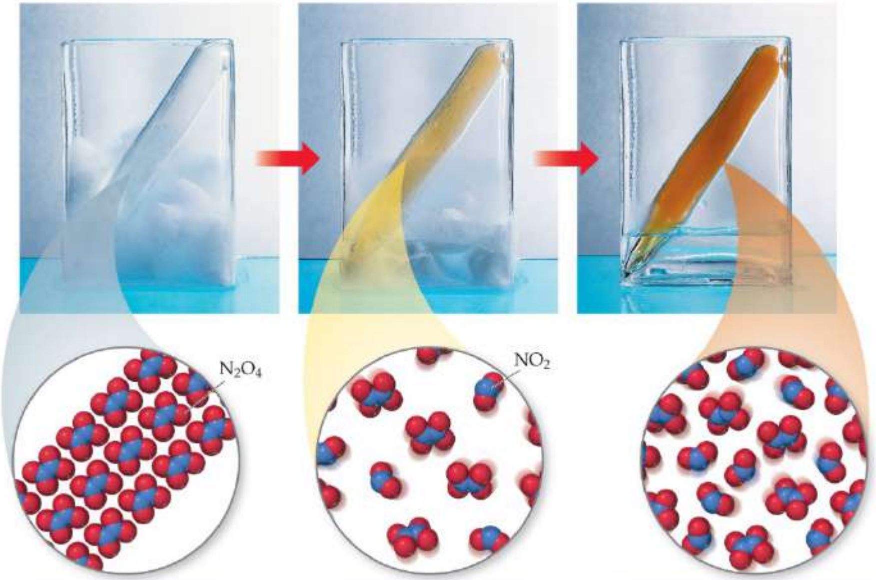
Chapter 15
Chemical Equilibrium

15.1 The Concept of Equilibrium

The Concept of Equilibrium



Frozen N_2O_4 sample is nearly colorless

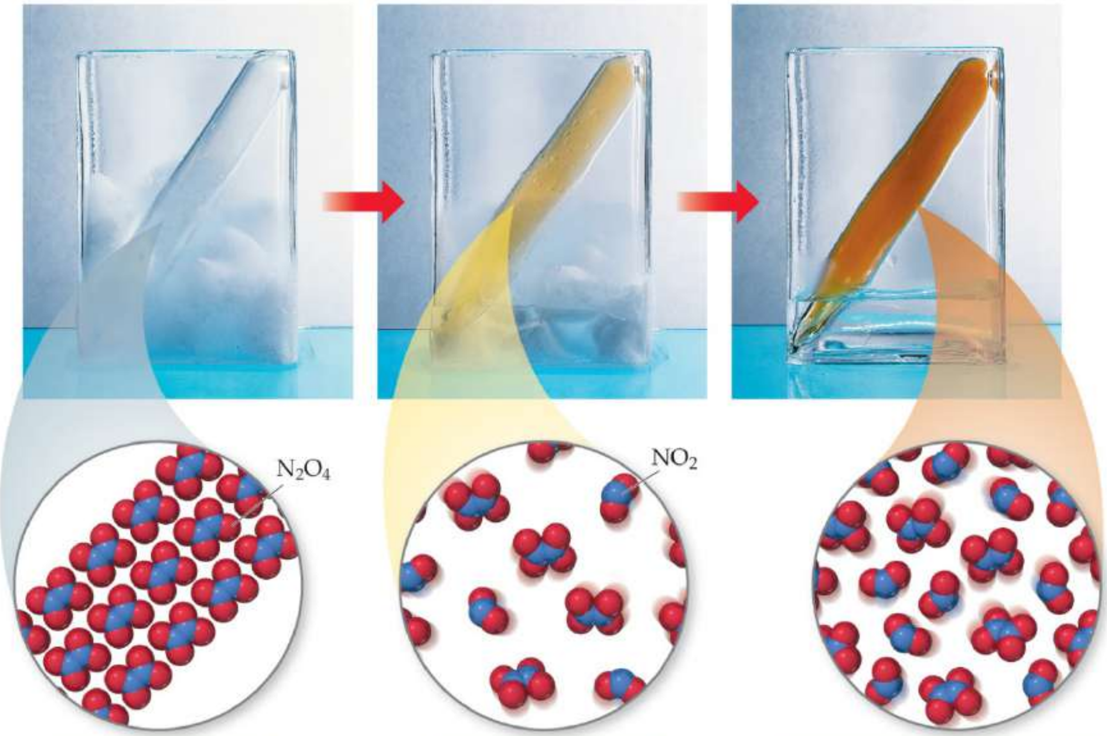
On warming, the N_2O_4 becomes a gas and partially dissociates to form brown $NO_2(g)$

Colors stop changing; equilibrium reached: rate of reaction $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ = rate of reaction $2\,NO_2(g) \longrightarrow N_2O_4(g)$

Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate. In the figure above, equilibrium is finally reached in the third picture.

If you were to let the tube on the right sit overnight and then take another picture would the brown color look darker, lighter, or the same?

a. Darker
b. Lighter
c. The same

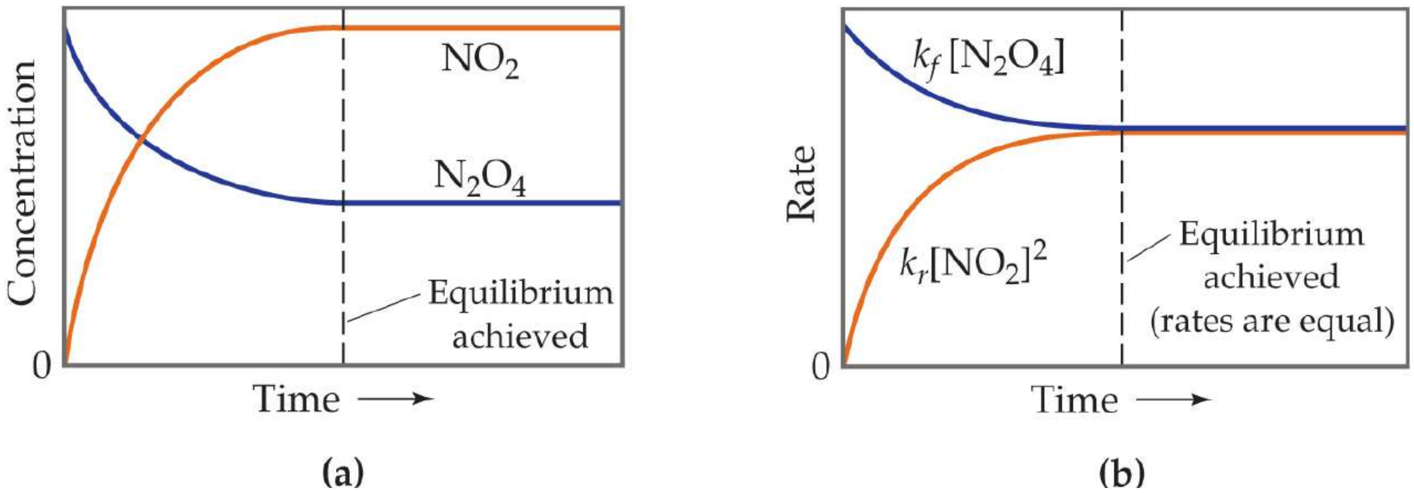


Frozen N_2O_4 sample is nearly colorless

On warming, the N_2O_4 becomes a gas and partially dissociates to form brown $NO_2(g)$

Colors stop changing, equilibrium reached: rate of reaction $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ = rate of reaction $2\,NO_2(g) \longrightarrow N_2O_4(g)$

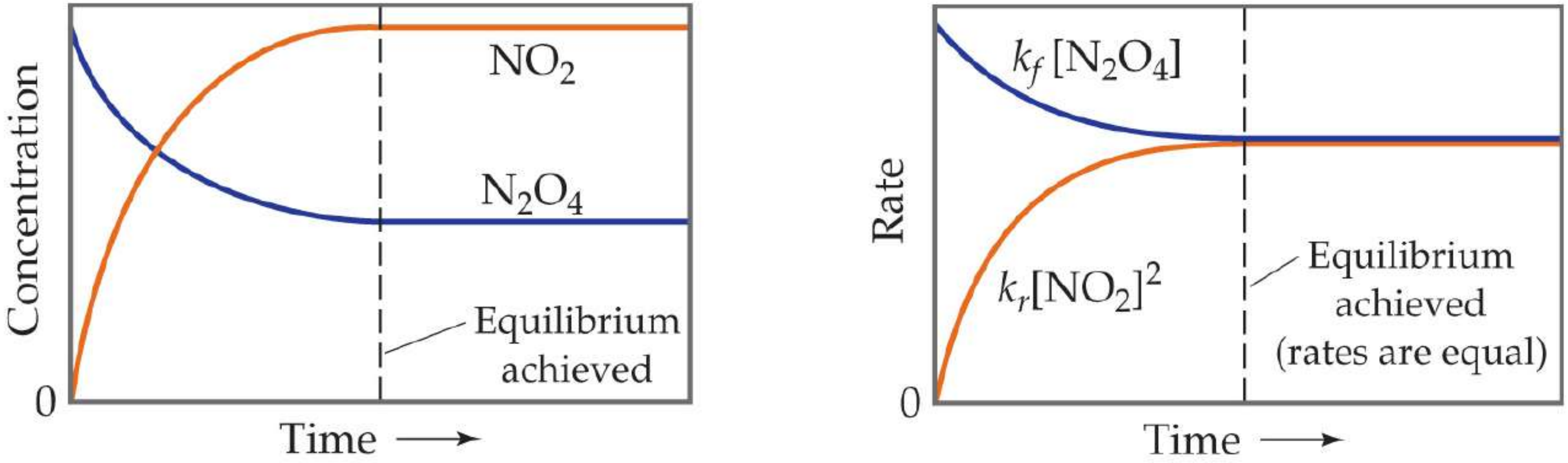
T



- As a system approaches equilibrium, both the forward and reverse reactions are occurring.
- At equilibrium, the forward and reverse reactions are proceeding *at the same rate*.
- Once equilibrium is achieved, the *amount* of each reactant and product remains constant.

At equilibrium, is the ratio [NO2] / [N2O4] less than, greater to, or equal to 1?

a. Less than 1
b. Greater than 1
c. Equal to 1
d.Cannot tell from the graph



(a)

(b)

Writing the Equation for an Equilibrium Reaction

Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow:

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

Comparing Rates

- For the forward reaction
  $N_2O_4(g) \rightarrow 2\ NO_2(g)$

The rate law is
  $\text{Rate} = k_f[N_2O_4]$

For the reverse reaction
  $2\ NO_2(g) \rightarrow N_2O_4(g)$

- The rate law is
  $\text{Rate} = k_r[NO_2]^2$

The Meaning of Equilibrium

- Therefore, at equilibrium

$\text{Rate}_f = \text{Rate}_r$

$k_f[N_2O_4] \;=\; k_r[NO_2]^2$

- Rewriting this, it becomes the expression for the equilibrium constant, K_{eq}.

