreasing enthalpy
2. the drive toward increasing entropy or disorder

Figure 2.4.2 *When the car moves, the book will fall into a more stable position.*

1. The Drive Toward Decreasing Enthalpy

Objects naturally adopt the lowest energy state available to them. This is illustrated by placing a book on its edge in the trunk of a car (Figure 2.4.2). Nobody would expect the book to remain in this position after the car had moved. A slight jostle causes the book to adopt a more stable orientation as it falls onto its face. The book lowers its gravitational potential energy as its center of mass moves closer to Earth. The jostle plays the role of the activation energy in this analogy. This principle applies to all objects including molecules, atoms, and subatomic particles. It is responsible for atoms forming stronger bonding associations with lower potential energy. In other words, chemical reactions tend to proceed in the exothermic direction.

For example, consider this reaction: $N_2(g) + 2\ O_2(g) + 68\text{ kJ/mol} \rightarrow 2\ NO_2(g)$

The tendency toward decreasing enthalpy (energy) pushes this reaction in the exothermic direction toward reactants (Figure 2.4.3).

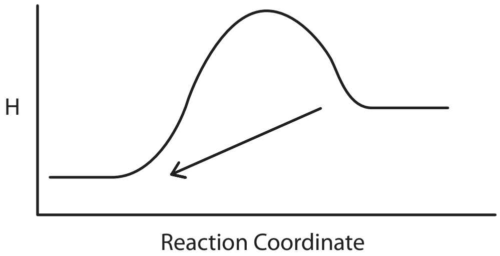


Figure 2.4.3 *Chemical reactions tend to proceed in the exothermic direction.*

2. The Drive Toward Increasing Entropy

Randomly moving objects such as liquid and gas molecules become disorganized when left on their own. It takes work to collect such objects and to keep them organized. Diffusion is an example of the tendency of objects toward disorder. Diffusion is the self-movement of chemicals from an area of greater concentration to an area of lesser concentration. If you open a bottle of perfume, its molecules will rapidly diffuse throughout the room. This tendency toward increasing entropy applies to chemical changes as well as to physical processes.

Enthalpy, Entropy, and Equilibrium

Chemical reactions are driven toward minimum or decreasing enthalpy and maximum or increasing entropy. If both drives are toward products then the reaction, having no opposition, will achieve an equilibrium position far to the right. If both drives are toward reactants, the forward reaction barely gets going before establishing equilibrium with a position far to the left. From a thermodynamic perspective, equilibria with a "reasonable" proportion of both reactants and products develop as a compromise between the two drives when they oppose each other.

> If the drive toward increasing entropy opposes the drive toward decreasing enthalpy, an equilibrium will develop with a "reasonable" proportion of both reactants and products.

Consider the following two examples:

$2\ CO_2(g) + 566\text{ kJ/mol} \rightarrow 2\ CO(g) + O_2(g)$	$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g) + 483.6\text{ kJ/mol}$
Decreasing enthalpy favors reactants. $\longleftarrow$	Decreasing enthalpy favors products. $\longrightarrow$
$\longrightarrow$ Increasing entropy favors products.	$\longleftarrow$ Increasing entropy favors reactants.

Figure 2.4.4 *The low enthalpy–low entropy option for water's movement*

The movement of rainwater is a good thermodynamic model of equilibrium. Water flows downhill and also seeps outward. Consider how rain distributes itself on a street. Some water covers the street but some also collects in the gutters and into puddles (Figure 2.4.4). The puddles and gutters are the low enthalpy–low entropy option while the street surface is the high enthalpy–high entropy option.

Figure 2.4.5 shows the four possible enthalpy-entropy combinations that could occur in a chemical reaction. Both the enthalpy and entropy could increase, they could both decrease, or one could increase and one could decrease. Although Figure 2.4.5 nicely lays out every possible thermodynamic scenario for reactions, there is absolutely no benefit to memorizing it. The thermodynamic drives themselves can easily be applied to any reaction rather than applying a table derived from them.

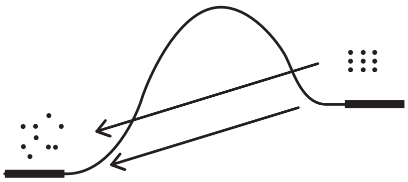
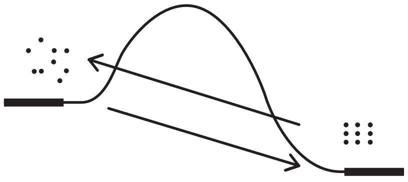
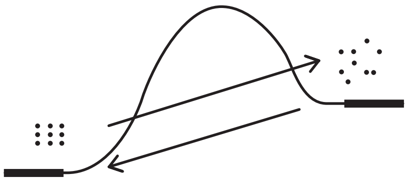
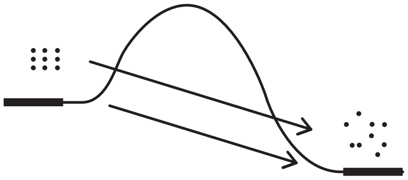
	Enthalpy increases	Enthalpy decreases
Entropy decreases	 Drive toward increasing entropy – opposes rxn Drive toward decreasing enthalpy – opposes rxn Virtually no reaction	 Drive toward increasing entropy – opposes rxn Drive toward decreasing enthalpy – favours rxn Equilibrium
Entropy increases	 Drive toward increasing entropy – favours rxn Drive toward decreasing enthalpy – opposes rxn Equilibrium	 Drive toward increasing entropy – favours rxn Drive toward decreasing enthalpy – favours rxn Goes virtually to completion

Figure 2.4.5 *The four thermodynamic categories of chemical reactions*

Why does a reaction not go entirely to completion when both drives are toward products? Maximum entropy is achieved just short of the completed reaction because even if the entropy of the products is much greater than the entropy of the reactants, a mixture containing a very small proportion of reactants will have a greater entropy than products alone. Chemists may say that such a reaction "goes to completion" because the equilibrium mixture consists of very nearly pure products.

Likewise, even if both drives are toward reactants, a mixture containing a very small proportion of products will still have greater entropy than the reactants alone. Chemists may say that such a reaction "does not occur" because the equilibrium mixture consists of very nearly pure reactants.

The relationship between enthalpy, entropy, and equilibrium facilitates a popular series of questions where students are directly or indirectly provided with two of these features of a reaction and asked for the third.

Sample Problem 2.4.2(a) — Predicting an Equilibrium's Position from Its Thermodynamics

State whether the following reaction will achieve *equilibrium* (with a reasonable proportion of reactants and products), go nearly to *completion*, or virtually *not occur*.

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \qquad \Delta H = -92\ \text{kJ/mol}$$

What to Think About	How to Do It
1. Consider the two thermodynamic drives: • The drive toward increasing entropy is toward reactants. • The drive toward decreasing enthalpy is toward products.	Since the two drives are opposing each other, the reaction will achieve equilibrium with a reasonable proportion of reactants and products.

Sample Problem 2.4.2(b) — Predicting an Equilibrium's Thermodynamics from Its Position

The following equilibrium has a reasonable proportion of reactants and products. State whether the forward reaction is endothermic or exothermic.

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$$

What to Think About	How to Do It
1. Determine from the equilibrium position whether the drives are opposed, both toward reactants, or both toward products.	The two thermodynamic drives are opposed because the reaction establishes equilibrium with a reasonable proportion of reactants and products.
2. By inspection, determine whether entropy is increasing or decreasing.	Entropy is increasing as one gas molecule reacts to produce two gas molecules.
3. Decide whether the reaction is endothermic or exothermic from steps 1 and 2.	The drives are opposed and the drive toward increasing entropy is toward products. Therefore the drive toward decreasing enthalpy must be toward reactants: the reaction is endothermic.

Practice Problems 2.4.2 — Predicting an Equilibrium's Position from Its Thermodynamics or Vice Versa

1. State whether the following reaction will achieve *equilibrium* (with a reasonable proportion of reactants and products), go nearly to *completion*, or almost *not occur*. $3\,O_2(g) \rightleftharpoons 2\,O_3(g)$ $\Delta H = +285$ kJ/mol

2. The following reaction establishes equilibrium with a reasonable proportion of reactants and products. State whether this reaction is endothermic or exothermic. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

3. The following equilibrium has a reasonable proportion of reactants and products. State whether entropy increases or decreases during the forward reaction. $CH_2O(g) + O_2(g) \rightleftharpoons CO_2(g) + H_2O(g)$ $\Delta H = -518$ kJ/mol

Enthalpy, Entropy, and Spontaneity

The spontaneity of a reaction is frequently a concern for chemists. A **spontaneous process** is one that happens "on its own" with no outside intervention.

> Chemical systems move spontaneously toward equilibrium.

The system's entropy change and enthalpy change both play a role in determining whether or not a reaction is spontaneous. You will learn much more about this in later chemistry courses. Do not confuse whether it's going to happen (spontaneity) with when it's going to happen (how quickly the final condition will be achieved). A spontaneous reaction can occur at a tediously slow rate. Nails spontaneously rust, and diamond spontaneously turns into graphite. Spontaneity is a thermodynamic function and depends only on the conditions at the start and the end of the process. Rate is a kinetic function and depends on the path taken between the two. The situation is loosely analogous to children telling their parents that they will take out the kitchen garbage but when this will occur is an entirely different matter.

