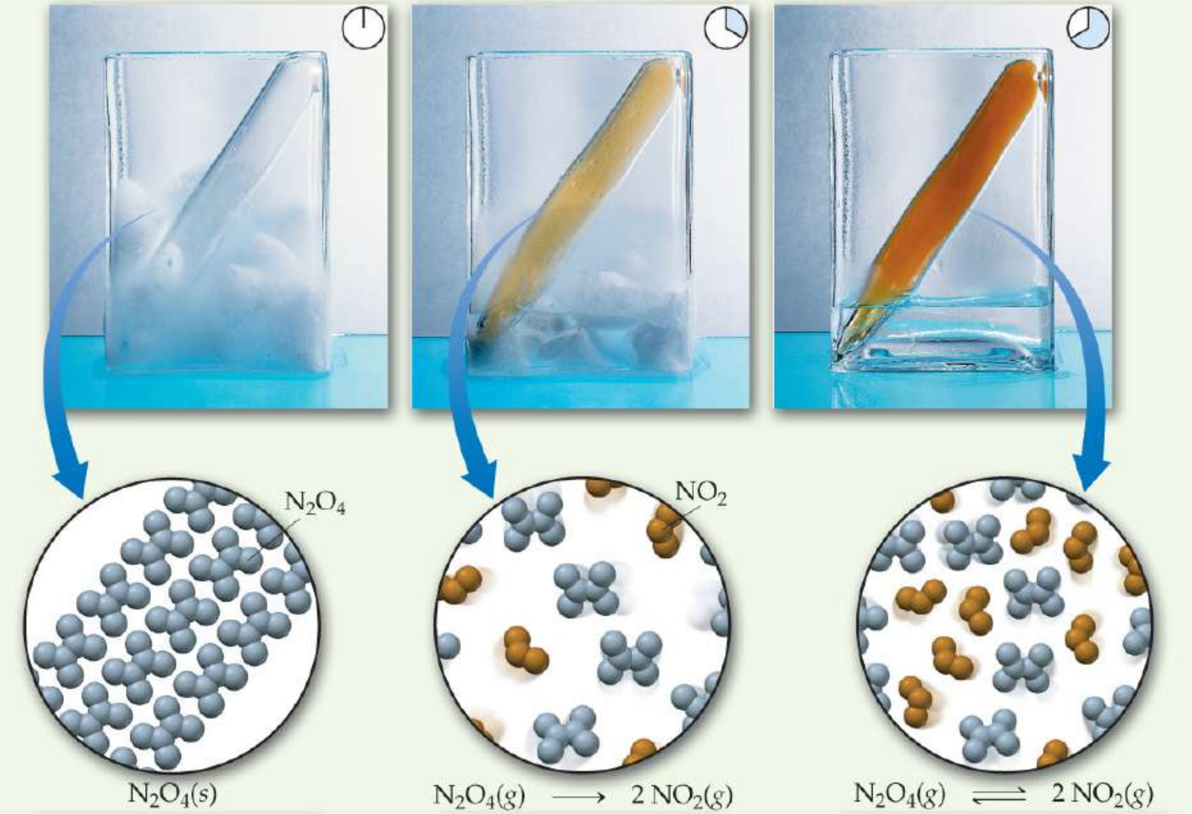
Chapter 15
Chemical Equilibrium

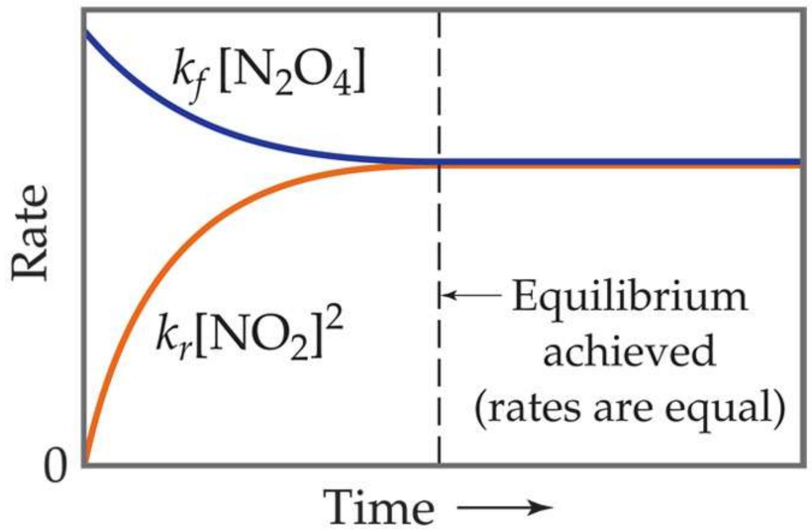
15.1 The Concept of Equilibrium

The Concept of Equilibrium



Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

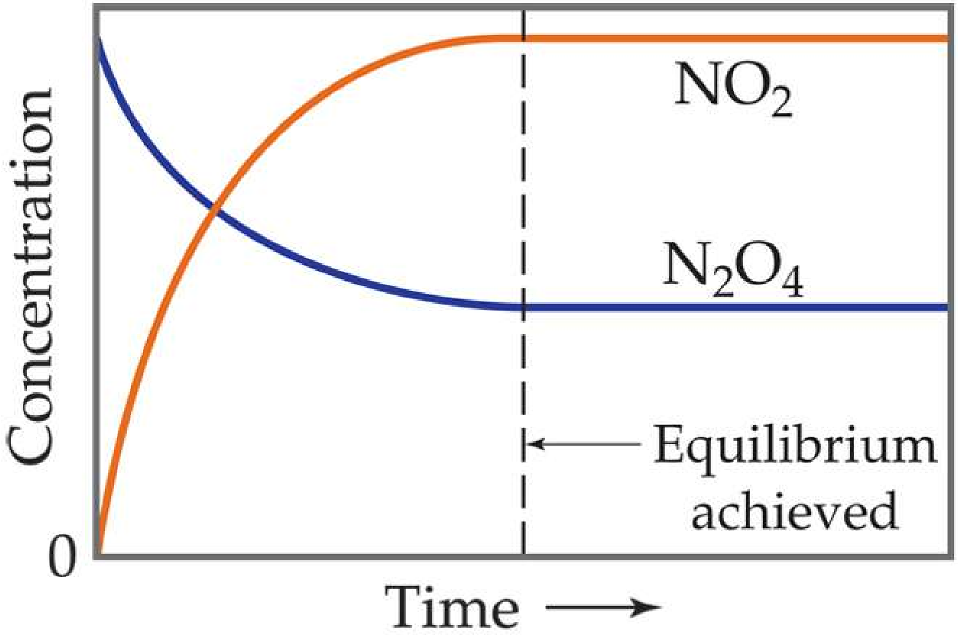
The Concept of Equilibrium



- 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*.

A System at Equilibrium

Once equilibrium is achieved, the *amount* of each reactant and product remains constant.



Depicting Equilibrium

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

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

p.630 GIST: 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

The Equilibrium Constant

- Forward reaction:

  $N_2O_4\ _{(g)} \longrightarrow 2\ NO_2\ _{(g)}$

- Rate Law:

  Rate = $k_f\ [N_2O_4]$

The Equilibrium Constant

- Reverse reaction:

  $2\ NO_{2\ (g)} \longrightarrow N_2O_{4\ (g)}$

- Rate Law:

  Rate = $k_r\ [NO_2]^2$

The Equilibrium Constant

- Therefore, at equilibrium

$$Rate_f = Rate_r$$

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

- Rewriting this, it becomes

$$\frac{kf}{kr} = \frac{[NO2]^2}{[N2O4]}$$

The Equilibrium Constant

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{eq} = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$$

The Equilibrium Constant

- Consider the generalized reaction

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium expression for this reaction would be

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

Writing Equilibrium Constant Expressions: 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) $Cd^{2+}_{(aq)} + 4\ Br^{-}_{(aq)} \leftrightarrow CdBr_4{}^{2-}_{(aq)}$
- How do you know when equilibrium has been reached in a chemical reaction?

