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Ninth  
Edition

# GENERAL CHEMISTRY

Principles and Modern Applications



## Chapter 15: Principles of Chemical Equilibrium

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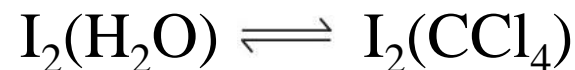
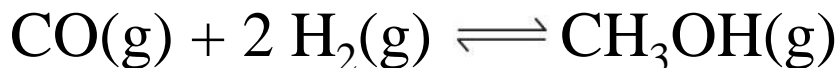
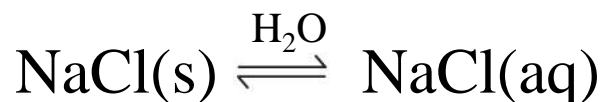
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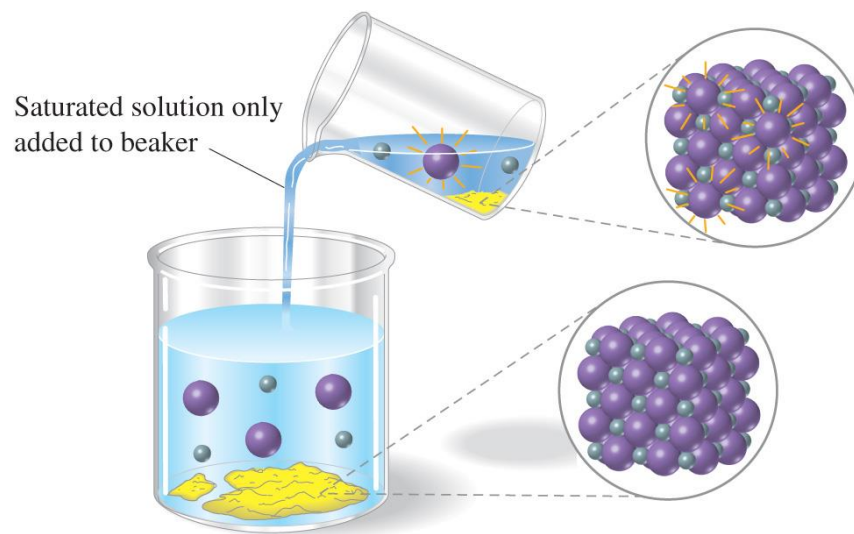
➤ *Focus On The Nitrogen Cycle and the Synthesis of Nitrogen Compounds*

# 15-1 Dynamic Equilibrium

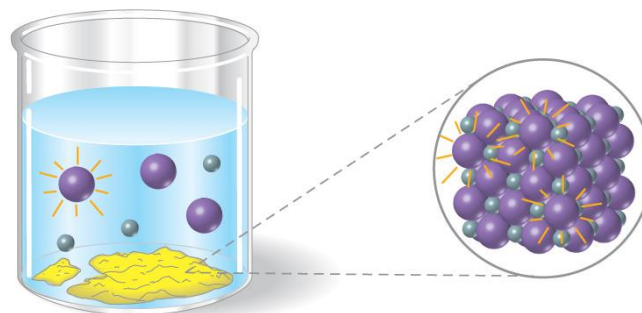
- ◆ Equilibrium – two opposing processes taking place at equal rates.



# Dynamic Equilibrium



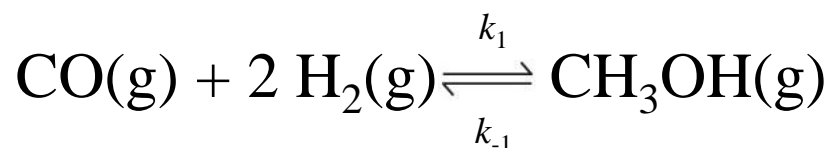
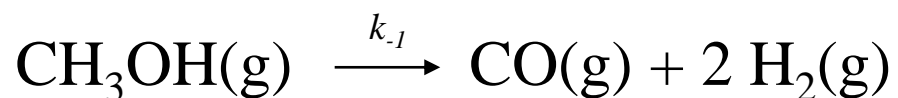
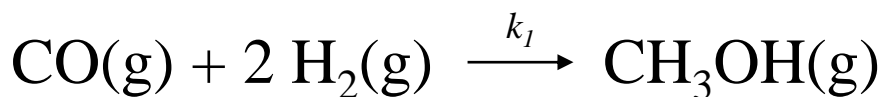
(a)



