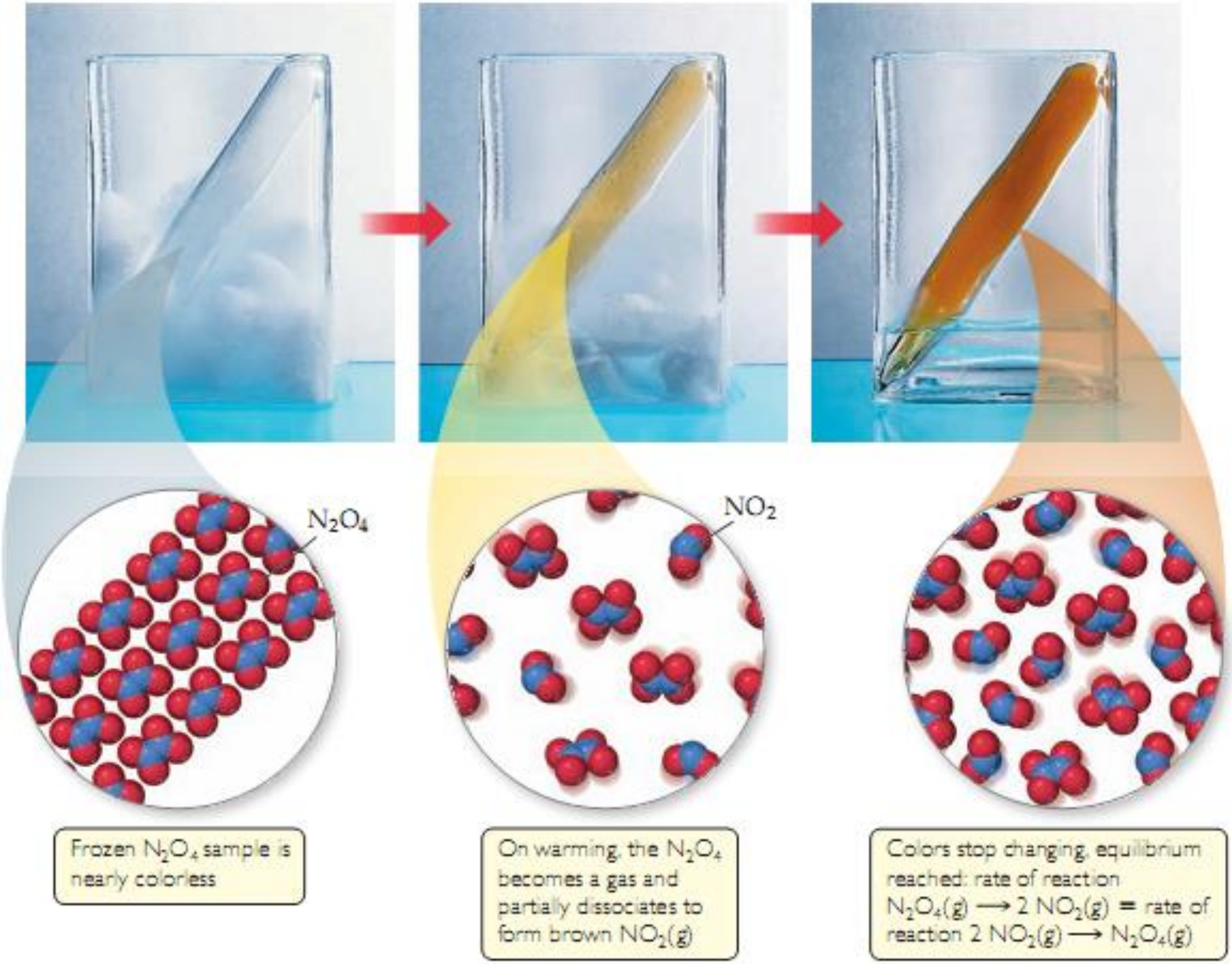
GENERAL
CHEMISTRY

Chapter 15
Chemical Equilibrium

Contents

15-1 The Concept of Equilibrium

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

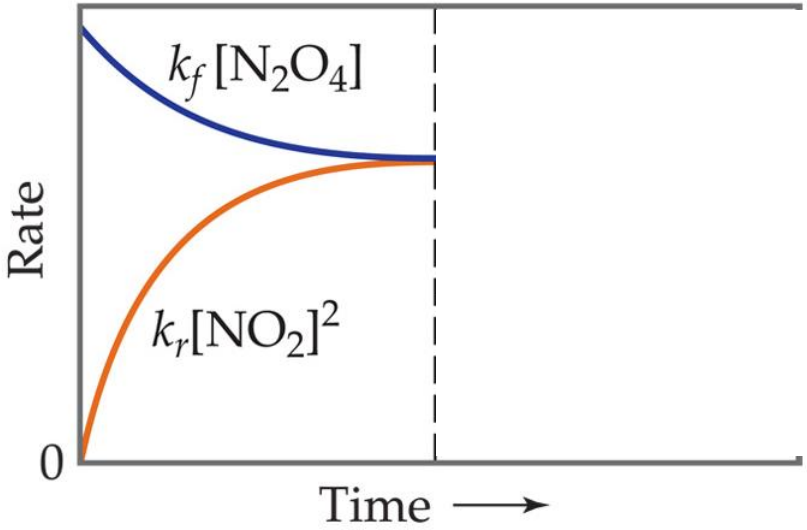


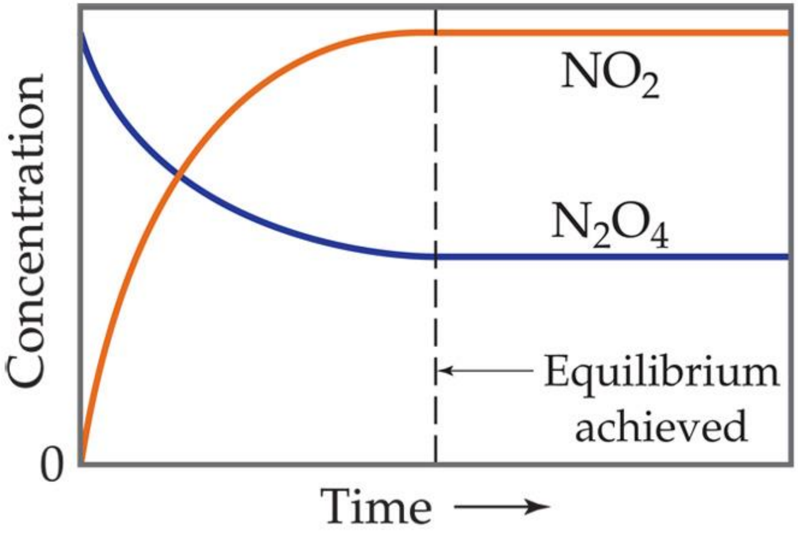
Frozen N_2O_4 sample is nearly colorless

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

The Concept of Equilibrium





- As a system approaches equilibrium, both the forward and reverse reactions are occurring.

$$N_2O_{4\,(g)} \rightleftharpoons 2\ NO_{2\,(g)}$$

- 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.

Dynamic Equilibrium

- A dynamic equilibrium exists when the rates of the forward and reverse reactions are equal.
- There is no further change in [reactant] or [product].
- How fast you get to equilibrium depends on kinetics.

The Equilibrium Constant

- Forward reaction:

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

Rate Law:

$\text{Rate}_f = k_f\,[N_2O_4]$

- Reverse reaction:

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

Rate Law:

$\text{Rate}_r = k_r\,[NO_2]^2$

- At equilibrium

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

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

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

The Equilibrium Constant

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

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

Summary

1. At equilibrium, the concentrations of reactants and products no longer change with time.

2. For equilibrium to occur, neither reactants nor products can escape from the system.

3. At equilibrium a particular ratio of concentration terms equals a constant.

15-2 The Equilibrium Constant

- Consider the generalized reaction

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

- The equilibrium expression for this reaction would be

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

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

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

K_{eq} vs K_c vs K_p

- K_{eq} = the general expression for equilibrium constant expressions.
- K_c = K_{eq} for which molar concentrations were used to evaluate the constant (i.e. subscript "c" = concentration).
- K_c includes
  - K_a (weak acids) and K_b (weak bases) (Chapter 16)
  - K_{sp} (solubility product) (Chapter 17)
  - K_w (water)
- K_p = K_{eq} where "p" stands for pressure

Relationship Between K_c and K_p

- From the Ideal Gas Law we know that

$$PV = nRT$$

- Rearranging it, we get

$$P = \frac{nRT}{V}$$

If we express volume in liters the quantity (n/V) is equivalent to molarity.

