

Chapter 15. Chemical Equilibrium

Common Student Misconceptions

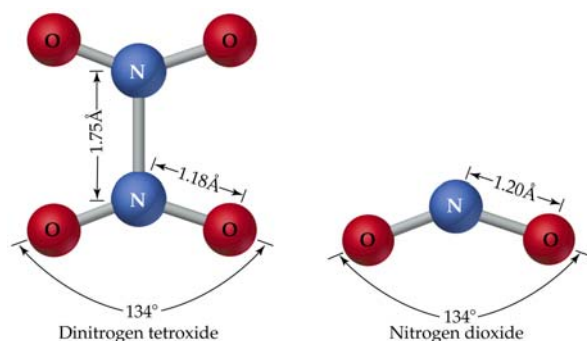
- Many students need to see how the numerical problems in this chapter are solved.
- Students confuse the arrows used for resonance (\leftrightarrow) and equilibrium (\rightleftharpoons).
- Students often have problems distinguishing between K and Q .
- Students who have difficulty with some of the mathematical manipulations in this chapter should be directed to Appendix A of the text.
- Sometimes students worry about approximations used in solving equilibrium problems. They feel that ignoring a small number when it is subtracted from a significantly larger number is wrong.

Lecture Outline

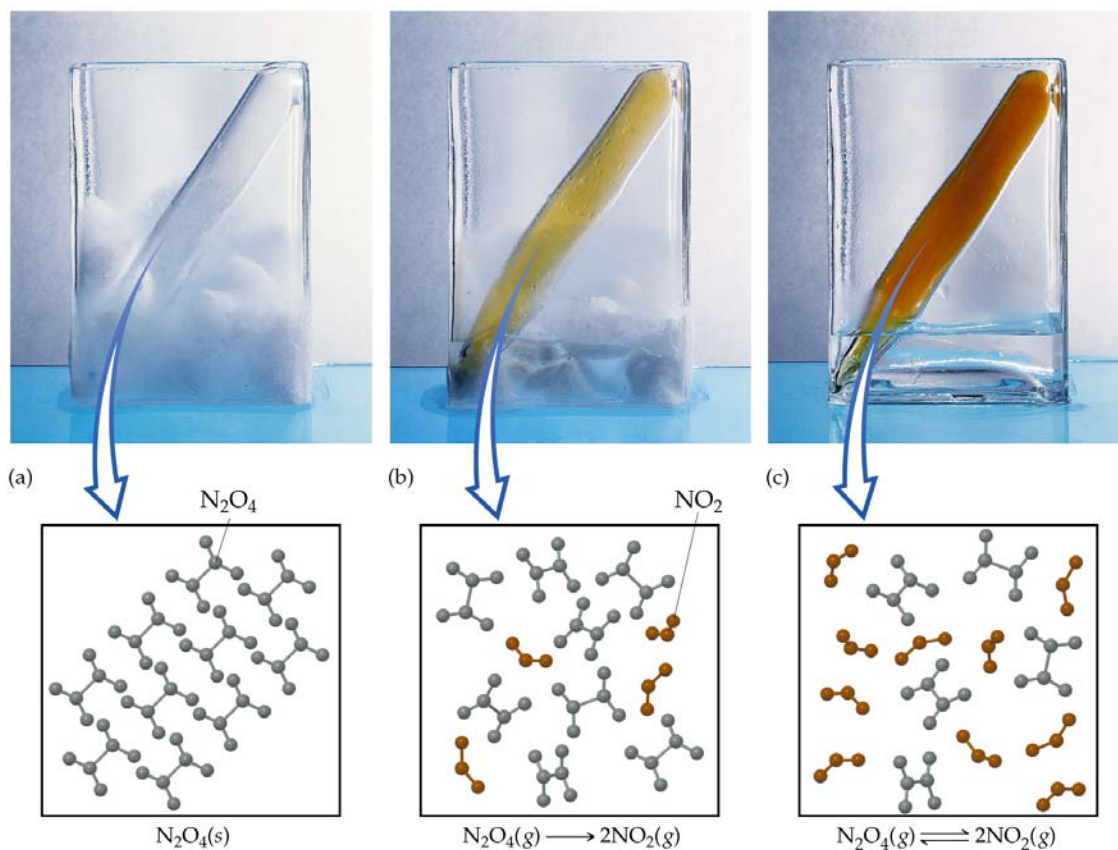
15.1 The Concept of Equilibrium

- Consider colorless frozen N_2O_4 .
 - At room temperature, it decomposes to brown NO_2 .
$$\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$$
 - At some time, the color stops changing and we have a mixture of N_2O_4 and NO_2 .
- **Chemical equilibrium** is the point at which the concentrations of all species are constant.
- Using the collision model:

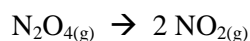
As the amount of NO_2 builds up, there is a chance that two NO_2 molecules will collide to form N_2O_4 . At the beginning of the reaction, there is no NO_2 so the reverse reaction ($2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$) does not occur.