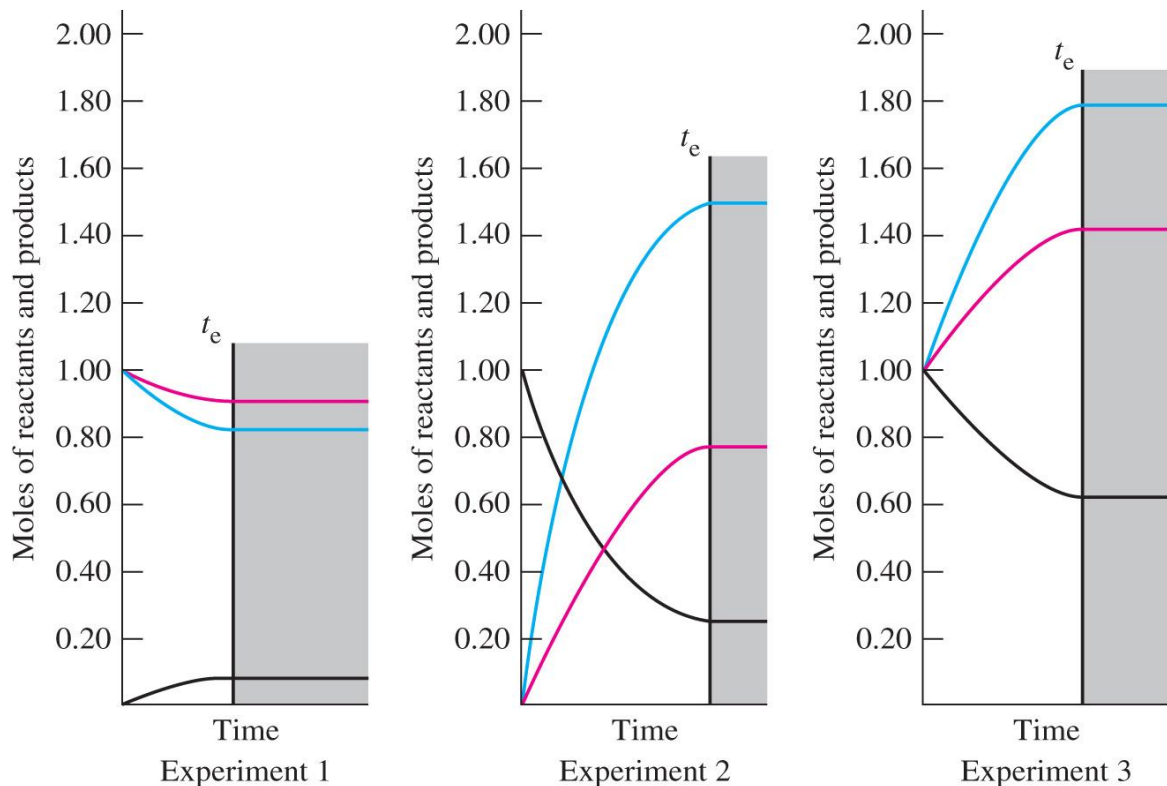
(b)

## 15-2 The Equilibrium Constant Expression

- ◆ Methanol synthesis is a reversible reaction.



# Three Approaches to the Equilibrium



$t_e$  = time for equilibrium to be reached

— mol CO

— mol  $H_2$

— mol  $CH_3OH$

**TABLE 15.1 Three Approaches to Equilibrium in the Reaction<sup>a</sup>**  
 $\text{CO(g)} + 2 \text{H}_2\text{(g)} \rightleftharpoons \text{CH}_3\text{OH(g)}$

	CO(g)	H <sub>2</sub> (g)	CH <sub>3</sub> OH(g)
<b>Experiment 1</b>			
Initial amounts, mol	1.000	1.000	0.000
Equilibrium amounts, mol	0.911	0.822	0.0892
Equilibrium concentrations, mol/L	0.0911	0.0822	0.00892
<b>Experiment 2</b>			
Initial amounts, mol	0.000	0.000	1.000
Equilibrium amounts, mol	0.753	1.506	0.247
Equilibrium concentrations, mol/L	0.0753	0.151	0.0247
<b>Experiment 3</b>			
Initial amounts, mol	1.000	1.000	1.000
Equilibrium amounts, mol	1.380	1.760	0.620
Equilibrium concentrations, mol/L	0.138	0.176	0.0620
The concentrations printed in blue are used in the calculations in Table 15.2.			
<sup>a</sup> Reaction carried out in a 10.0-L flask at 483 K.			