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{a constant}$$

15.1 Give It Some Thought

a) Which quantities are equal in a dynamic equilibrium?
b) If the rate constant for the forward reaction is larger than the rate constant for the reverse reaction, will the constant be greater than or smaller than 1?

15.2 The Equilibrium Constant

Another Equilibrium—The Haber Process

- Consider the Haber Process, which is the industrial preparation of ammonia:

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

- The equilibrium constant depends on stoichiometry:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

15.2 Give It Some Thought

- How do we know when equilibrium has been reached in a chemical reaction?

The Equilibrium Constant

- Consider the generalized reaction

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons d\,\mathrm{D} + e\,\mathrm{E}$$

- The equilibrium expression for this reaction would be

$$K_c = \frac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b} \begin{array}{l} \longleftarrow \text{products} \\ \longleftarrow \text{reactants} \end{array}$$

- Also, since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$K_p = \frac{(P_{\mathrm{D}})^d(P_{\mathrm{E}})^e}{(P_{\mathrm{A}})^a(P_{\mathrm{B}})^b}$$

Sample Exercise 15.1

- Write the equilibrium-constant expression for the following reactions:
  - A) $2\ O_{3(g)} \leftrightarrow 3\ O_{2(g)}$
  - B) $2\ NO_{(g)} + Cl_{2(g)} \leftrightarrow 2\ NOCl_{(g)}$
  - C) $Ag^{+}{}_{(aq)} + 2\ NH_{3(aq)} \leftrightarrow Ag(NH_3)_2{}^{+}{}_{(aq)}$
  - D) $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$
  - E) $Cd^{2+}{}_{(aq)} + 4\ Br^{-}{}_{(aq)} \leftrightarrow CdBr_4{}^{2-}{}_{(aq)}$

Practice Exercise 1

For the reaction $2\ SO_2(g) + O_2(g) \leftrightarrow 2\ SO_3(g)$ which of the following is the correct equilibrium-constant expression?

(a) $K_C = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$

(b) $K_C = \dfrac{2[SO_2][O_2]}{2[SO_3]}$

(c) $K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(d) $K_C = \dfrac{2[SO_3]}{2[SO_2][O_2]}$

Equilibrium Can Be Reached from Either Direction

- As you can see, the ratio of $[NO_2]^2$ to $[N_2O_4]$ remains constant at this temperature no matter what the initial concentrations of NO_2 and N_2O_4 are.

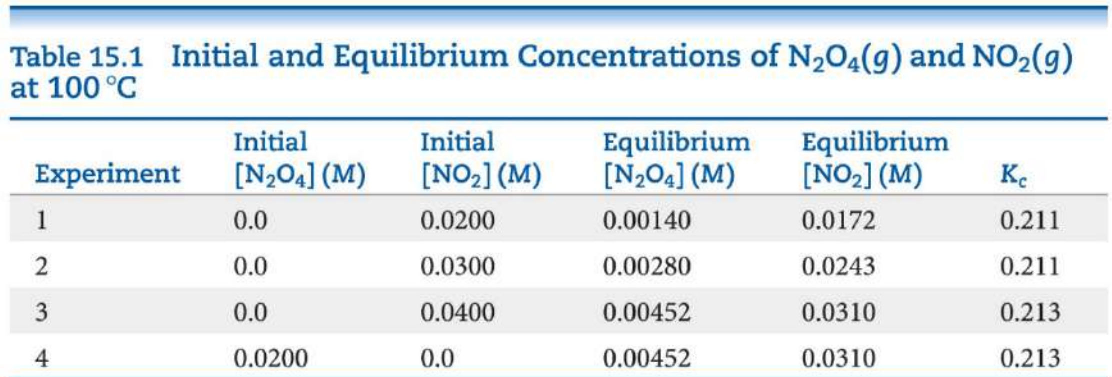
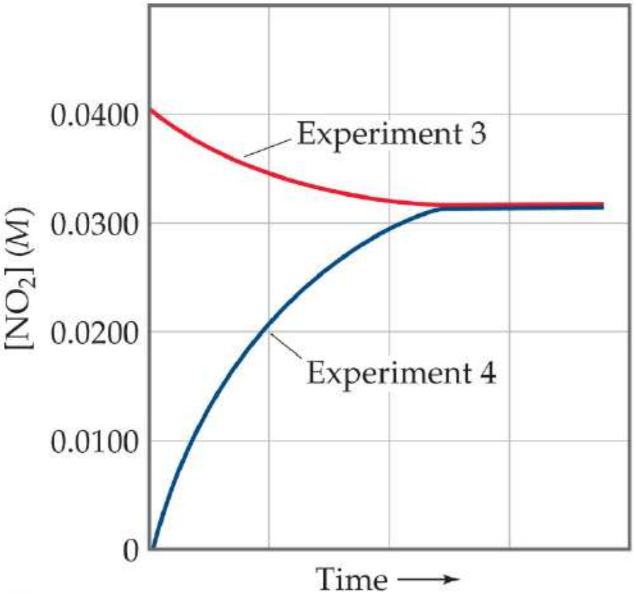


Table 15.1 Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

Experiment	Initial $[N_2O_4]$ (*M*)	Initial $[NO_2]$ (*M*)	Equilibrium $[N_2O_4]$ (*M*)	Equilibrium $[NO_2]$ (*M*)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213



The Equilibrium Constant

Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written

$$Kp = \frac{(PC)^c\,(PD)^d}{(PA)^a\,(PB)^b}$$

15.2 Give It Some Thought

- How does the value of K_c in the equation depend on the starting concentrations of NO_2 and N_2O_4?
  - $K_c = [NO_2]^2/[N_2O_4]$
- What is the difference between the equilibrium constant K_c and the equilibrium constant K_p?

More with Gases and Equilibrium

- We can compare the equilibrium constant based on concentration to the one based on pressure.
- For gases, $PV = nRT$ (the Ideal Gas Law).
- Rearranging, $P = (n/V)RT$; (n/V) is [ ].
- The result is

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

- where

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$$

15.2 Give It Some Thought

- Is it possible to have a reaction where $K_c = K_p$? If so, under what conditions would this relationship hold?

Sample Exercise 15.2

- In the synthesis of ammonia from nitrogen and hydrogen,

  $N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)}$

  K_c = 9.60 at 300ºC. Calculate K_p for this reaction at this temperature.

Practice Exercise 1

For which of the following reactions is the ratio K_p/K_c largest at 300 K?

(a) $N_2(g) + O_2(g) \leftrightarrow 2\ NO(g)$

(b) $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

(c) $Ni(CO)_4(g) \leftrightarrow Ni(s) + 4\ CO(g)$

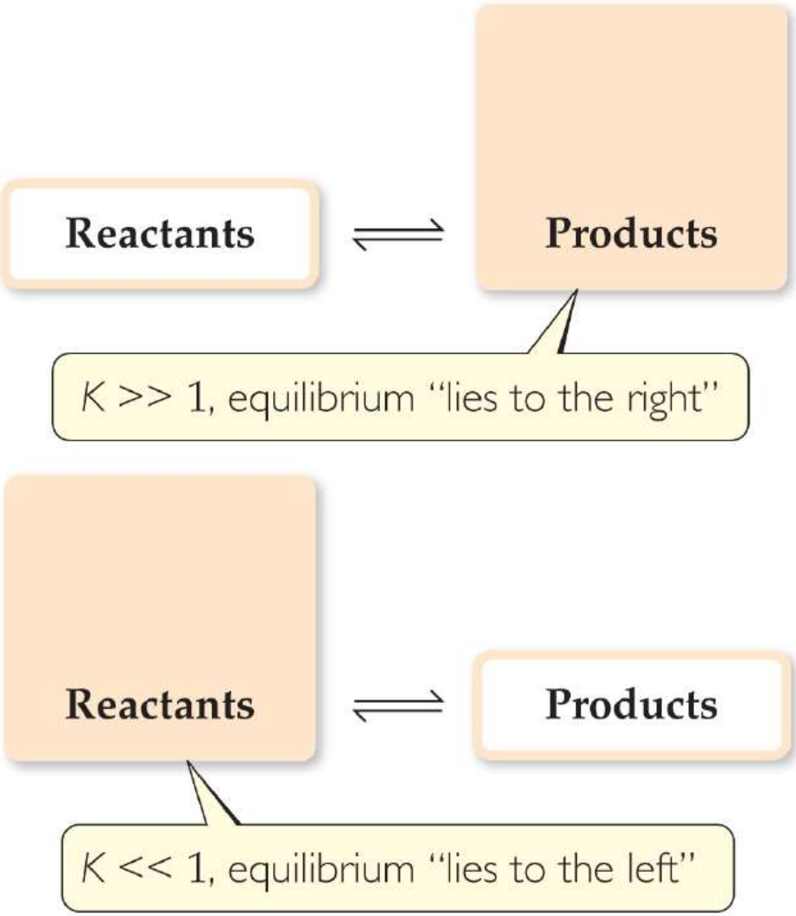
(d) $C(s) + 2\ H_2(g) \leftrightarrow CH_4(g)$

Practice Exercise 2

- For the equilibrium $2\ SO_{3(g)} \leftrightarrow 2\ SO_{2(g)} + O_{2(g)}$, K_c is 4.08×10^{-3} at 1000 K. Calculate the value for K_p.

15.3 Understanding and Working with Equilibrium Constants

Magnitude of *K*



Reactants $\rightleftharpoons$ Products

$K >> 1$, equilibrium "lies to the right"

Reactants $\rightleftharpoons$ Products

$K << 1$, equilibrium "lies to the left"

- If $K >> 1$, the reaction favors products; products predominate at equilibrium.
- If $K << 1$, the reaction favors reactants; reactants predominate at equilibrium.

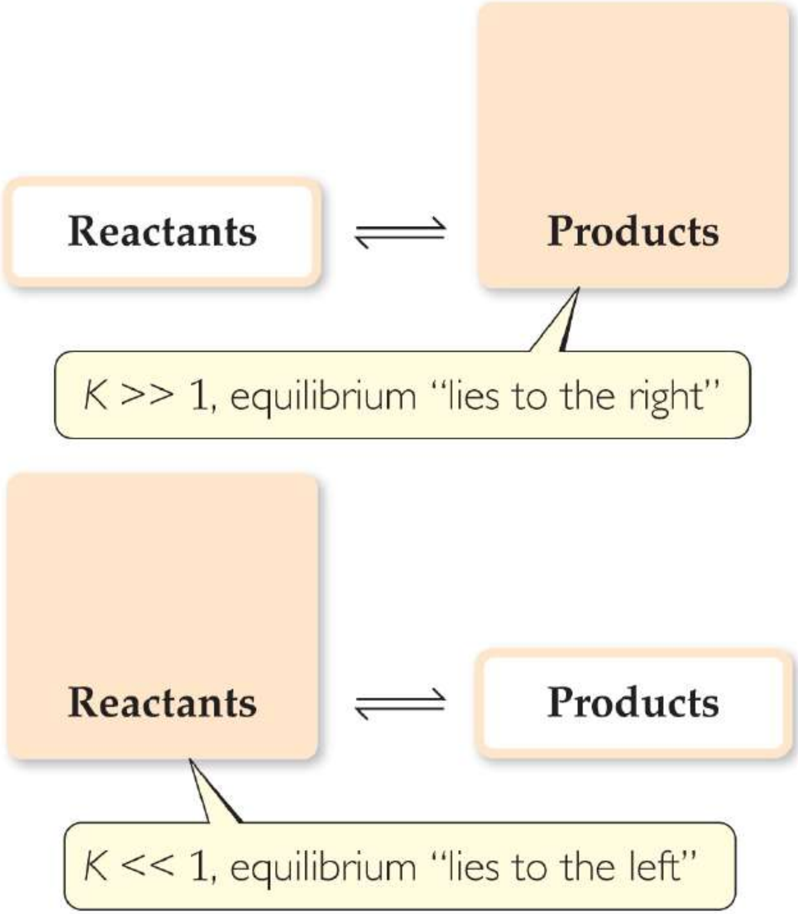
What would this figure look like for a reaction in which *K* ≈ 1?

a. The boxes would be extremely small.

b. The boxes would be extremely big.