2.4 Activity: Imitating Disorder

Question

Can you place some black dots in a matrix so that they appear to your classmates to be randomly distributed?

Background

When people attempt to randomize objects in space or time, they tend to err toward an even distribution. Let's see if you and your classmates can identify which of each other's two matrices contains the set of dots that are actually randomly distributed.

Procedure

1. Attempt to randomly distribute 12 dots within the squares of one of the two matrices below. You may place more than one dot within a square.
2. Randomly place a single dot *in the other matrix* by rolling a pair of dice twice to determine the row and column to place the dot in (e.g., a 1-1 roll would place the dot in the upper left hand corner of the matrix). Repeat this technique 11 more times to produce a matrix that actually contains 12 randomly distributed dots.

	1	2	3	4	5	6
1						
2						
3						
4						
5						
6						

	1	2	3	4	5	6
1						
2						
3						
4						
5						
6						

3. Exchange books with 10 classmates. Each time, attempt to identify which of your classmate's two matrices contains the set of dots that are actually randomly distributed.

Continued on next page

2.4 Activity: *Continued*

Results and Discussion

1. Keep a record (𝍸) in the table below of how many of your classmates chose correctly and how many times you chose correctly.

Your Guesses	
Correct	**Incorrect**

Your Classmates' Guesses	
Correct	**Incorrect**

If a person can't tell the difference between the two matrices then there is still a 50% chance that the person will choose the correct matrix. There is only a 17% probability that 7 or more of the 10 people could pick the correct (random) matrix by chance. If this happens, we'll declare your fake "busted." Likewise, if you can correctly identify the random distribution 7 out of 10 times then we'll declare you "randomly gifted."

Each trial tests two things: a person's ability to fake a random distribution and another person's ability to spot the fake. Correctly spotting the random distribution could indicate a "poor" fake or a "good" spotter.

2. Look around the room at your classmates' results and comment on whether there is a relationship between people who are good at faking random patterns and people who are good at recognizing random patterns.

2.4 Review Questions

1. Which substance in each of the following pairs would likely have the greater entropy? Explain.
   (a) $Br_2(l)$ or $Br_2(g)$

   (b) $SO_3(g)$ or $SO_2(g)$

   (c) $Sn(s)$ or $Pb(s)$

2. For each of the following state whether entropy is increasing or decreasing and briefly state your reasoning.
   (a) $2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$

   (b) $NOCl_2(g) + NO(g) \rightarrow 2\ NOCl(g)$

   (c) $4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$

   (d) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$

   (e) $WO_3(s) + 3\ H_2(g) \rightarrow W(s) + 3\ H_2O(g)$

3. State whether each of the following reactions will achieve *equilibrium* with a reasonable amount of reactants and products, go almost to *completion*, or virtually *not occur*.
   (a) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$ $\Delta H = -907.2$ kJ/mol

   (b) $N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$ $\Delta H = +68$ kJ/mol

   (c) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ $\Delta H = -92.5$ kJ/mol

   (d) $S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -297$ kJ/mol

4. For the following reaction, state whether the forward reaction is endothermic or exothermic, given that the two thermodynamic drives are opposed to each other. Explain your reasoning.
   $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

5. Describe the thermodynamics of a reaction that establishes equilibrium so far toward reactants that it is said to virtually not occur.

6. The following equilibrium has a reasonable proportion of reactants and products. State whether entropy is increasing or decreasing during the forward reaction. Explain your reasoning.
$CO_2(g) + NO(g) \rightleftharpoons NO_2(g) + CO(g) \quad \Delta H = +82\ \text{kJ/mol}$

7. Given that equilibrium is established with a reasonable proportion of reactants and products, in what direction will the system shift when the temperature is decreased? Explain your reasoning.
$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$

8. Why does a reaction that has both thermodynamic drives toward products (the drive toward increasing entropy and the drive toward decreasing enthalpy) not go entirely to completion?

2.5 The Equilibrium Constant

Warm Up

A **constant** is a specific piece of information that does not change value, possibly within a set of described parameters. You have already used many constants in your science and mathematics classes. Some constants simply relate one system of measurement to another. For example, there are 2.54 cm in an inch.

1. Pi (π) is a mathematical constant that relates the circumference of a circle to its radius. What is the approximate value of pi?

   ____

2. The speed of light (c) in a vacuum is a physical constant with a value of 3.00×10^8 m/s. What famous formula of Albert Einstein's uses the speed of light to relate energy to mass?

   ____

3. State the name, symbol, and value of a chemical constant that provides the number of items in a mole of anything.

   ____

4. Why is it important to scientists to have accurate constants?

   ____

Deriving the Equilibrium Expression

Figure 2.5.1 provides the forward and reverse rate equations for the following reaction at equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

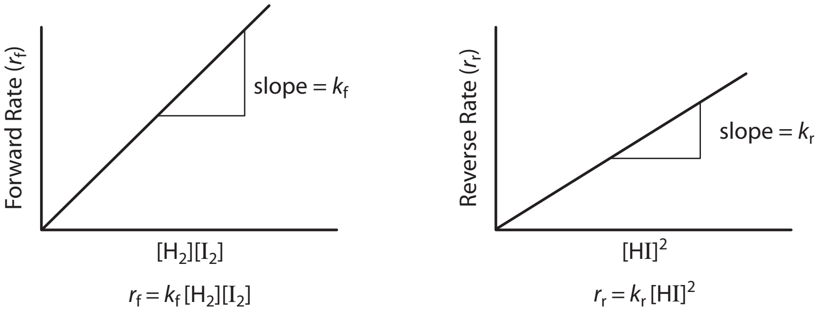


Figure 2.5.1 *Forward and reverse reaction rates for the equation above*

At equilibrium: $r_f = r_r$

Therefore: $k_f[H_2][I_2] = k_r[HI]^2$

Rearranging to isolate the constants we get:

$$\frac{k_f}{k_r} = \frac{[HI]^2}{[H_2][I_2]}$$

A constant divided by another constant equals a third constant. In this case $k_f \div k_r$ provides a constant that chemists call the equilibrium constant, K_{eq}.

Therefore: $K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$

Regardless of the initial concentrations of reactants and possibly products, when equilibrium is achieved and the equilibrium concentrations are substituted into this expression, the calculated value will always be the same at any given temperature. Since the rate constants k_f and k_r are temperature dependent, so too is the equilibrium constant, K_{eq}, that can be derived from them. This relationship is the mathematical "hook" we needed to quantify our understanding and descriptions of equilibrium. It provides chemists and chemical engineers with the ability to predict the concentrations that will be present when equilibrium is achieved.

The **equilibrium expression** refers to *the formula* for the equilibrium constant in terms of the equilibrium concentrations of reactants and products. The **equilibrium constant** refers to *the numerical value* provided by the equilibrium expression. The units of equilibrium constants vary too much from equation to equation to be useful and are therefore not required for this course.

> The *equilibrium law* states that for the general equation:
>
> $$p\,\mathrm{A} + q\,\mathrm{B} \rightleftharpoons r\,\mathrm{C} + s\,\mathrm{D}$$
>
> $$K_{eq} = \frac{[\mathrm{C}]^r[\mathrm{D}]^s}{[\mathrm{A}]^p[\mathrm{B}]^q}$$
>
> where *p*, *q*, *r*, and *s* are the coefficients in the balanced chemical equation.

The equilibrium law is valid for both single-step equilibria and multiple-step equilibria. In other words, the equilibrium expression and constant are independent of the reaction mechanism. Consider the following reaction mechanism:

$$\begin{array}{ll} \text{Step 1} & NO_2 + F_2 \rightleftharpoons NO_2F + \cancel{F} \\ \text{Step 2} & \cancel{F} + NO_2 \rightleftharpoons NO_2F \\ \hline \text{Net reaction} & 2\,NO_2 + F_2 \rightleftharpoons 2\,NO_2F \end{array}$$

If the reaction is at equilibrium, then step 1 must be at equilibrium to maintain the reactants at a constant concentration. Step 2 must be at equilibrium to maintain the products at a constant concentration. The equilibrium expression for the overall reaction can be derived from the equilibrium expressions for each individual step:

$$K_{eq1} = \frac{[NO_2F][F]}{[NO_2][F_2]} \qquad K_{eq2} = \frac{[NO_2F]}{[F][NO_2]}$$

$$K_{eq1} \times K_{eq2} = \frac{[NO_2F][\cancel{F}]}{[NO_2][F_2]} \times \frac{[NO_2F]}{[\cancel{F}][NO_2]} = \frac{[NO_2F]^2}{[NO_2]^2[F_2]} = K_{eq}$$

The most common and reliable means of determining a reaction's equilibrium constant is to simply substitute equilibrium concentrations into the equilibrium expression.

Sample Problem 2.5.1 — Determining K_{eq} from the Equilibrium Concentrations

For the following equation, 0.19 mol NO_2 and 0.64 mol N_2O_4 are found at equilibrium in a 250 mL flask at 92°C.