# Three Approaches to Equilibrium

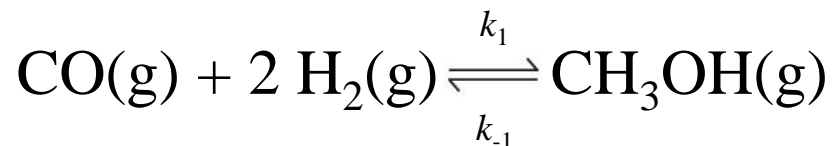


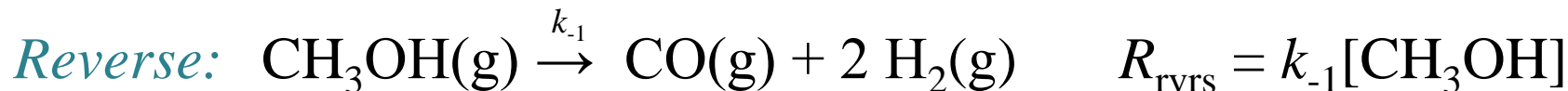
TABLE 15.2

Expt	Trial 1: $\frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]}$	Trial 2: $\frac{[\text{CH}_3\text{OH}]}{[\text{CO}](2 \times [\text{H}_2])}$	Trial 3: $\frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$
1	$\frac{0.00892}{0.0911 \times 0.0822} = 1.19$	$\frac{0.00892}{0.0911 \times (2 \times 0.0822)} = 0.596$	$\frac{0.00892}{0.0911 \times (0.0822)^2} = 14.5$
2	$\frac{0.0247}{0.0753 \times 0.151} = 2.17$	$\frac{0.0247}{0.0753 \times (2 \times 0.151)} = 1.09$	$\frac{0.0247}{0.0753 \times (0.151)^2} = 14.4$
3	$\frac{0.0620}{0.138 \times 0.176} = 2.55$	$\frac{0.0620}{0.138 \times (2 \times 0.176)} = 1.280$	$\frac{0.0620}{0.138 \times (0.176)^2} = 14.5$

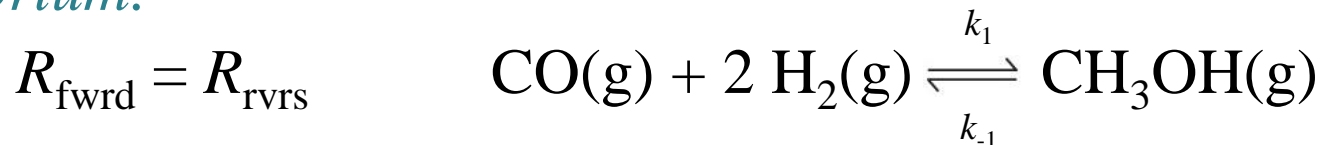
Equilibrium concentration data are from Table 15.1. In Trial 1, the equilibrium concentration of CH<sub>3</sub>OH is placed in the numerator and the product of the equilibrium concentrations, [CO][H<sub>2</sub>], in the denominator. In Trial 2, each concentration is multiplied by its stoichiometric coefficient. In Trial 3, each concentration is raised to a power equal to its stoichiometric coefficient. Trial 3 has essentially the same value for each experiment. This value is the equilibrium constant  $K_c$ .



# The Equilibrium Constant Expression



*At Equilibrium:*



$$k_1[\text{CO}][\text{H}_2]^2 = k_{-1}[\text{CH}_3\text{OH}]$$

$$\frac{k_1}{k_{-1}} = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = K_c$$

# The Equilibrium Constant and Activities

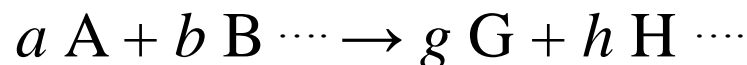
## ◆ Activity

- Thermodynamic concept introduced by Lewis.
- Dimensionless ratio referred to a chosen reference state.

$$a_B = \frac{[B]}{c_B^0} = \gamma_B[B] \quad c_B^0 \text{ is a standard reference state} \\ = 1 \text{ mol L}^{-1} \text{ (ideal conditions)}$$

- Accounts for non-ideal behaviour in solutions and gases.
- An *effective* concentration.

# General Expressions



$$\text{Equilibrium constant} = K_c = \frac{[G]^g[H]^h \cdots}{[A]^m[B]^n \cdots}$$

Thermodynamic

$$\text{Equilibrium constant} = K_{\text{eq}} = \frac{(a_G)^g(a_H)^h \cdots}{(a_A)^a(a_B)^b \cdots}$$

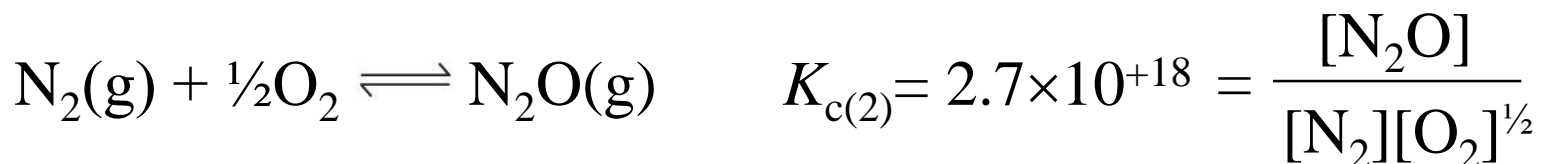
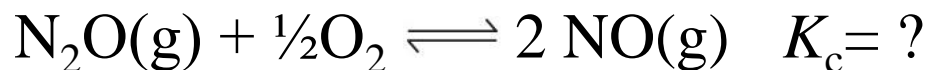
$$= \left( \frac{[G]^g[H]^h \cdots}{[A]^m[B]^n \cdots} \right) \times \left( \frac{(\gamma_G)^g(\gamma_H)^h \cdots}{(\gamma_A)^a(\gamma_B)^b \cdots} \right)$$

$\approx 1$   
under ideal conditions

## 15-3 Relationships Involving the Equilibrium Constant

- ◆ Reversing an equation causes inversion of  $K$ .
- ◆ Multiplying by coefficients by a common factor raises the equilibrium constant to the corresponding power.
- ◆ Dividing the coefficients by a common factor causes the equilibrium constant to be taken to that root.