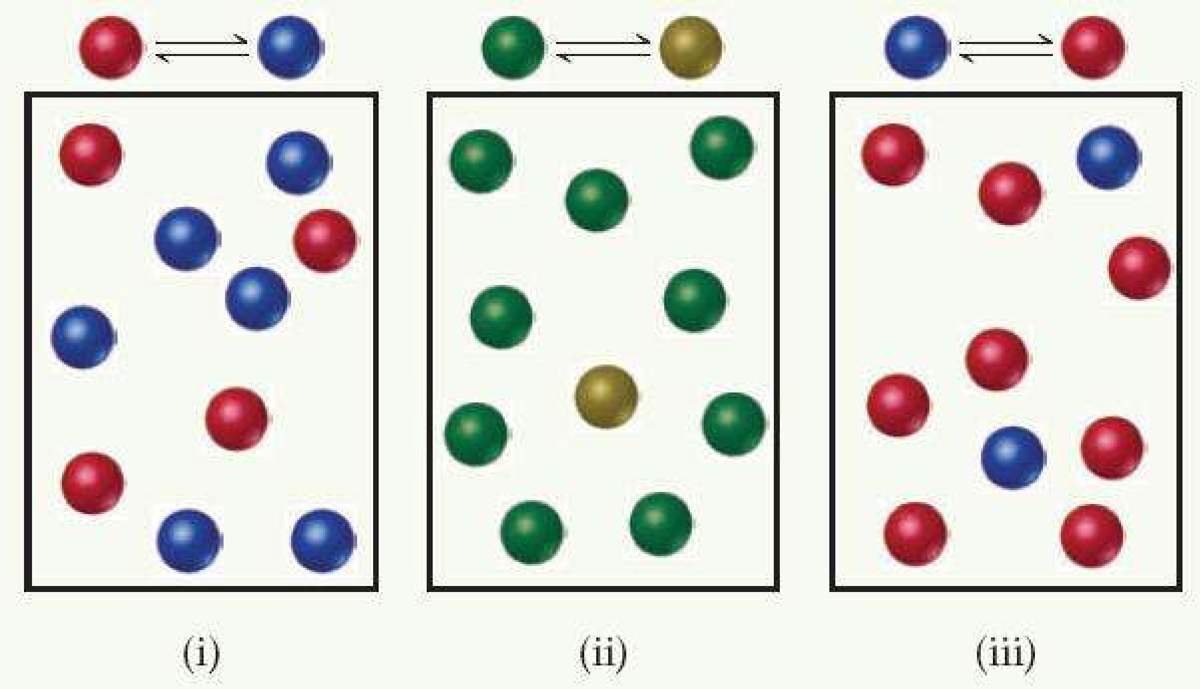
c. The boxes would be quite different in size.

d. The boxes would be approximately the same size.



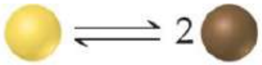
Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

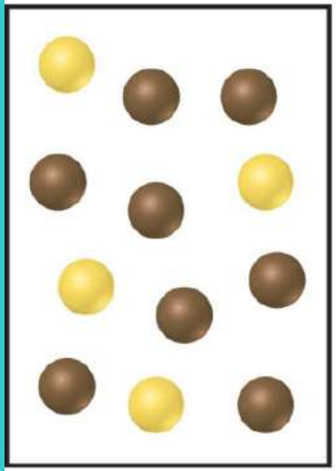
The following diagrams represent three different systems at equilibrium, all in the same size containers. **(a)** Without doing any calculations, rank the three systems in order of increasing equilibrium constant, *Kc*. **(b)** If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate *Kc* for each system.

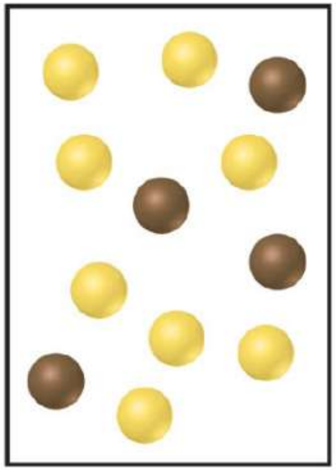


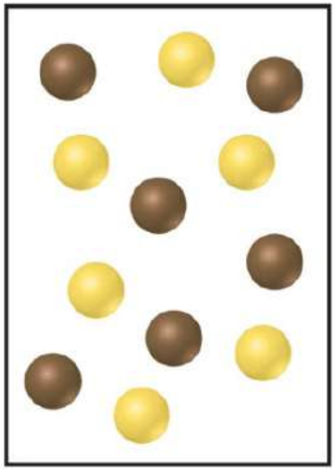
Practice Exercise 1

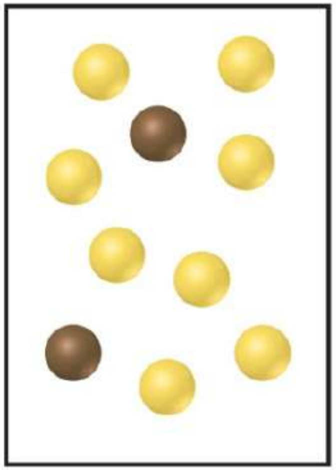
- The equilibrium constant for the reaction $N_2O_4(g) \leftrightarrow 2\ NO_2(g)$ at 2 °C is $K_c = 2.0$. If each yellow sphere represents 1 mol of N_2O_4 and each brown sphere 1 mol of NO_2 which of the following 1.0 L containers represents the equilibrium mixture at 2 °C?

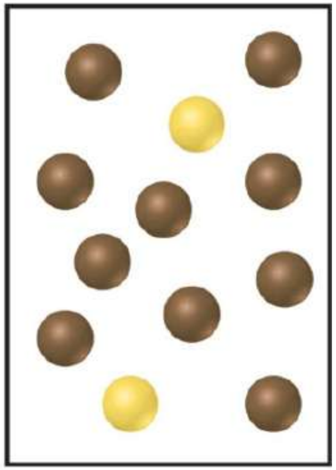



(a)


(b)


(c)


(d)


(e)

Practice Exercise 2

For the reaction $H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)$, K_p = 794 at 298 K and K_p = 55 at 700 K. Is the formation of HI favored more at the higher or lower temperature?

The Direction of the Chemical Equation and *K*

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.

$$N_2O_4(g) \leftrightarrow 2\,NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ at } 100\ ^\circ C$$

$$2\,NO_2(g) \leftrightarrow N_2O_4(g) \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 \text{ at } 100\ ^\circ C$$

Stoichiometry and Equilibrium Constants

The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.

$N_2O_4(g) \leftrightarrow 2\ NO_2(g)$ $\quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$ at 100 °C

$2\ N_2O_4(g) \leftrightarrow 4\ NO_2(g)$ $\quad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2$ at 100 °C

15.3 Give It Some Thought

For the reaction $PCl_5(g) \leftrightarrow PCl_3(g) + Cl(g)$, $K_c = 1.1 \times 10^{-2}$ at 400 K. What is the equilibrium constant for the reaction $PCl_3(g) + Cl(g) \leftrightarrow PCl_5(g)$ at 400 K?

How does the magnitude of K_p for the reaction $2\ HI(g) \leftrightarrow H_2(g) + I_2(g)$ change if the equilibrium is written $6\ HI(g) \leftrightarrow 3\ H_2(g) + 3\ I_2(g)$?

Consecutive Equilibria

- When two consecutive equilibria occur, the equations can be added to give a single equilibrium.
- The equilibrium constant of the new reaction is the *product* of the two constants:

$K_3 = K_1 \times K_2$

- Example

➢ $2\ NOBr \rightleftharpoons 2\ NO + Br_2 K_1 = 0.014$

➢ $Br_2 + Cl_2 \rightleftharpoons 2\ BrCl K_2 = 7.2$

➢ $2\ NOBr + Cl_2 \rightleftharpoons 2\ NO + 2\ BrCl$

$K_3 = K_1 \times K_2 = 0.014 \times 7.2 = 0.10$

Sample Exercise 15.4

Given the reactions:

$HF(aq) \leftrightarrow H^+(aq) + F^-(aq)$ $K_c = 6.8 \times 10^{-4}$

$H_2C_2O_4(aq) \leftrightarrow 2\ H^+(aq) + C_2O_4^{2-}(aq)$ $K_c = 3.8 \times 10^{-6}$

Determine the value of K_c for the reaction

$2\ HF(aq) + C_2O_4^{2-}(aq) \leftrightarrow 2\ F^-(aq) + H_2C_2O_4(aq)$

Practice Exercise 1

Given the equilibrium constants for the following two reactions in aqueous solution at 25 °C:

$HNO_2(aq) \leftrightarrow H^+(aq) + NO_2^-(aq)$ $K_c = 4.5 \times 10^{-4}$

$H_2SO_3(aq) \leftrightarrow 2\,H^+(aq) + SO_3^-(aq)$$K_c = 1.1 \times 10^{-9}$

What is the value of K_c for the reaction?

$2\,HNO_2(aq) + SO_3^{2-}(aq) \leftrightarrow H_2SO_3(aq) + 2\,NO_2^-(aq)$

(a) 4.9×10^{-13}**(b)** 4.1×10^{5}

(c) 8.2×10^{5}**(d)** 1.8×10^{2}

(e) 5.4×10^{-3}

Practice Exercise 2

- Given that, at 700 K, $K_p = 54.0$ for the reaction $H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $N_2(g) + 3\ H_2(g) \leftrightarrow 2\ NH_3(g)$, determine the value of K_p for the reaction $2\ NH_3(g) + 3\ I_2(g) \leftrightarrow 6\ HI(g) + N_2(g)$ at 700 K

To summarize

- 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.