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

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

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

EXAMPLE

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

a) $2\ O_{3(g)} \leftrightarrows 3\ O_{2(g)}$

$$K_c = \frac{[O_2]^3}{[O_3]^2}$$

b) $2\ NO_{(g)} + Cl_{2(g)} \leftrightarrows 2\ NOCl_{(g)}$

$$K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$$

c) $Ag^+_{(aq)} + 2\ NH_{3(g)} \leftrightarrows Ag(NH_3)_2{}^+_{(aq)}$

$$K_c = \frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$$

Equilibrium Can Be Reached from Either Direction

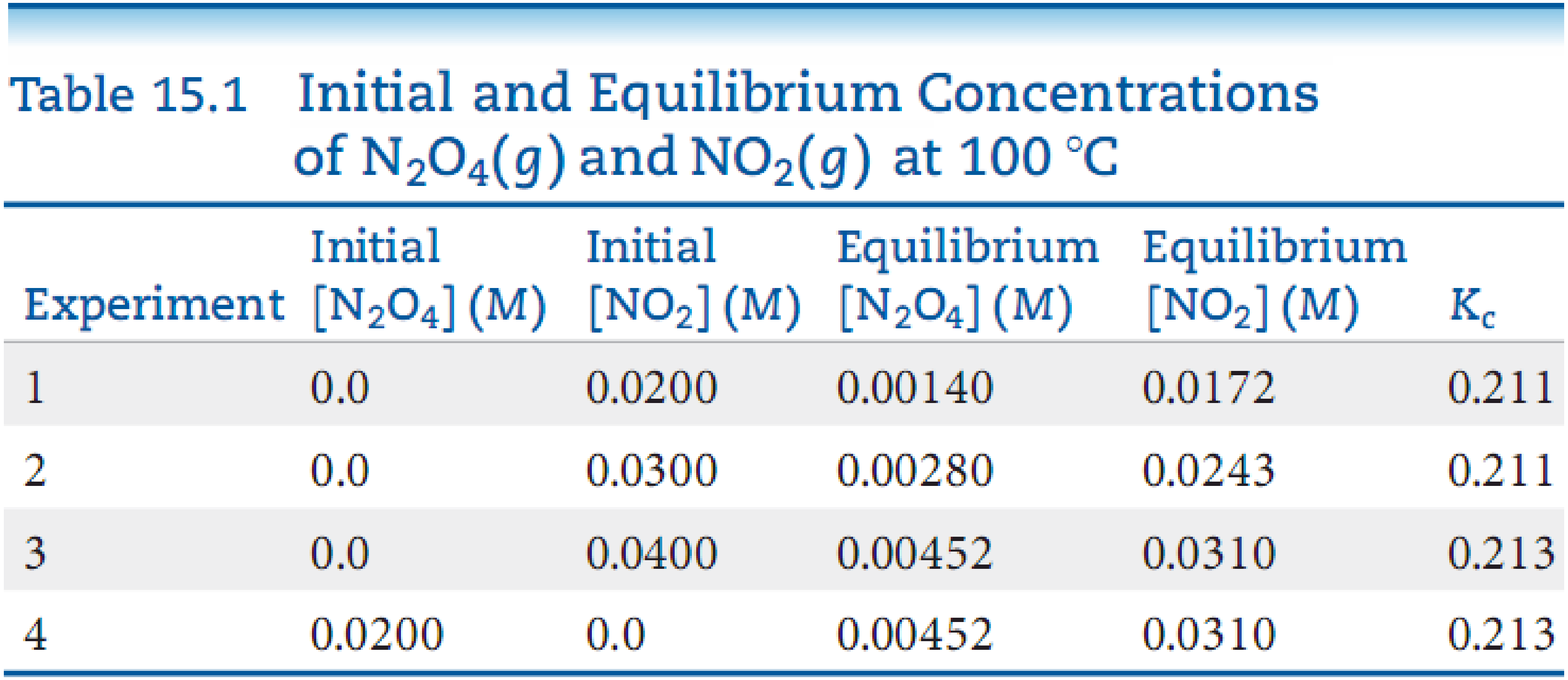
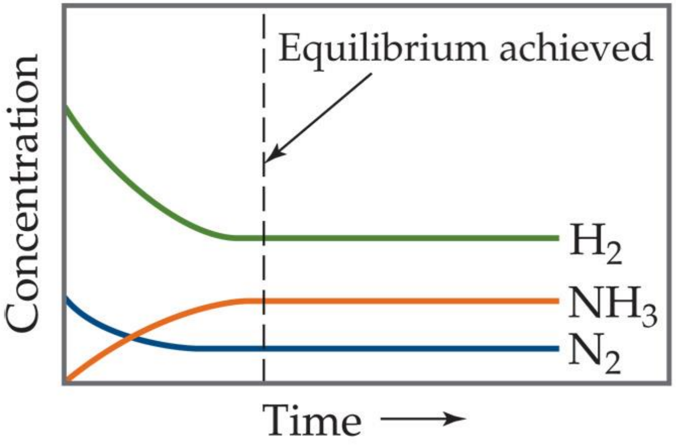


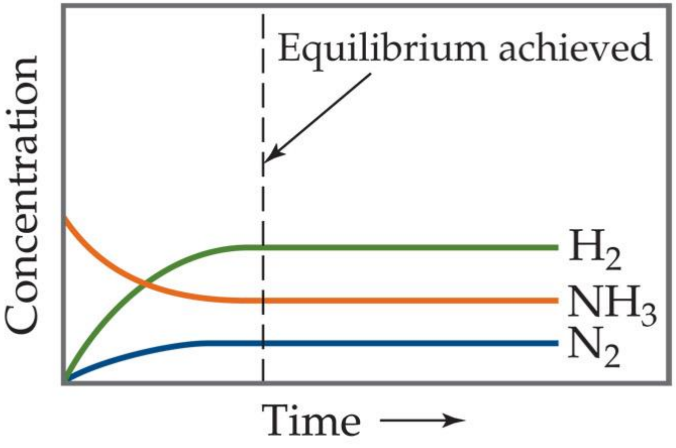
Table 15.1 Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

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 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.

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.

EXAMPLE

In the synthesis of ammonia from nitrogen and hydrogen,

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

$K_c = 9.60$ at 300°C, calculate K_p for this reaction at this temperature.

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

R = 0.08206 L.atm/mol.K

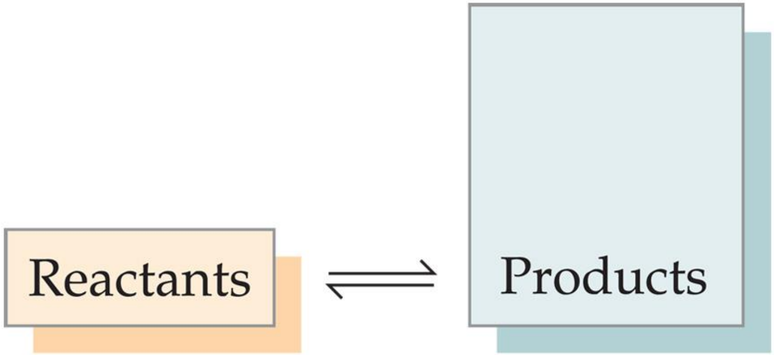
T= 300 + 273 = 573 K

2 mol of gaseous products (2 NH_3) and 4 mol of gaseous reactants (1 N_2 + 3 H_2)