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

What is the equilibrium constant for this reaction at 92°C?

What to Think About	How to Do It
1. Write the equilibrium expression for the reaction. As indicated by the notation [ ], K_{eq} values are determined using molar concentrations so it is important to consider the units provided for the reacting species (moles or M) and the container size if the concentrations need to be calculated.	$K_{eq} = \dfrac{[N_2O_4]}{[NO_2]^2}$
2. Substitute the equilibrium concentrations into the expression.	$K_{eq} = \dfrac{(0.64\ mol/0.25\ L)}{(0.19\ mol/0.25\ L)^2} = 4.4$

Practice Problems 2.5.1 — Determining K_{eq} from the Equilibrium Concentrations

1. The following gases are at equilibrium in a flask at 423°C: 4.56×10^{-3} M H_2, 7.4×10^{-4} M I_2, and 1.35×10^{-2} M HI. What is the equilibrium constant for the reaction at this temperature?

   $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$

2. A quantity of 3.88×10^{-3} M NO_2 is at equilibrium with 1.73×10^{-4} M N_2O_4 at 60°C.

   $2\,NO_2(g) \rightleftharpoons N_2O_4(g)$

   (a) What is the equilibrium constant for the reaction at 60°C?

   (b) State whether this reaction is endothermic or exothermic by comparing the equilibrium constant for this reaction at 60°C to the constant at 92°C provided in the preceding sample problem. Explain your reasoning.

3. As a slight variation on this type of problem, you could be asked to determine an equilibrium concentration from the K_{eq} and the other equilibrium concentrations. For example, 0.14 M NH_3 is at equilibrium with 0.020 M N_2 at 225°C. What is the equilibrium concentration of H_2 in the reacting mixture?

   $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_{eq} = 1.7 \times 10^2$ at 225°C

What Does a Bigger Equilibrium Constant Mean?

Recall our derivation of K_{eq}. For the equilibrium system, $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$:

$$\frac{k_f}{k_r} = \frac{[HI]^2}{[H_2][I_2]} = K_{eq} \qquad \text{but } \frac{k_r}{k_f}\text{, which equals } \frac{[H_2][I_2]}{[HI]^2}\text{, is also a constant.}$$

Presumably, chemists chose the numerical value provided by the first expression, $[HI]^2/[H_2][I_2]$ to be K_{eq} because the product concentration is in its numerator and the reactant concentrations are in its denominator. This means that the size of the equilibrium constant indicates the extent of the reaction's progress towards products.

> The further a given reaction progresses to the right to achieve equilibrium, the greater its equilibrium constant will be.

This appeals to us because it is consistent with the number line, which also has numbers increasing from left to right. Here we are combining the chemical equation metaphor that changing from reactants to products is proceeding to the right with the number line metaphor that proceeding to the right is increasing in numerical value.

Knowing what a bigger equilibrium constant *does not mean* is perhaps just as important as knowing what it *does mean*. Chemists must be careful not to attempt to infer too much from equilibrium constants. The following two points outline important information about interpreting equilibrium constants:

1. It is impossible to infer anything about an equilibrium's position solely from its equilibrium constant. An equilibrium's position depends on the initial reactant concentrations as well as the equilibrium constant. A given reaction therefore has a wide range of equilibrium positions that result from the same equilibrium constant. Consider the following equilibrium:

   $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ $\qquad K_{eq} = 1.8 \times 10^{-5}$

   If the initial concentration of CH_3COOH is 1.0 M then there will be a 0.42% yield at equilibrium, but if its initial concentration is 1.0×10^{-6} M then there will be a 95% yield at equilibrium. From Le Châtelier's perspective, diluting the system causes a shift to the right to partially restore the osmotic pressure.

2. Even with the same initial reactant concentrations, it is difficult to make meaningful comparisons between the equilibrium constants of different equilibria unless their expressions have identical forms. The following two equilibria have radically different percent yields even when they have the same equilibrium constant (at different temperatures) and the same initial reactant concentrations. The first equilibrium can have a greater K_{eq} than the second one and still have a lower percent yield.

   $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$ $\qquad K_{eq} = 1$

   When the initial $[Ni(CO)_4]$ = 1.0 M there is a 23% yield at equilibrium.

   $2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$ $\qquad K_{eq} = 1$

   When the initial [NO] = 1.0 M there is an 83% yield at equilibrium.

Does an Equilibrium Constant Change When the Equilibrium System Shifts?

When an equilibrium is stressed by changing concentration(s), the new concentrations will not provide the equilibrium constant when plugged into the equilibrium expression. The equilibrium will shift to restore a set of concentrations that once again provide the equilibrium constant. It is after all, a constant.

On the other hand, the shift caused by a temperature change makes all the product concentrations increase and all the reactant concentrations decrease or vice versa so it must change the equilibrium constant. Equilibrium constants are temperature dependent. A shift to the right in response to a temperature change causes the equilibrium constant to increase. A shift to the left in response to a temperature change causes the equilibrium constant to decrease.

> Changing the temperature is the only way to change a chemical equation's equilibrium constant.

When a temperature change causes an equilibrium system to shift to the right, its [products] increase and its [reactants] decrease; therefore its equilibrium position also shifts to the right. Conversely, when a temperature change causes an equilibrium system to shift to the left, its [reactants] increase and its [products] decrease; therefore its equilibrium position also shifts to the left.

Table 2.5.1 *The Effect of Stresses on the Equilibrium System, Position, and Constant*

$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \qquad \Delta H = -198$ kJ/mol

Stress	Equilibrium System	Equilibrium Position	Equilibrium Constant
Add reactant	shifts right	may shift left or right	no change
Decrease volume	shifts right	shifts right	no change
Decrease temperature	shifts right	shifts right	increases

Quick Check

1. Consider the following equilibrium: $Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$
   (a) In what direction will the system shift if some ammonia (NH_3) is added to it? __________
   (b) How will this affect the equilibrium constant? ____________________________________
2. Consider the following equilibrium: $PCl_5(g) + 92.5\ kJ \rightleftharpoons PCl_3(g) + Cl_2(g)$
   A decrease in temperature will cause the equilibrium system to shift ____________________
   causing its percent yield to __________________ and its equilibrium constant to
   _________________.
3. Consider the following equilibrium: $C_2H_2(g) + 3\ H_2(g) \rightleftharpoons 2\ CH_4(g)$ $K_{eq} = 0.36$
   True or False? We know that reactants are favored in this reaction because $K_{eq} < 1$. _________

No Liquids or Solids in Equilibrium Expressions

Chemicals in liquid or solid states are not included in equilibrium expressions.

For example, the equilibrium formed when common salt dissolves in water is:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

Its equilibrium expression is simply: $K_{eq} = [Na^+][Cl^-]$

While the term *concentration* normally refers the amount of one chemical per unit volume of a mixture, it is sometimes used to describe how concentrated particles of pure matter are. For example, [pure $H_2O(l)$] = 55.6 M. However, the *concentration* of a pure solid or liquid is fixed by its density while the concentration of a solute is not. Regardless, this is a heterogeneous reaction, and it is the surface area of the NaCl that affects the reaction rate, not its concentration. So why is the surface area of the salt not part of the equilibrium expression? Increasing the surface area by grinding the salt or by adding more salt increases the rate of dissolving but does not affect the equilibrium concentrations because the rate of recrystallizing increases equally.

Although our example was a physical equilibrium, this principle holds true for heterogeneous chemical equilibria as well. A solid's surface area, although affecting the rate at which equilibrium is achieved, does not affect the equilibrium position. Solids therefore do not appear in equilibrium expressions. Likewise, adding or removing solids from an equilibrium affects the forward and reverse rates equally and therefore does not cause a shift.

The same logic applies to pure liquids involved in heterogeneous reactions but liquids involved as solvents are not included for a different reason. For example:

$$Cr_2O_7{}^{2-}(aq) + H_2O(l) \rightleftharpoons 2\ H^+(aq) + 2\ CrO_4{}^{2-}(aq)$$

$$K_{eq} = \frac{[H^+]^2[CrO_4{}^{2-}]^2}{[Cr_2O_7{}^{2-}]}$$

The $[H_2O(l)]$ is not included in any equilibrium expression. In the above chemical equation, water is a reactant and a solvent for the reactant and product ions. Since water's concentration is nearly constant, we omit it from equilibrium expressions.

There is one situation where liquids appear in equilibrium expressions. When there is more than one liquid in the chemical equation, the liquids dilute each other so these chemicals are included in the equilibrium expression.

