大 学 化 学 (双语)

College Chemistry

College of Chemistry and Materials Science

Chapter 5

Chemical Equilibrium

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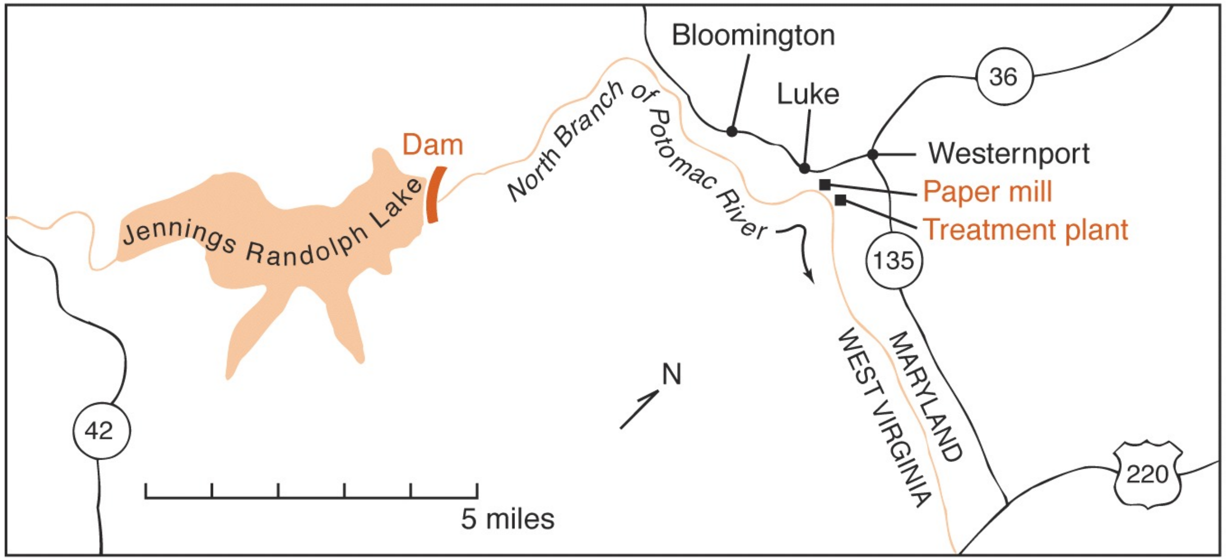
Chemical Equilibrium in the Environment

Paper mill on the Potomac River near Westernport, Maryland, neutralizes acid mine drainage in the water. Upstream of the mill, the river is acidic and lifeless; below the mill, the river teems(充满) with life.



$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + HCO_3^-$$

$$HCO_3^- + H^+ = CO_2 + H_2$$

Contents

5-1 Dynamic Equilibrium(动态平衡)