$\Delta n = 2 - 4 = -2$

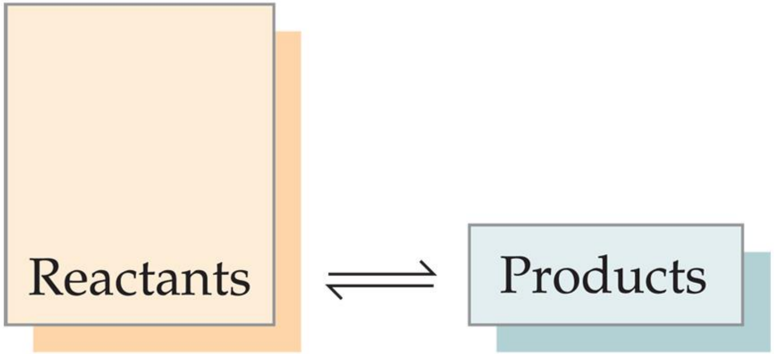
$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.08206 \times 573)^{-2} = 4.34 \times 10^{-3}$$

15-3 Understanding and Working with Equilibrium Constants



$K \gg 1$

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



$K \ll 1$

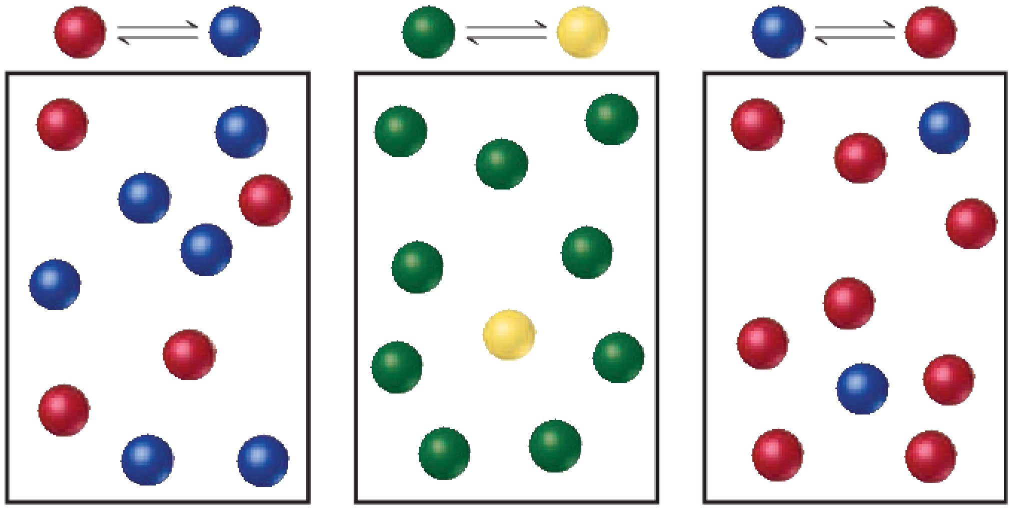
- If *K*<<1, the reaction is *reactant-favored*; reactant predominates at equilibrium.

EXAMPLE

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, K_c.

b) If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate K_c for each system.



(i) (ii) (iii)

a) **(ii) < (i) < (iii)**

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

(i) $K_c = 0.60/0.40 = 1.5$

(ii) $K_c = 0.10/0.90$

(iii) $K_c = 0.80/0.20 = 4.0$

Relating Chemical Equation Stoichiometry and Equilibrium Constants

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

$$\mathrm{A + B \rightleftharpoons C + D} \quad K_1$$

$$\mathrm{C + D \rightleftharpoons A + B} \quad K = 1/K_1$$

2. 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.

$$\mathrm{A + B \rightleftharpoons C + D} \qquad K_1$$

$$n\mathrm{A} + n\mathrm{B} \rightleftharpoons n\mathrm{C} + n\mathrm{D} \quad K = K_1^{\,n}$$

3. 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.

$$\begin{array}{ll} \mathrm{A + B \rightleftharpoons C + D} & K_1 \\ \mathrm{C + F \rightleftharpoons G + A} & K_2 \\ \hline \mathrm{B + F \rightleftharpoons D + G} & K_3 = (K_1)(K_2) \end{array}$$

Manipulating Equilibrium Constants

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

In the opposite direction:

$N_2O_{4\,(g)} \leftrightarrows 2\ NO_{2\,(g)}$

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$$

$2\ NO_{2\,(g)} \leftrightarrows N_2O_{4\,(g)}$

$$K_{eq} = \frac{[N_2O_4]}{[NO_2]^2} = 4.72$$

K_{eq} for these reactions are reciprocals of each other.

Manipulating Equilibrium Constants

2. 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.

$N_2O_{4(g)} \leftrightarrows 2\ NO_{2(g)}$ $$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$$

$2\ N_2O_{4(g)} \leftrightarrows 4\ NO_{2(g)}$ $$K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2$$

Manipulating Equilibrium Constants

3. 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.

$$1.\ 2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g) \quad K_{c1} = \frac{[NO]^2[Br_2]}{[NOBr]^2} = 0.014$$

$$2.\ Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_{c2} = \frac{[BrCl]^2}{[Br_2][Cl_2]} = 7.2$$

The net sum of these two equations is

$$2\,NOBr(g) + Cl_2(g) \rightleftharpoons 2\,NO(g) + 2\,BrCl(g)$$

$$K_{c3} = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]} = \frac{[NO]^2[Br_2]}{[NOBr]^2} \times \frac{[BrCl]^2}{[Br_2][Cl_2]}$$

$$K_{c3} = (K_{c1})(K_{c2}) = (0.014)(7.2) = 0.10$$

EXAMPLE

The equilibrium constant for the reaction of N_2 with O_2 to form NO equals $K_c = 1 \times 10^{-30}$ at 25°C.

$$N_{2(g)} + O_{2(g)} \leftrightarrows 2\,NO_{(g)}$$

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

$$2\,NO_{(g)} \leftrightarrows N_{2(g)} + O_{2(g)}$$

$$K_{c\text{ forward}} = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_{c\text{ reverse}} = \frac{[N_2][O_2]}{[NO]^2}$$

$$K_{c\text{ reversed}} = 1/K_{c\text{ forward}} = 1/(1 \times 10^{-30}) = 10^{30}$$

EXAMPLE

Given the following information,

$HF_{(aq)} \leftrightarrows H^{+}_{(aq)} + F^{-}_{(aq)}$ $K_c = 6.8 \text{ x } 10^{-4}$

$H_2C_2O_{4(aq)} \leftrightarrows 2\,H^{+}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)}$ $K_c = 3.8 \text{ x } 10^{-6}$

determine the value of K_c for the following reaction:

$2\,HF_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \leftrightarrows 2\,F^{-}_{(aq)} + H_2C_2O_{4(aq)}$

$2HF_{(aq)} \leftrightarrows 2H^{+}_{(aq)} + 2\,F^{-}_{(aq)}$ $K_c = (6.8 \text{ x } 10^{-4})^2 = 4.6 \text{ x} 10^{-7}$

$2\,H^{+}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \leftrightarrows H_2C_2O_{4(aq)}$ $K_c = (3.8 \text{ x } 10^{-6})^{-1} = 2.6 \text{ x} 10^{5}$

$2\,HF_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \leftrightarrows 2\,F^{-}_{(aq)} + H_2C_2O_{4(aq)}$

$Kc = (4.6 \text{ x} 10^{-7})(2.6 \text{ x} 10^{5}) = 0.12$

15-4 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**.