15.4 Heterogeneous Equilibria

Homogeneous vs. Heterogeneous

- **Homogeneous equilibria** occur when all reactants and products are in the same phase.
- **Heterogeneous equilibria** occur when something in the equilibrium is in a different phase.
- The value used for the concentration of a pure substance is always 1.
  - Concentrations of liquids and solids are constant

15.4 Give It Some Thought

- Write the equilibrium constant expression for the evaporation of water, $H_2O(l) \leftrightarrow H_2O(g)$, in terms of partial pressures.

The Decomposition of $CaCO_3$—A Heterogeneous Equilibrium

- The equation for the reaction is

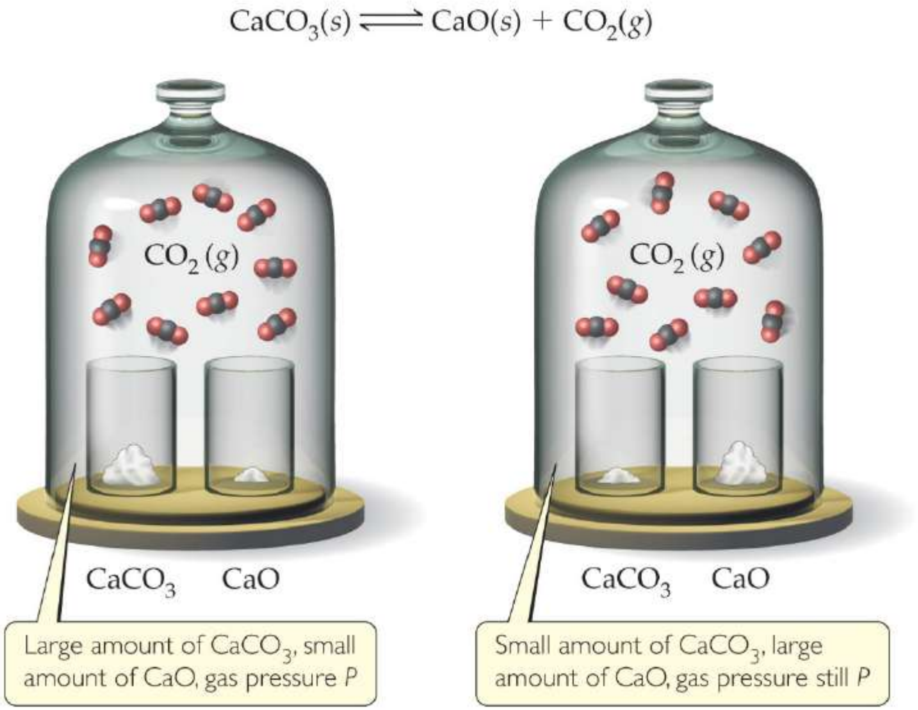
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

- This results in

$K_c = [CO_2]$

and

$K_p = P_{CO_2}$



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

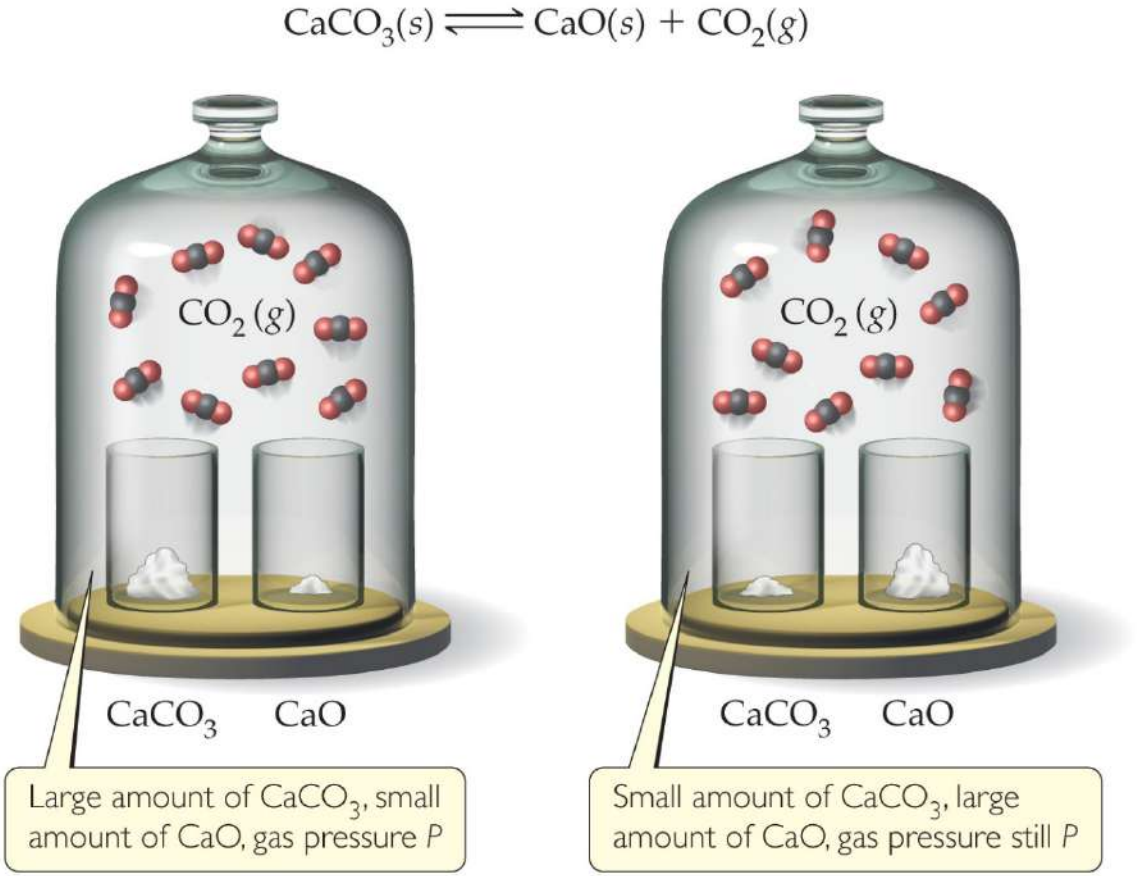
Large amount of $CaCO_3$, small amount of CaO, gas pressure *P*

Small amount of $CaCO_3$, large amount of CaO, gas pressure still *P*

If some of the CO2 (*g*) were released from the upper bell jar and the seal then restored and the system allowed to return to equilibrium, would the amount of CaCO3 (*s*) increase, decrease, or remain the same?

$$CaCO3(s) \rightleftharpoons CaO(s) + CO2(g)$$

a. Increase
b. Decrease
c. Remain the same



Sample Exercise 15.5

- Write the equilibrium constant expression for K_c for each of the following reactions:
  - A) $CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(l)}$
  - B) $SnO_{2(s)} + 2\ CO_{(g)} \leftrightarrow Sn_{(s)} + 2\ CO_{2(g)}$

Practice Exercise 1

Consider the equilibrium that is established in a saturated solution of silver chloride, $Ag^+(aq) + Cl^-(aq) \leftrightarrow AgCl(s)$. If solid AgCl is added to this solution, what will happen to the concentration of Ag^+ and Cl^- ions in solution?

(a) $[Ag^+]$ and $[Cl^-]$ will both increase

(b) $[Ag^+]$ and $[Cl^-]$ will both decrease

(c) $[Ag^+]$ will increase and $[Cl^-]$ will decrease

(d) $[Ag^+]$ will decrease and $[Cl^-]$ will increase

(e) neither $[Ag^+]$ nor $[Cl^-]$ will change

Practice Exercise 2

- Write the following equilibrium-constant expressions:
  - A) K_c for $Cr_{(s)} + 3\,Ag^+_{(aq)} \leftrightarrow Cr^{3+}_{(aq)} + 3\,Ag_{(s)}$
  - B) K_p for $3\,Fe_{(s)} + 4\,H_2O_{(g)} \leftrightarrow Fe_3O_{4(s)} + 4\,H_{2(g)}$

Sample Exercise 15.6

- Each of the following mixtures was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium $CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$:
  - A) $CaCO_3(s)$
  - B) $CaO(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p
  - C) $CaCO_3(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p
  - D) $CaCO_3(s)$ and $CaO(s)$

Practice Exercise 1

If 8.0 g of $NH_4HS(s)$ is placed in a sealed vessel with a volume of 1.0 L and heated to 200 °C the reaction $NH_4HS(s) \leftrightarrow NH_3(g) + H_2S(g)$ will occur. When the system comes to equilibrium, some $NH_4HS(s)$ is still present. Which of the following changes will lead to a reduction in the amount of $NH_4HS(s)$ that is present?

(a) Adding more $NH_3(g)$ to the vessel

(b) Adding more $H_2S(g)$ to the vessel

(c) Adding more $NH_4HS(s)$ to the vessel

(d) Increasing the volume of the vessel

(e) decreasing the volume of the vessel

Practice Exercise 2

- When added to $Fe_3O_{4(s)}$ in a closed container, which one of the following substances – $H_{2(g)}$, $H_2O_{(g)}$, $O_{2(g)}$ – will allow equilibrium to be established in the reaction $3\ Fe_{(s)} + 4\ H_2O_{(g)} \leftrightarrow Fe_3O_{4(s)} + 4\ H_{2(g)}$?

15.4 Give It Some Thought

Write the equilibrium constant expression for the reaction:

$NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

15.5 Calculating Equilibrium Constants

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 H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant *Kp* for the reaction.

$$3H_{2(g)} + N_{2(g)} \leftrightarrow 2NH_{3(g)}$$

Practice Exercise 1

A mixture of gaseous sulfur dioxide and oxygen are added to a reaction vessel and heated to 1000 K where they react to form $SO_3(g)$. If the vessel contains 0.669 atm $SO_2(g)$, 0.395 atm $O_2(g)$, and 0.0851 atm $SO_3(g)$ after the system has reached equilibrium, what is the equilibrium constant K_p for the reaction $2\ SO_2(g) + O_2(g) \leftrightarrow 2\ SO_3(g)$?

(a) 0.0410**(b)** 0.322

(c) 24.4**(d)** 3.36

(e) 3.11

Practice Exercise 2

- An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25ºC: $[CH_3COOH] = 1.65 \times 10^{-2}$ M; $[H^+] = 5.44 \times 10^{-4}$ M; and $[CH_3COO^-] = 5.44 \times 10^{-4}$ M. Calculate the equilibrium constant, K_c, for the ionization of acetic acid at 25ºC: $CH_3COOH_{(aq)} \leftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)}$

Deducing Equilibrium Concentrations

1) Tabulate all known initial and equilibrium concentrations.
2) For anything for which initial *and* equilibrium concentrations are known, calculate the change.
3) Use the balanced equation to find change for all other reactants and products.
4) Use initial concentrations and changes to find equilibrium concentration of all species.
5) Calculate the equilibrium constant using the equilibrium concentrations.

Sample Exercise 15.8

A closed system initially containing 1.000×10^{-3} *M* H_2 and 2.000×10^{-3} *M* I_2 at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} *M*. Calculate K_c at 448 °C for the reaction taking place, which is

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

What Do We Know?