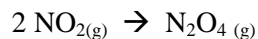
- The point at which the rate of decomposition:
$$\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$$
equals the rate of dimerization: $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ is **dynamic equilibrium**.
- The equilibrium is dynamic because the reaction has not stopped: the opposing rates are equal.
- Consider frozen N_2O_4 : only white solid is present. On the microscopic level, only N_2O_4 molecules are present.



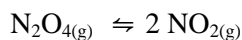
- As the substance warms it begins to decompose:



- A mixture of N_2O_4 (initially present) and NO_2 (initially formed) appears light brown.
- When enough NO_2 is formed, it can react to form N_2O_4

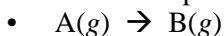


- At equilibrium, as much N_2O_4 reacts to form NO_2 as reacts to re-form N_2O_4 :



- The **double arrow** implies the process is **dynamic**.

- Consider a simple reaction:



- Assume that both the forward and reverse reactions are elementary processes.

- We can write rate expressions for each reaction.

- Forward reaction:



- Rate = $k_f[\text{A}]$

k_f = rate constant (forward reaction)

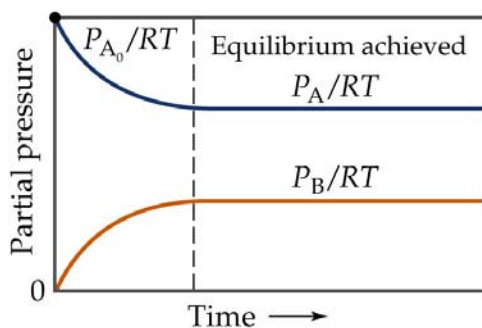
- Reverse reaction:



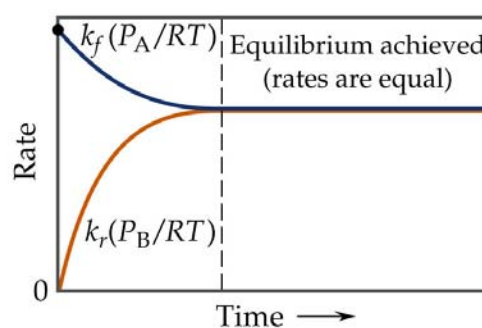
- Rate = $k_r[\text{B}]$

k_r = rate constant (reverse reaction)

- For gaseous substances we can use the ideal gas equation to convert between concentration and pressure:
 - $PV = nRT$ so $M = (n/V) = (P/RT)$
 - For substances A and B:
 - $[A] = (P_A/RT)$ and $[B] = (P_B/RT)$
 - $\text{Rate}_{\text{fwd}} = k_f P_A/RT$ and $\text{Rate}_{\text{rev}} = k_r P_B/RT$
- Place some pure compound A into a closed container.
 - As A reacts to form B, the partial pressure of A will decrease and the partial pressure of B will increase.



(a)



(b)

- Thus we expect the forward reaction rate to slow and the reverse reaction rate to increase.
- Eventually we get to equilibrium where the forward and reverse rates are equal.
- At equilibrium:

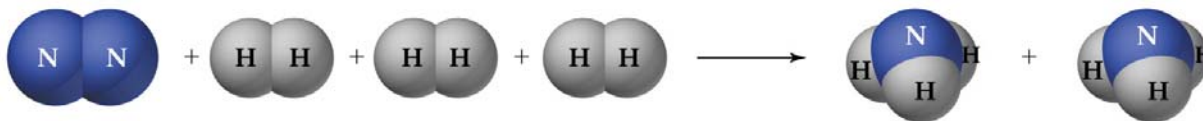
$$k_f P_A/RT = k_r P_B/RT$$

- Rearranging, we get:

$$\frac{(P_B / RT)}{(P_A / RT)} = \frac{P_B}{P_A} = \frac{k_f}{k_r} = \text{a constant}$$

- At equilibrium the partial pressures of A and B do not change.
 - This mixture is called an *equilibrium mixture*.
 - This is an example of a *dynamic* equilibrium.
 - A dynamic equilibrium exists when the rates of the forward and reverse reactions are equal.
 - No further net change in reactant or product concentration occurs.
 - The double arrow \rightleftharpoons implies that the process is dynamic.
- Haber process:** industrial preparation of ammonia from nitrogen and hydrogen:

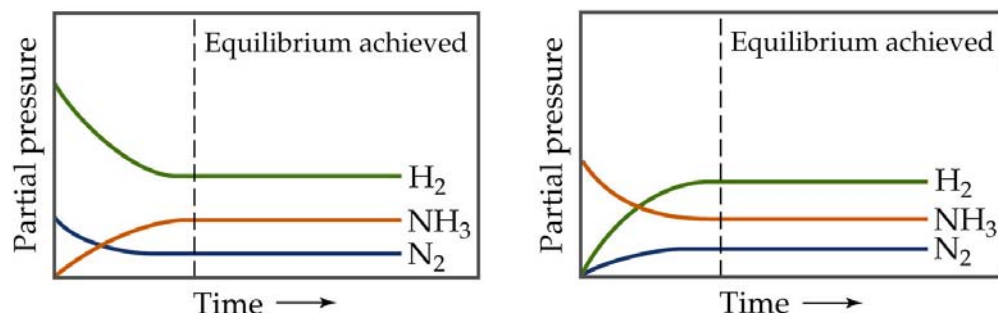
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$



- The process is carried out at high temperature (500°C) and pressure (200 atm).
- Ammonia is a good source of fixed nitrogen for plants.
 - Much of the NH_3 produced industrially is used as a fertilizer.

15.2 The Equilibrium Constant

- Consider the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
- If we start with a mixture of nitrogen and hydrogen (in any proportions), the reaction will reach equilibrium with constant concentrations of nitrogen, hydrogen and ammonia.
- However, if we start with just ammonia and no nitrogen or hydrogen, the reaction will proceed and N_2 and H_2 will be produced until equilibrium is achieved.
- No matter the starting composition of reactants and products is, the equilibrium mixture contains the same relative concentrations of reactants and products.
 - Equilibrium can be reached from either direction.



- We can write an expression for the relationship between the concentration of the reactants and products at equilibrium.
 - This expression is based on the **law of mass action**.
 - For a general reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$
 - The **equilibrium expression** is given by:

$$K_{eq} = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- Where K_{eq} is the **equilibrium constant**.
- Note that the equilibrium constant expression has products in the numerator and reactants in the denominator.
- When the reactants and products are all in solution, the equilibrium constant is expressed in terms of molarities:

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

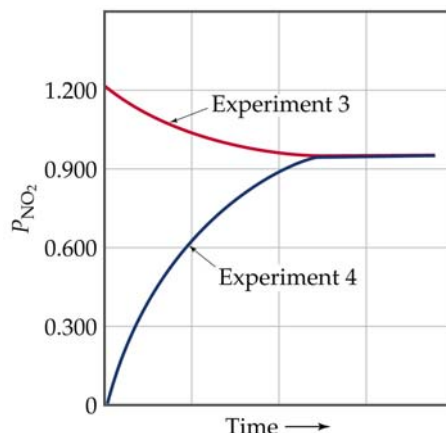
- The value of K_{eq} does not depend on initial concentrations of products or reactants.
 - Consider the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 - The equilibrium constant is given by:

$$K_{eq} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

- The value of this constant (at 100°C) is 6.49 (regardless of the initial $\text{N}_2\text{O}_4(\text{g})$ or $\text{NO}_2(\text{g})$ partial pressures.

TABLE 15.1 Initial and Equilibrium Partial Pressures (P) of N_2O_4 and NO_2 at 100°C

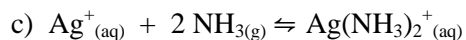
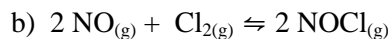
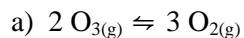
Experiment	Initial N_2O_4 Partial Pressure (atm)	Initial NO_2 Partial Pressure (atm)	Equilibrium N_2O_4 Partial Pressure (atm)	Equilibrium NO_2 Partial Pressure (atm)	K_{eq}
1	0.0	0.612	0.0429	0.526	6.45
2	0.0	0.919	0.0857	0.744	6.46
3	0.0	1.22	0.138	0.944	6.46
4	0.612	0.0	0.138	0.944	6.46



- The equilibrium expression depends on stoichiometry.
 - It does not depend on the reaction mechanism.
 - The value of K_{eq} varies with temperature.
- We generally omit the units of the equilibrium constant.