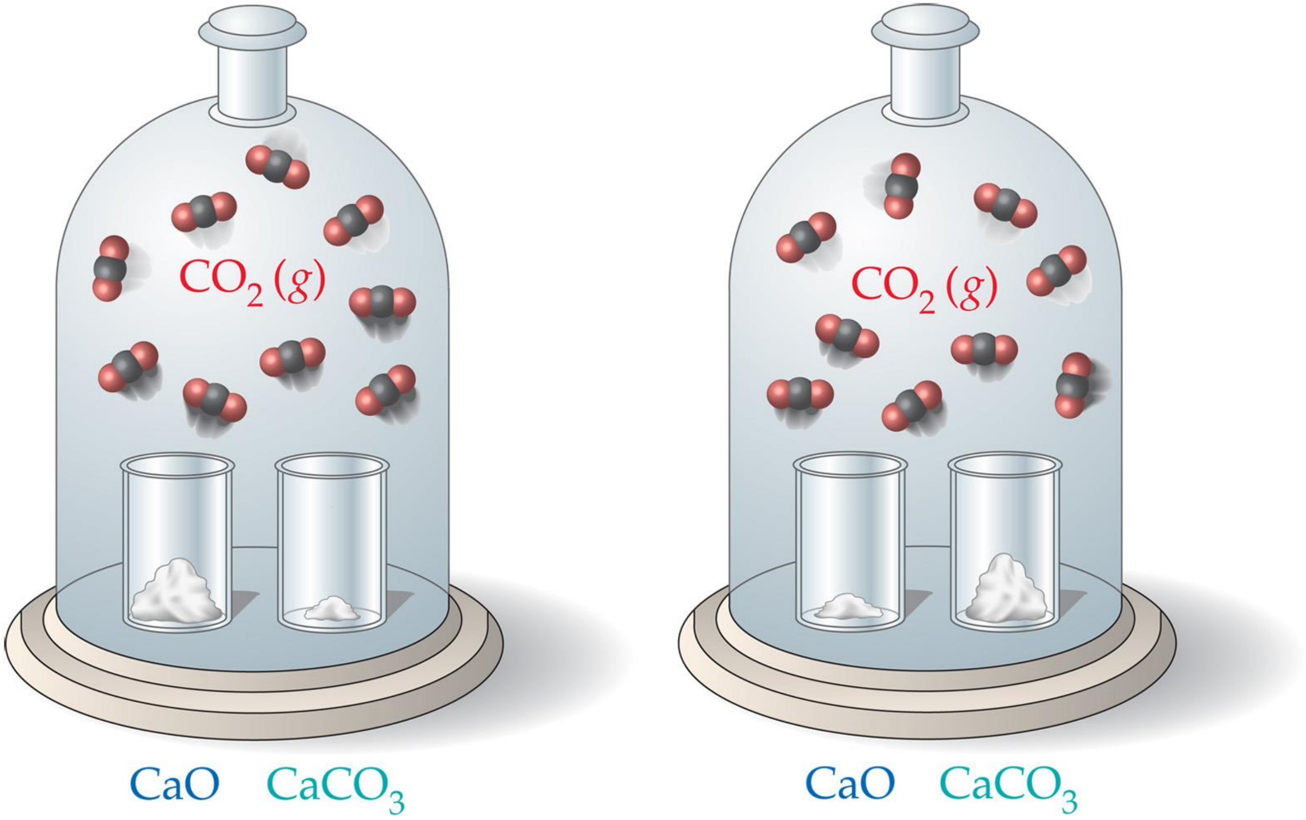
$$PbCl_{2(s)} \leftrightarrows Pb^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)}$$

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

Whenever a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium constant expression

Heterogeneous Equilibria
Pure solids & gases

$$CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}$$



At a given temperature, the equilibrium pressure of CO_2 in the bell jars is the same no matter how much of each solid is present

$$K_c = [CO_2] \text{ and } K_p = P_{CO2}$$

Heterogeneous Equilibria
Low solute concentration

Systems where the solvent is involved as a reactant or product and the solutes are present at **low** concentrations.

e.g. dissociation of a weak acid

$$H_2O_{(l)} + CO_3^{2-}{}_{(aq)} \leftrightarrows OH^-{}_{(aq)} + HCO_3^-{}_{(aq)}$$

$$K_c = [OH^-][HCO_3^-] / [CO_3^{2-}]$$

EXAMPLE

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

a) $CO_{2(g)} + H_{2(g)} \leftrightarrows CO_{(g)} + H_2O_{(l)}$

$$K_c = \frac{[CO]}{[CO_2][H_2]}$$

b) $SnO_{2(s)} + 2\ CO_{(g)} \leftrightarrows Sn_{(s)} + 2\ CO_{2(g)}$

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

EXAMPLE

Each of these mixtures was placed in a closed container and allowed to stand:

(a) $CaCO_3(s)$

(b) $CaO(s)$ and CO_2 (g) at a pressure greater than the value of Kp

(c) $CaCO_3$ (s) and CO_2 (g) at a pressure greater than the value of Kp

(d) $CaCO_3$ (s) and CaO (s)

Determine whether or not each mixture can attain the equilibrium

$$CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}$$

$$K_p = P_{CO2}$$

(a) $CaCO_3$ simply decomposes, forming CaO(s) and CO_2 (g) until the equilibrium pressure of CO_2 is attained. There must be enough $CaCO_3$, however, to allow the CO_2 pressure to reach equilibrium.

(b) CO_2 continues to combine with CaO until the partial pressure of the CO_2 decreases to the equilibrium value.

(c) Because there is no CaO present, equilibrium cannot be attained; there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some CO2 to react with CaO).

(d) The situation is essentially the same as in (a)

15-5 Calculating Equilibrium Constants Using ICE charts

An ICE Chart should be used when we are **missing more than one** equilibrium amount for compounds in our balanced equation.

I = initial concentrations (or pressures) for each species
C = change in the concentrations (or pressures) for each species
E = equilibrium concentrations (or pressures)

K_c ← **M** **atm** → **K_p**

$$2\,NO\,(g) + Br_2\,(l) \rightleftharpoons 2\,NOBr\,(g)$$

Initial	0.10 M or atm		0
Change	– 2 x		+ 2 x
Equilibrium	0.10 – 2 x		+ 2 x

Equilibrium Calculations

Often, we do not know the equilibrium concentrations of all species in an equilibrium mixture. If we know the initial concentrations and the equilibrium concentration of at least one species, then:

1. ***Tabulate all known initial and equilibrium concentrations*** of the species that appear in the equilibrium-constant expression.
2. For those species for which initial and equilibrium concentrations are known, ***calculate the change in concentration*** that occurs as the system reaches equilibrium.
3. Use the stoichiometry of the reaction (that is, the coefficients in the balanced chemical equation) to ***calculate the changes in concentration for all other species*** in the equilibrium-constant expression.
4. Use initial concentrations from step 1 and changes in concentration from step 3 to ***calculate any equilibrium concentrations not tabulated*** in step 1.
5. ***Determine the value of the equilibrium constant***.

EXAMPLE

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

$$H_{2(g)} + I_{2(g)} \leftrightarrows 2\ HI_{(g)}$$

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\ HI(g)$
Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)	**-x**	**-x**	**+2x**
Equilibrium concentration (*M*)	$1.000*10^{-3} - x$	$2.000*10^{-3} - x$	1.87×10^{-3}

$$+2x = 1.87*10^{-3}$$

$$x = 1.87*10^{-3}/2 = 9.35*10^{-3}$$

$$[H_2] = 1.000 \times 10^{-3}\,M - 0.935 \times 10^{-3}\,M = 0.065 \times 10^{-3}\,M$$

$$[I_2] = 2.000 \times 10^{-3}\,M - 0.935 \times 10^{-3}\,M = 1.065 \times 10^{-3}\,M$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

15-6 Applications of Equilibrium

- Predicting the Direction of Reaction
- Calculating Equilibrium Concentrations

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 of reactants and products into the equilibrium expression.