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

$$H_2O(l) \rightleftharpoons H_2O(g)$$

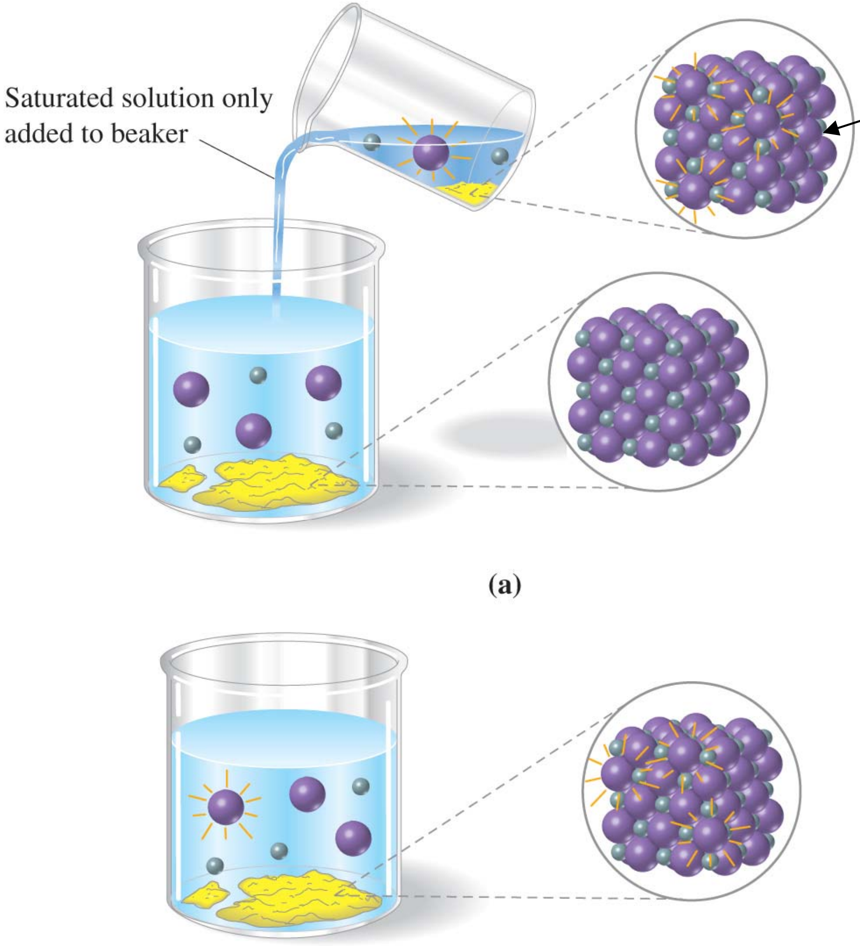
$$NaCl(s) \overset{H_2O}{\rightleftharpoons} NaCl(aq)$$

$$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$$

(a) (b)

$$I_2(H_2O) \rightleftharpoons I_2(CCl_4)$$

Dynamic Equilibrium



(a)

(b)

Saturated solution of AgI made from AgI containing radioactive iodine-131 as iodide ion.

$$\mathrm{AgI(s)} \rightleftharpoons \mathrm{AgI(satd\ aq)}$$

Dynamic equilibrium illustrated