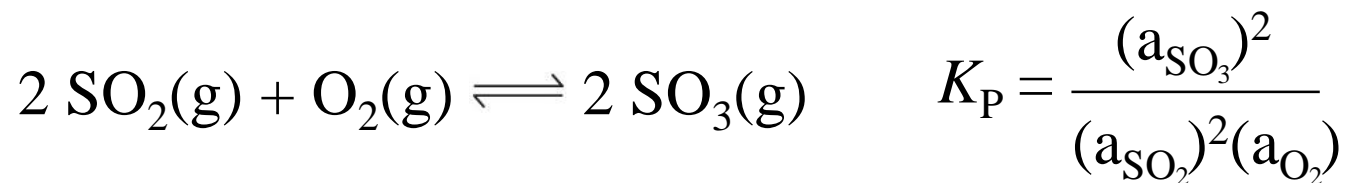
# Combining Equilibrium Constant Expressions



$$K_{\text{c}} = \frac{[\text{NO}]^2}{[\text{N}_2\text{O}][\text{O}_2]^{1/2}} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \frac{[\text{N}_2][\text{O}_2]^{1/2}}{[\text{N}_2\text{O}]} = K_{\text{c}(3)} \frac{1}{K_{\text{c}(2)}} = 1.7 \times 10^{-13}$$

# Gases: The Equilibrium Constant, $K_P$

- ◆ Mixtures of gases are solutions just as liquids are.
- ◆ Use  $K_P$ , based upon *activities* of gases.



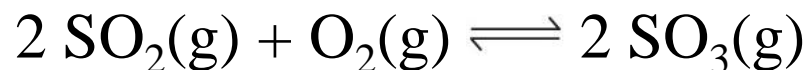
$$a_{\text{SO}_3} = \frac{P_{\text{SO}_3}}{P^\circ} \quad a_{\text{SO}_2} = \frac{P_{\text{SO}_2}}{P^\circ} \quad a_{\text{O}_2} = \frac{P_{\text{O}_2}}{P^\circ}$$

$$K_P = \left( \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})} \right) P^\circ$$



# Gases: The Equilibrium Constant, $K_C$

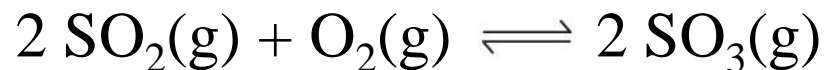
- ◆ In *concentration* we can do another substitution



$$[\text{SO}_3] = \frac{n_{\text{SO}_3}}{V} = \frac{P_{\text{SO}_3}}{RT} \quad [\text{SO}_2] = \frac{P_{\text{SO}_2}}{RT} \quad [\text{O}_2] = \frac{P_{\text{O}_2}}{RT}$$

$$(a_X) = \frac{[X]}{c^\circ} = \frac{\frac{P_X}{RT}}{c^\circ} \quad P_X = [X] RT$$

# Gases: The Equilibrium Constant, $K_C$

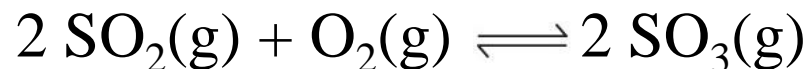


$$K_P = \frac{(a_{\text{SO}_3})^2}{(a_{\text{SO}_2})^2(a_{\text{O}_2})} = P^\circ \left( \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})} \right) \quad P_X = [X] RT$$

$$= \left( \frac{([\text{SO}_3] RT)^2}{([\text{SO}_2] RT)^2([\text{O}_2] RT)} \right) P^\circ$$

$$= \frac{P^\circ}{RT} \left( \frac{([\text{SO}_3])^2}{([\text{SO}_2])^2([\text{O}_2])} \right) = \frac{K_C}{RT} \quad \text{Where } P^\circ = 1 \text{ bar}$$

# An Alternative Derivation



$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2]^2[\text{O}_2]} = \frac{\left(\frac{P_{\text{SO}_3}}{RT}\right)^2}{\left(\frac{P_{\text{SO}_2}}{RT}\right)^2 \frac{P_{\text{O}_2}}{RT}} = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} RT$$

Where  $P^\circ = 1 \text{ bar}$

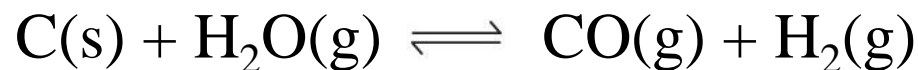
$$K_c = K_p(RT)$$

$$K_p = K_c(RT)^{-1}$$

In general terms:  $K_p = K_c(RT)^{\Delta n}$

# Pure Liquids and Solids

- ◆ Equilibrium constant expressions do not contain concentration terms for solid or liquid phases of a single component (that is, pure solids or liquids).



$$K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]^2} = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}^2} (RT)^1$$

# Burnt Lime



$$K_c = [\text{CO}_2]$$

$$K_p = P_{\text{CO}_2}(RT)$$



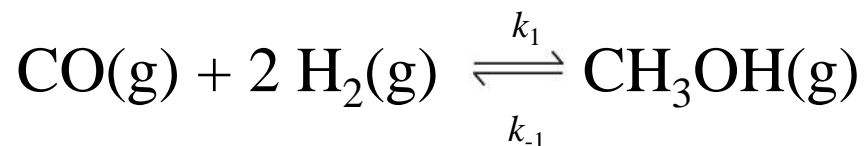
# 15-4 The Significance of the Magnitude of the Equilibrium Constant.