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

The Reaction Quotient

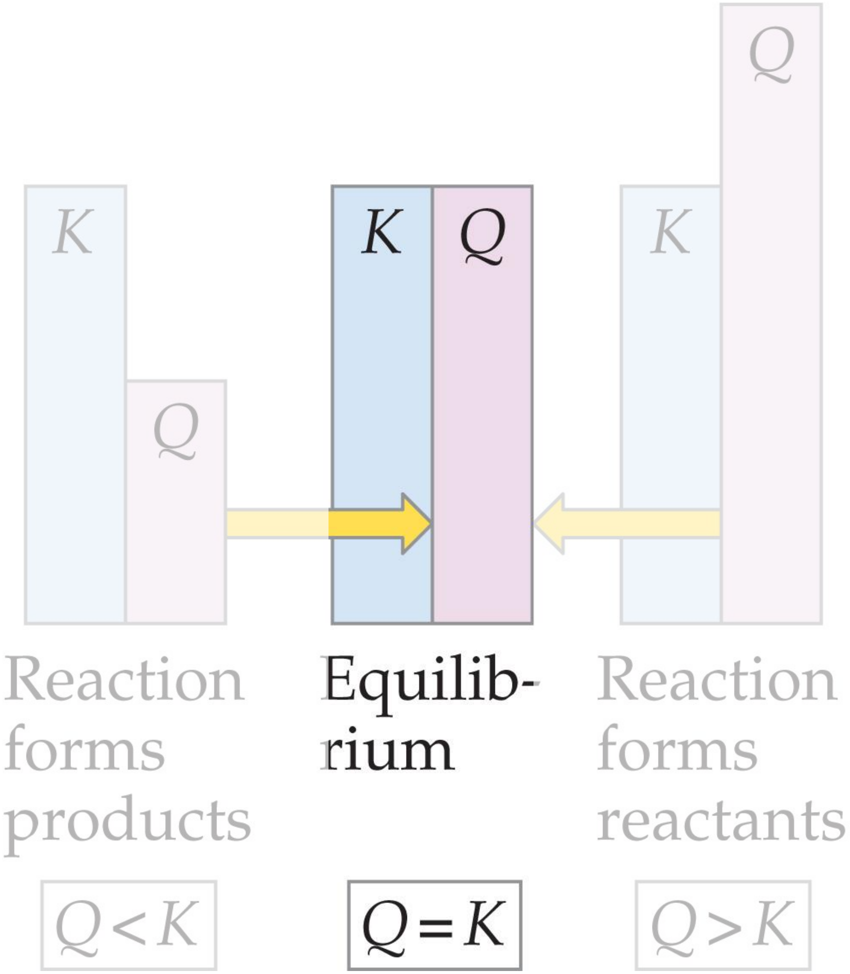
- Note: $Q = K_{eq}$ only at equilibrium.
- If $Q < K_{eq}$ then the forward reaction must occur to reach equilibrium.
- If $Q > K_{eq}$ then the reverse reaction must occur to reach equilibrium.

  Products are consumed, reactants are formed.

  Q decreases until it equals K_{eq}.

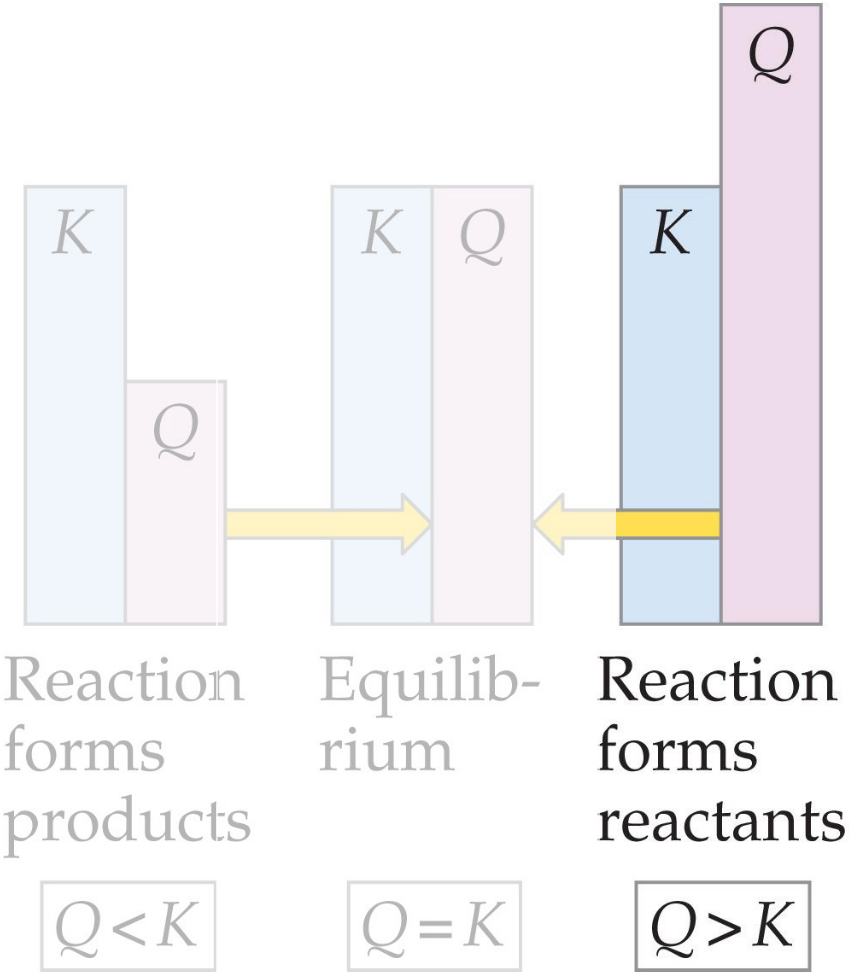
If $Q = K$,

The system is at equilibrium.



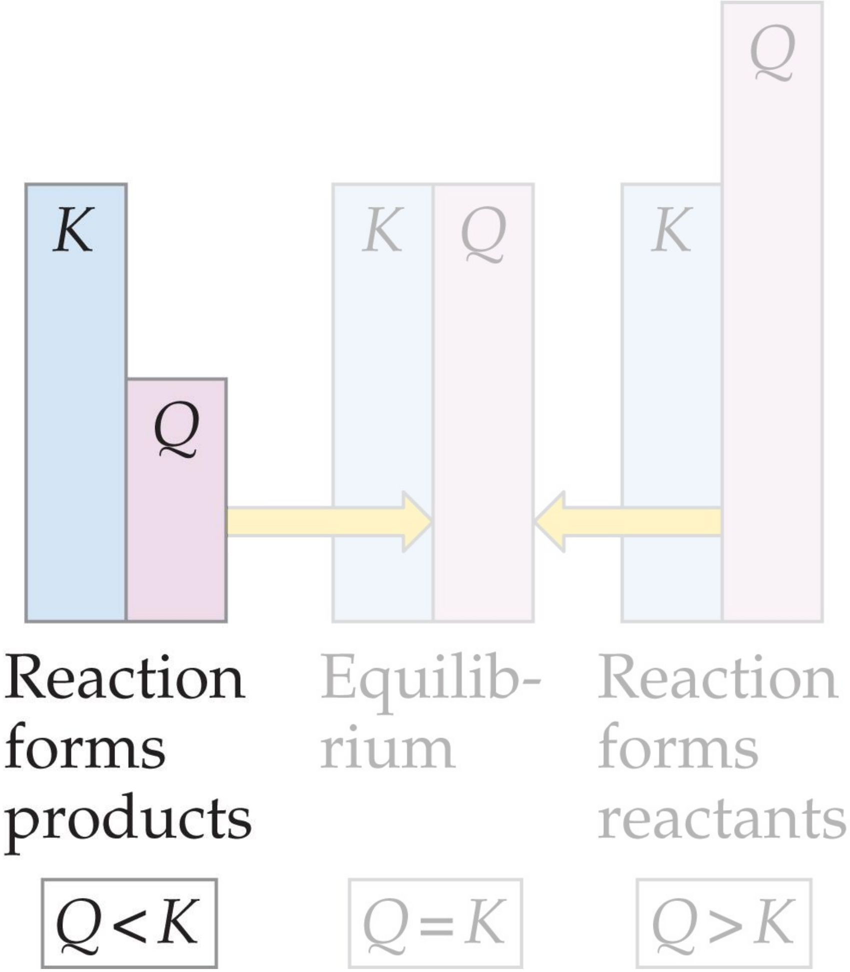
If $Q > K$,

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

At 448°C the equilibrium constant, K_c, for the reaction

$$H_{2(g)} + I_{2(g)} \rightarrow 2\,HI_{(g)}$$

is 50.5.

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.