Quick Check

Write the equilibrium expression for the following reactions:

1. $B_2H_6(g) + 3\ O_2(g) \rightleftharpoons B_2O_3(s) + 3\ H_2O(g)$ __________________________
2. $4\ HCl(g) + O_2(g) \rightleftharpoons 2\ Cl_2(g) + 2\ H_2O(g)$ __________________________
3. $H_2(g) + Br_2(l) \rightleftharpoons 2\ HBr(g)$ __________________________
4. $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ __________________________

The Equilibrium Constant and the Form of the Chemical Equation

The form in which a chemical equation is written affects its K_{eq} expression and constant. To avoid possible ambiguity, chemists should provide the chemical equation with the K_{eq} value.

$$H_2(g) + ½\ O_2(g) \rightleftharpoons H_2O(g)$$

At a particular temperature, 2.0 mol H_2, 4.0 mol O_2, and 12.0 mol H_2O are discovered at equilibrium in a 1.0 L flask.

$$K_{eq} = \frac{[H_2O]}{[H_2][O_2]^{½}} = \frac{12.0}{(2.0)(4.0)^{½}} = 3.0$$

The same reaction has a different equilibrium expression and a different constant when the coefficients in its equation are doubled:

$$2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(g)$$

$$K_{eq} = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{(12.0)^2}{(2.0)^2(4.0)} = 9.0$$

The exact same equilibrium concentrations, when substituted into the new expression, provide a value that is the square of the original chemical equation's constant. Doubling a chemical equation's coefficients has the effect of squaring its K_{eq}. This is reasonable since the coefficients in the chemical equation appear as powers in the equilibrium expression.

Reversing a chemical equation has the effect of inverting its equilibrium expression and constant. The K_{eq} for any reaction is the reciprocal of the K_{eq} for its reverse reaction. Reversing the original equation we get:

$$H_2O(g) \rightleftharpoons H_2(g) + ½\ O_2(g)$$

$$K_{eq} = \frac{[H_2][O_2]^{½}}{[H_2O]} = \frac{(2.0)(4.0)^{½}}{12.0} = 0.33$$

Quick Check

$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $K_{eq} = 0.018$ at 423°C

1. What is the K_{eq} at 423°C of $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$? ____________
2. What is the K_{eq} at 423°C of $HI(g) \rightleftharpoons ½\ H_2(g) + ½\ I_2(g)$? ____________
3. What is the K_{eq} at 423°C of $½\ H_2(g) + ½\ I_2(g) \rightleftharpoons HI(g)$? ____________

The Reaction Quotient

The numerical value derived when *any* set of reactant and product concentrations is plugged into an equilibrium expression is called the **trial K_{eq}** or the **reaction quotient, Q**. This value tells chemists whether a reaction is at equilibrium and, if not, the direction that the reaction will proceed or shift to achieve equilibrium. If the trial K_{eq} is less than the actual K_{eq} then the reaction must proceed to the right to achieve equilibrium. The reaction quotient's numerator must increase and its denominator decrease until the quotient itself has risen to equal the equilibrium constant. If the trial K_{eq} is greater than the actual K_{eq} then the reaction must proceed to the left to achieve equilibrium. The reaction quotient's numerator must decrease and its denominator increase until the quotient itself has dropped to equal the equilibrium constant.

Sample Problem 2.5.2 — Determining the Direction a System Will Proceed to Achieve Equilibrium, Given its Reactant and Product Concentrations

The following gases are introduced into a closed flask: 0.057 M SO_2, 0.057 M O_2, and 0.12 M SO_3. In which direction will the reaction proceed to establish equilibrium?

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \qquad K_{eq} = 85$$

What to Think About	How to Do It
1. Write the equilibrium expression for the reaction provided.	$\text{Trial } K_{eq} = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$
2. Substitute the concentrations into the equilibrium expression and solve for the trial K_{eq}. Compare the trial K_{eq} to the actual K_{eq}.	$= \dfrac{(0.12)^2}{(0.057)^2\,0.057} = 78 < 85$
3. Note that, by shifting to the right, the $[SO_3]$ will rise while the $[SO_2]$ and $[O_2]$ fall, causing the trial K_{eq} to increase toward 85 and the establishment or restoration of equilibrium.	Therefore this reaction must proceed or shift to the right to achieve equilibrium.

Practice Problems 2.5.2 — Determining the Direction a System Will Proceed to Achieve Equilibrium, Given its Reactant and Product Concentrations

1. The industrial synthesis of hydrogen involves the reaction of steam and methane to produce *synthesis gas*, a mixture of hydrogen and carbon monoxide.

   $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$ $K_{eq} = 4.7$ at 1127°C

   A mixture at 1127°C contains 0.045 M H_2O, 0.025 M CH_4, 0.10 M CO, and 0.30 M H_2. In which direction will the reaction proceed to establish equilibrium?

2. The following gases are introduced into a closed 0.50 L flask: 1.5 mol NO_2 and 4.0 mol N_2O_4. In which direction will the reaction proceed to achieve equilibrium?

   $2\,NO_2(g) \rightleftharpoons N_2O_4(g)$ $K_{eq} = 0.940$.

3. In a container, 0.10 M H^+ and 0.10 M SO_4^{2-} exist in equilibrium with 0.83 M HSO_4^-. A buffer is added that increases the concentration of both the bisulphate and sulphate ions by 0.10 M. What happens to the $[HSO_4^-]$ as equilibrium is restored?

   $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$

Reactants or Products?

It is awkward to call some chemicals "reactants" and others "products" if they are all present when the reaction starts. It is nevertheless convenient to use these terms so chemists write the chemical equation with the chemicals on the left side of the arrow being called the reactants and those on the right side of the arrow being called the products. Which direction the equation is written and therefore which chemicals are called reactants and which chemicals are called products is arbitrary. Of course, once decided, reversing the equation would invert the equilibrium expression and provide a K_{eq} that is the reciprocal of the original one.

An Addendum to Le Châtelier's Principle

Le Châtelier's principle of *partially* alleviating a stress is based on more than one chemical concentration being involved in the equilibrium process. When an equilibrium removes some of an added chemical, other chemicals' concentrations also change along with it. The changing concentrations of these others essentially prevent the stressed chemical from reaching its original equilibrium concentration before equilibrium is re-established. Consider the following hypothetical equilibrium's response to the stress of adding some A.

$$A + B \rightleftharpoons AB$$

If all the added A were removed (by reacting it with B to form AB) then the forward rate would be less than it was at the original equilibrium (due to the decreased [B]) but the reverse rate would be greater than at the original equilibrium (due to the increased [AB]). To re-establish equilibrium the forward rate must be greater than it was at the original equilibrium and therefore all the added A cannot be removed.

Some heterogeneous chemical reactions and physical processes involve only one chemical concentration. When such a system is stressed by changing that concentration, equilibrium is not re-established until the entire stress is removed and the original concentration restored.

Equilibria that have only one chemical concentration in their equilibrium expression *completely* alleviate any stress that changes that concentration.

For example, any stress that changes the concentration of the lone gaseous product in the following equilibria will be completely, rather than partially, alleviated.

- Water evaporating and condensing in a closed vessel
  $H_2O(l) \rightleftharpoons H_2O(g) \qquad K_{eq} = [H_2O(g)]$
- Calcium carbonate decomposing and synthesizing within a closed vessel
  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad K_{eq} = [CO_2]$

These equilibrium expressions have only one chemical concentration in them. As this implies, this value is constant at a given temperature. When these systems are stressed by removing some of this chemical, the entire loss must be replaced to restore the reaction quotient back to that of the equilibrium constant.

Quick Check

State whether each of the following equilibria would partially or completely alleviate a stress that changes a reactant's or product's concentration.

1. $CoCl_2(s) + 6\,H_2O(g) \rightleftharpoons CoCl_2\cdot 6\,H_2O(s)$ ____________________
2. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ ____________________
3. $CO_2(g) + NaOH(s) \rightleftharpoons NaHCO_3(s)$ ____________________

2.5 Activity: What's My Constant?

Question

How can you determine the mathematical relationship that is common to three sets of numbers? Of course, it's a lot easier to discover the relationship when you know that one actually exists!

Background

Do you think that you could have reasoned or recognized that different sets of equilibrium concentrations have a common mathematical relationship? The Norwegian chemists Cato Maximilian Guldberg and Peter Waage proposed the equilibrium law in 1864 after observing many different sets of equilibrium concentrations.

Procedure

Each set of numbers in the table below satisfies the formula A – B + C = 5.

Set	A	B	C
1	10	6	1
2	3	1	3
3	– 4	2	11

A – B + C = 5 ____________

Continued on next page

2.5 Activity: *Continued*

1. Each set of numbers in the table below can also be substituted into a common formula yielding a constant. Determine that formula.

Set	A	B	C
1	18	3	9
2	6	22	2
3	5	10	15

Easy

2. Repeat procedure step 1 for each table below.

Set	A	B	C
1	3	4	20
2	5	37	3
3	14	24	88

Challenging

Set	A	B	C
1	7	13	20
2	0	5	9
3	3	10	33

Really Hard

Results and Discussion

1. Briefly describe the method(s) you used to determine the expression for each collection of data.

2. How successful were you and your colleagues at this task?

3. Why do you not need anyone to mark this activity to know whether or not you were successful?

2.5 Review Questions

1. At a given temperature the forward and reverse rate equations for the following reaction are as shown (the units for the rate constants are left out for simplicity):
   $2\ N_2O_5(g) \rightleftharpoons 2\ N_2O_4(g) + O_2(g)$
   $r_f = 2.7 \times 10^{-3}\ [N_2O_5]^2$ $r_r = 4.3 \times 10^{-2}\ [N_2O_4]^2[O_2]$
   Derive the equilibrium constant, K_{eq}, for this reaction at this temperature.