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

[HI] Increases by 1.87×10^{-3} *M*

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			**$+1.87 \times 10^{-3}$**
At equilibrium			1.87×10^{-3}

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

	[H2], *M*	[I2], *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	**-9.35×10^{-4}**	**-9.35×10^{-4}**	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

We can now calculate the equilibrium concentrations of all three compounds.

	[H2], *M*	[I2], *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium	$\mathbf{6.5 \times 10^{-5}}$	$\mathbf{1.065 \times 10^{-3}}$	1.87×10^{-3}

And, therefore, the equilibrium constant…

$$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}]\,[\mathrm{I_2}]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

$$= 51$$

Practice Exercise 1

In Section 15.1, we discussed the equilibrium between $N_2O_4(g)$ and $NO_2(g)$. Let's return to that equation in a quantitative example. When 9.2 g of frozen N_2O_4 is added to a 0.50 L reaction vessel and the vessel is heated to 400 K and allowed to come to equilbrium, the concentration of N_2O_4 is determined to be 0.057 M. Given this information, what is the value of K_c for the reaction $N_2O_4(g) \rightarrow 2\ NO_2(g)$ at 400 K?

(a) 0.23**(b)** 0.36

(c) 0.13**(d)** 1.4

(e) 2.5

Practice Exercise 2

The gaseous compound BrCl decomposes at high temperature in a sealed container: $2\ BrCl(g) \leftrightarrow Br_2(g) + Cl_2(g)$. Initially, the vessel is charged at 500 K with BrCl(*g*) at a partial pressure of 0.500 atm. At equilibrium, the BrCl(*g*) partial pressure is 0.040 atm. Calculate the value of K_p at 500 K.

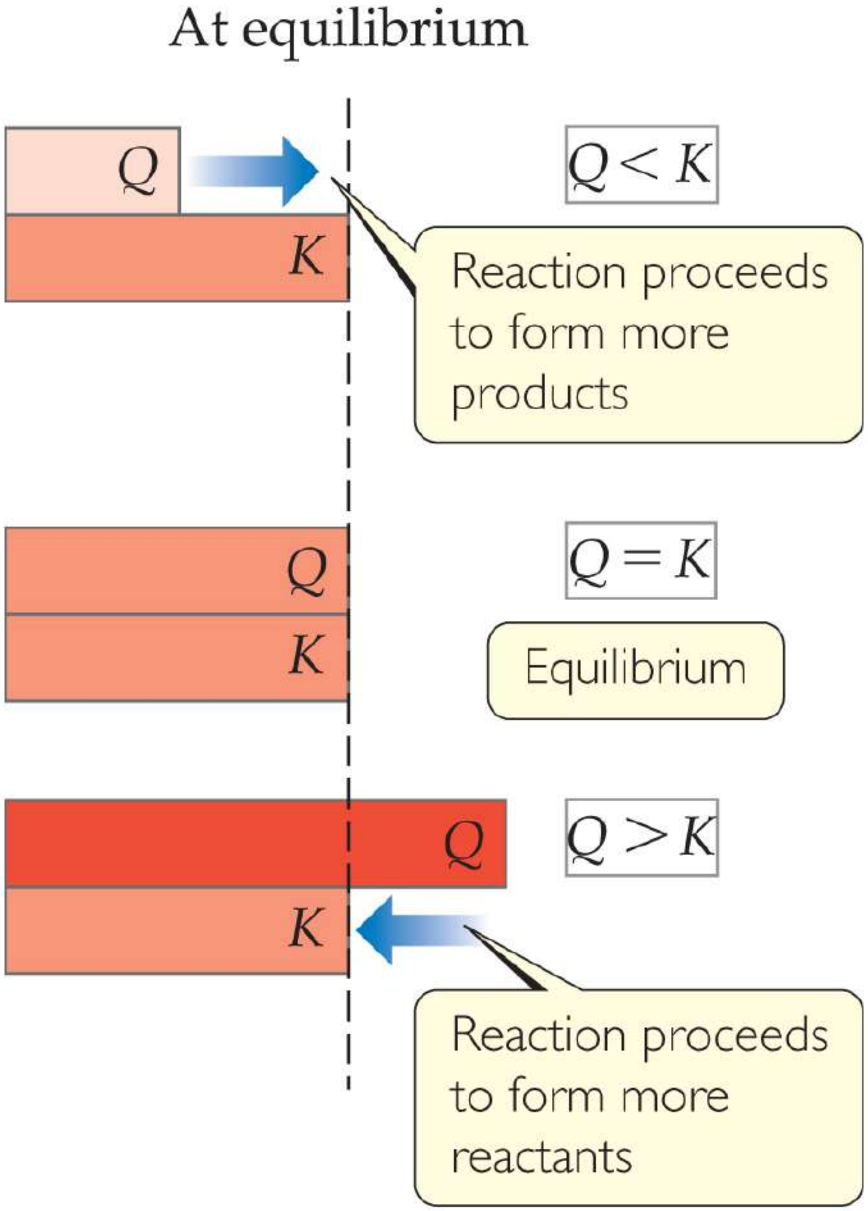
15.6 Applications of Equilibrium Constants

Is a Mixture in Equilibrium? Which Way Does the Reaction Go?

- To answer these questions, we calculate the **reaction quotient**, *Q*.
- Q looks like the equilibrium constant, *K*, but the values used to calculate it are the current conditions, not necessarily those for equilibrium.
- To calculate *Q*, one substitutes the initial concentrations of reactants and products into the equilibrium expression.

Comparing *Q* and *K*

- Nature wants $Q = K$.
- If $Q < K$, nature will make the reaction proceed to products.
- If $Q = K$, the reaction is in equilibrium.
- If $Q > K$, nature will make the reaction proceed to reactants.



Sample Exercise 15.9

- At 448ºC the equilibrium constant K_c for the reaction $H_{2(g)} + I_{2(g)} \leftrightarrow 2\ HI_{(g)}$ is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448ºC if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol H_2, and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

Practice Exercise 2

- At 1000 K the value of K_p for the reaction 2 $SO_{3(g)} \leftrightarrow 2\ SO_{2(g)} + O_{2(g)}$ is 0.338. Calculate the value for Q_p and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are P_{SO3} = 0.16 atm; P_{SO2} = 0.41 atm; P_{O2} = 2.5 atm.

Sample Exercise 15.10

- For the Haber process, $N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)}$, $K_p = 1.45 \times 10^{-5}$ at 500ºC. In an equilibrium mixture of the three gases at 500ºC, 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?

Practice Exercise 1

At 500 K, the reaction $2\ NO(g) + Cl_2(g) \leftrightarrow 2\ NOCl(g)$ has $K_p = 51$. In an equilibrium mixture at 500 K, the partial pressure of NO is 0.125 atm and Cl_2 is 0.165 atm. What is the partial pressure of NOCl in the equilibrium mixture?

(a) 0.13 atm

(b) 0.36 atm

(c) 1.0 atm

(d) 5.1×10^{-5} atm

(e) 0.125 atm.

Practice Exercise 2

- At 500 K, the reaction $PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$ has $K_p = 0.497$. 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?

Calculating Equilibrium Concentrations

- If you know the equilibrium constant, you can find equilibrium concentrations from initial concentrations and changes (based on stoichiometry).
- You will set up a table similar to the ones used to find the equilibrium concentration, but the "change in concentration" row will simple be a factor of "*x*" based on the stoichiometry.

Sample Exercise 15.11

A 1.000 L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 448 °C. Given a K_c of 50.5 at 448 °C, what are the equilibrium concentrations of H_2, I_2, and HI?

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

initial concentration (*M*)	**1.000**	**2.000**	**0**
change in concentration (*M*)	$-x$	$-x$	$+2x$
equilibrium concentration (*M*)	$1.000 - x$	$2.000 - x$	$2x$

Example (continued)

- Set up the equilibrium constant expression, filling in equilibrium concentrations from the table.
- $$K_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

- Solving for *x* is done using the quadratic formula, resulting in *x* = 2.323 *or* 0.935.

Example (completed)

- Since *x* must be subtracted from 1.000 *M*, 2.323 makes no physical sense. (It results in a negative concentration!) The value *must* be 0.935.

So

- $[H_2]_{eq}$ = 1.000 – 0.935 = 0.065 *M*
- $[I_2]_{eq}$ = 2.000 – 0.935 = 1.065 *M*
- $[HI]_{eq}$ = 2(0.935) = 1.87 *M*

Practice Exercise 1

For the equilibrium $Br_2(g) + Cl_2(g) \leftrightarrow 2\,BrCl(g)$, the equilibrium constant K_p is 7.0 at 400 K. If a cylinder is charged with $BrCl(g)$ at an initial pressure of 1.00 atm and the system is allowed to come to equilibrium what is the final (equilibrium) pressure of BrCl?

(a) 0.57 atm**(b)** 0.22 atm

(c) 0.45 atm**(d)** 0.15 atm

(e) 0.31 atm

Practice Exercise 2

- For the equilibrium $PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$, the equilibrium constant K_p has a value of 0.497 at 500 K. A gas cylinder at 500 K is charged with $PCl_{5(g)}$ at an initial pressure 1.66 atm. What are the equilibrium pressures of PCl_5, PCl_3 and Cl_2 at this temperature?

15.7 Le Châtelier’s Principle

LeChâtelier's Principle

"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

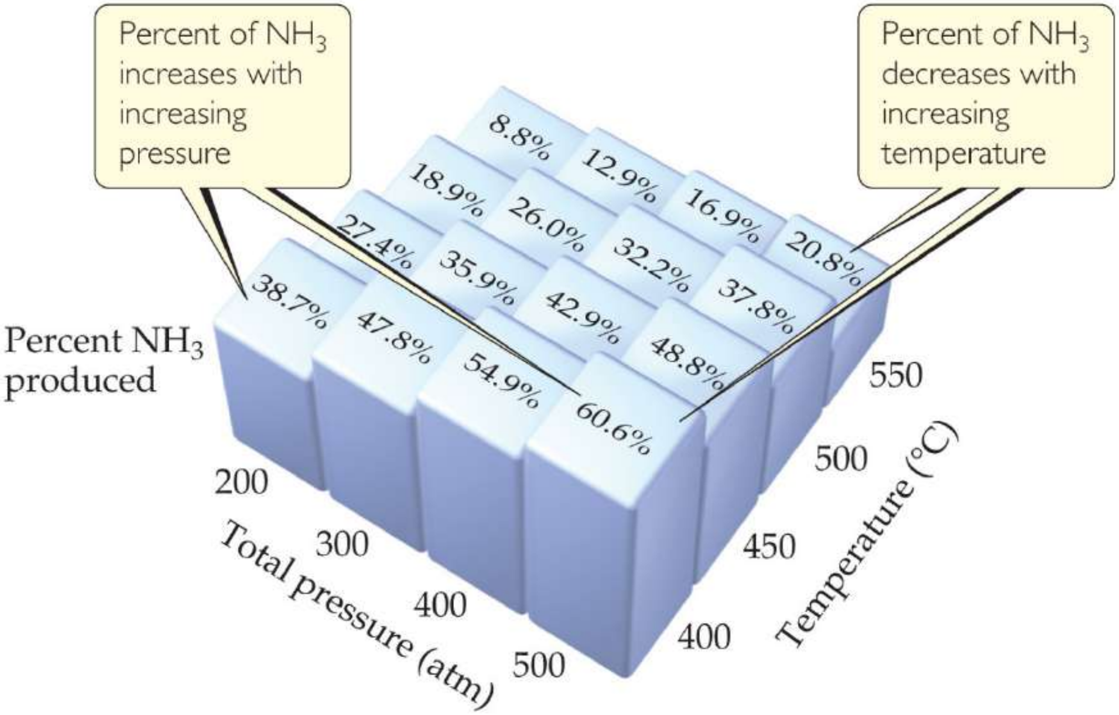
At what combination of pressure and temperature should you run the reaction to maximize NH3 yield?