The initial concentrations are

$$[HI] = 2.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 1.0 \times 10^{-2}\ M$$

$$[H_2] = 1.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 5.0 \times 10^{-3}\ M$$

$$[I_2] = 3.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 1.5 \times 10^{-2}\ M$$

The reaction quotient is therefore

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

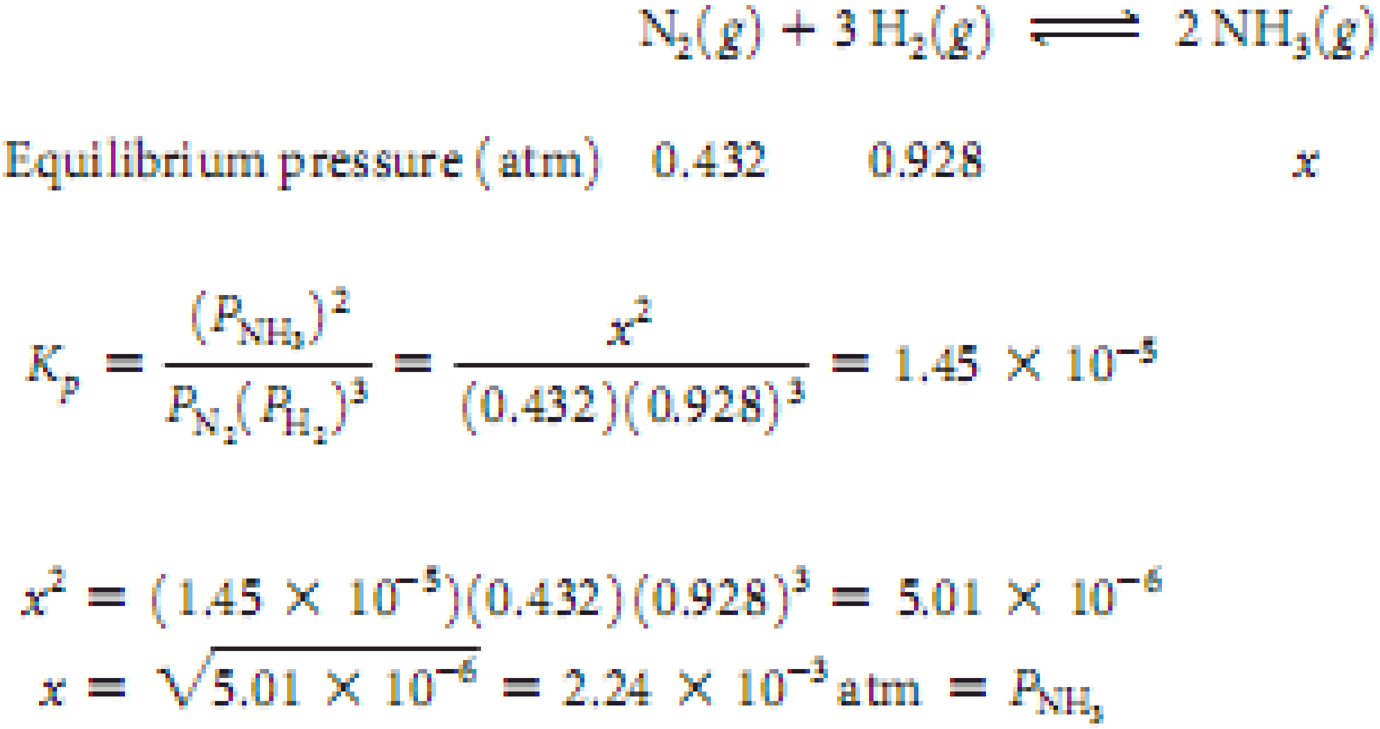
Because $Q_c < K_c$, the reaction proceeds left to right to attain equilibrium

EXAMPLE

For the Haber process,

$$N_{2(g)} + 3\,H_{2(g)} \leftrightarrows 2\,NH_{3(g)},\ K_p = 1.45 \times 10^{-5} \text{ at } 500^{o}C.$$

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?



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

	$N_2(g)$	$3\,H_2(g)$	$2\,NH_3(g)$
Equilibrium pressure (atm)	0.432	0.928	x

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

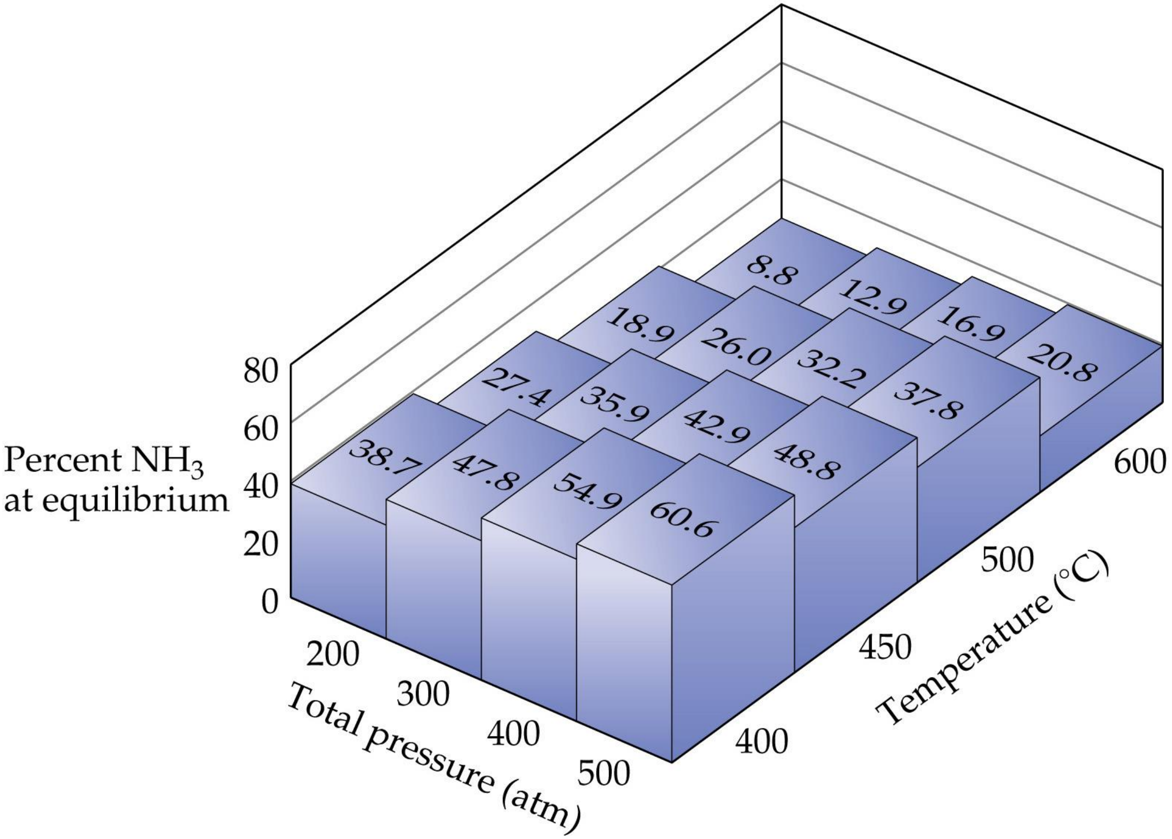
$$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3}\,\text{atm} = P_{NH_3}$$