2. A student claims that the coefficients in balanced chemical equations provide the ratio of the chemicals present at equilibrium? For example, consider the following equation.
   $2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$
   The student asserts that the equation tells us that the ratio of the equilibrium concentrations will be
   2 NO: 1 Cl_2: 2 NOCl. Is the student correct? If not, what do the coefficients represent?

3. Write the equilibrium expression for each of the following:
   (a) $HNO_2\ (aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

   (b) $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$

   (c) $4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g)$

4. A 2.0 L flask contains 0.38 mol $CH_4(g)$, 0.59 mol $C_2H_2(g)$, and 1.4 mol $H_2(g)$ at equilibrium.
   Calculate the equilibrium constant, K_{eq}, for the reaction:
   $2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$

5. A cylinder contains 0.12 M $COBr_2$, 0.060 M CO, and 0.080 M Br_2 at equilibrium. The volume of the cylinder is suddenly doubled.
   $COBr_2(g) \rightleftharpoons CO(g) + Br_2(g)$
   (a) What is the molar concentration of each gas immediately after the volume of the cylinder is doubled?

   (b) Explain, in terms of Le Châtelier's principle, why the system shifts right to restore equilibrium.

   (c) The system re-equilibrates by converting 0.010 M $COBr_2$ into CO and Br_2. Verify that the original equilibrium concentrations and the re-established equilibrium concentrations provide the same value when substituted into the reaction's equilibrium expression.

6. A closed flask contains 0.65 mol/L N_2 and 0.85 mol/L H_2 at equilibrium. What is the $[NH_3]$?
   $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_{eq} = 0.017$

7. A 1.0 L flask is injected simultaneously with 4.0 mol N_2, 3.0 mol H_2, and 8.0 mol NH_3. In what direction will the reaction proceed to achieve equilibrium? Show your mathematical reasoning.
   $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_{eq} = 1.0$

8. Write the equilibrium expression for each of the following:
   (a) $Fe(s) + 2\,H^+(aq) \rightleftharpoons H_2(g) + Fe^{2+}(aq)$

   (b) $2\,I^-(aq) + Cl_2(aq) \rightleftharpoons I_2(s) + 2\,Cl^-(aq)$

   (c) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

(d) $CO_2(g) \rightleftharpoons CO_2(aq)$ (Include each chemical's phase in the equilibrium expression.)

(e) $2\ Na_2O(s) \rightleftharpoons 4\ Na(l) + O_2(g)$

9. Write the chemical equation and the equilibrium expression for the equilibrium that develops when:
   (a) Gaseous chlorine dissolves in water.

   (b) Gaseous carbon tetrachloride decomposes into solid carbon and chlorine gas.

   (c) Solid magnesium oxide reacts with sulphur dioxide gas and oxygen gas to produce solid magnesium sulphate.

10. $2\ NOCl(g) \rightleftharpoons 2\ NO(g) + Cl_2(g)$ $K_{eq} = 8.0 \times 10^{-2}$ at 462°C
    For each of the following, what is the K_{eq} at 462°C?
    (a) $NOCl(g) \rightleftharpoons NO(g) + ½\ Cl_2(g)$

    (b) $2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$

    (c) $NO(g) + ½\ Cl_2(g) \rightleftharpoons NOCl(g)$

11. How would each of the following stresses affect the equilibrium constant, K_{eq}, for:
$2\ CO(g) + O_2(g) \rightleftharpoons 2\ CO_2(g)$ $\Delta H = -31$ kJ/mol
(a) Add some $CO_2(g)$?

(b) Decrease the volume of the reaction vessel (at a constant temperature)?

(c) Increase the temperature?

(d) Add a catalyst?

12. Can you infer that reactants are favored in the reaction below because $K_{eq} < 1$? Explain.
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ $K_{eq} = 0.16$

13. Consider the following two equilibria:
(a) $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$ $K_{eq} = 0.25$
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $K_{eq} = 0.50$
Given that their initial reactant concentrations are equal, can you infer from their equilibrium constants that the first equilibrium has a lower percent yield than the second equilibrium? Explain.

14. Consider the following equilibrium:
$2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$ $\Delta H = 56$ kJ/mol
Compare the $[O_2]$ when equilibrium is re-established to its concentration before:
(a) some $KClO_3(s)$ is added.

(b) some $O_2(g)$ is removed.

(c) the temperature is decreased.

2.6 Equilibrium Problems

Warm Up

Chemists use a simple table called an **ICE table** to help solve equilibrium problems. ICE is an acronym for **I**nitial concentration, **C**hange in concentration, and **E**quilibrium concentration. All the units are molarity (M). ICE tables are like Sudoku for chemists and are fun to solve!

The following ICE table shows a system that initially had 3.0 M N_2 and an unknown concentration of Cl_2. In the system, 2.0 M of the N_2 was consumed before achieving equilibrium. Complete the ICE table to determine the initial concentration of Cl_2. The steps following the table will assist you if you need help.

$K_{eq} = 0.128$	$N_2(g)$ +	$3\ Cl_2(g)$ $\rightleftharpoons$	$2\ NCl_3(g)$
I	3.0	?	0
C	– 2.0		
E			

1. Solve for the equilibrium concentration (E) of N_2. 3.0 – 2.0 = ?
2. Solve for the change of concentration (C) of Cl_2 and NCl_3 using the coefficients in the balanced chemical equation.
3. Solve for the equilibrium concentration (E) of NCl_3.
4. Solve for the equilibrium concentration (E) of Cl_2 using K_{eq}.
5. Solve for the initial concentration (I) of Cl_2.

Solving Equilibrium Problems

There are three related values in any chemical system that develops an equilibrium:

- the equilibrium constant
- the initial concentrations
- the equilibrium concentrations

In equilibrium problems, you will be given two of these values and asked to determine the third. The only two chemical concepts used to solve equilibrium problems are:

- reaction stoichiometry — the mole ratio in which the reactants are consumed and the products are formed
- the equilibrium law — the relationship between the equilibrium constant and any set of equilibrium concentrations

Determining K_{eq} from Initial Concentrations and One Equilibrium Concentration

The coefficients in a balanced chemical equation provide the mole ratios in which the reactants are consumed and the products are formed. Thus, if you know how much the concentration of one chemical changed in reaching equilibrium, you can easily determine how much the others have changed. The C in the ICE table stands for *change* but it can also remind you to pay attention to the *coefficients*.

It's important as well to pay attention to the units provided and requested in equilibrium problems. In this type of problem, you may be given the number of moles and liters, thus requiring you to calculate the molar concentrations, or you may have the molarity provided directly.

Sample Problem 2.6.1 — Determining K_{eq} from Initial Concentrations and One Equilibrium Concentration

A student placed 7.00 mol NH_3 in a 0.500 L flask. At equilibrium, 6.2 M N_2 was found in the flask. What is the equilibrium constant, K_{eq}, for this reaction?

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$$

What to Think About

1. Draw an ICE table and fill in the information provided in the question.

$$\frac{7.00 \text{ mol}}{0.500 \text{ L}} = 14.0 \text{ M}$$

How to Do It

	$2\,NH_3(g)$ ⇌	$N_2(g)$	+ $3\,H_2(g)$
I	**14.0**	**0**	**0**
C			
E		**6.2**	

2. Use the coefficients in the balanced chemical equation to relate (in the C row) the moles of reactant consumed to the moles of each product formed.
   For every 2 mol of NH_3 that are consumed,
   1 mol of N_2 and 3 mol of H_2 are produced.

	$2\,NH_3(g)$ ⇌	$N_2(g)$	+ $3\,H_2(g)$
I	14.0	0	0
C	**−12.4**	**+ 6.2**	**+ 18.6**
E		6.2	

3. Do the math.

4. Calculate K_{eq} using the equilibrium expression and concentrations.
   Exercise caution indicating your final answer to the appropriate degree of certainty. ICE tables involve subtraction and addition. In subtraction and addition, the answer must be rounded to the number of decimal places that the least precise piece of data is rounded to.

	$2\,NH_3(g)$ ⇌	$N_2(g)$	+ $3\,H_2(g)$
I	14.0	0	0
C	−12.4	+ 6.2	+ 18.6
E	**1.6**	6.2	**18.6**

$$K_{eq} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(6.2)(18.6)^3}{(1.6)^2} = 1.6 \times 10^4$$

Practice Problems 2.6.1 — Determining K_{eq} from Initial Concentrations and One Equilibrium Concentration

1. The following gases were placed in a 4.00 L flask: 8.00 mol N_2 and 10.00 mol H_2. After equilibrium was achieved, 1.20 M NH_3 was found in the flask. Complete the ICE table below and determine the equilibrium constant, K_{eq}.

	$N_2(g)$ +	$3\,H_2(g)$ ⇌	$2\,NH_3(g)$
I			
C			
E			

Continued opposite

Practice Problems 2.6.1 — *Continued*

2. Equal volumes of 1.60 M Ag^+ and 2.60 M $S_2O_3^{2-}$ were mixed. The $[Ag(S_2O_3)_2^{3-}]$ at equilibrium was 0.35 M. Complete the ICE table below and determine K_{eq}. (Reminder: Whenever you mix aqueous solutions, there is a dilution effect. Mixing equal volumes doubles the solution's volume and halves the concentration of both solutes.)