(a) A saturated solution of radioactive AgI is added to a saturated solution of AgI. **(b)** Radiation is detectable in *both* the solution and the previously nonradioactive AgI(s). The only explanation must be that the radioactive iodide ions distribute themselves throughout the solution and the solid AgI, showing that the equilibrium is dynamic.

5-2 The Equilibrium Constant Expression

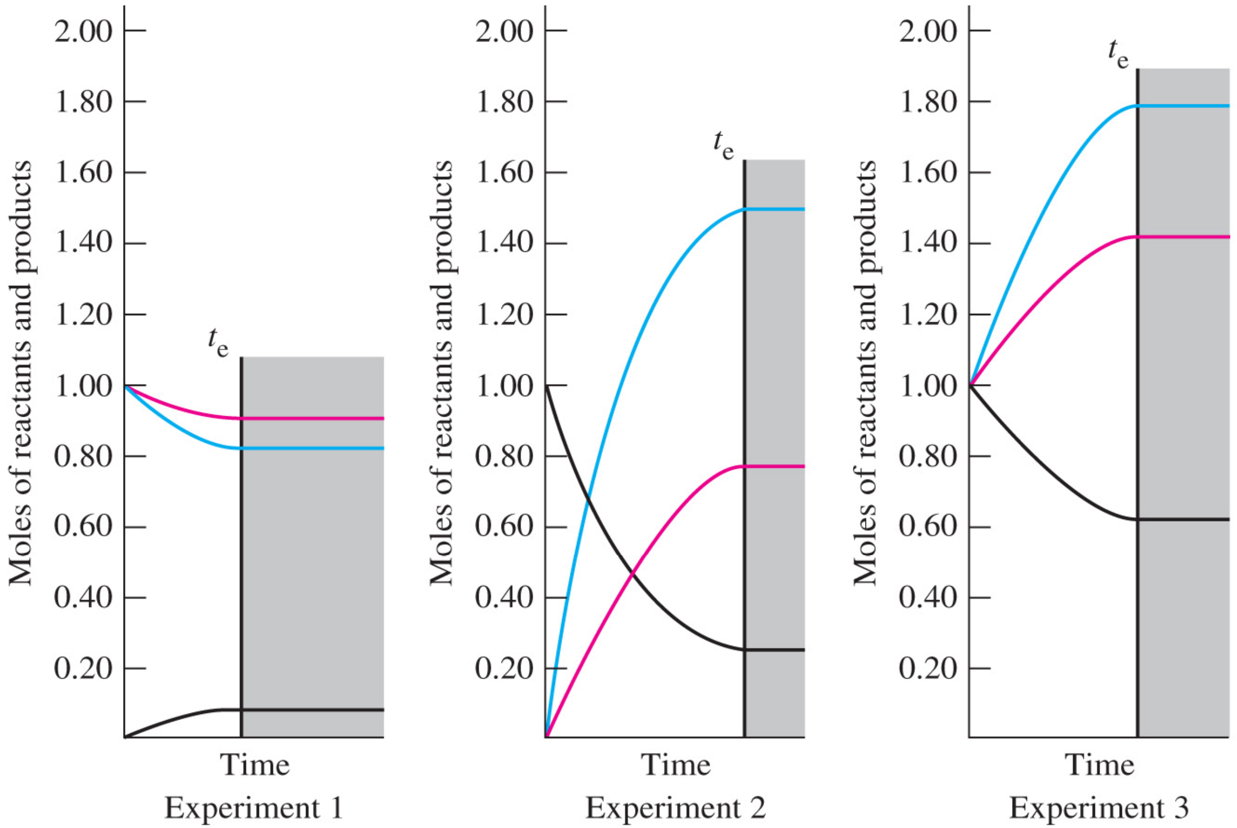
- **Methanol is synthesized from a carbon monoxide-hydrogen mixture called synthesis gas.**
- **Methanol synthesis is a reversible reaction.**