a. 300 atm, 550 °C

b. 500 atm, 400 °C

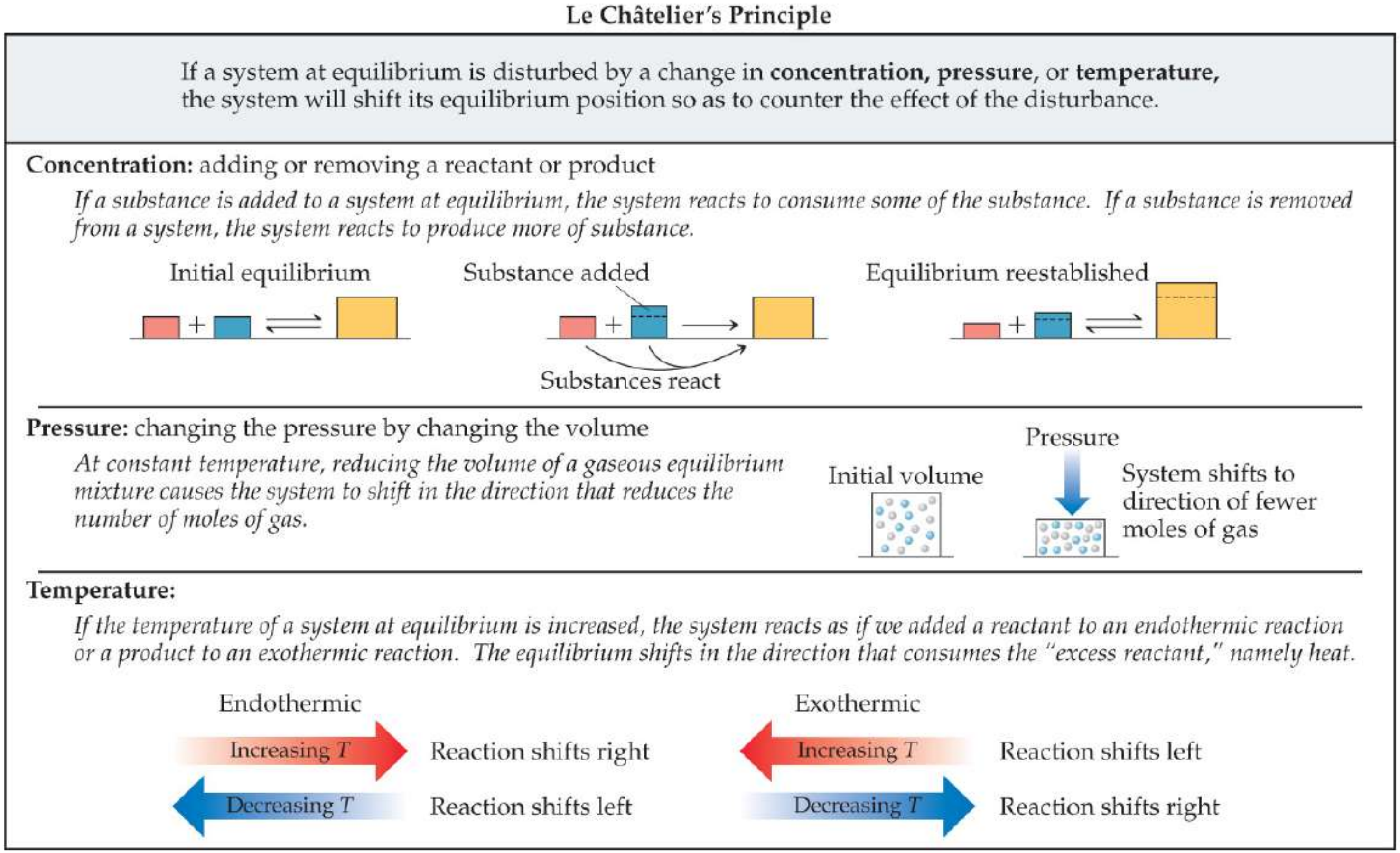
c. 400 atm, 450 °C

d.200 atm, 500 °C



How Conditions Change Equilibrium

We will use LeChâtelier's Principle qualitatively to predict shifts in equilibrium based on changes in conditions.



Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in **concentration, pressure**, or **temperature,** the system will shift its equilibrium position so as to counter the effect of the disturbance.

Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.

Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.

Temperature:

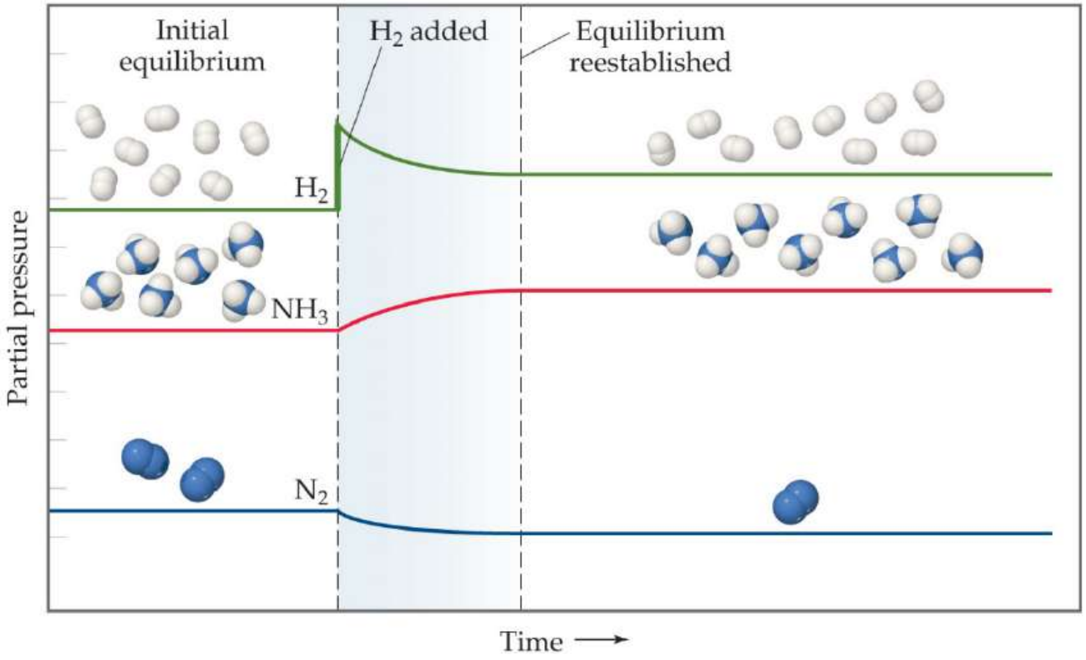
If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reactant," namely heat.

Endothermic		Exothermic	
Increasing T	Reaction shifts right	Increasing T	Reaction shifts left
Decreasing T	Reaction shifts left	Decreasing T	Reaction shifts right

Change in Reactant or Product Concentration

- If the system is in equilibrium
  - adding a reaction component will result in some of it being used up.
  - removing a reaction component will result in some if it being produced.

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



Why does the nitrogen concentration decrease after hydrogen is added?

$$N2(g) + 3\ H2(g) \rightleftharpoons 2\ NH3(g)$$

a. Adding nitrogen changes the temperature, and the reaction shifts to the right.

b. Adding nitrogen changes the total pressure, and the reaction shifts to the left.

c. Nitrogen along with hydrogen gas is converted into ammonia.

d. Nitrogen decomposes over time to nitrogen atoms, and this decreases its concentration.

15.7 Give It Some Thought

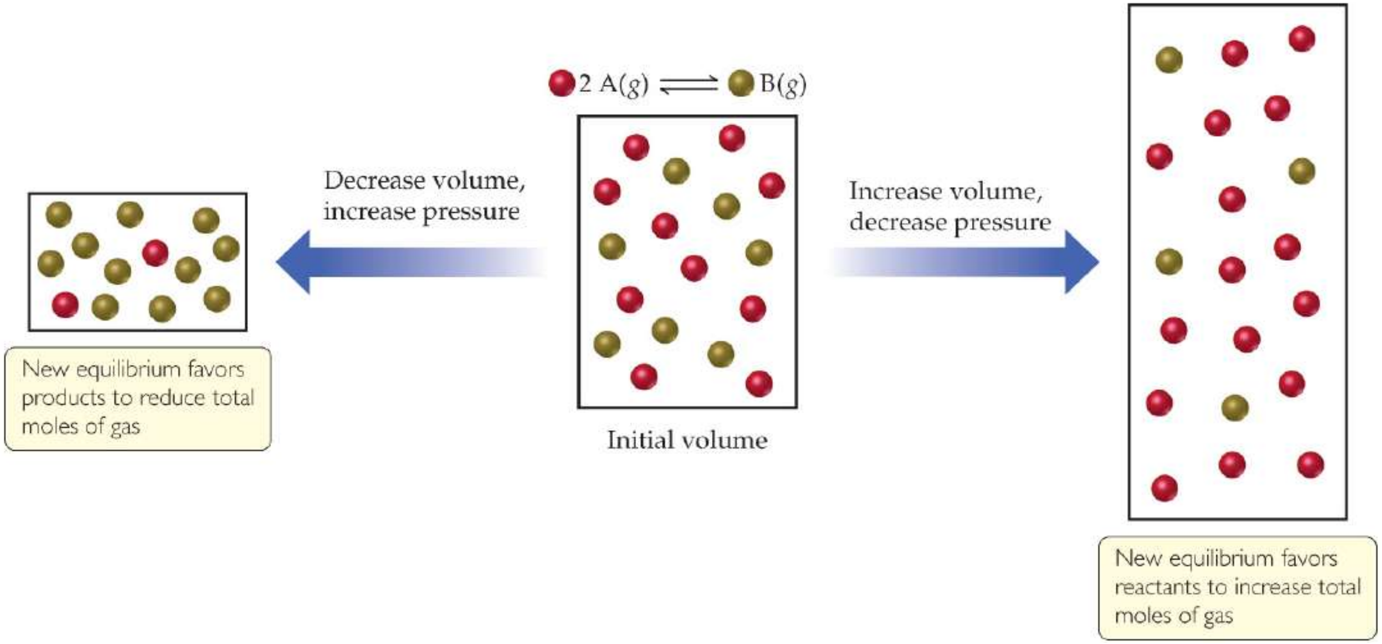
Does the equilibrium $2\ NO(g) + O_2(g) \leftrightarrow 2\ NO_2(g)$ shift to the right (more products) or left (more reactants) if:

a) O_2 is added to the system

b) NO is removed?