Equilibrium Can Be Reached from Either Direction

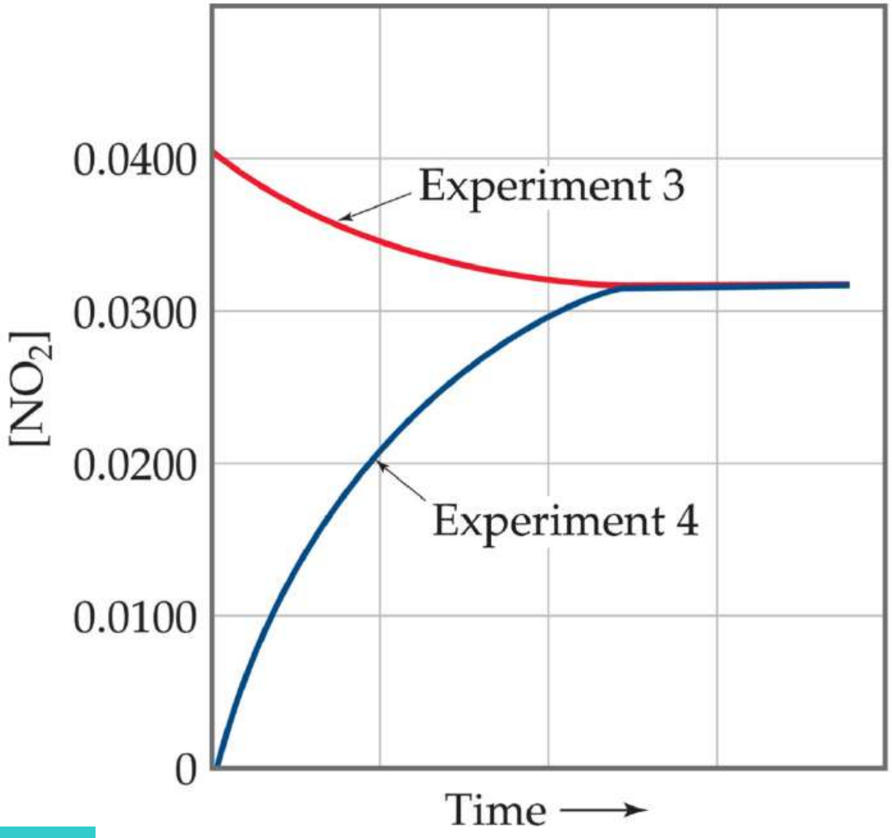
TABLE 15.1 ■ Initial and Equilibrium Concentrations of N_2O_4 and NO_2 in the Gas Phase at 100 °C

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

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.

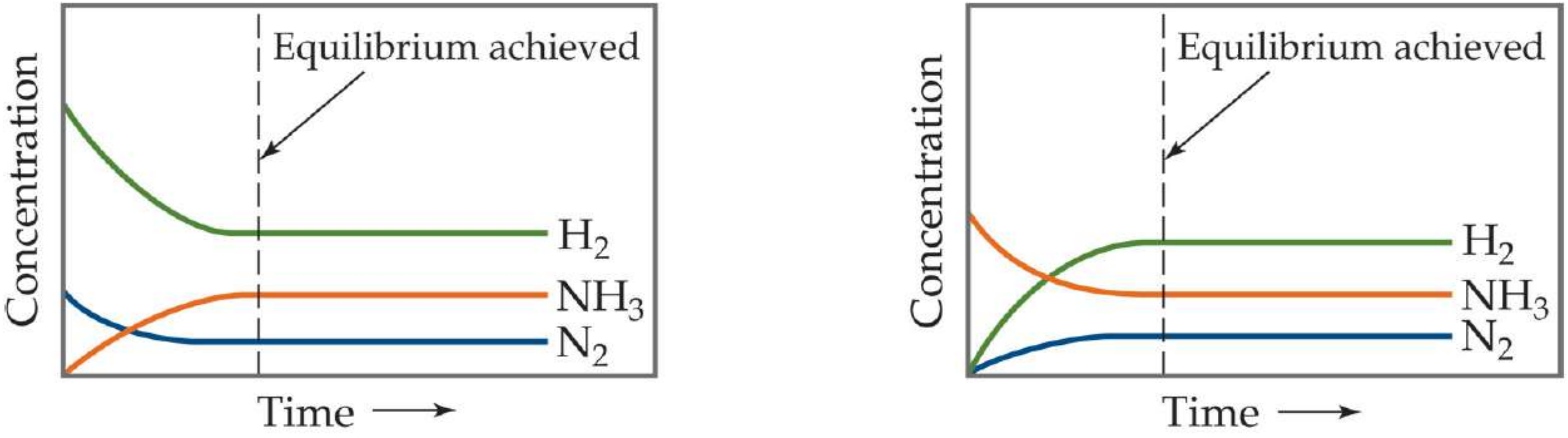
$$Kc = \frac{[NO2]^2}{[N2O4]}$$

Equilibrium Can Be Reached from Either Direction



This is the data from the last two trials from the table on the previous slide.

Equilibrium Can Be Reached from Either Direction



It doesn't matter whether we start with N_2 and H_2 or whether we start with NH_3: we will have the same proportions of all three substances at equilibrium.

The Equilibrium Constant

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

$$K_p = \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b}$$

Relationship Between K_c and K_p

- From the Ideal Gas Law we know that

$$PV = nRT$$

Rearranging it, we get

$$P = \frac{n}{V}RT$$

Relationship Between K_c and K_p

Plugging this into the expression for K_p for each substance, the relationship between K_c and K_p becomes

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

where

Δn = (moles of gaseous product) − (moles of gaseous reactant)

Ex 15.2 Converting between K_c and K_p

- In the synthesis of ammonia from nitrogen and hydrogen,

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

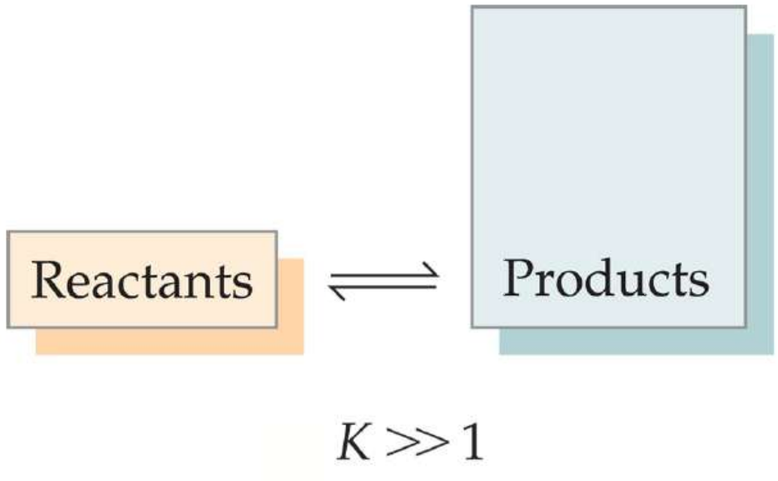
  $K_c = 9.60$ at 300ºC. Calculate K_p for this reaction at this temperature.