	$Ag^+(aq)$ +	$2\ S_2O_3^{2-}(aq)$ $\rightleftharpoons$	$Ag(S_2O_3)_2^{3-}(aq)$
I			
C			
E			

3. A sample of 6.0 g of carbon was placed in a 1.0 L flask containing 1.4 mol O_2. When equilibrium is established, 1.2 g of carbon remains. Determine K_{eq}. (Note: Because carbon is a solid it is crossed out in the ICE table but the moles of carbon consumed must be calculated — outside the ICE table — to determine the equilibrium concentrations of O_2 and CO.)

	$2\ C(s)$ +	$O_2(g)$ $\rightleftharpoons$	$2\ CO(g)$
I			
C			
E			

Determining Equilibrium Concentrations from K_{eq} and the Initial Concentrations

The equilibrium law provides chemists with the ability to predict the concentrations that will be present when equilibrium is achieved from any initial set of concentrations. This includes determining the concentrations that will be reached when a stressed system restores equilibrium. In re-equilibration problems, the initial concentrations are created by stressing a previous equilibrium. Such calculations will allow you to verify Le Châtelier's principle.

Chemists solve this type of problem algebraically. There are no questions in Chemistry 12 that require the quadratic equation or synthetic division to obtain the answer. The course is limited, in problems of this type, to perfect squares or to solving by trial and error.

Sample Problem 2.6.2(a) — Determining Equilibrium Concentrations from K_{eq} and the Initial Concentrations

The following gases are injected into a 1.00 L flask: 1.20 mol of $H_2(g)$ and 1.20 mol of $F_2(g)$. What will the concentration of HF be when equilibrium is achieved? (Note: There is no dilution effect when gases are mixed because the mixture's volume isn't increased. Injecting another gas into the same flask is possible because there is so much space between gas particles.)

$$H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g) \qquad K_{eq} = 2.50$$

What to Think About | **How to Do It**

1. Draw an ICE table and fill in the information provided in the question.

	$H_2(g)$ +	$F_2(g)$ ⇌	$2\,HF(g)$
I	**1.20**	**1.20**	**0**
C			
E			

2. Set up an algebraic solution using the coefficients in the balanced chemical equation to relate the moles of reactants consumed to each other and to the moles of the product formed.
For every x moles of H_2 and F_2 that are consumed, $2x$ moles of HF are produced.

	$H_2(g)$ +	$F_2(g)$ ⇌	$2\,HF(g)$
I	1.20	1.20	0
C	**$-x$**	**$-x$**	**$+2x$**
E			

3. Complete the ICE table.

	$H_2(g)$ +	$F_2(g)$ ⇌	$2\,HF(g)$
I	1.20	1.20	0
C	$-x$	$-x$	$+2x$
E	**$1.20 - x$**	**$1.20 - x$**	**$2x$**

4. Solve for x using the equilibrium expression and constant:

$$K_{eq} = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2x)^2}{(1.20 - x)^2} = 2.50$$

(i) Find the square root of each side.

$$\frac{2x}{1.20 - x} = (2.50)^{1/2} = 1.58$$

(ii) Multiply each side by $1.20 - x$.
(iii) Expand.
(iv) Add $1.58x$ to both sides.
(v) Divide each side by 3.58.

$$2x = 1.58\,(1.20 - x)$$
$$2x = 1.896 - 1.58x$$
$$3.58x = 1.896$$
$$x = 0.530\ M$$

5. Don't forget to answer the question!
How could you check your answer?

$$[HF]_{eq} = 2x = 2(0.530\ M) = 1.06\ M$$

Sample Problem 2.6.2(b) — Determining Equilibrium Concentrations from K_{eq} and the Initial Concentrations

A 3.00 L flask contains 6.00 M H_2, 6.00 M Cl_2, and 3.00 M HCl at equilibrium. An additional 15 mol of HCl is injected into the flask. What is $[Cl_2]$ when equilibrium is re-established?

$$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$$

What to Think About

1. Draw an ICE table and fill in the information provided in the question.
   E_o = original equilibrium
   E_f = final (re-established) equilibrium

   Adding $\frac{15.0 \text{ mol}}{3.00 \text{ L}}$ increases the [HCl] by 5.00 M.

2. Le Châtelier predicts that the system will shift to the left to remove some of the added HCl.
   For every x moles of H_2 and Cl_2 that are produced in the shift, $2x$ moles of HCl are consumed.

3. Complete the ICE table.

4. Calculate K_{eq} by substituting the original equilibrium concentrations into the equilibrium expression.

5. Solve for x using the equilibrium expression and constant and by taking the square root of each side.

   Note that this value corroborates our qualitative prediction based on Le Châtelier's principle. The system re-establishes equilibrium by removing only 4 M of the added 5 M HCl.

6. Don't forget to answer the question!

7. Check your answer by substituting your value for x back into the equilibrium expression.

How to Do It

	$H_2(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$2\,HCl(g)$
E_o	**6.00**	**6.00**	**3.00**
I	**6.00**	**6.00**	**8.00**
C			
E_f			

	$H_2(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$2\,HCl(g)$
E_o	6.00	6.00	3.00
I	6.00	6.00	8.00
C	**+x**	**+x**	**−2x**
E_f	**6.00 + x**	**6.00 + x**	**8.00 − 2x**

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(3.00)^2}{(6.00)^2} = 0.250$$

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(8.00 - 2x)^2}{(6.00 + x)^2} = 0.250$$

$$\frac{8.00 - 2x}{6.00 + x} = (0.250)^{½} = 0.500$$

$$x = 2.00 \text{ M}$$

$[Cl_2]$ when equilibrium is restored is:
6.00 M + x = 6.00 M + 2.00 M = 8.00 M

$\frac{(8.00 - 4.00)^2}{(6.00 + 2.00)^2}$ does indeed equal 0.250.

Practice Problems 2.6.2 — Determining the Equilibrium Concentrations from K_{eq} and the Initial Concentrations

1. In the lab, 4.5 mol of HCl(*g*) are pumped into a 3.00 L flask and heated to 80°C. How many moles of Cl_2 will be found in the flask after equilibrium is established? K_{eq} at 80°C = 0.36

	$2\,HCl(g) \rightleftharpoons$	$H_2(g)$ +	$Cl_2(g)$
I			
C			
E			

2. As part of an experiment, 4.00 mol H_2, 4.00 mol C_2N_2, and 8.00 mol HCN are injected into a 2.00 L flask where they establish equilibrium. What is the $[C_2N_2]$ when equilibrium is achieved? $K_{eq} = 5.00$

	$H_2(g)$ +	$C_2N_2(g) \rightleftharpoons$	$2\,HCN(g)$
I			
C			
E			

3. The table below shows the molarity of three gases at equilibrium. The concentration of HCl is then decreased as shown. What is the [HCl] when equilibrium is re-established?

	$H_2(g)$ +	$Cl_2(g) \rightleftharpoons$	$2\,HCl(g)$
E_o	6.00	6.00	12.0
I	6.00	6.00	5.00
C			
E_f			

Determining Initial Concentrations from K_{eq} and the Equilibrium Concentrations

Determining past conditions from present ones is perhaps even more remarkable than predicting future conditions. In solving the previous type of problem, we predicted a future event by determining the concentrations that will be reached at equilibrium from the system's initial concentration. In solving the type of problem covered in this section, we will do exactly the opposite as we travel back into the past to determine what initial concentrations would have resulted in the current equilibrium concentrations. We've outlined one method of solving this type of problem below but many variations exist.

Sample Problem 2.6.3 — Determining Initial Concentrations from K_{eq} and the Equilibrium Concentrations

Some CH_3OH was injected into a flask where it established equilibrium with a [CO] = 0.15 M. What was the initial concentration of CH_3OH?

$$CH_3OH(g) \rightleftharpoons 2\,H_2(g) + CO(g) \qquad K_{eq} = 0.040$$

What to Think About

How to Do It

1. Draw an ICE table and fill in the information provided in the question.

	$CH_3OH(g)$ ⇌	$2\,H_2(g)$ +	$CO(g)$
I	x	0	0
C			
E			0.15

2. Use the coefficients in the balanced chemical equation to relate the moles of reactant consumed to the moles of each product formed.
   For each mole of CH_3OH that is consumed,
   2 mol of H_2 and 1 mol of CO are produced.