$$CO(g) + 2\ H_2(g) \xrightarrow[1]{k} CH_3OH(g)$$

$$CH_3OH(g) \xrightarrow{k_{-1}} CO(g) + 2\ H_2(g)$$

$$CO(g) + 2\ H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OH(g)$$

Three Approaches to the Equilibrium



Three approaches to equilibrium in the reaction $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

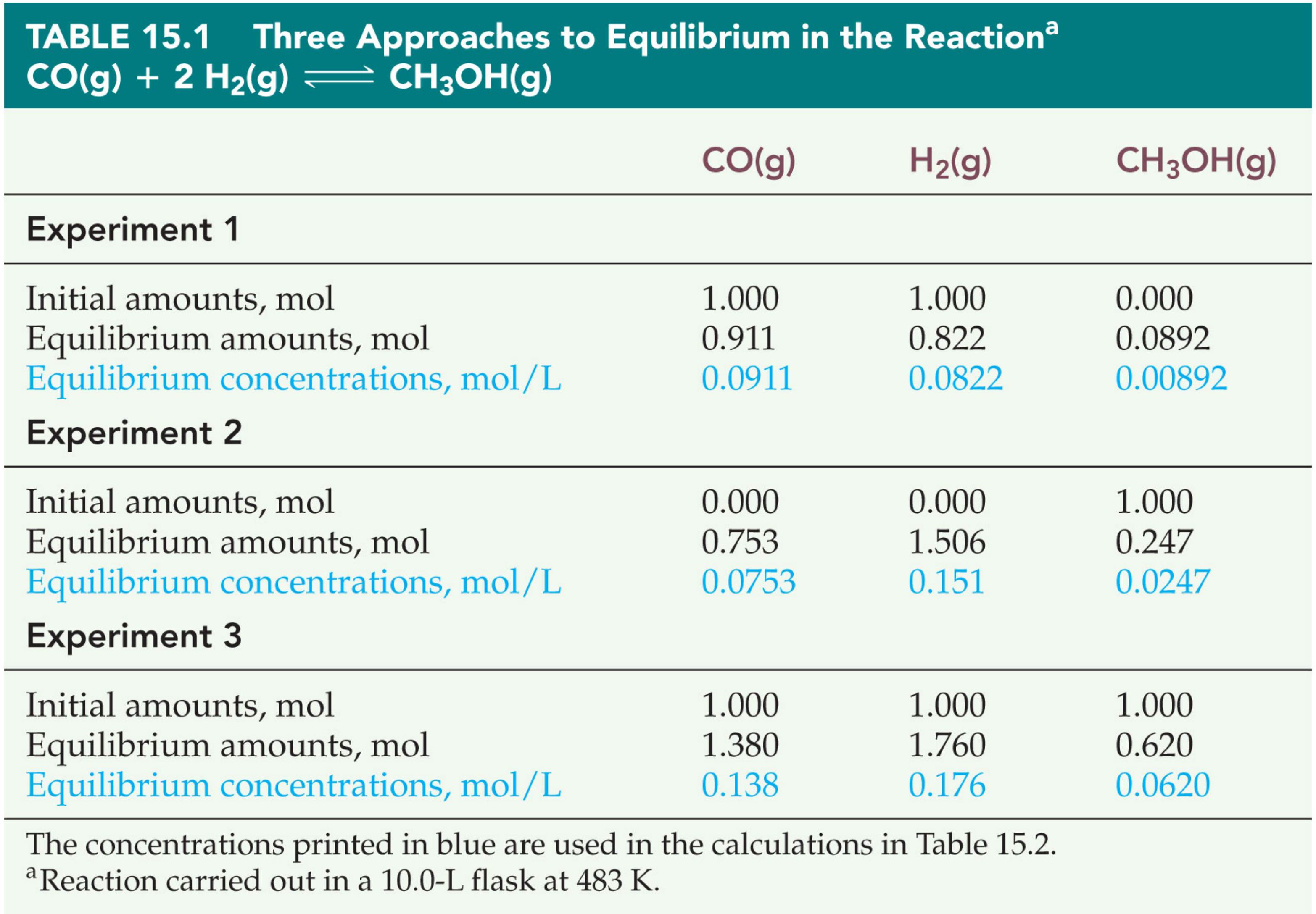


TABLE 15.1 Three Approaches to Equilibrium in the Reaction[a] $CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$

	$CO(g)$	$H_2(g)$	$CH_3OH(g)$
Experiment 1			
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
Experiment 2			
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
Experiment 3			
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.

[a] Reaction carried out in a 10.0-L flask at 483 K.