Practice

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

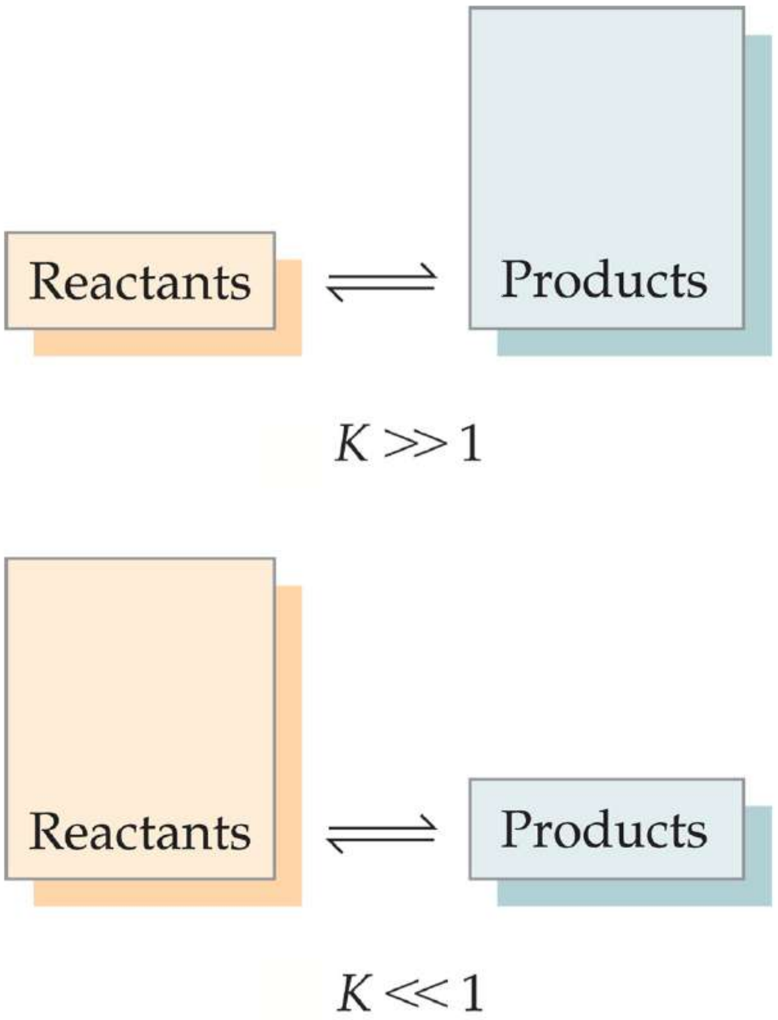
15.3 Interpreting and Working with Equilibrium Constants

What Does the Value of *K* Mean?



- If *K*>>1, the reaction is *product-favored*; product predominates at equilibrium.

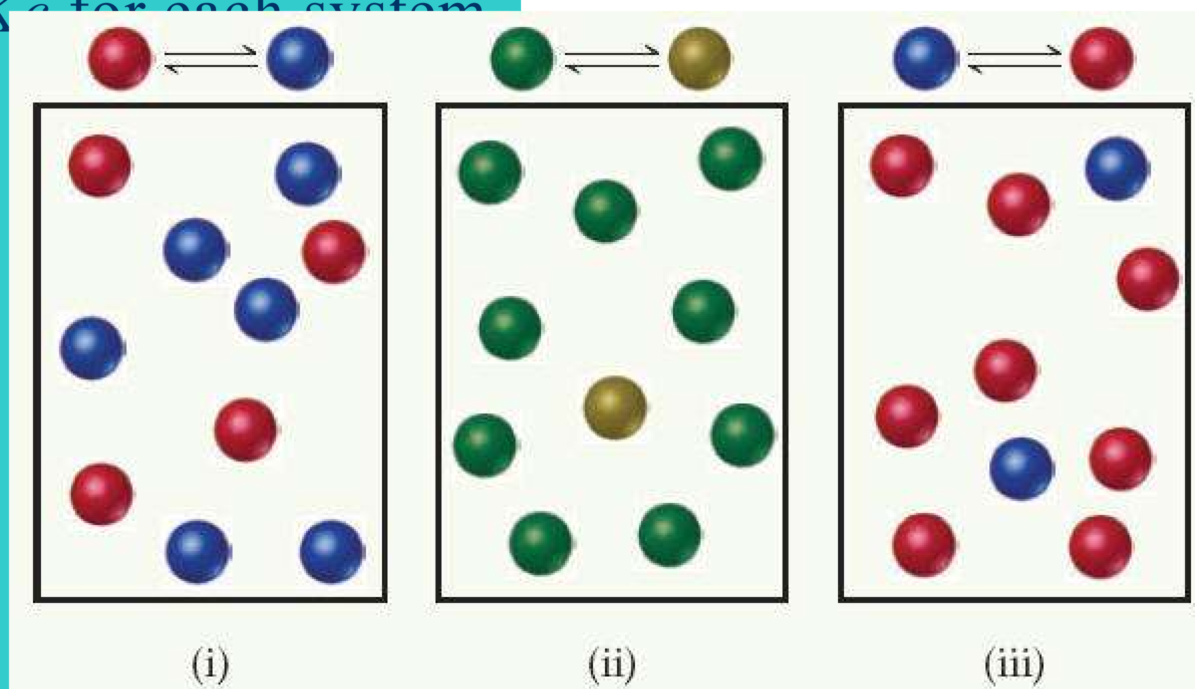
What Does the Value of *K* Mean?



- If *K*>>1, the reaction is *product-favored*; product predominates at equilibrium.

If *K*<<1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

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

For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_p = 794$ at 298 K and $K_p = 54$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?

Manipulating Equilibrium Constants

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

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

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

Manipulating 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.

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

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

Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

The equilibrium constant for the reaction of N2 with O2 to form NO equals $Kc = 1 \times 10^{-30}$ at 25 ° C:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad K_c = 1 \times 10^{-30}$$

Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction:

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

Practice

- For the formation of NH_3 from N_2 and H_2, $N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)}$, $K_p = 4.34 \times 10^{-3}$ at 300ºC. What is the value of K_p for the reverse reaction?

Manipulating Equilibrium Constants

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.

p.638 GIST

- How does the magnitude of the equilibrium constant, K_p, for the reaction

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

change if the equilibrium is written

$6HI(g) \leftrightarrow 3H_2(g) + 3H_2(g)$?

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.

Exercise 15.5

- Given the following information: $HF_{(aq)} \leftrightarrow H^+_{(aq)} + F^-_{(aq)}$ $K_c = 6.8 \times 10^{-4}$

$H_2C_2O_{4(aq)} \leftrightarrow 2\ H^+_{(aq)} + C_2O_4^{2-}{}_{(aq)}$ $K_c = 3.8 \times 10^{-6}$ 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

- 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.

15.4 Heterogeneous Equilibria

The Concentrations of Solids and Liquids Are Essentially Constant

Both can be obtained by multiplying the density of the substance by its molar mass — and both of these are constants at constant temperature.