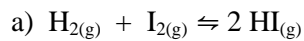
Sample Exercise 15.1

Write the equilibrium expression for K_{eq} for these three reactions:



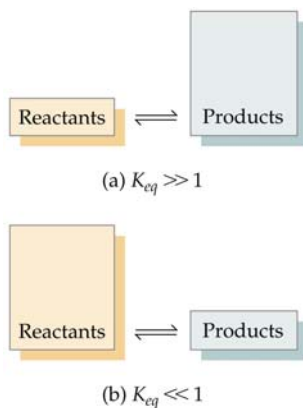
Practice Exercise 15.1

Write the equilibrium expression for K_{eq} for these three reactions:



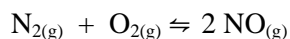
The Magnitude of Equilibrium Constants

- The equilibrium constant, K_{eq} , is the ratio of products to reactants.
 - Therefore, the larger K_{eq} the more products are present at equilibrium.
 - Conversely, the smaller K_{eq} the more reactants are present at equilibrium.
 - If $K_{eq} \gg 1$, then products dominate at equilibrium and equilibrium lies to the right.
 - If $K_{eq} \ll 1$, then reactants dominate at equilibrium and the equilibrium lies to the left.



Sample Exercise 15.2

The reaction of N_2 with O_2 to form NO might be considered a means of “fixing” nitrogen.



The value for the equilibrium constant for this reaction at 25°C is $K_{eq} = 1 \times 10^{-30}$.

Describe the feasibility of this reaction for nitrogen fixation.

Practice Exercise 15.2

The equilibrium constant for the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2 HI_{(g)}$ varies with temperature as follows:

$K_{eq} = 792$ at 298 K ; $K_{eq} = 54$ at 700 K .

Is the formation of HI favored more at the higher or lower temperature?

The Direction of the Chemical Equation and K

- An equilibrium can be approached from any direction.
- Consider the reaction: $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 - The equilibrium constant for this reaction (at 100°C) is:

$$K_{eq} = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 6.49$$

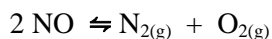
- However, when we write the equilibrium expression for the reverse reaction,
 $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$
- The equilibrium constant for this reaction (at 100°C) is:

$$K_{eq} = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = 0.154$$

- The equilibrium constant for a reaction in one direction is the reciprocal of the equilibrium constant of the reaction in the opposite direction.

Sample Exercise 15.3:

- a) Write the expression for K_{eq} for the following reaction:



- b) Using information in Sample Exercise 15.2, determine the value of this equilibrium constant at 25°C. (1×10^{30})

Practice Exercise 15.3:

For the formation of NH_3 from N_2 and H_2 , $\text{N}_{2(g)} + \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$, $K_{eq} = 4.34 \times 10^{-3}$ at 300°C.

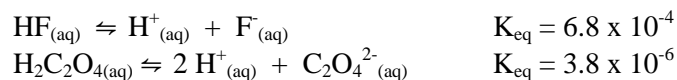
What is the value of K_{eq} for the **reverse** reaction? (2.30×10^2)

Other Ways to Manipulate Chemical Equations and K_{eq} Values

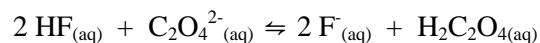
- The equilibrium constant of a reaction in the reverse direction is the inverse of the equilibrium constant of the reaction in the forward direction.
- The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power equal to that number.
- The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.

Sample Exercise 15.4

Given the following information,



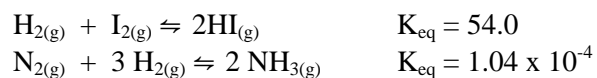
determine the value of the equilibrium constant for the following reaction:



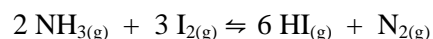
(0.12)

Practice Exercise 15.4

Given the following information at 700 K,



determine the value of the equilibrium constant for the reaction (at 700 K)



(1.51 x 10⁹)

15.3 Heterogeneous Equilibria

- Equilibria in which all reactants and products are present in the same phase are called **homogeneous equilibria**.
- Equilibria in which one or more reactants or products are present in a different phase are called **heterogeneous equilibria**.
- Consider the decomposition of calcium carbonate: $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$
 - Experimentally, the amount of CO_2 does not depend on the amounts of CaO and CaCO_3 .
 - Why?
 - The concentration of a pure solid or pure liquid equals its density divided by its molar mass.
 - Neither density nor molar mass is a variable.
 - Thus the concentrations of solids and pure liquids are constant.
 - For the decomposition of CaCO_3 :

$$K_{eq} = \frac{[\text{CaO}]P_{\text{CO}_2}}{[\text{CaCO}_3]}$$

- CaO and CaCO_3 are pure solids and have constant concentrations.

$$K_{eq} = \frac{(\text{constant 1})P_{\text{CO}_2}}{(\text{constant 2})}$$

- Rearranging:

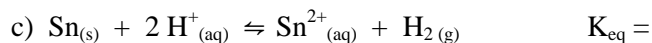
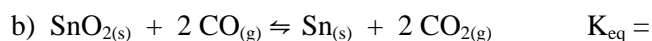
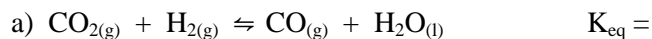
$$\therefore K_{eq}' = K_{eq} \frac{(\text{constant 2})}{(\text{constant 1})} = P_{\text{CO}_2}$$

- If a pure solid or pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium constant expression.
- Therefore, we anticipate that the amount of CO_2 formed will not depend on the amounts of CaO and CaCO_3 present.
- Note: Although the *concentrations* of these species are not included in the equilibrium expression, they *do* participate in the reaction and *must* be present for an equilibrium to be established!