**TABLE 15.3** Equilibrium Constants of Some Common Reactions

Reaction	Equilibrium constant, $K_p$
$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$	$1.4 \times 10^{83}$ at 298 K
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	$1.9 \times 10^{-23}$ at 298 K 1.0 at about 1200 K
$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$	3.4 at 1000 K
$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$	$1.6 \times 10^{-21}$ at 298 K 10.0 at about 1100 K



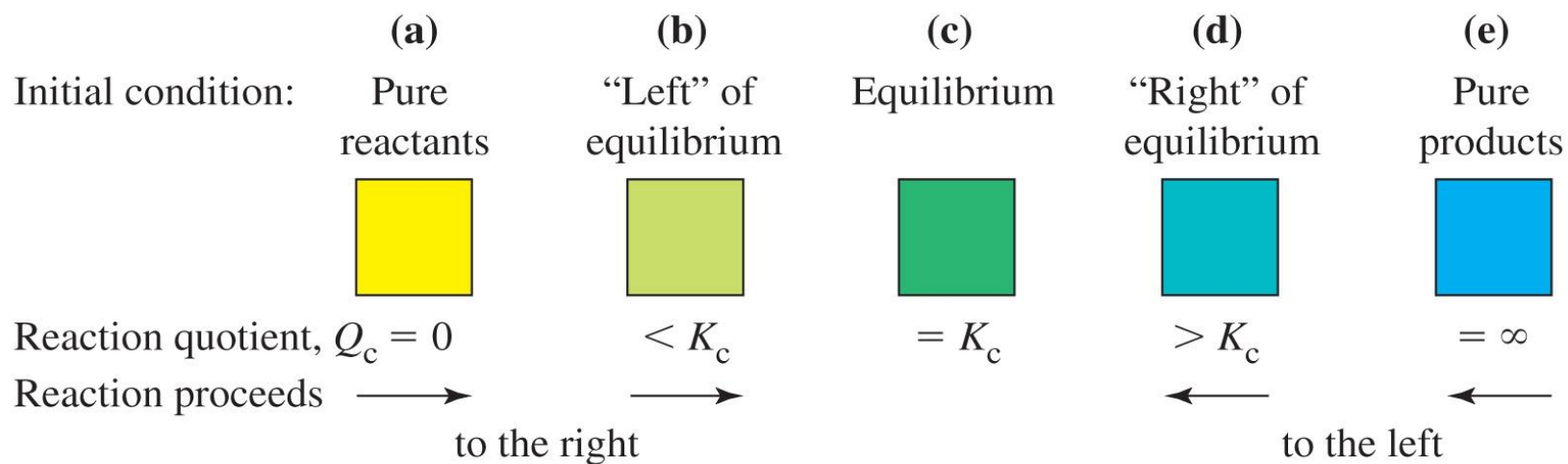
## 15-5 The Reaction Quotient, $Q$ : Predicting the Direction of Net Change.



- ◆ Equilibrium can be approached various ways.
- ◆ Qualitative determination of change of initial conditions as equilibrium is approached is needed.

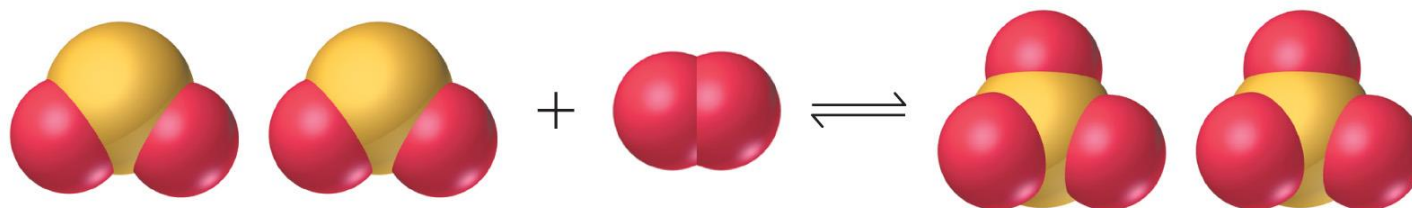
$$Q_c = \frac{[\text{G}]_t^g [\text{H}]_t^h}{[\text{A}]_t^m [\text{B}]_t^n} \quad \text{At equilibrium } Q_c = K_c$$

# Reaction Quotient



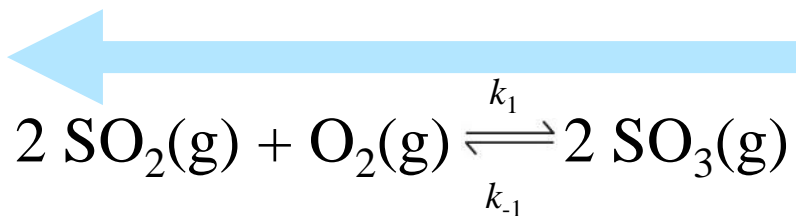
## 15-6 Altering Equilibrium Conditions: Le Châtelier's Principle

- ◆ When an equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that *partially* offsets the impact of the change.