Three Approaches to Equilibrium

$$CO(g) + 2\ H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OH(g)$$

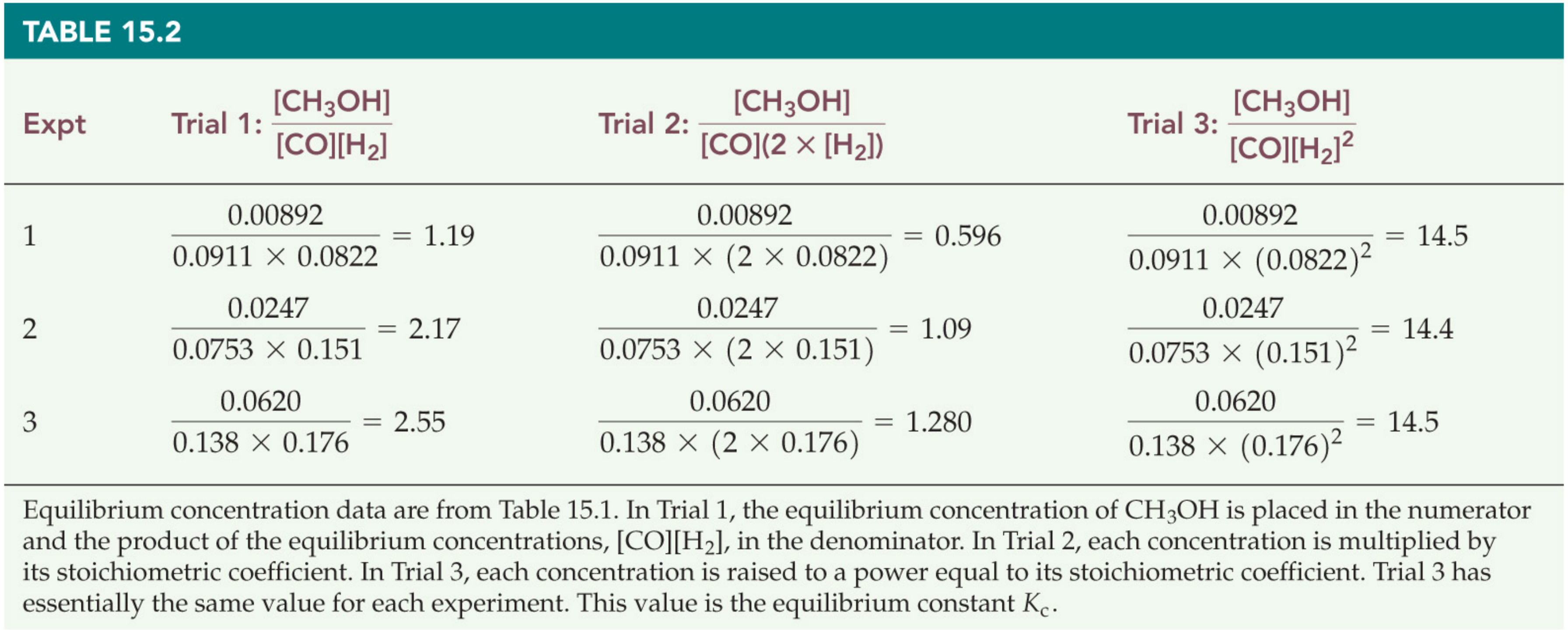


TABLE 15.2

Expt	Trial 1: $\frac{[CH_3OH]}{[CO][H_2]}$	Trial 2: $\frac{[CH_3OH]}{[CO](2 \times [H_2])}$	Trial 3: $\frac{[CH_3OH]}{[CO][H_2]^2}$
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_3OH is placed in the numerator and the product of the equilibrium concentrations, $[CO][H_2]$, 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

Forward: $CO(g) + 2\ H_2(g) \xrightarrow{k_1} CH_3OH(g)$ $\quad R_{fwrd} = k_1[CO][H_2]^2$

Reverse: $CH_3OH(g) \xrightarrow{k_{-1}} CO(g) + 2\ H_2(g)$ $\quad R_{rvrs} = k_{-1}[CH_3OH]$

At Equilibrium:

$R_{fwrd} = R_{rvrs}$ $\qquad CO(g) + 2\ H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OH(g)$