The Concentrations of Solids and Liquids Are Essentially Constant

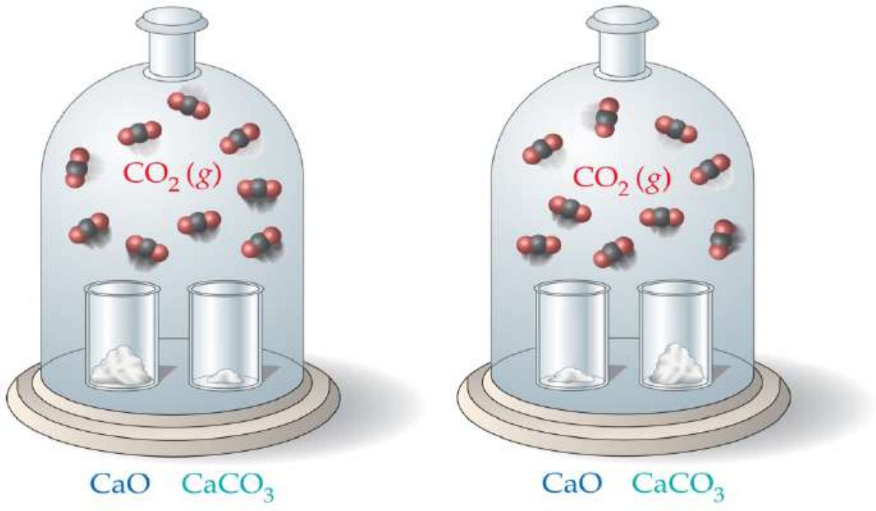
Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.

$$PbCl2\ (s) \leftrightarrow Pb^{2+}\ (aq) + 2\ Cl^{-}\ (aq)$$

$$Kc = [Pb^{2+}]\ [Cl^{-}]^{2}$$

CaCO3 (*s*) ⟷ CO2 (*g*) + CaO(*s*)

As long as *some* $CaCO_3$ or CaO remain in the system, the amount of CO_2 above the solid will remain the same.



P.639 & 641 GIST

- Write the equilibrium constant expression for the evaporation of water

$H_2O(l) \leftrightarrow H_2O(g)$,

in terms of partial pressures, K_p.

Write the equilibrium expression for the following:

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

Exercise 15.6

- 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

- 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 $3\ Fe_{(s)} + 4\ H_2O_{(g)} \leftrightarrow Fe_3O_{4(s)} + 4\ H_{2(g)}$

Exercise 15.7

- 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) pure $CaCO_3$
  - B) CaO and a CO_2 pressure greater than the value of K_p
  - C) some $CaCO_3$ and a CO_2 pressure greater than the value of K_p
  - D) $CaCO_3$ and CaO

Practice

- 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 $3\ Fe_{(s)} + 4\ H_2O_{(g)} \leftrightarrow Fe_3O_{4(s)} + 4\ H_{2(g)}$?

15.5 Calculating Equilibrium Constants

Exercise 15.8

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

- An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25ºC: $[HC_2H_3O_2] = 1.65 \times 10^{-2}$ M; $[H^+] = 5.44 \times 10^{-4}$ M; and $[C_2H_3O_2^-] = 5.44 \times 10^{-4}$ M. Calculate the equilibrium constant, K_c, for the ionization of acetic acid at 25ºC: $HC_2H_3O_{2(aq)} \leftrightarrow H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$

Equilibrium Constant

- if we know the value of K, we can predict:
  - tendency of a reaction to occur
  - if a set of concentrations could be at equilibrium
  - equilibrium position, given initial concentrations

Equilibrium Constant

- If you start a reaction with only reactants:
  - concentration of reactants will decrease by a certain amount
  - concentration of products will increase by a same amount

Exercise 15.9

A closed system initially containing 1.000 x 10^{-3} M H_2 and 2.000 x 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 x 10^{-3} M. Calculate K_c at 448 °C for the reaction taking place, which is

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

What Do We Know?

	[H2], *M*	[I2], *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

Practice 15.9

- Sulfur trioxide decomposes at high temperature in a sealed container:
  - $2SO_{3(g)} \leftrightarrow 2SO_{2(g)} + O_{2(g)}$
- Initially, the vessel is charged at 1000 K with $SO_{3(g)}$ at a partial pressure of 0.500 atm. At equilibrium the SO_3 partial pressure is 0.200 atm. Calculate the value of *Kp* at 1000 K.

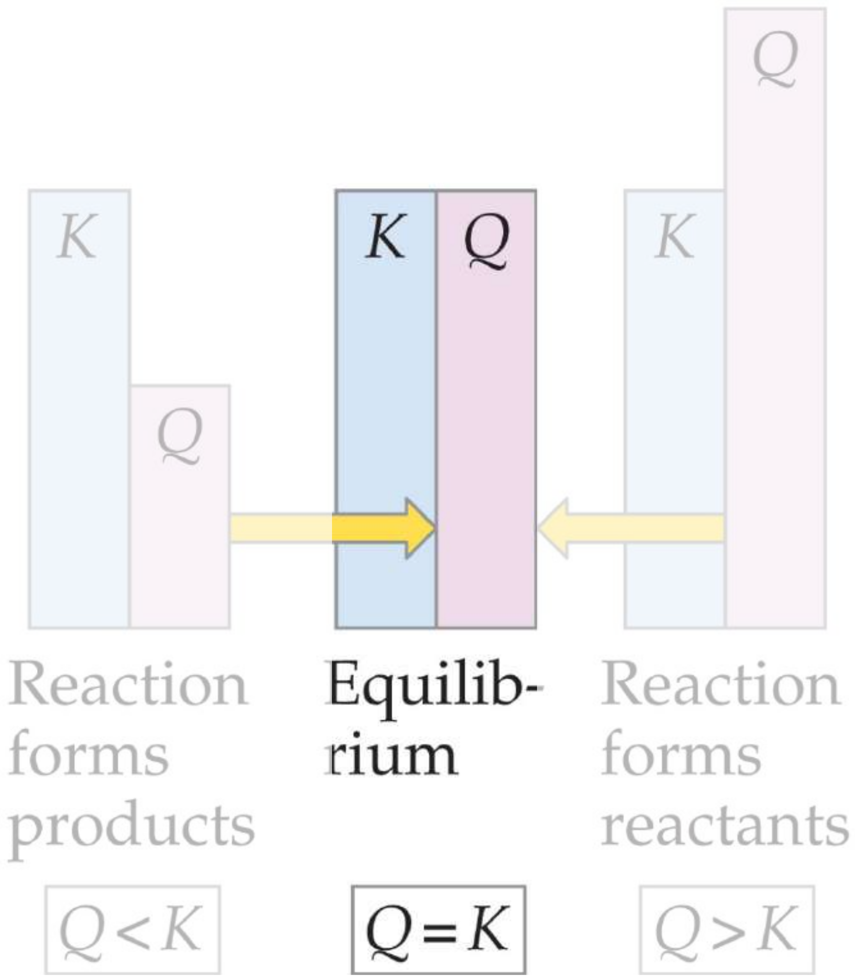
15.6 Applications of Equilibrium Constants

The Reaction Quotient (*Q*)

- *Q* gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- To calculate *Q*, one substitutes the initial concentrations on reactants and products into the equilibrium expression.