	$CH_3OH(g)$ ⇌	$2\,H_2(g)$ +	$CO(g)$
I	x	0	0
C	−0.15	+0.30	+0.15
E			

3. Complete the ICE table.

	$CH_3OH(g)$ ⇌	$2\,H_2(g)$ +	$CO(g)$
I	x	0	0
C	−0.15	+0.30	+0.15
E	x − 0.15	0.30	0.15

4. Solve for x using the equilibrium expression and constant.

$$K_{eq} = \frac{[H_2]^2[CO]}{[CH_3OH]} = \frac{(0.30)^2(0.15)}{x - 0.15} = 0.040$$

$$\frac{(0.30)^2(0.15)}{0.040} = x - 0.15$$

$$x = 0.49\ M$$

Practice Problems 2.6.3 — Determining Initial Concentrations from K_{eq} and the Equilibrium Concentrations

1. NiS reacted with O_2 in a 2.0 L flask. When equilibrium was achieved 0.36 mol of SO_2 were found in the flask. What was the original $[O_2]$ in the flask? $K_{eq} = 0.30$

	$2\,NiS(s)$ +	$3\,O_2(g)$ ⇌	$2\,SO_2(g)$ +	$2\,NiO(s)$
I				
C				
E				

2. Some HI is pumped into a flask. At equilibrium, the [HI] = 0.60 mol/L. What was the initial [HI]? $K_{eq} = 0.25$

	$2\,HI(g)$ ⇌	$H_2(g)$ +	$I_2(g)$
I			
C			
E			

3. Some SO_2 and O_2 are injected into a flask. At equilibrium, the $[SO_2] = 0.050$ M and the $[O_2] = 0.040$ M. What was the initial $[O_2]$? $K_{eq} = 100$

	$2\,SO_2(g)$ +	$O_2(g)$ ⇌	$2\,SO_3(g)$
I			
C			
E			

The Equilibrium Constant and Partial Pressures

The equilibrium position of a reaction is characterized by a mathematical value often referred to as the **mass action expression**. For the reaction:

$$dD + eE \rightleftharpoons fF + gG$$

where D, E, F, and G represent chemical formulas, and *d*, *e*, *f*, and *g* are coefficients, the mass action expression is:

$$\frac{(aF)^f\,(aG)^g}{(aD)^d\,(aE)^e}$$

where *a* stands for the *activity* of each of the species in the equation.

The activity of a chemical species may be represented by its concentration (e.g., [F]) in the case of species present in solution or as gases, or by its partial pressure (e.g., P_F) in the case of a reaction where all species are present as gases. If the activities are represented by concentrations and the system is at equilibrium, the mass action expression is called an equilibrium constant K_c (as described in section 2.5). If, however, the activities are represented by partial pressures and the system is at equilibrium, the expression is still called an equilibrium constant, but it is represented by K_p. To summarize:

$$K_c = \frac{[F]^f\,[G]^g}{[D]^d\,[E]^e} \qquad K_P = \frac{[P_F]^f\,[P_G]^g}{[P_D]^d\,[P_E]^e}$$

Note: K_p should always be *calculated* using partial pressures in *atmospheres*.

The numerical values of K_C and K_P are usually different. Their relationship becomes clear if you remember the ideal gas law, which states that $PV = nRT$. Rearrangement of the ideal gas law shows:

Concentration, $C = n/V$ and $n/V = P/RT$, hence $C = P/RT$, thus $P = CRT$

Substitution of *CRT* for *P* into the K_P expression above allows you to derive the relationship between K_P and K_C as follows:

$$\boldsymbol{K_P = K_C(RT)^{\Delta n}}$$

Because K_p is determined using partial pressures in atmospheres, it follows that the ideal gas constant value, $R = 0.08206$ L·atm/mol·K. Additionally,

T = temperature in K, and
$\Delta n = (f + g) - (d + e)$ (the difference in the sums of the coefficients for the *gaseous* reactants and products)

Sample Problem 2.6.4 — Conversion Between K_c and K_p

The Haber process for the formation of ammonia establishes equilibrium at 498 K. Under these circumstances, $[N_2] = 0.020$ mol/L, $[H_2] = 0.18$ mol/L, and $[NH_3] = 0.14$ mol/L. Determine the numerical value of K_c and K_p.

What to Think About	How to Do It
1. Determine the balanced chemical equation that describes the equilibrium.	$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$
2. Write an appropriate K_c expression for the equation. 3. Substitute concentrations and solve for K_c.	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.14)^2}{(0.020)(0.18)^3} = 170$
4. Determine Δn and substitute into the appropriate equation to determine K_p. (Be sure to apply the exponent Δn to the *entire product* of $R \times T$. Also take care with the *sign* of Δn and substitution of the correct R value.)	$\Delta n = 2 - (1 + 3) = -2 \qquad K_p = K_c(RT)^{\Delta n}$ $= 170(0.08206\ \text{L atm/mol}\ \cancel{K} \times 498\ \cancel{K})^{-2}$ $= 170 \times 0.000599 = 0.10$ Notice that NO units are included in a K_c or K_p value.

Practice Problems 2.6.4 — Conversion Between K_c and K_p

1. Given the equilibrium quantities stated below each species, determine K_p for the following reactions at a fixed temperature:

(a) $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
2.71 atm 0.600 atm

(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
15.6 g/L 0.02 g/L 1.04 atm

2. Given the equilibrium partial pressures stated below each species, and the K_p value at a fixed temperature, determine the missing partial pressure.

(a) $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \qquad K_p = 1.6 \times 10^{12}$
6.5×10^{-5} atm 4.5×10^{-5} atm ?

(b) $N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad K_p = 0.715$
? 15.8 atm

3. At 500.°C, the reaction between N_2 and H_2 to form ammonia has a $K_p = 1.5 \times 10^{-5}$. What is the numerical value of K_c for this reaction?

4. For which of the following reactions would $K_P = K_C$? Explain your choice.

(a) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$

(b) $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$

2.6 Activity: Visualizing Equilibria

Question

How could you determine an equilibrium system's constant if you were able to count the number of molecules present at equilibrium?

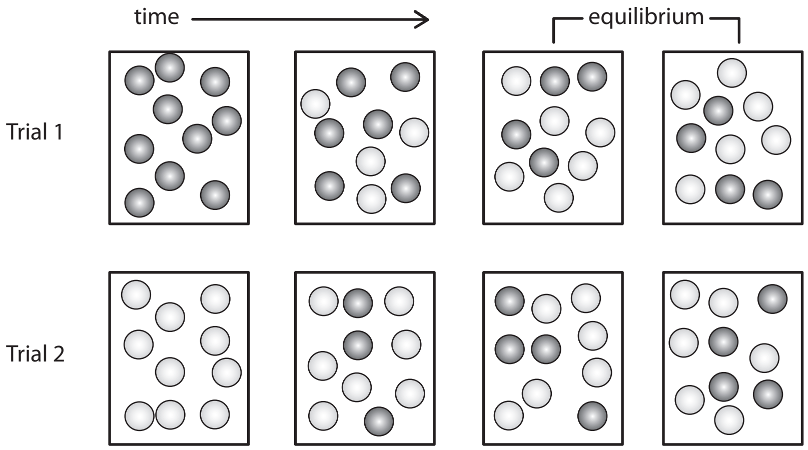
Background

The amount of each reactant and product remains constant at equilibrium because each chemical is being produced at the same rate that it is being consumed. The diagrams below represent the interconversion of A (dark) molecules and B (light) molecules:

$$\text{A (dark)} \rightleftharpoons \text{B (light)}$$

Procedure

1. Each row of drawings represents a separate trial that results in equilibrium. Answer the questions below about the trials.



Results and Discussion

1. State a property of chemical equilibrium that is evident by observing trials 1 and 2.

2. What is the equilibrium constant for A $\rightleftharpoons$ B? The container could be any volume because the volumes cancel in this particular equilibrium expression.

3. In another trial, 20 A molecules and 50 B molecules were counted in a reaction vessel. How many A molecules will there be in the vessel when equilibrium is established?

4. After equilibrium was established in trial 2, the temperature was decreased. When equilibrium was restored, there were 7 A molecules and 3 B molecules in the container. State whether A $\rightleftharpoons$ B is exothermic or endothermic.

2.6 Review Questions

1. Complete the following ICE tables.

(a)

	$2\ CH_4(g)$ $\rightleftharpoons$	$C_2H_2(g)$ +	$3\ H_2(g)$
I	6.0	0	0
C			
E		1.5	

(b)

	$N_2(g)$ +	$3\ H_2(g)$ $\rightleftharpoons$	$2\ NH_3(g)$
I		5.0	0
C			
E	2.0		1.0

2. During an experiment, 3.0 mol of NO_2 are injected into a 1.0 L flask at 55°C. At equilibrium, the flask contains 1.2 mol of N_2O_4.
$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$
(a) What is the $[NO_2]$ at equilibrium?

(b) What is K_{eq} for this reaction at 55°C?

3. Equal volumes of 3.60 M A^{2+} and 6.80 M B^- are mixed. After the reaction, equilibrium is established with $[B^-] = 0.40$ M.
$A^{2+}(aq) + 3B^-(aq) \rightleftharpoons AB_3^-(aq)$
(a) What is the $[A^{2+}]$ at equilibrium?

(b) Determine K_{eq}.

4. Complete the following ICE tables:

(a)

K_{eq} = 1.20	$H_2(g)$ +	$C_2N_2(g)$ $\rightleftharpoons$	2 HCN(g)
I			0
C			
E	5.0	1.5	

(b)

K_{eq} = 1.20	$H_2(g)$ +	$C_2N_2(g)$ $\rightleftharpoons$	2 HCN(g)
I	5.4		0
C			
E			3.6

5. The interconversion of the structural isomers glyceraldehyde-3-phospate (G3P) and dihydroxyacetone phosphate (DHAP) is a biochemical equilibrium that occurs during the breakdown of glucose in our cells. What will their concentrations be at equilibrium if the initial concentration of each isomer is 0.020 M?