$$k_1[CO][H_2]^2 = k_{-1}[CH_3OH]$$

$$\frac{k_1}{k_{-1}} = \frac{[CH_3OH]}{[CO][H_2]^2} = K_c$$

The Equilibrium Constant and Activities

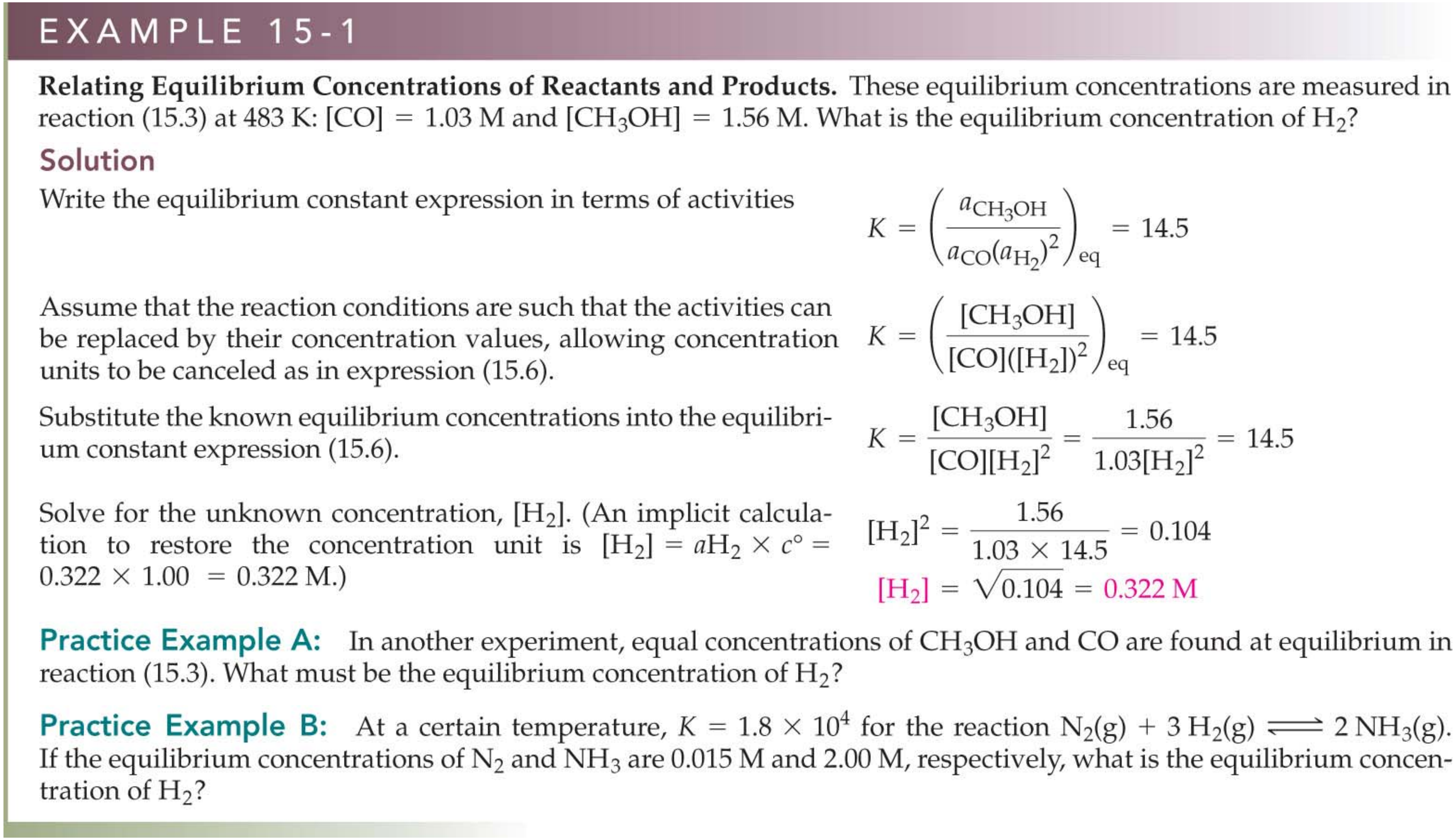
- **Activity**
  - **Thermodynamic concept introduced by Lewis.**
  - **Dimensionless ratio referred to a chosen reference state.**

$$a_B = \frac{[B]}{c_B^{\,0}} = \gamma_B[B]$$

$c_B^{\,0}$ is a standard reference state

$= 1$ mol L^{-1} (ideal conditions)

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



EXAMPLE 15-1

Relating Equilibrium Concentrations of Reactants and Products. These equilibrium concentrations are measured in reaction (15.3) at 483 K: [CO] = 1.03 M and $[CH_3OH]$ = 1.56 M. What is the equilibrium concentration of H_2?

Solution

Write the equilibrium constant expression in terms of activities

$$K = \left(\frac{a_{CH_3OH}}{a_{CO}(a_{H_2})^2}\right)_{eq} = 14.5$$

Assume that the reaction conditions are such that the activities can be replaced by their concentration values, allowing concentration units to be canceled as in expression (15.6).

$$K = \left(\frac{[CH_3OH]}{[CO]([H_2])^2}\right)_{eq} = 14.5$$

Substitute the known equilibrium concentrations into the equilibrium constant expression (15.6).

$$K = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{1.56}{1.03[H_2]^2} = 14.5$$

Solve for the unknown concentration, $[H_2]$. (An implicit calculation to restore the concentration unit is $[H_2] = aH_2 \times c° = 0.322 \times 1.00 = 0.322$ M.)

$$[H_2]^2 = \frac{1.56}{1.03 \times 14.5} = 0.104$$

$$[H_2] = \sqrt{0.104} = 0.322 \text{ M}$$

Practice Example A: In another experiment, equal concentrations of CH_3OH and CO are found at equilibrium in reaction (15.3). What must be the equilibrium concentration of H_2?

Practice Example B: At a certain temperature, $K = 1.8 \times 10^4$ for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$. If the equilibrium concentrations of N_2 and NH_3 are 0.015 M and 2.00 M, respectively, what is the equilibrium concentration of H_2?