15-7 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

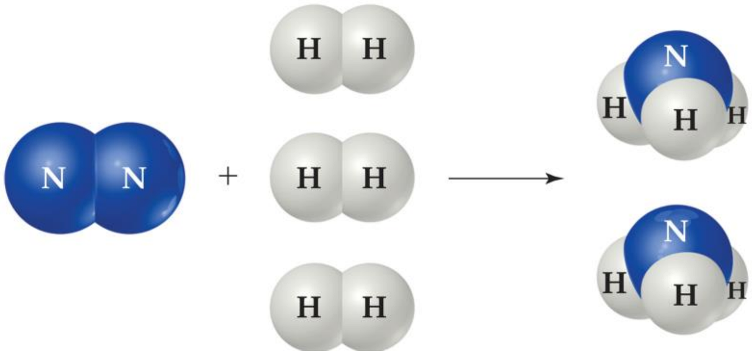


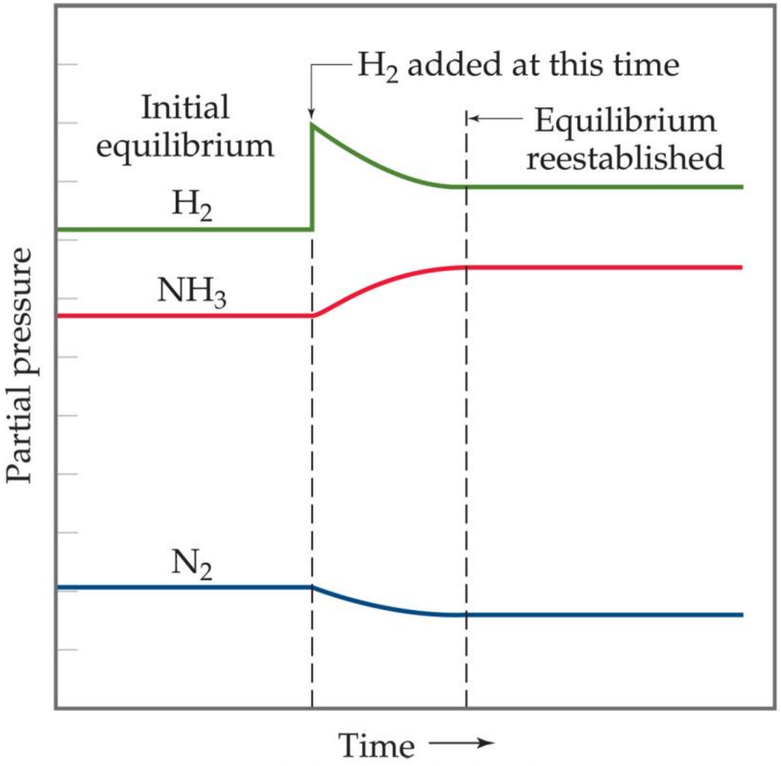
As P increases, the amount of ammonia present at equilibrium increases.
As T increases, the amount of ammonia at equilibrium decreases.

Can this be predicted?

The Haber Process

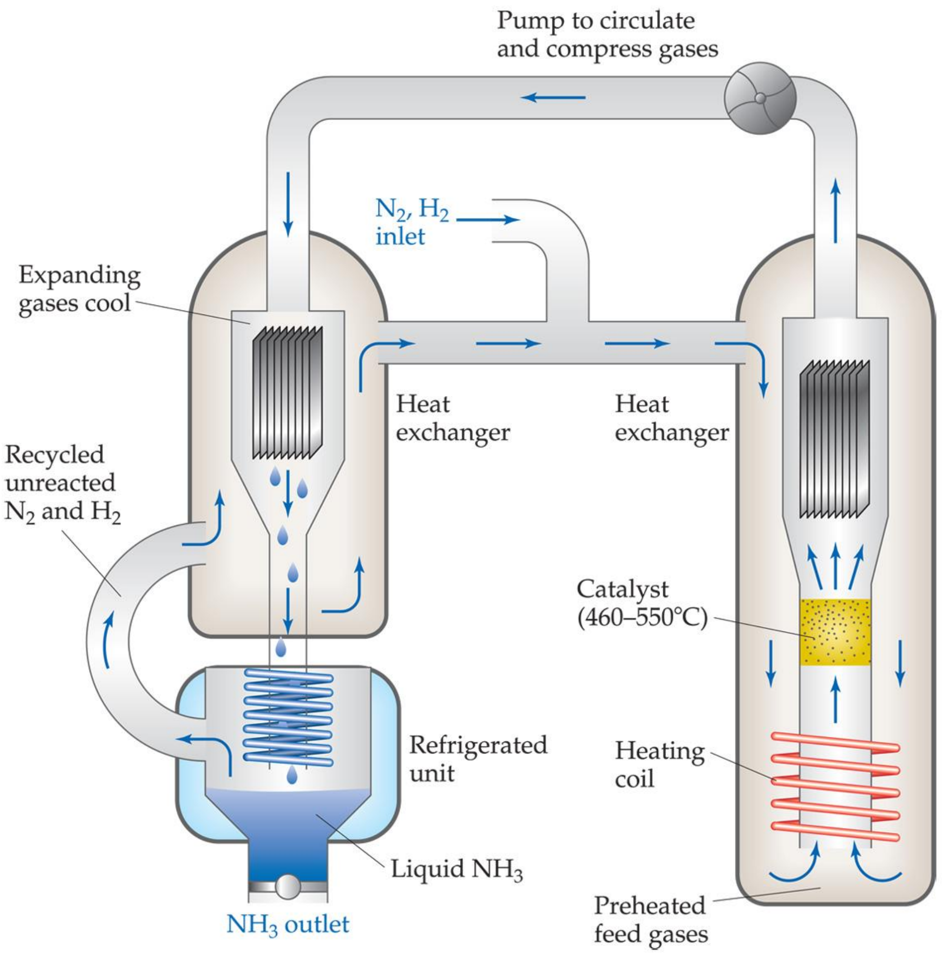
The transformation of nitrogen and hydrogen into ammonia (NH_3) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.





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.

Effects of Volume and Pressure Changes

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.

Effects of Volume and Pressure Changes

- 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.

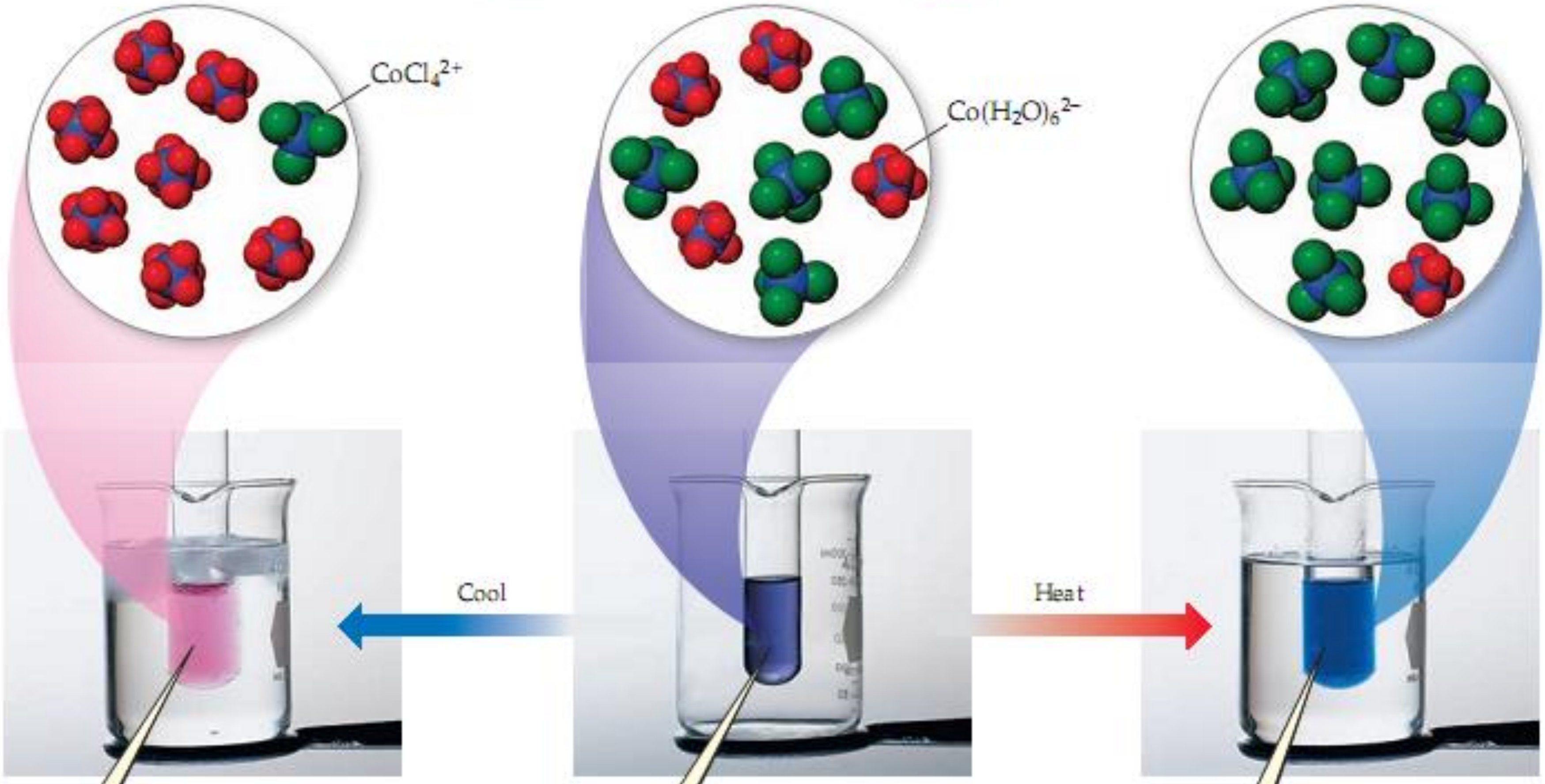
- No change will occur if we increase the total gas pressure by the addition of a gas that is not involved in the reaction.