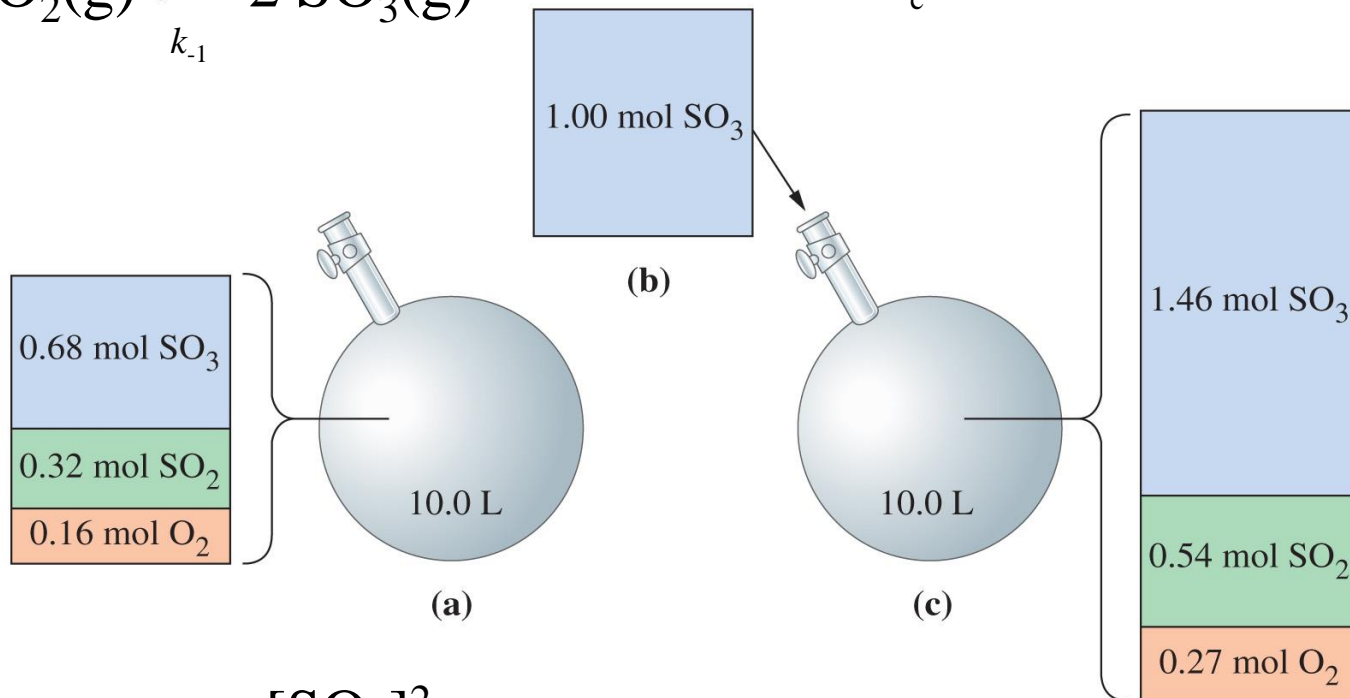


What happens if we add  $\text{SO}_3$  to this equilibrium?

# Le Châtelier's Principle



$$K_c = 2.8 \times 10^2 \text{ at } 1000\text{K}$$



$$Q = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = K_c$$

$$Q > K_c$$

# Effect of Condition Changes

- ◆ Adding a gaseous reactant or product changes  $P_{\text{gas}}$ .
- ◆ Adding an inert gas changes the total pressure.
  - Relative partial pressures are unchanged.
- ◆ Changing the volume of the system causes a change in the equilibrium position.

$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2]^2[\text{O}_2]} = \frac{\left(\frac{n_{\text{SO}_3}}{V}\right)^2}{\left(\frac{n_{\text{SO}_2}}{V}\right)^2 \frac{n_{\text{O}_2}}{V}} = \frac{n_{\text{SO}_3}^2}{n_{\text{SO}_2}^2 n_{\text{O}_2}} V$$