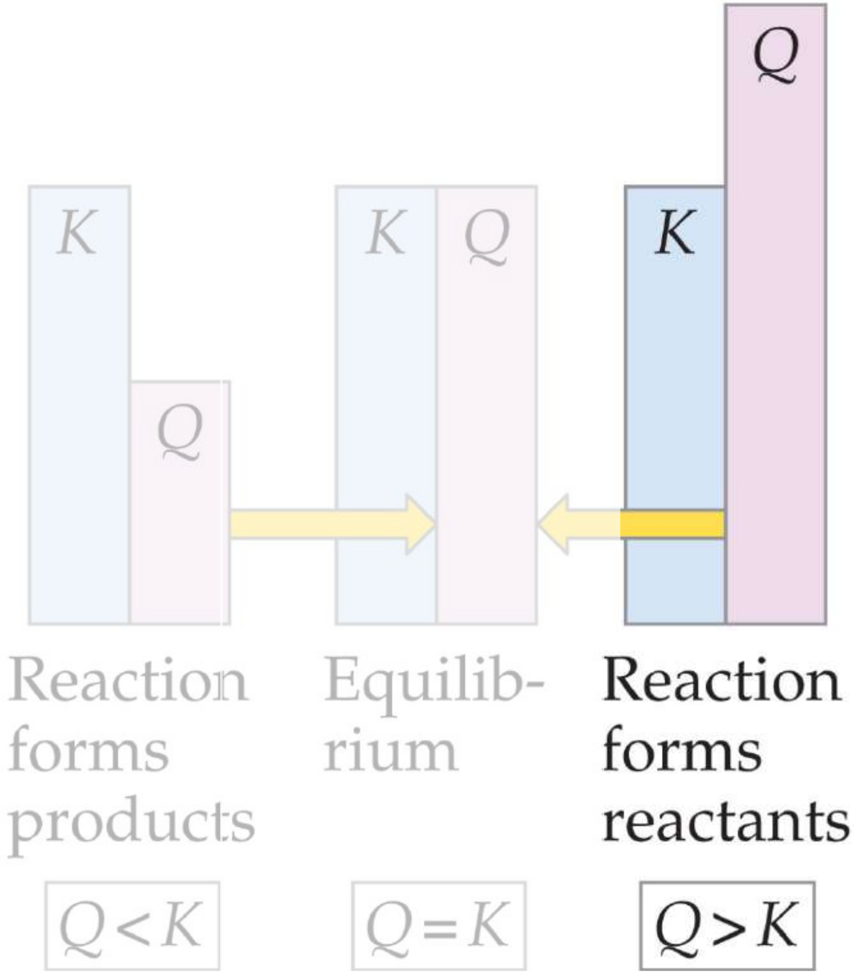
If $Q = K$,

the system is at equilibrium.



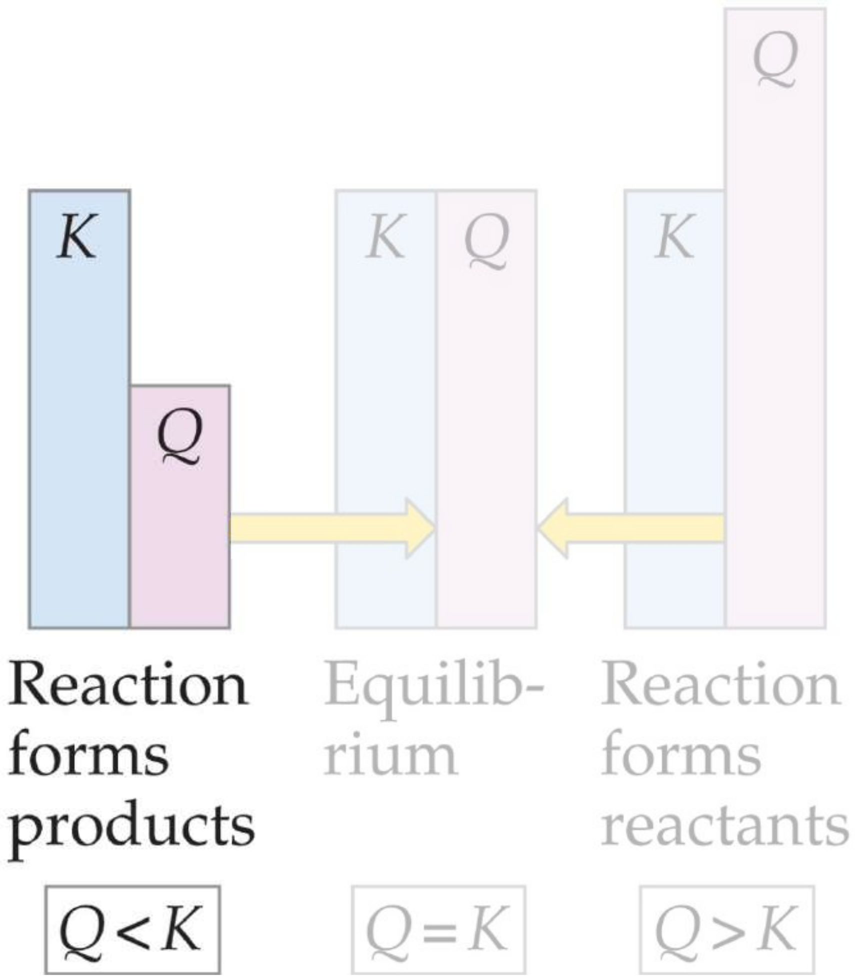
If *Q* > *K*,

there is too much product, and the equilibrium shifts to the left.



If *Q* < *K*,

there is too much reactant, and the equilibrium shifts to the right.



Example

- For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0 x 10^{-2}. Predict the direction the system will shift to reach equilibrium in the following case:

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

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.0 \times 10^{-2}$$

Example

- $[NH_3]_0$ = 1.0x10^{-3} M,

$[N_2]_0$=1.0x10^{-5} M

$[H_2]_0$=2.0x10^{-3} M

$$Q = \frac{[1.0 \times 10^{-3}]^2}{[1.0 \times 10^{-5}][2.0 \times 10^{-3}]^3} = 1.3 \times 10^7$$

Q > K so forms reactants, shifts to left

Exercise 15.10

- 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 x 10^{-2} mol of HI, 1.0 x 10^{-2} mol H_2, and 3.0 x 10^{-2} mol of I_2 in a 2.00-L container.

Practice

- 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.

Example

- In the gas phase, dinitrogen tetroxide decomposes to gaseous nitrogen dioxide:

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

- Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a T where K_P = 0.133. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm.
- Calculate the equilibrium pressure of NO_2.

Example

$$K_P = \frac{{P_{NO_2}}^2}{P_{N_2O_4}} = 0.133$$

$${P_{NO_2}}^2 = K_P \cdot P_{N_2O_4} = (0.133)(2.71) = 0.360$$

$$P_{NO_2} = \sqrt{0.360} = 0.600$$

Exercise 15.11

- For the Haber process, $N_{2(g)}$ + 3 $H_{2(g)}$ $\leftrightarrow$ 2 $NH_{3(g)}$, K_p = 1.45 x 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

- 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?

Example

- At a certain temperature a 1.00 L flask initially contained 0.298 mol $PCl_3(g)$ and 8.70×10^{-3} mol $PCl_5(g)$. After the system had reached equilibrium, 2.00×10^{-3} mol $Cl_2(g)$ was found in the flask.

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

- Calculate the equilibrium concentrations of all the species and the value of K.

Example

	$PCl_5(g)$ →	$PCl_3(g)$ +	$Cl_2(g)$
I	8.70×10^{-3}	0.298	0
C	-x	+x	+x
E	8.70×10^{-3}-x = (8.70-2.00) $\times10^{-3}$ = **6.70×10^{-3}**	0.298+**x =** 0.298+2.00×10^{-3} = **0.300**	x = **2.00×10^{-3}**

$$K = \frac{(0.300)(2.00\times10^{-3})}{6.70\times10^{-3}} = 8.96\times 10^{-2}$$

Exercise 15.12

- 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_c for the reaction at 448 °C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?
- $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

Practice

- 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?

Approximation example

- At a particular temperature, K = 4.0×10^{-7} for the reaction

$N_2O_{4(g)} \leftrightarrow 2NO_{2(g)}$

❿ In an experiment, 1.0 mol N_2O_4 is placed in a 10.0 L vessel. Calculate the concentrations of N_2O_4 and NO_2 when this reaction reaches equilibrium.