Change in Volume or Pressure

- When gases are involved in an equilibrium, a change in pressure or volume will affect equilibrium:
- Higher volume or lower pressure favors the side of the equation with more moles (and vice versa)



$2\,A(g) \rightleftharpoons B(g)$

New equilibrium favors products to reduce total moles of gas

Initial volume

New equilibrium favors reactants to increase total moles of gas

15.7 Give It Some Thought

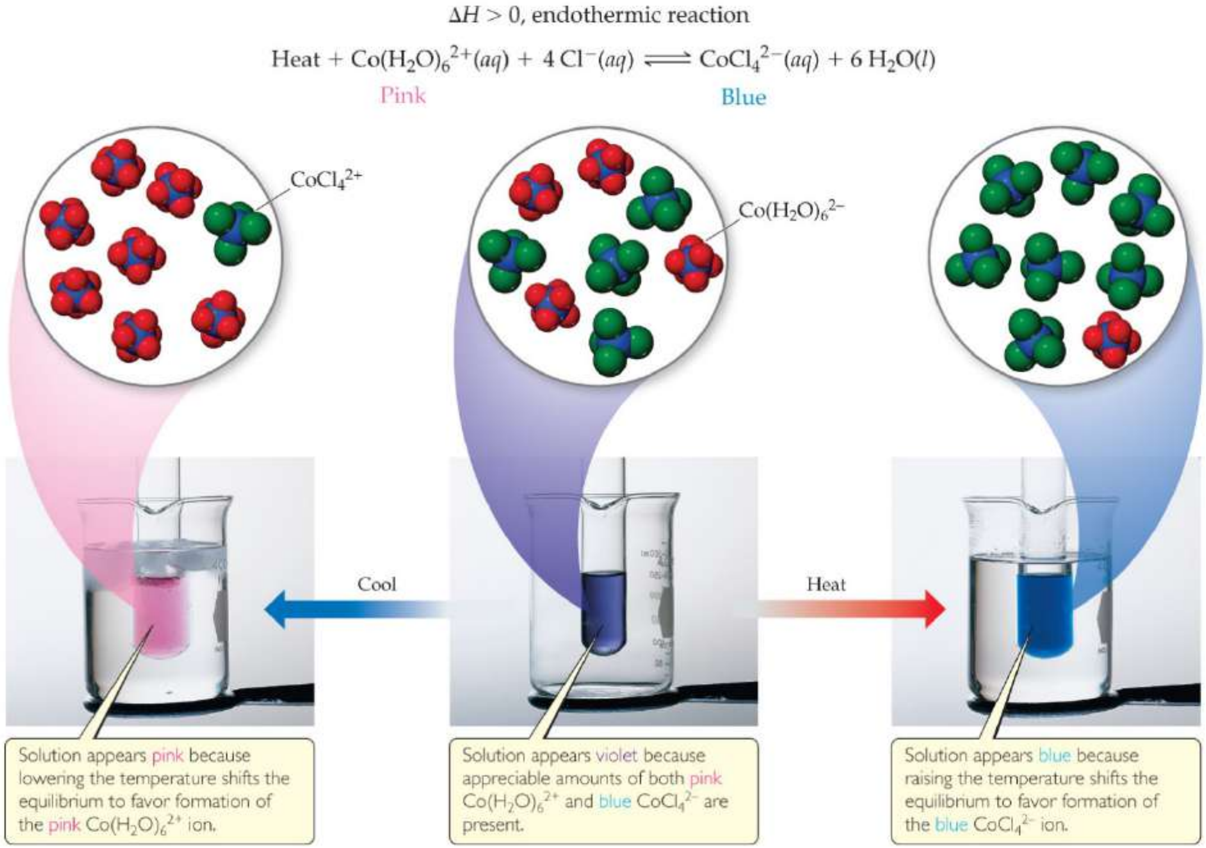
- What happens to the equilibrium $2\ SO_2(g) + O_2(g) \leftrightarrow 2\ SO_3(g)$ if the volume of the system is increased?

Change in Temperature

- Is the reaction endothermic or exothermic as written? That matters!
- Endothermic: Heats acts *like* a reactant; adding heat drives a reaction toward products.
- Exothermic: Heat acts *like* a product; adding heat drives a reaction toward reactants.

An Endothermic Equilibrium

$$\underset{\text{Pale pink}}{Co(H_2O)_6^{2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{Deep blue}}{CoCl_4^{2-}(aq)} + 6\,H_2O(l) \qquad \Delta H > 0$$



$\Delta H > 0$, endothermic reaction

$$\text{Heat} + \underset{\text{Pink}}{Co(H_2O)_6^{2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{Blue}}{CoCl_4^{2-}(aq)} + 6\,H_2O(l)$$

Solution appears pink because lowering the temperature shifts the equilibrium to favor formation of the pink $Co(H_2O)_6^{2+}$ ion.

Solution appears violet because appreciable amounts of both pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ are present.

Solution appears blue because raising the temperature shifts the equilibrium to favor formation of the blue $CoCl_4^{2-}$ ion.

An Exothermic Equilibrium

- The Haber Process for producing ammonia from the elements is exothermic.
- One would think that cooling down the reactants would result in more product.
- However, the activation energy for this reaction is high!
- This is the *one* instance where a system in equilibrium can be affected by a catalyst!

15.7 Give It Some Thought

- Use Le Chatelier’s Principle to explain why the equilibrium vapor pressure of a liquid increases with increasing themperature.

$As_4O_6(s) + 6C(s) \rightleftarrows As_4(g) + 6CO(g)$

- add CO
- add C
- remove C
- add As_4O_6
- remove As_4O_6
- remove As_4
- decrease volume
- add Ne gas

$P_4(s) + 6Cl_2(g) \rightleftarrows 4PCl_3(l)$

- decrease volume
- increase volume
- add P_4
- remove Cl_2
- add Kr gas
- add PCl_3

$\text{energy} + N_2(g) + O_2(g) \rightleftarrows 2NO(g)$

- endo or exo?
- increase temp
- increase volume
- decrease temp

Sample Exercise 15.12

Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H^\circ = 58.0\ \text{kJ}$$

In which direction will the equilibrium shift when **(a)** N2O4 is added, **(b)** NO2 is removed, **(c)** the total pressure is increased by addition of N2(*g*), **(d)** the volume is increased, **(e)** the temperature is decreased?

Practice Exercise 1

For the following reaction, $\Delta H° = -904$ kJ:

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

Which of the following changes will shift the equilibrium to the right, toward the formation of more products?

(a) Adding more water vapor
(b) Increasing the temperature
(c) Increasing the volume of the reaction vessel
(d) Removing $O_2(g)$
(e) Adding 1 atm of Ne(*g*) to the reaction vessel

Practice Exercise 2

- For the reaction $PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$

$\Delta H° = 87.9$ kJ, in which direction will the equilibrium shift when:

  - A) Cl_2 is removed
  - B) the temperature is decreased
  - C) the volume of the reaction system is increased
  - D) PCl_3 is added

Sample Exercise 15.13

- Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)}$
- Determine how the equilibrium constant for this reaction should change with temperature.

Practice Exercise 1

The standard enthalpy of formation of HCl(*g*) is –92.3 kJ/mol. Given only this information, in which direction would you expect the equilibrium for the reaction

$H_2(g) + Cl_2(g) \leftrightarrow 2\ HCl(g)$ to shift as the temperature increases:

(a) to the left

(b) to the right

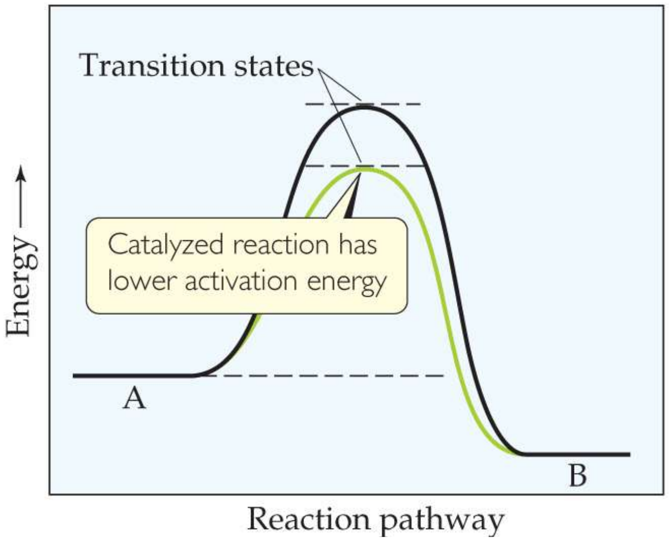
(c) no shift in equilibrium

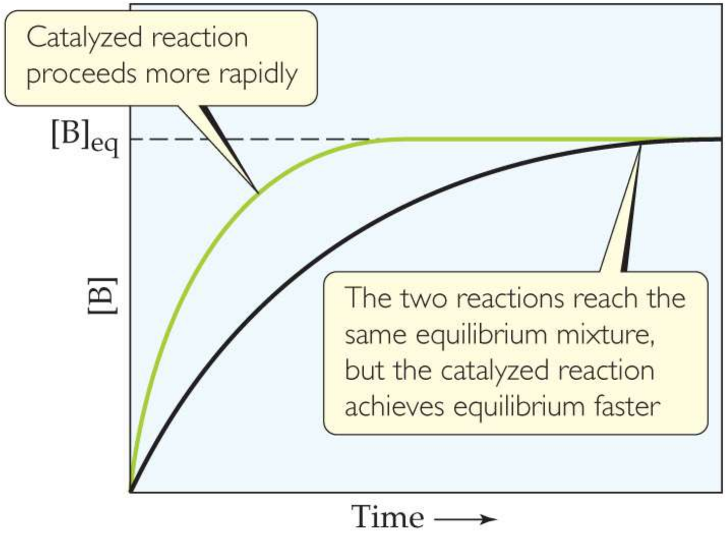
Practice Exercise 2

- Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction2 $2\ POCl_{3(g)} \leftrightarrow 2\ PCl_{3(g)} + O_{2(g)}$
- Use this result to determine how the equilibrium constant for the reaction should change with temperature.

Catalysts

- **Catalysts** increase the rate of both the forward *and* reverse reactions.
- Equilibrium is achieved faster, but the equilibrium composition remains unaltered.
- Activation energy is lowered, allowing equilibrium to be established at lower temperatures.