The Effect of Changes in Temperature

$\Delta H > 0$, endothermic reaction

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

Pink　　Blue



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.

The Effect of Changes in Temperature

Endothermic: Reactants + heat → products
Exothermic: Reactants → products + heat

When 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 (or product), namely heat.

EXAMPLE

Consider the following equilibrium:

$$N_2O_{4(g)} \leftrightarrows 2\ NO_{2(g)} \qquad \Delta H^o = 58.0\ kJ$$

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

a) add N_2O_4 →

b) remove NO_2 →

c) increase the total pressure by adding $N_{2(g)}$ No shift

d) increase the volume →

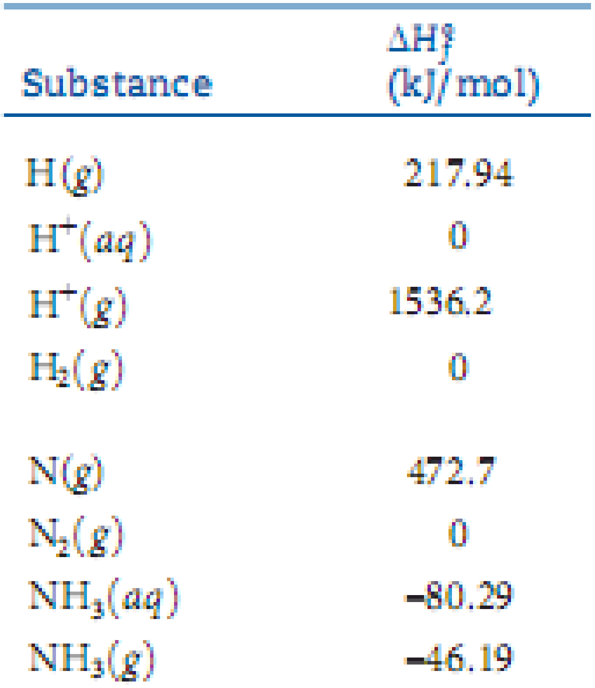
e) decrease the temperature? ←

EXAMPLE

a) Using the standard heat of formation, determine the standard enthalpy change for the reaction

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

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



Substance	ΔH_f° (kJ/mol)
$H(g)$	217.94
$H^+(aq)$	0
$H^+(g)$	1536.2
$H_2(g)$	0
$N(g)$	472.7
$N_2(g)$	0
$NH_3(aq)$	−80.29
$NH_3(g)$	−46.19

a)

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

0 0 2 mol x -46.19 kJ/mol

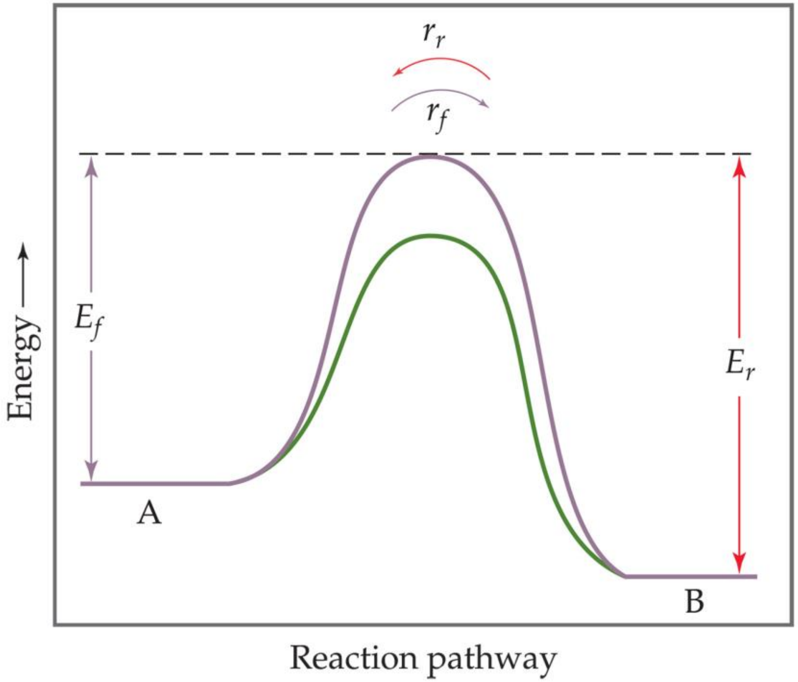
ΔH_{rctn} = - 92.38 kJ/mol

b) Because the reaction in the forward direction is exothermic, we can consider heat a product of the reaction. An increase in temperature causes the reaction to shift in the direction of less NH_3 and more N_2 and H_2.

TABLE 15.2 ■ Variation in K_p for the Equilibrium $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$ as a Function of Temperature

Temperature (°C)	K_p
300	4.34×10^{-3}
400	1.64×10^{-4}
450	4.51×10^{-5}
500	1.45×10^{-5}
550	5.38×10^{-6}
600	2.25×10^{-6}

The Effect of Catalysts



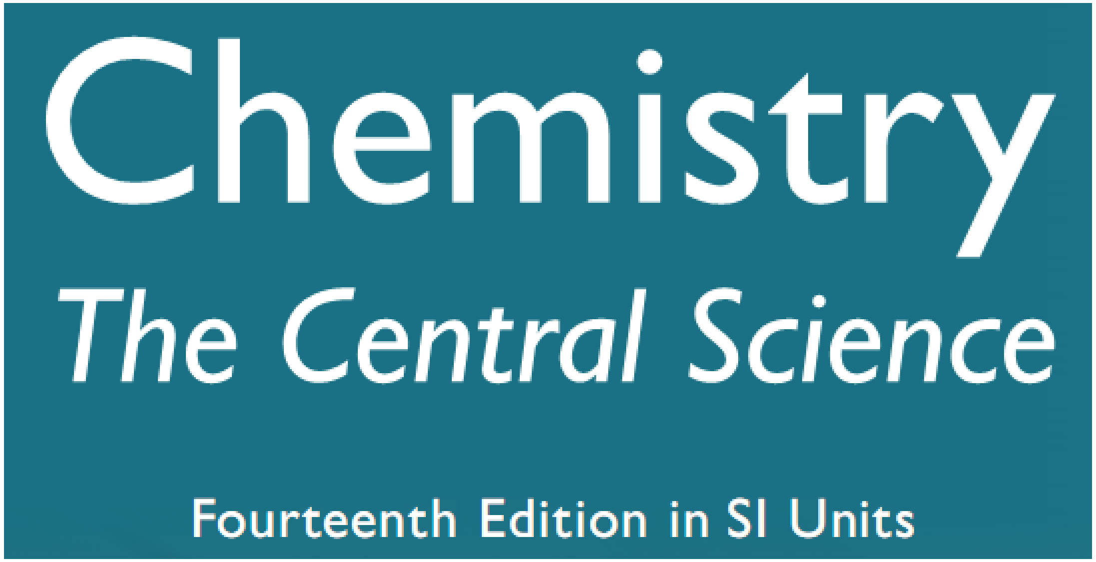
- Catalysts increase the rate of both the forward *and* reverse reactions.
- When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.

Homeworks

15.93

15.94

Due: August 7th 2019



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