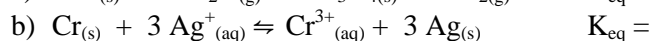
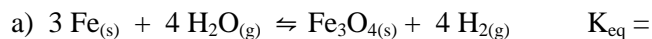
Sample Exercise 15.5

Write the equilibrium-constant expressions for each of the following reactions:



Practice Exercise 15.5

Write the equilibrium-constant expressions for each of the following reactions:



Sample Exercise 15.6

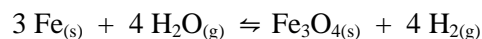
Each of the following mixtures was placed in a closed container and allowed to stand. Which of these mixtures is capable of attaining the equilibrium expressed by the following equation:



- a) pure CaCO_3
- b) CaO and a pressure of CO_2 greater than the value of K_{eq}
- c) Some CaCO_3 and a pressure of CO_2 greater than the value of K_{eq}
- d) CaCO_3 and CaO

Practice Exercise 15.6

Which one of the following substances – $\text{H}_{2(g)}$, $\text{H}_2\text{O}_{(g)}$, $\text{O}_{2(g)}$ – when added to $\text{Fe}_3\text{O}_{4(s)}$ in a closed container will allow equilibrium to be established in the reaction



15.4 Calculating Equilibrium Constants

- Proceed as follows:
 - Tabulate initial and equilibrium concentrations (or partial pressures) for all species in the equilibrium.
 - If an initial *and* an equilibrium concentration is given for a species, calculate the change in concentration.
 - Use the coefficients in the balanced chemical equation to calculate the changes in concentration of all species.
 - Deduce the equilibrium concentrations of all species.
 - Use these equilibrium concentrations to calculate the value of the equilibrium constant.

15.5 Applications of Equilibrium Constants

Predicting the Direction of Reaction

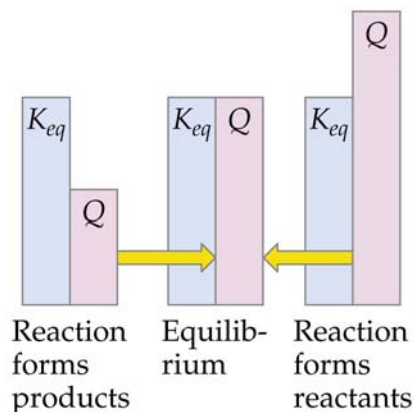
- For a general reaction: $aA + bB \rightleftharpoons cC + dD$
- We define Q , the **reaction quotient**, as:

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

- Where $[A]$, $[B]$, $[C]$, and $[D]$ are molarities (for substances in solution) or partial pressures (for gases) at any given time.
- Note: $Q = K_{eq}$ only at equilibrium.
 - If $Q < K_{eq}$ then the forward reaction must occur to reach equilibrium.
 - If $Q > K_{eq}$ then the reverse reaction must occur to reach equilibrium.
 - Products are consumed, reactants are formed.
 - Q decreases until it equals K_{eq} .

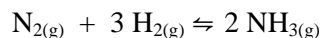
Calculating Equilibrium Concentrations

- The same steps used to calculate equilibrium constants are used to calculate equilibrium concentrations.
- Generally, we do not have a number for the change in concentration.
 - Therefore, we need to assume that x mol/L of a species is produced (or used).
- The equilibrium concentrations are given as algebraic expressions.



Sample Exercise 15.7

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472°C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm H₂, 2.46 atm N₂, and 0.166 atm NH₃. From these data calculate the equilibrium constant, K_{eq}, for



(2.79 x 10⁻⁵)

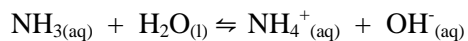
Practice Exercise 15.7

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25°C: [HC₂H₃O₂] = 1.65 x 10⁻² M; [H⁺] = 5.44 x 10⁻⁴ M; and [C₂H₃O₂⁻] = 5.44 x 10⁻⁴ M. Calculate the equilibrium constant, K_{eq}, for the ionization of acetic acid at 25°C.