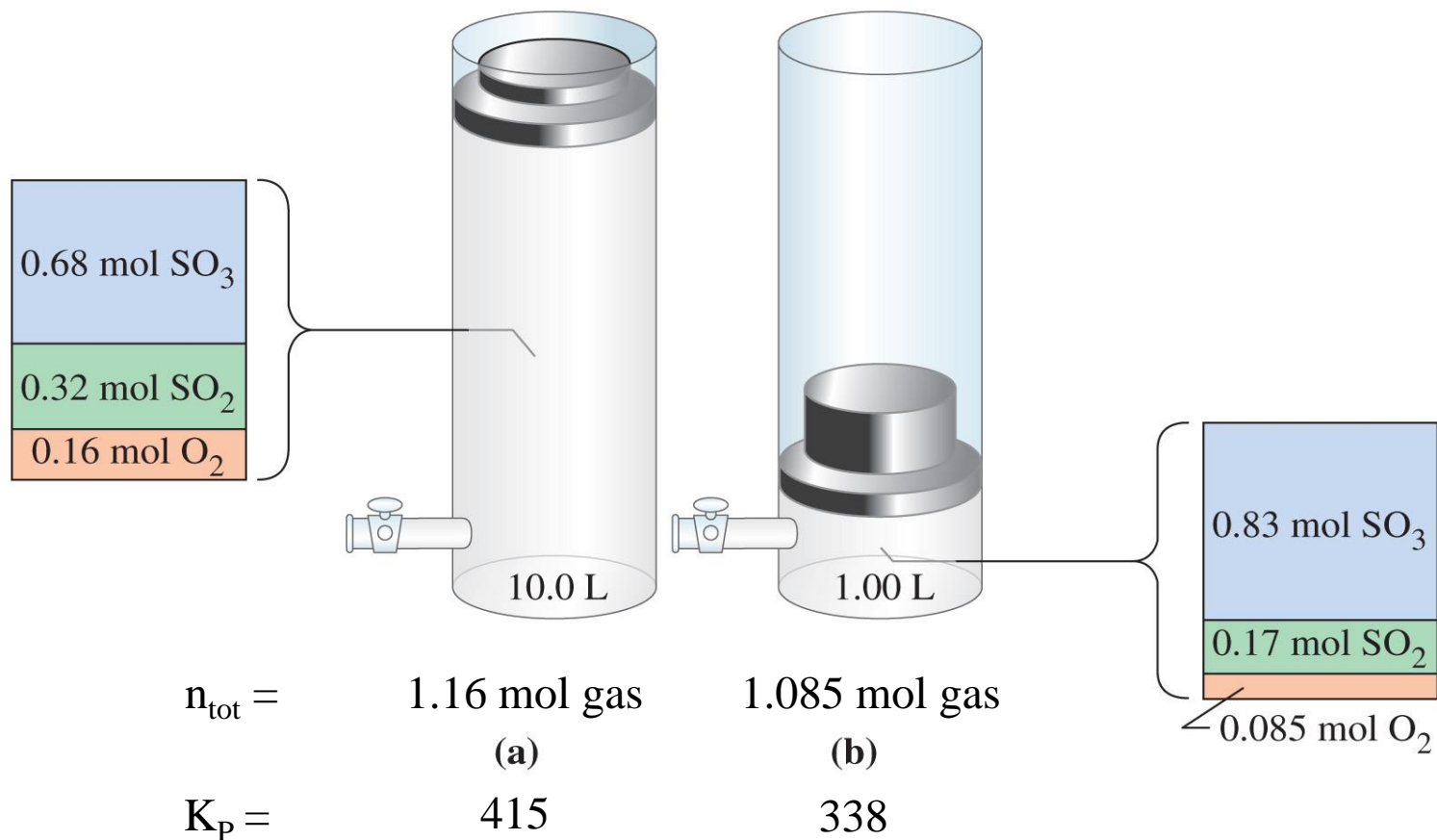
# Effect of Change in Volume

$$K_c = \frac{[G]^g[H]^h}{[C]^c[D]^d} = \frac{n_G^g n_H^h}{n_A^a n_B^a} V^{(a+b)-(g+h)}$$
$$= \frac{n_G^g n_H^h}{n_A^a n_B^a} V^{-\Delta n}$$

- ◆ When the volume of an equilibrium mixture of gases is *reduced*, a net change occurs in the direction that produces *fewer moles of gas*. When the volume is *increased*, a net change occurs in the direction that produces *more moles of gas*.



# Effect of the Change of Volume



# Effect of Temperature on Equilibrium

- ◆ *Raising the temperature* of an equilibrium mixture shifts the equilibrium condition in the *direction of the endothermic* reaction.
- ◆ *Lowering the temperature* causes a shift in the *direction of the exothermic* reaction.

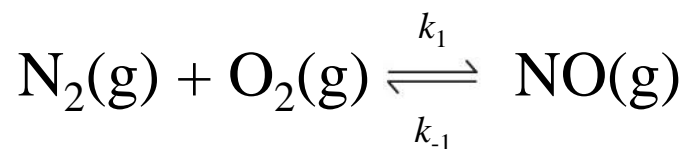
# Effect of a Catalyst on Equilibrium

- ◆ A catalyst changes the mechanism of a reaction to one with a lower activation energy.
- ◆ A catalyst has no effect on the condition of equilibrium.
  - But does affect the *rate* at which equilibrium is attained.