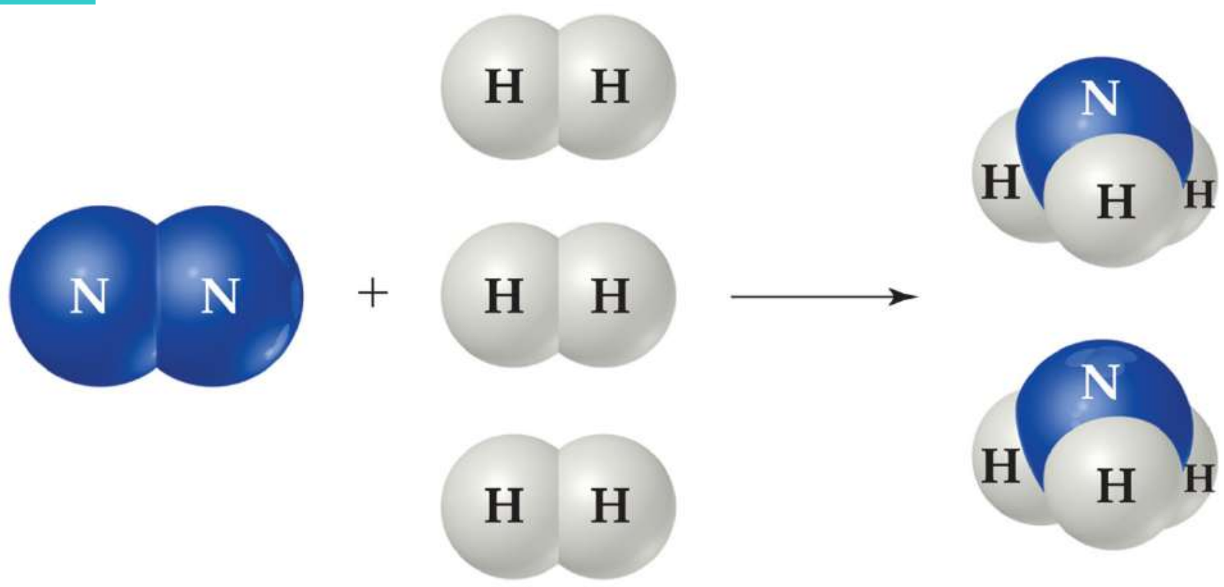
15.7 Le Châtelier's Principle

Le Châtelier's Principle

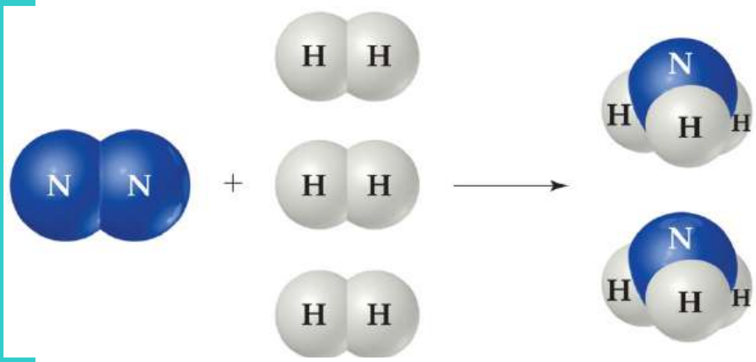
"If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance."

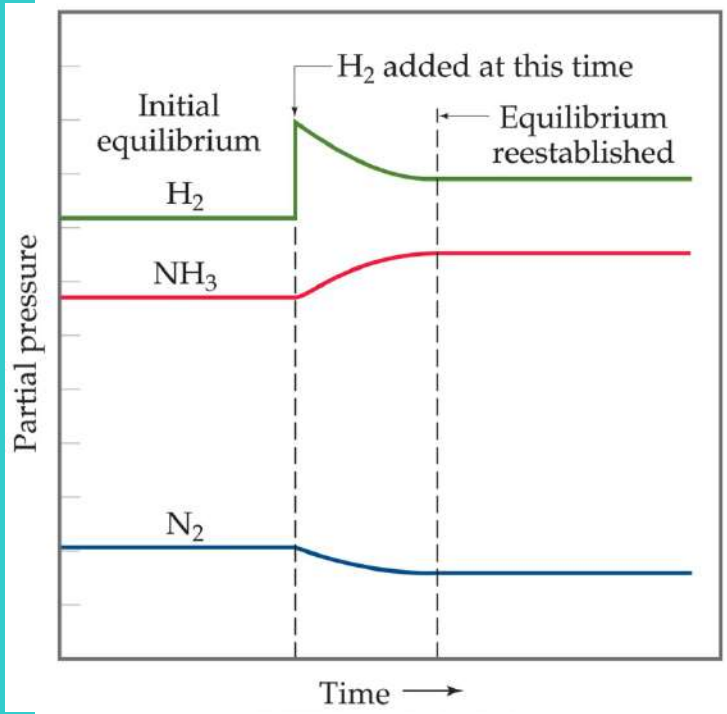
The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.



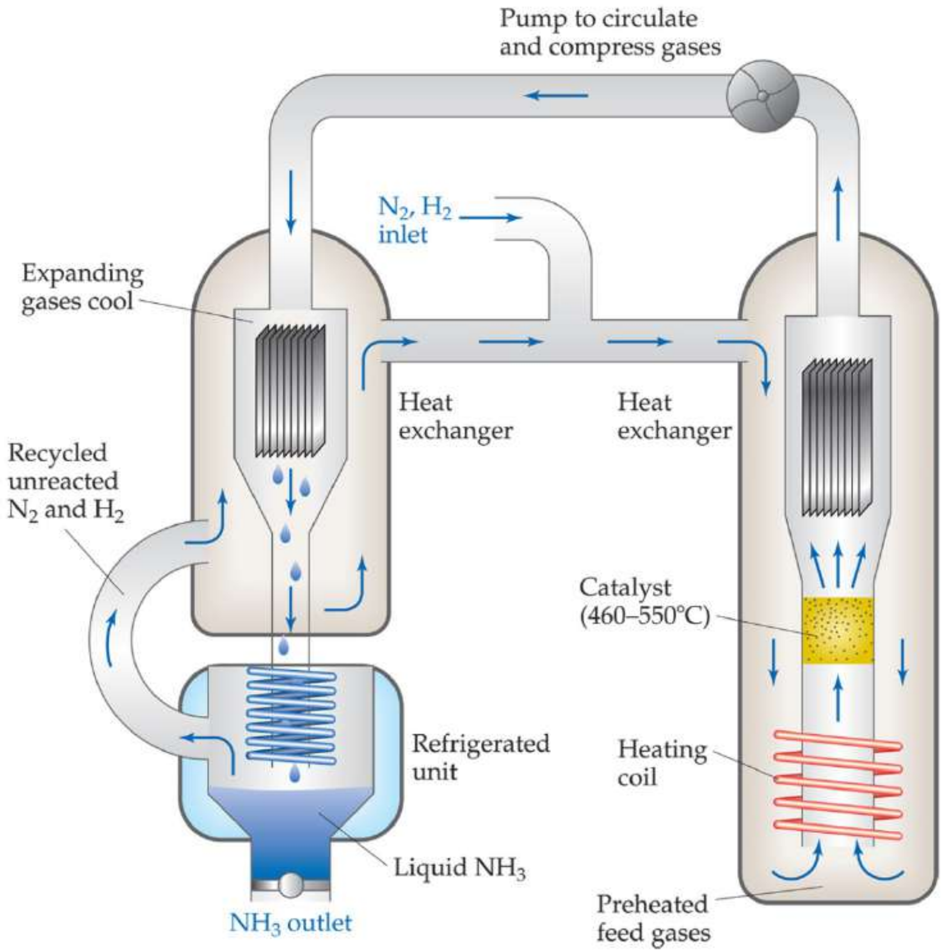
The Haber Process





If H_2 is added to the system, N_2 will be consumed and the two reagents will form more NH_3.