(1.79 x 10⁻⁵)

Sample Exercise 15.8

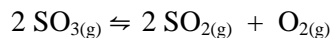
Enough ammonia is dissolved in 5.00 liters of water at 25°C to produce a solution that is 0.0124 M in ammonia. The solution is then allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of OH⁻ is 4.64 x 10⁻⁴ M. Calculate K_{eq} at 25°C for the reaction



(1.81 x 10⁻⁵)

Practice Exercise 15.8

Sulfur trioxide decomposes at high temperature in a sealed container:

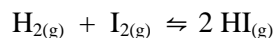


Initially the vessel is charged at 1000 K with SO_{3(g)} at a partial pressure of 0.500 atm. At equilibrium the SO₃ partial pressure is 0.200 atm. Calculate the value of K_{eq} at 1000 K.

(0.338)

Sample Exercise 15.9

At 448°C the equilibrium constant, K_{eq} , for the reaction



is 51. Predict how the reaction will proceed to reach equilibrium at 448°C if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mole of H_2 , and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

($Q = 1.3$, so reaction must proceed from left to right)

Practice Exercise 15.9

At 1000 K the value of K_{eq} for the reaction $2 \text{SO}_{3(g)} \rightleftharpoons 2 \text{SO}_{2(g)} + \text{O}_{2(g)}$ is 0.338. Calculate the value for Q , and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures of reactants are $P_{\text{SO}_3} = 0.16$ atm; $P_{\text{SO}_2} = 0.41$ atm; $P_{\text{O}_2} = 2.5$ atm.

($Q = 16$; $Q > K_{eq}$, so reaction will proceed from right to left)

Sample Exercise 15.10

For the Haber process, $\text{N}_{2(\text{g})} + 3 \text{H}_{2(\text{g})} \rightleftharpoons 2 \text{NH}_{3(\text{g})}$, $K_{\text{eq}} = 1.45 \times 10^{-5}$ at 500°C . In an equilibrium mixture of the three gases at 500°C , the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

$(2.24 \times 10^{-3} \text{ atm})$

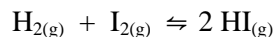
Practice Exercise 15.10

At 500 K the reaction $\text{PCl}_{5(\text{g})} \rightleftharpoons \text{PCl}_{3(\text{g})} + \text{Cl}_{2(\text{g})}$ has $K_{\text{eq}} = 0.497$. In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

(1.22 atm)

Sample Exercise 15.11

A 1.000-L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 at 448°C . The value of the equilibrium constant, K_{eq} , for the reaction



at 448°C is 50.5. What are the partial pressures of H_2 , I_2 , and HI in the flask at equilibrium?

($P_{\text{H}_2} = 3.9 \text{ atm}$, $P_{\text{I}_2} = 63.1 \text{ atm}$, $P_{\text{HI}} = 110.6 \text{ atm}$)

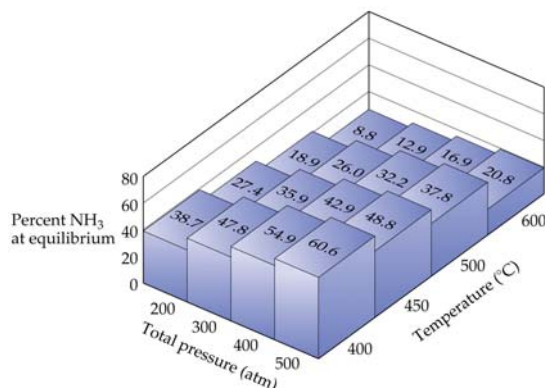
Practice Exercise 15.11

For the equilibrium, $\text{PCl}_{5(\text{g})} \rightleftharpoons \text{PCl}_{3(\text{g})} + \text{Cl}_{2(\text{g})}$, the equilibrium constant, K_{eq} , has the value 0.497 at 500 K. A gas cylinder at 500 K is charged with $\text{PCl}_{5(\text{g})}$ at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5 , PCl_3 , and Cl_2 at this temperature?

($P_{\text{PCl}_5} = 0.967 \text{ atm}$, $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.693 \text{ atm}$)

15.6 Le Châtelier's Principle

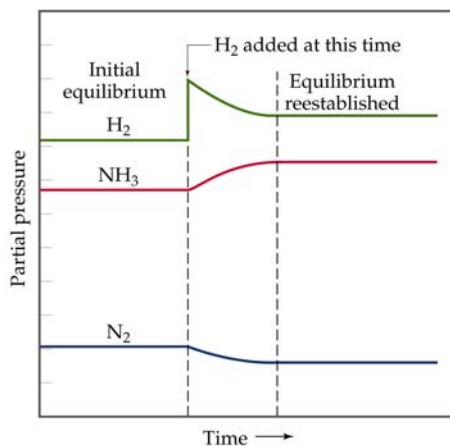
- Consider the Haber process: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - As the pressure increases, the amount of ammonia present at equilibrium increases.
 - As the temperature increases, the amount of ammonia at equilibrium decreases.
 - Can this be predicted?