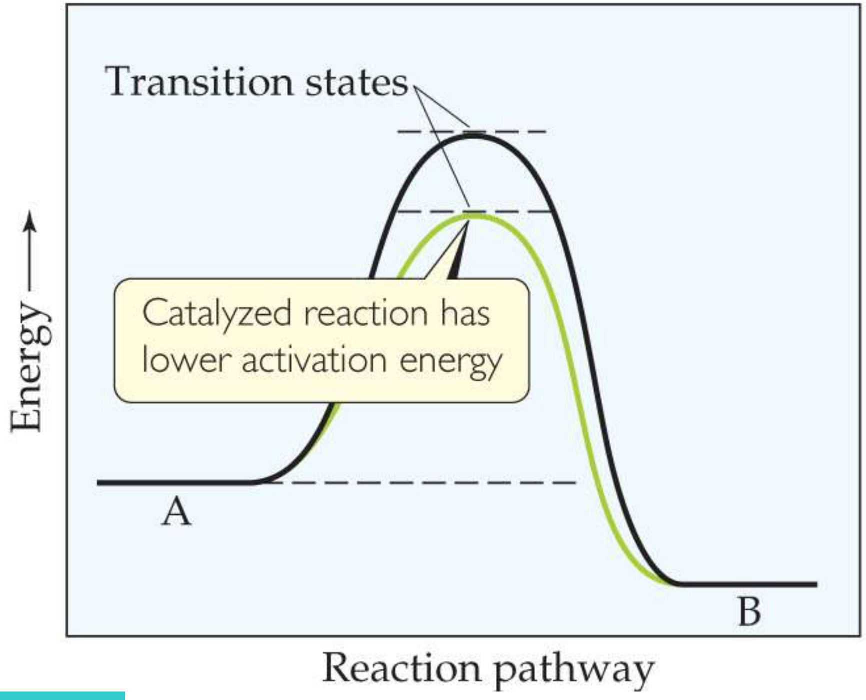


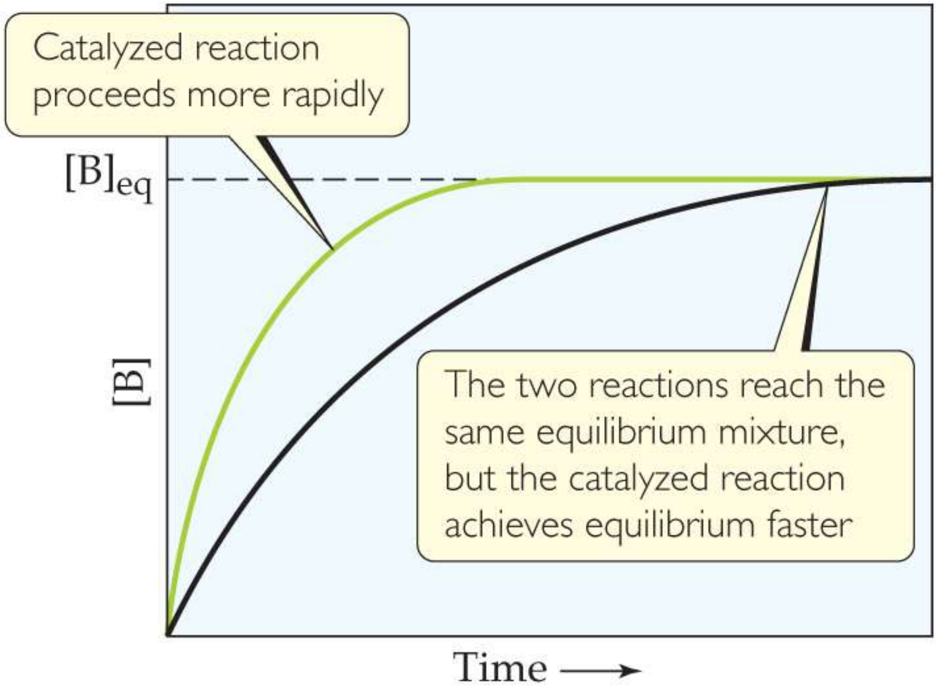


What quantity dictates the speed of a reaction:

(a) the energy difference between the initial state and the transition state or

(b) the energy difference between the initial state and the final state?





Integrative Exercise

At temperatures near 800ºC, steam passed over hot coke (a form of carbon from coal) reacts to form CO and $H_2C_{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)}$ This produces an important industrial fuel called water gas.

- A) At 800ºC the equilibrium constant is $K_p = 14.1$. What are the equilibrium partial pressures of H_2O, CO and H_2 in the equilibrium mixture if we start with solid carbon and 0.100 mol of H_2O in a 1.00-L vessel?
- B) What is the minimum amount of carbon required to achieve equilibrium under these conditions?
- C) What is the total pressure in the vessel at equilibrium?
- D) At 25ºC the value of K_p for this reaction is 1.7×10^{-21}. Is the reaction exothermic or endothermic?
- E) To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased?

19.7 Free Energy and the Equilibrium Constant

Free Energy and Equilibrium

Under any conditions, standard or nonstandard, the free energy change can be found this way:

$\Delta G = \Delta G^\circ + RT \ln Q$

R is 8.31 J/mol·K

(Under standard conditions, concentrations are 1 *M*, so $Q = 1$ and $\ln Q = 0$; the last term drops out.)

Sample Exercise 19.10

(a) Write the chemical equation that defines the normal boiling point of liquid carbon tetrachloride, $CCl_4(l)$.

(b) What is the value of $\Delta G°$ for the equilibrium in part (a)?

(c) Use data from Appendix C and Equation 19.12 to estimate the normal boiling point of CCl_4.

Practice Exercise 1

If the normal boiling point of a liquid is 67 °C, and the standard molar entropy change for the boiling process is +100 J/K, estimate the standard molar enthalpy change for the boiling process.

(a) +6700 J

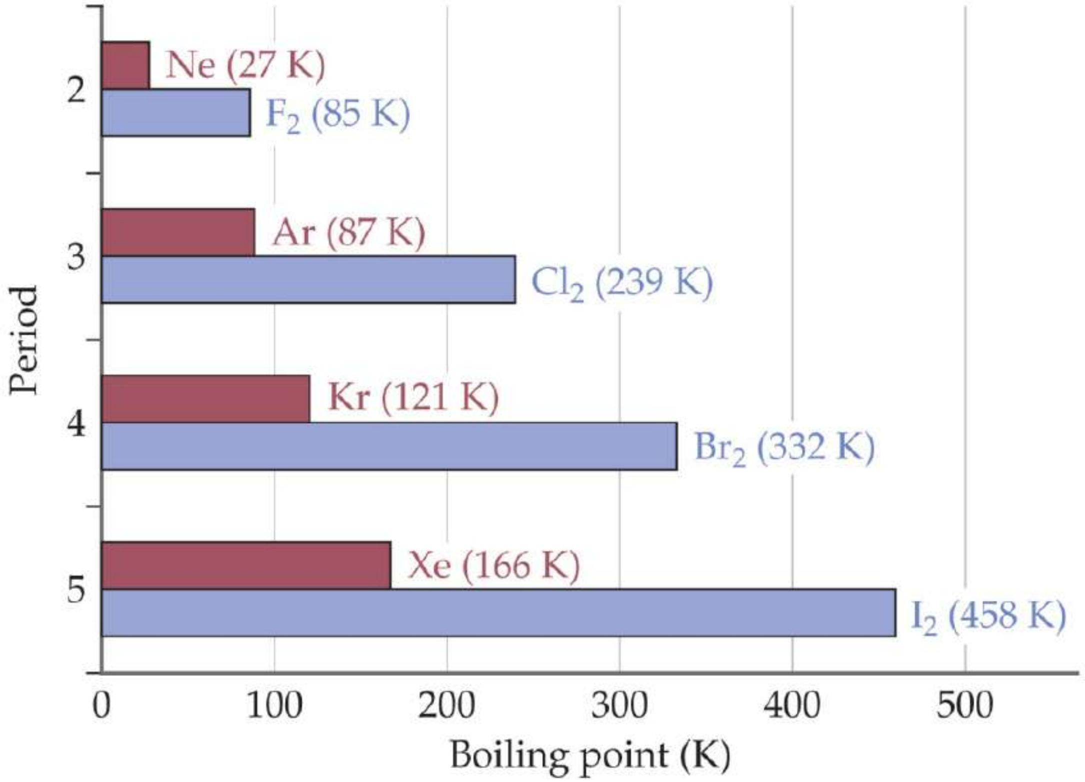
(b) −6700 J

(c) +34,000 J

(d) −34,000 J

Practice Exercise 2

Use data in Appendix C to estimate the normal boiling point, in K, for elemental bromine, $Br_2(l)$. (The experimental value is given in Figure 11.5.)



Sample Exercise 19.11

Calculate ΔG at 298 K for a mixture of 1.0 atm N_2, 3.0 atm H_2, and 0.50 atm NH_3 being used in the Haber process:

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

Practice Exercise 2

Calculate ΔG at 298 K for the Haber reaction if the reaction mixture consists of 0.50 atm N_2, 0.75 atm H_2, and 2.0 atm NH_3.

Free Energy and Equilibrium

- At equilibrium, $Q = K$, and $\Delta G = 0$.
- The equation becomes

$$0 = \Delta G^\circ + RT \ln K$$

- Rearranging, this becomes

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{-\Delta G^\circ / RT}$$

Sample Exercise 19.12

The standard free-energy change for the Haber process at 25 °C was obtained in Sample Exercise 19.9 for the Haber reaction:

$$N_2(g) + 3\ H_2(g) \leftrightarrow 2\ NH_3(g)$$

$$\Delta G° = -33.3\ \text{kJ/mol} = -33{,}300\ \text{J/mol}$$

Use this value of $\Delta G°$ to calculate the equilibrium constant for the process at 25 °C.

Practice Exercise 1

The K_{sp} for a very insoluble salt is 4.2×10^{-47} at 298 K. What is $\Delta G°$ for the dissolution of the salt in water?

(a) −265 kJ/mol

(b) −115 kJ/mol

(c) −2.61 kJ/mol

(d) +115 kJ/mol

(e) +265 kJ/mol

Practice Exercise 2

Use data from Appendix C to calculate the standard free-energy change, ΔG° , and the equilibrium constant, K, at 298 K for the reaction:

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

Sample Integrative Exercise

Consider the simple salts NaCl(*s*) and AgCl(*s*):

$$\mathrm{NaCl}(s) \leftrightarrow \mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{AgCl}(s) \leftrightarrow \mathrm{a} \quad \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

(a) Calculate the value of ΔG° at 298 K for each of the preceding reactions.

(b) The two values from part (a) are very different. Is this difference primarily due to the enthalpy term or the entropy term of the standard free-energy change?

(c) Use the values of ΔG° to calculate the K_{sp} values for the two salts at 298 K.

(d) Sodium chloride is considered a soluble salt, whereas silver chloride is considered insoluble. Are these descriptions consistent with the answers to part (c)?

(e) How will ΔG° for the solution process of these salts change with increasing T? What effect should this change have on the solubility of the salts?