The Haber Process



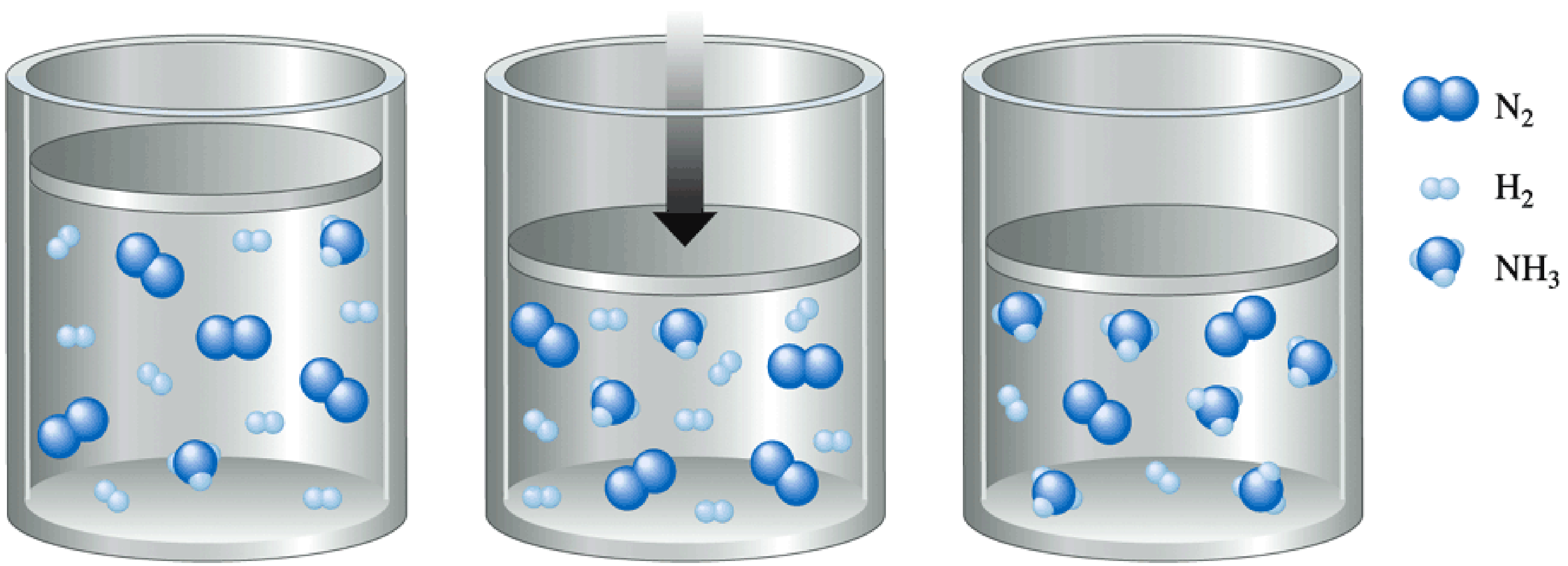
This apparatus helps push the equilibrium to the right by removing the ammonia (NH_3) from the system as a liquid.

Changing Concentration

- system will shift away from the added component or towards a removed component
- Ex: $N_2 + 3H_2 \rightarrow 2NH_3$
  - if more N_2 is added, then equilibrium position shifts to right
  - if some NH_3 is removed, then equilibrium position shifts to right

Change in Pressure

- adding or removing gaseous reactant or product is same as changing conc.
- adding inert or uninvolved gas
  - increase the total pressure
  - doesn't effect the equilibrium position



Change in Pressure

- changing the volume
  - decrease V (increase in pressure)
    - decrease in # gas molecules
    - shifts towards the side of the reaction with less gas molecules
  - increase V (decrease in pressure)
    - increase in # of gas molecules
    - shifts towards the side of the reaction with more gas molecules

Change in Temperature

- all other changes alter the concentration at equilibrium position but don't actually change value of K
- value of K does change with temperature

TABLE 13.3
Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	*K*
500	90
600	3
700	0.3
800	0.04

Change in Temperature

- if energy is added, the reaction will shift in direction that consumes energy
- treat energy as a
  - reactant: for endothermic reactions
  - product: for exothermic reactions

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

- add CO
  - to left
- add C
  - to right
- remove C
  - to left
- add As_4O_6
  - to right
- remove As_4O_6
  - to left
- remove As_4
  - to right
- decrease volume
  - to left
- add Ne gas
  - no shift

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

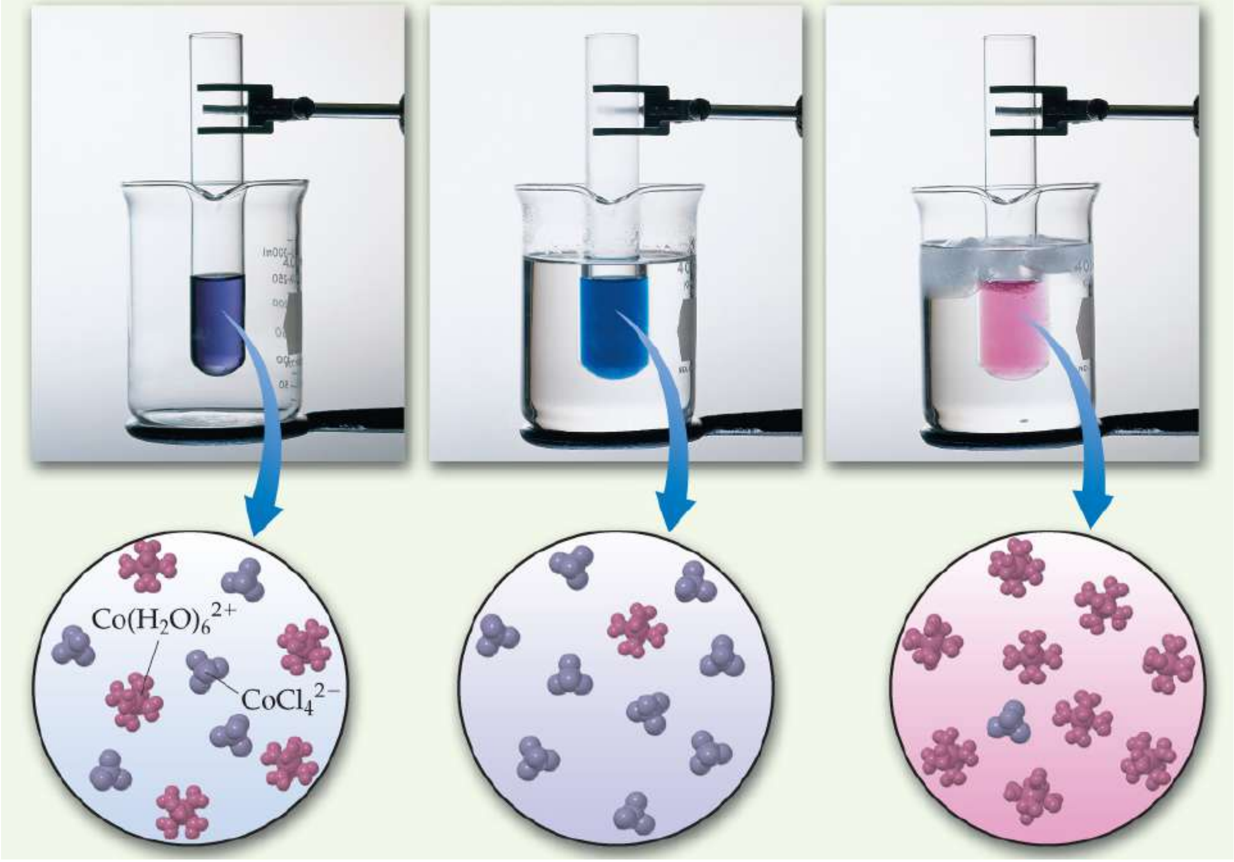
- decrease volume
  - to right
- increase volume
  - to left
- add P_4
  - to right
- remove Cl_2
  - to left
- add Kr gas
  - no shift
- add PCl_3
  - to left

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

- endo or exo?
  - $\Delta H = 181$ kJ
  - endothermic
- increase temp
  - to right
- increase volume
  - no shift
- decrease temp
  - to left

The Effect of Changes in Temperature

$Co(H_2O)_6^{2+}(aq) + 4\ Cl(aq) \leftrightarrow CoCl_4\ (aq) + 6\ H_2O\ (l)$



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

TABLE 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure*

	Total Pressure		
Temperature (°C)	*300 atm*	*400 atm*	*500 atm*
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

Section 15.7 GIST

- What happens to the equilibrium

$2NO(g) + O_2(g) \leftrightarrow 2NO_2(g)$ if

a) O_2 is addedb) NO is removed

What happens to the equilibrium

$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$ if the volume of the system is increased?