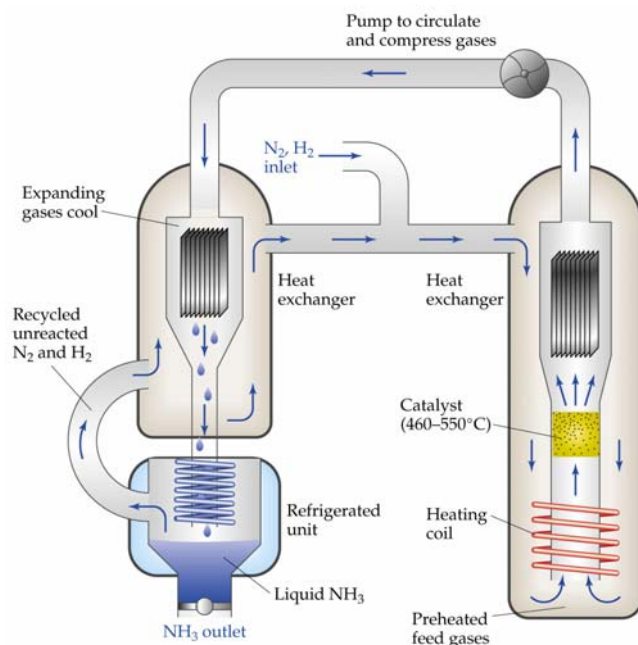
- Le Châtelier's principle:** If a system at equilibrium is disturbed by a change in temperature, a change in pressure, or a change in the concentration of one or more components, the system will shift its equilibrium position in such a way as to counteract the effects of the disturbance.

Change in Reactant or Product Concentration

- If a chemical system is at equilibrium and we add or remove a product or reactant, the reaction will shift so as to reestablish equilibrium.
 - For example, consider the Haber process again: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - If H₂ is added while the system is at equilibrium, $Q < K_{\text{eq}}$.
 - The system must respond to counteract the added H₂ (by Le Châtelier's principle).
 - That is, the system must consume the H₂ and produce products until a new equilibrium is established.
 - Therefore, [H₂] and [N₂] will decrease and [NH₃] increase until $Q = K_{\text{eq}}$.



- We can exploit this industrially.
 - Suppose that we wanted to optimize the amount of ammonia we formed from the Haber process.
 - We might flood the reaction vessel with reactants and continuously remove product.
 - The amount of ammonia produced is optimized because the product (NH_3) is continuously removed and the reactants (N_2 and H_3) are continuously being added.

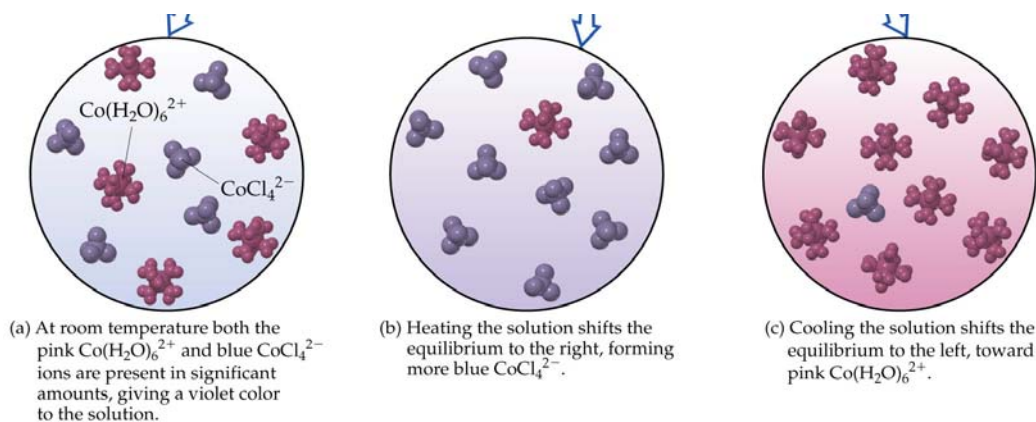


Effects of Volume and Pressure Changes

- Consider a system at equilibrium.
- If the equilibrium involves gaseous products or reactants, the concentration of these species will be changed if we change the volume of the container.
 - For example, if we decrease the volume of the container, the partial pressures of each gaseous species will increase.
 - Le Châtelier's principle predicts that if pressure is increased, the system will shift to counteract the increase.
 - That is, the system shifts to remove gases and decrease pressure.
 - An increase in pressure favors the direction that has fewer moles of gas.
- Consider the following system: $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 - An increase in pressure (by decreasing the volume) favors the formation of colorless N_2O_4 .
 - The instant the pressure increases, the concentration of both gases increases and the system is not at equilibrium.
 - The system moves to reduce the number moles of gas.
 - A new equilibrium is established.
 - The mixture is lighter in color.
 - Some of the brown NO_2 has been converted into colorless $\text{N}_2\text{O}_4(g)$
- In a reaction with the same number of moles of gas in the products and reactants, changing the pressure has no effect on the equilibrium.
- In addition, no change will occur if we increase the total gas pressure by the addition of a gas that is not involved in the reaction.