G3P(aq) $\rightleftharpoons$ DHAP(aq) $K_{eq} = 19$

6. A 1.00 L flask is injected with 0.600 mol of each of the following four gases: H_2, CO_2, H_2O, and CO.

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $K_{eq} = 1.69$

(a) What is the $[H_2]$ at equilibrium?

(b) What is the [CO] at equilibrium?

7. A 500 mL flask is injected with 0.72 mol of C_2N_2 and 0.72 mol of H_2. What will the [HCN] be when the system reaches equilibrium?

$H_2(g) + C_2N_2(g) \rightleftharpoons 2\,HCN(g)$ $K_{eq} = 1.20$

8. A 1.0 L flask containing 4.0 mol of H_2 and a 1.0 L flask containing 4.0 mol of F_2 are connected by a valve. The valve is opened to allow the gases to mix in the 2.0 L combined volume.

   $H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)$ $K_{eq} = 121$

   How many moles of H_2 will be present in the system when it equilibrates?

9. A 250 mL flask containing 1.0 g of excess BN(*s*) is injected with 0.21 mol of $Cl_2(g)$.

   $2\,BN(s) + 3\,Cl_2(g) \rightleftharpoons 2\,BCl_3(g) + N_2(g)$ $K_{eq} = 0.045$

   (a) What will the $[BCl_3]$ equal when the system attains equilibrium? (Hint: The math is a bit trickier on this one; you need to take the cube root of each side.)

   (b) Would the reaction achieve equilibrium if the flask initially contained 1.0 g of BN(s)? Support your answer with calculations.

10. A flask is injected with 0.60 M C_2H_2 and 0.60 M H_2. Determine the $[H_2]$ at equilibrium by trial and error. Lower the $[C_2H_2]$ and the $[H_2]$ and raise the $[CH_4]$ in appropriate increments until you find a set of concentrations that provides the K_{eq} value when substituted into the equilibrium expression.

    $2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g)$ $K_{eq} = 2.8$

11. In a 2.00 L flask, 3.00 M H_2, 3.00 M Cl_2, and 7.50 M HCl coexist at equilibrium. A student removes 7.00 mol of HCl from the flask.

    (a) What would the concentration of each gas be when equilibrium re-establishes?

	$H_2(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$2\,HCl(g)$
E_o			
I			
C			
E_f			

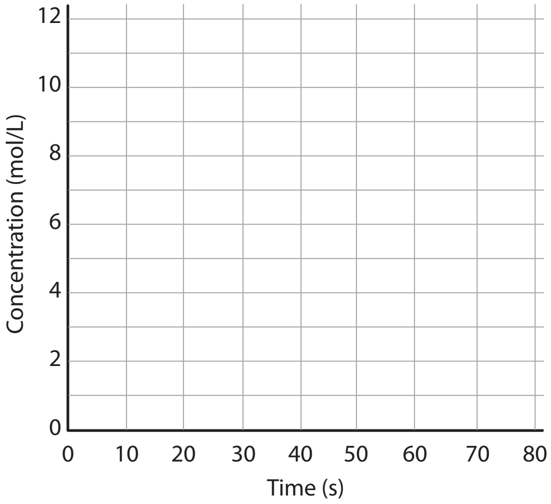
(b) Describe how the system's response is consistent with Le Châtelier's principle.

12. A 200.0 mL solution of 0.10 M Fe^{3+}, 0.10 M SCN^-, and 1.8 M $FeSCN^{2+}$ is at equilibrium. The solution is diluted by adding water up to 500.0 mL. Complete the ICE table below and show the algebraic equation that would allow you to solve for the ion concentrations when equilibrium is restored. Do **NOT** solve for *x*.

	$Fe^{3+}(aq)$ +	$SCN^-(aq)$ $\rightleftharpoons$	$FeSCN^{2+}(aq)$
E_o	0.10	0.10	1.8
I			
C			
E_f			

13. In a 500.0 mL flask, 2.5 mol of H_2, 2.5 mol of Br_2, and 5.0 mol of HBr coexist at equilibrium. At 35 s, 2.5 mol of Br_2 is injected into the flask, and the system re-establishes equilibrium at 55 s. Use three different-colored plots on the graph below to show how the concentration of each chemical changes during this period. (This question can be solved algebraically without using the quadratic formula despite not providing a perfect square.)

$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$



14. Some SO_3 is injected into a 500 mL flask. At equilibrium the $[O_2] = 1.80$ M.
    $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_{eq} = 3.83 \times 10^{-2}$
    (a) What is the $[SO_3]$ at equilibrium?

    (b) How many moles of SO_3 were originally injected into the flask?

15. Equal quantities of $H_2(g)$ and $I_2(g)$ are pumped into a flask. At equilibrium the [HI] = 1.0 M. What was the initial $[H_2]$?
    $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ $K_{eq} = 4.0$

16. Some PCl_5 is pumped into a 500 mL flask. The $[PCl_3] = 1.50$ M at equilibrium. What was the initial $[PCl_5]$?
    $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $K_{eq} = 2.14$

17. A reaction mixture contains 0.24 mol of NO, 0.10 mol of O_2, and 1.20 mol of NO_2 at equilibrium in a 1.0 L container. How many moles of O_2 would need to be added to the mixture to increase the amount of NO_2 to 1.30 mol when equilibrium is re-established?
    $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$

18. Write the K_p expression for each of the following equations:
    (a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

    (b) $P_4(s) + 5\,O_2(g) \rightleftharpoons 2\,P_2O_5(g)$

    (c) $CO_2(g) + CaO(s) \rightleftharpoons CaCO_3(s)$

19. Calculate K_p for the equilibria in Review Questions 4, 6, and 7 in section 2.5.
    Review Question 4:

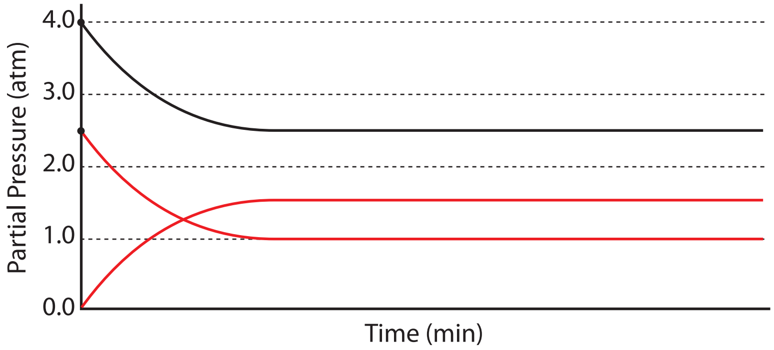
    Review Question 6:

    Review Question 7:

20. Consider the following reaction:
    $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ $K_p = 0.14$ at 625°C

    If a reaction vessel is filled with SO_3 at a partial pressure of 0.10 atm and 0.20 atm each of SO_2 and O_2 gas, is the reaction at equilibrium? If not, in which direction does it proceed to reach equilibrium?

21. The following graph represents partial pressure vs. time for the reaction between A and B gas to form C gas. Gas A is present in excess.



(a) Write a balanced chemical equation for the equilibrium in the question.

(b) Write the equilibrium expression K_p for the reaction.

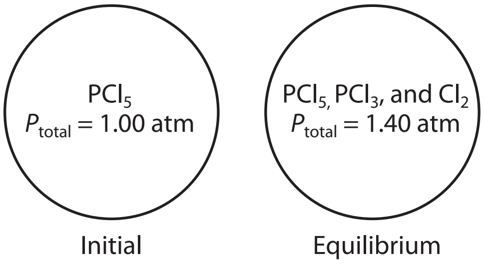
(c) Calculate the numerical value for K_p for this reaction.

(d) Calculate the numerical value for K_c for this reaction.

22. In a container, 1.00 mol of N_2 and 3.00 mol of H_2 are mixed together to produce ammonia. At equilibrium, the total pressure of the system is 1.8×10^6 Pa and the mixture contains only 50% of the N_2 that was present originally. Calculate K_p for this reaction at this temperature.

23. A lab technician places 0.300 atm of SO_2, 0.400 atm O_2, and 0.020 atm of SO_3 into a 10.0 L bulb. Once equilibrium is established, the partial pressure of SO_3 is found to be 0.140 atm. What is the value of K_p for the reaction under these conditions?

24. $PCl_5(g)$ decomposes into $PCl_3(g)$ and $Cl_2(g)$. A pure sample of phosphorus pentachloride is placed into an evacuated 1.00 L glass bulb. The temperature remains constant while the pure sample decomposes as shown below:



(a) Explain why the pressure increases in the container as the reaction reaches equilibrium.

(b) Determine the partial pressure of each gas when the system reaches equilibrium.

(c) Calculate K_p for the equilibrium system.

(d) If the decomposition were to go to completion, what would the total pressure be in the system?