Use Le Châtelier's principle to explain why the vapor pressure of a liquid increases with increasing temperature.

Sample Exercise 15.13 Using Le Châtelier's Principal to Predict shifts in Equilibrium

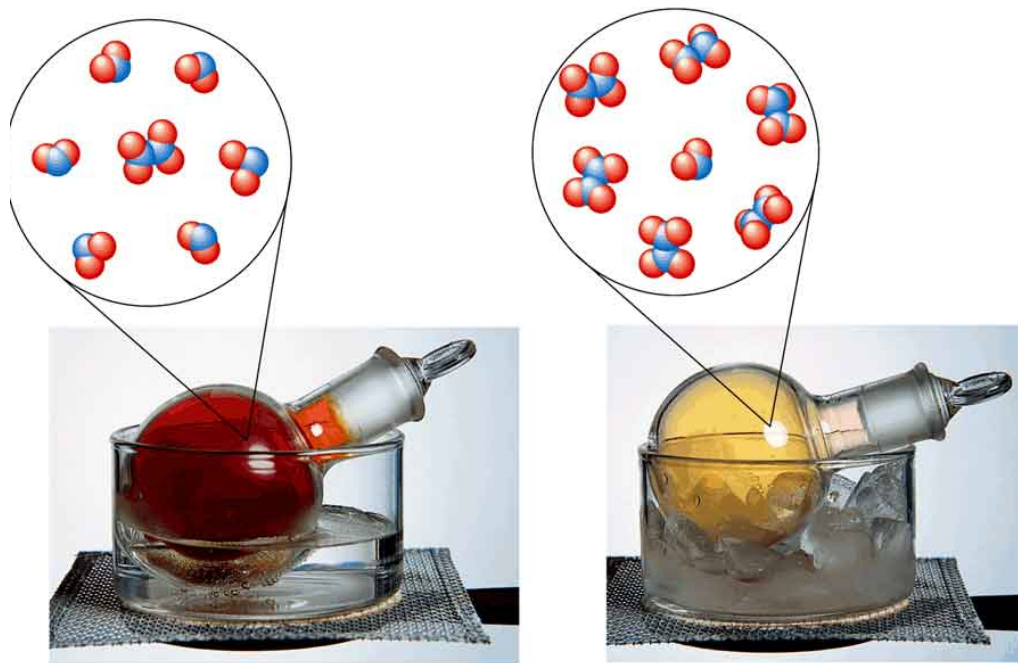
Consider the equilibrium

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

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?

TABLE 13.4 Shifts in the Equilibrium Position for the Reaction 58 kJ + $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Change	Shift
Addition of $N_2O_4(g)$	Right
Addition of $NO_2(g)$	Left
Removal of $N_2O_4(g)$	Left
Removal of $NO_2(g)$	Right
Addition of $He(g)$	None
Decrease container volume	Left
Increase container volume	Right
Increase temperature	Right
Decrease temperature	Left



Practice Exercise 15.13

- 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

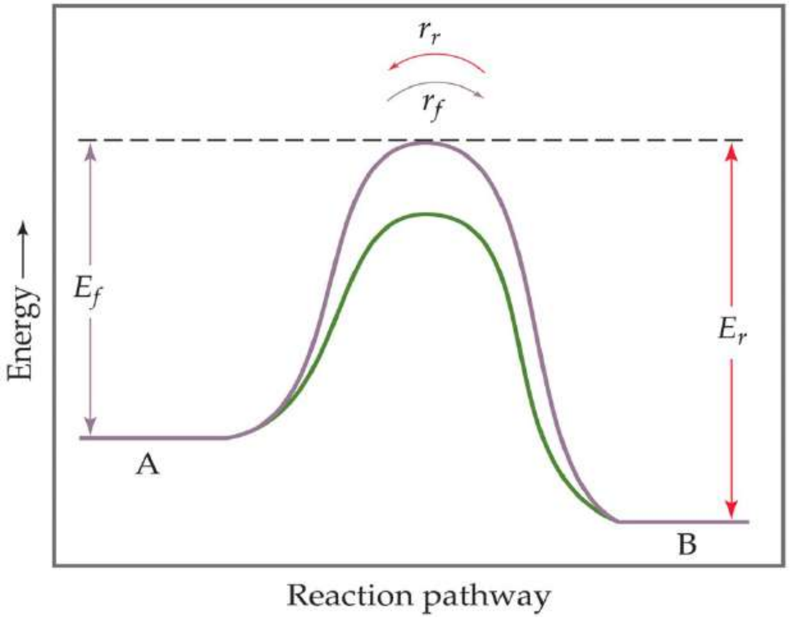
Sample Exercise15.14

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

Practice

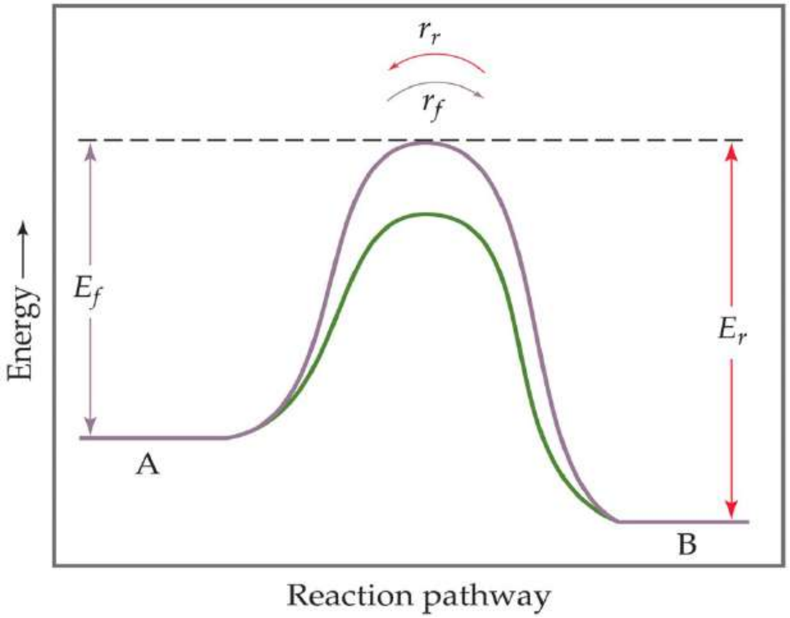
- Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction2 $POCl_{3(g)} \leftrightarrow 2\ PCl_{3(g)} + O_{2(g)}$
- Use this result to determine how the equilibrium constant for the reaction should change with temperature.

Catalysts



Catalysts increase the rate of both the forward *and* reverse reactions.

Catalysts



When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.

p.655 GIST: Does the addition of a catalyst have any effect on the position of an equilibrium?

Integrative Exercise

- At temperatures near 800ºC, steam pased over hot coke (a form of carbon from coal) reacts to form CO and $H_2C_{(s)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)}$ producing 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?