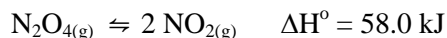
Effect of Temperature Changes

- The equilibrium constant is temperature dependent.
- How will a change in temperature alter a system at equilibrium?
 - It depends on the particular reaction.
 - For example, consider the endothermic reaction:
$$\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4\text{Cl}^{-}(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \quad \Delta H > 0$$
 - $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pale pink and CoCl_4^{2-} is a deep blue.
 - At room temperature, an equilibrium mixture (light purple) is placed in a beaker of warm water.
 - The mixture turns deep blue.
 - This indicates a shift toward products (blue CoCl_4^{2-}).
 - This reaction is endothermic.
 - For an endothermic reaction ($\Delta H > 0$), heat can be considered as a reactant.
 - Thus adding heat causes a shift in the forward direction.
 - The room-temperature equilibrium mixture is placed in a beaker of ice water.
 - The mixture turns bright pink.
 - This indicates a shift toward reactants (pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$).
 - In this case, by cooling the system we are removing a reactant (heat).
 - Thus the reaction is shifted in the reverse reaction.



Sample Exercise 15.12

Consider the following equilibrium:

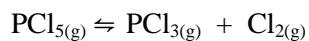


In what direction will the equilibrium shift when each of the following changes is made to a system at equilibrium:

- add N_2O_4
- remove NO_2
- increase the total pressure by adding $\text{N}_{2(\text{g})}$
- increase the volume
- decrease the temperature?

Practice Exercise 15.12

For the reaction

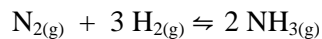


in what direction will the equilibrium shift when

- a) $\text{Cl}_{2(g)}$ is removed;
- b) The temperature is decreased;
- c) The volume of the reaction system is increased;
- d) $\text{PCl}_{3(g)}$ is added?

Sample Exercise 15.13

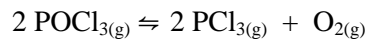
Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction



Determine how the equilibrium constant for this reaction should change with temperature.

Practice Exercise 15.13

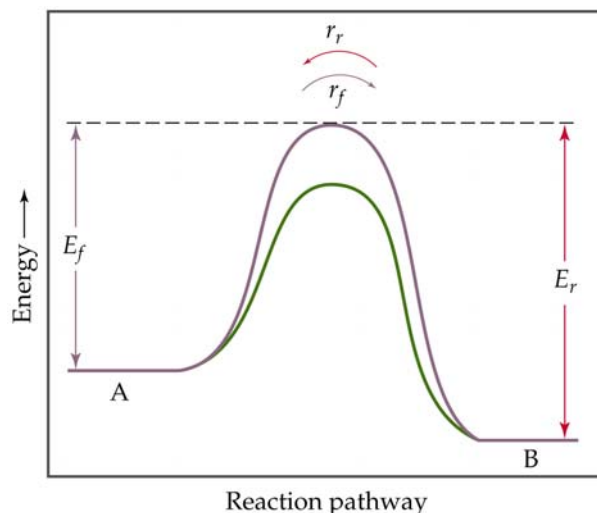
Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction



Use this result to determine how the equilibrium constant for the reaction should change with temperature.

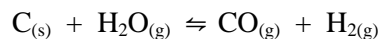
The Effect of Catalysts

- A catalyst lowers the activation energy barrier for the reaction.
 - Therefore, a catalyst will decrease the time taken to reach equilibrium.
 - A catalyst *does not* affect the composition of the equilibrium mixture.



Sample Integrative Exercise 15

At temperatures near 800°C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H₂:



The mixture of gases that results is an important industrial fuel called water gas.

- At 800°C the equilibrium constant for this reaction is $K_{\text{eq}} = 14.1$. What are the equilibrium partial pressures of H₂O, CO, and H₂ in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H₂O in a 1.00-L vessel?
- What is the minimum amount of carbon required to achieve equilibrium under these conditions?
- What is the total pressure in the vessel at equilibrium?
- At 25°C the value of K_{eq} for this reaction is 1.7×10^{-21} . Is the reaction exothermic or endothermic?
- To produce the maximum amount of CO and H₂ at equilibrium, should the pressure of the system be increased or decreased?