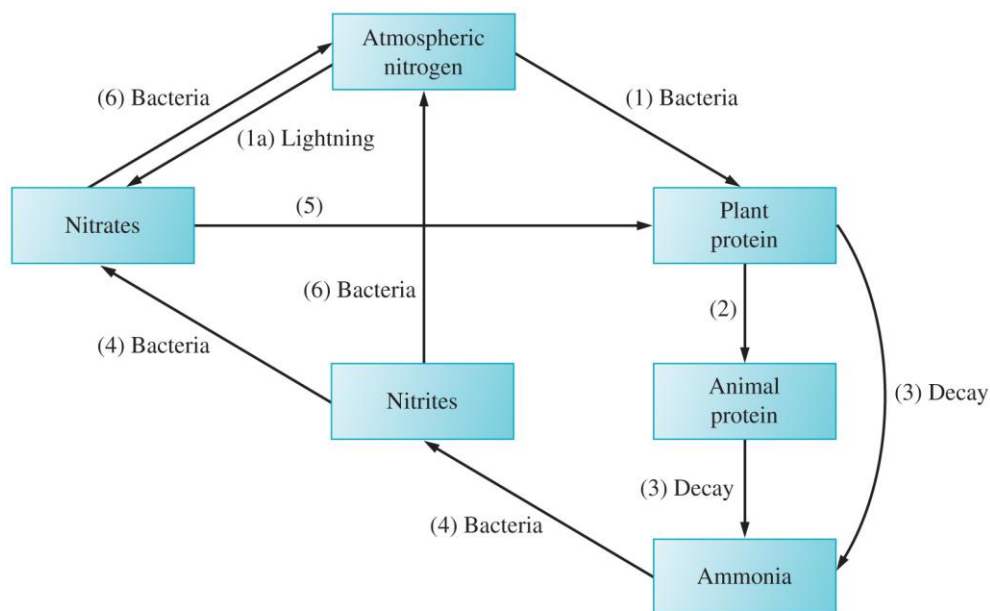
## 15-7 Equilibrium Calculations: Some Illustrative Examples.

- ◆ Five numerical examples are given in the text that illustrate ideas that have been presented in this chapter.
- ◆ Refer to the “comments” which describe the methodology. These will help in subsequent chapters.
- ◆ Exercise your understanding by working through the examples with a pencil and paper.

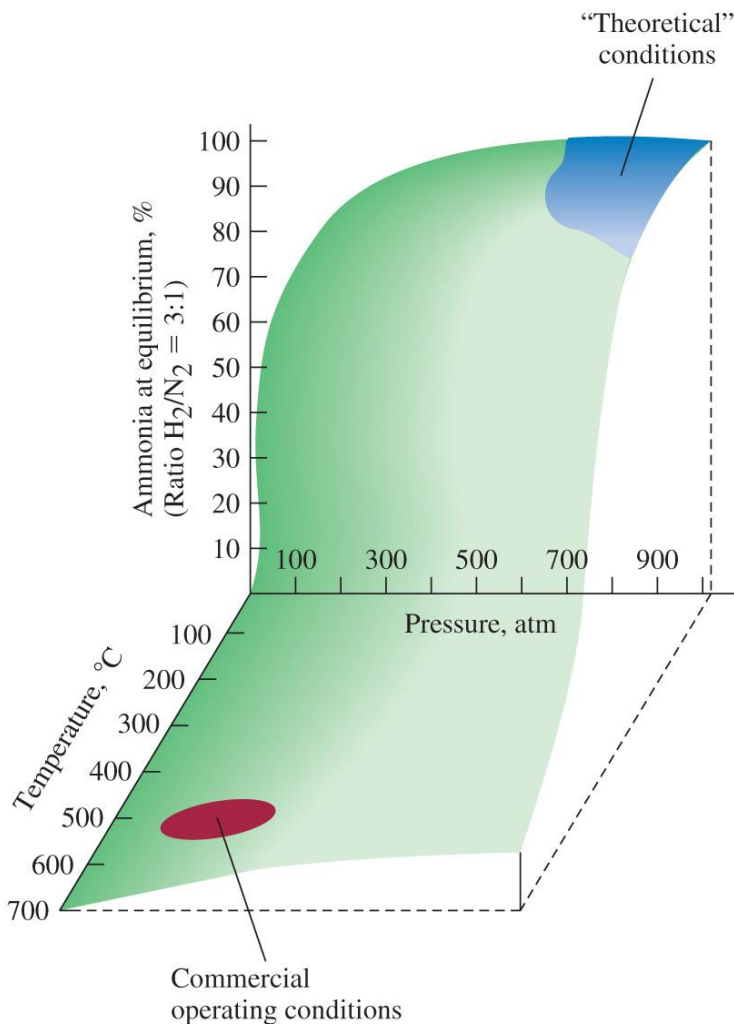
# Focus on the Nitrogen Cycle and the Synthesis of Nitrogen Compounds.



$$K_p = 4.7 \cdot 10^{-31} \text{ at } 298\text{K and } 1.3 \times 10^{-4} \text{ at } 1800\text{K}$$



# Synthesis of Ammonia



The optimum conditions are only for the equilibrium position and do not take into account the *rate* at which equilibrium is attained.



# End of Chapter Questions

- ◆ Problems can be solved by eliminating errors from your approach.
  - There may be nothing wrong with your strategy, but for some reason the problem is not solving.
- ◆ Be willing to make errors.
- ◆ Be able to recognize them.