General Expressions

$$a\,\mathrm{A} + b\,\mathrm{B} \cdots \rightarrow g\,\mathrm{G} + h\,\mathrm{H} \cdots$$

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

Thermodynamic

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

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

≈ 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(次方).**
- **Dividing the coefficients by a common factor causes the equilibrium constant to be taken to that root(根号).**

EXAMPLE 15-2

Relating K to the Balanced Chemical Equation. The following K value is given at 298 K for the synthesis of $NH_3(g)$ from its elements.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K = 3.6 \times 10^8$$

What is the value of K at 298 K for the following reaction?

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \qquad K = ?$$

Solution

First, reverse the given equation. This puts $NH_3(g)$ on the left side of the equation, where we need it.

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

The equilibrium constant K' becomes

$$K' = 1/(3.6 \times 10^8) = 2.8 \times 10^{-9}$$

Then, to base the equation on 1 mol $NH_3(g)$, divide all coefficients by 2.

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

This requires the square root of K'.

$$K = \sqrt{2.8 \times 10^{-9}} = 5.3 \times 10^{-5}$$

Practice Example A: Use data from Example 15-2 to determine the value of K at 298 K for the reaction

$$\frac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \frac{2}{3}NH_3(g)$$

Practice Example B: For the reaction $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ at 184 ° C, $K = 7.5 \times 10^2$. What is the value of K at 184 °C for the reaction $2\,NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$?

Combining Equilibrium Constant Expressions

When individual equations are combined (added), their equilibrium constants are multiplied to obtain the equilibrium constant for the overall reaction.

$$N_2O(g) + \tfrac{1}{2}O_2 \rightleftharpoons 2\ NO(g) \qquad K_c = ?$$

$$N_2(g) + \tfrac{1}{2}O_2 \rightleftharpoons N_2O(g) \qquad K_{c(2)} = 2.7\times10^{+18} = \frac{[N_2O]}{[N_2][O_2]^{1/2}}$$

$$N_2(g) + O_2 \rightleftharpoons 2\ NO(g) \qquad K_{c(3)} = 4.7\times10^{-31} = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_c = \frac{[NO]^2}{[N_2O][O_2]^{1/2}} = \frac{[NO]^2}{[N_2][O_2]}\,\frac{[N_2][O_2]^{1/2}}{[N_2O]} = K_{c(3)}\frac{1}{K_{c(2)}} = 1.7\times10^{-13}$$

Gases: The Equilibrium Constant, K_P

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

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \qquad K_P = \frac{(a_{SO_3})^2}{(a_{SO_2})^2(a_{O_2})}$$

$$a_{SO_3} = \frac{P_{SO_3}}{P^\circ} \qquad a_{SO_2} = \frac{P_{SO_2}}{P^\circ} \qquad a_{SO_3} = \frac{P_{O_2}}{P^\circ}$$

$$K_P = \left(\frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} \right) P^\circ$$

Gases: The Equilibrium Constant, K_C

- **In *concentration* we can do another substitution**

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

$$[SO_3] = \frac{n_{SO_3}}{V} = \frac{P_{SO_3}}{RT} \qquad [SO_2] = \frac{P_{SO_2}}{RT} \qquad [O_2] = \frac{P_{O_2}}{RT}$$

$$(a_X) = \frac{[X]}{c°} = \frac{\frac{P_X}{RT}}{c°} \qquad P_X = [X]\,RT$$

Gases: The Equilibrium Constant, K_C

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

$$K_P = \frac{(a_{SO_3})^2}{(a_{SO_2})^2(a_{O_2})} = P^\circ\left(\frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})}\right) \qquad P_X = [X]\,RT$$

$$= \left(\frac{([SO_3]\,RT)^2}{([SO_2]\,RT)^2([O_2]\,RT)}\right)P^\circ$$

$$= \frac{P^\circ}{RT}\left(\frac{([SO_3])^2}{([SO_2])^2([O_2])}\right) = \frac{K_C}{RT}$$

Where $P^\circ = 1$ bar

An Alternative Derivation

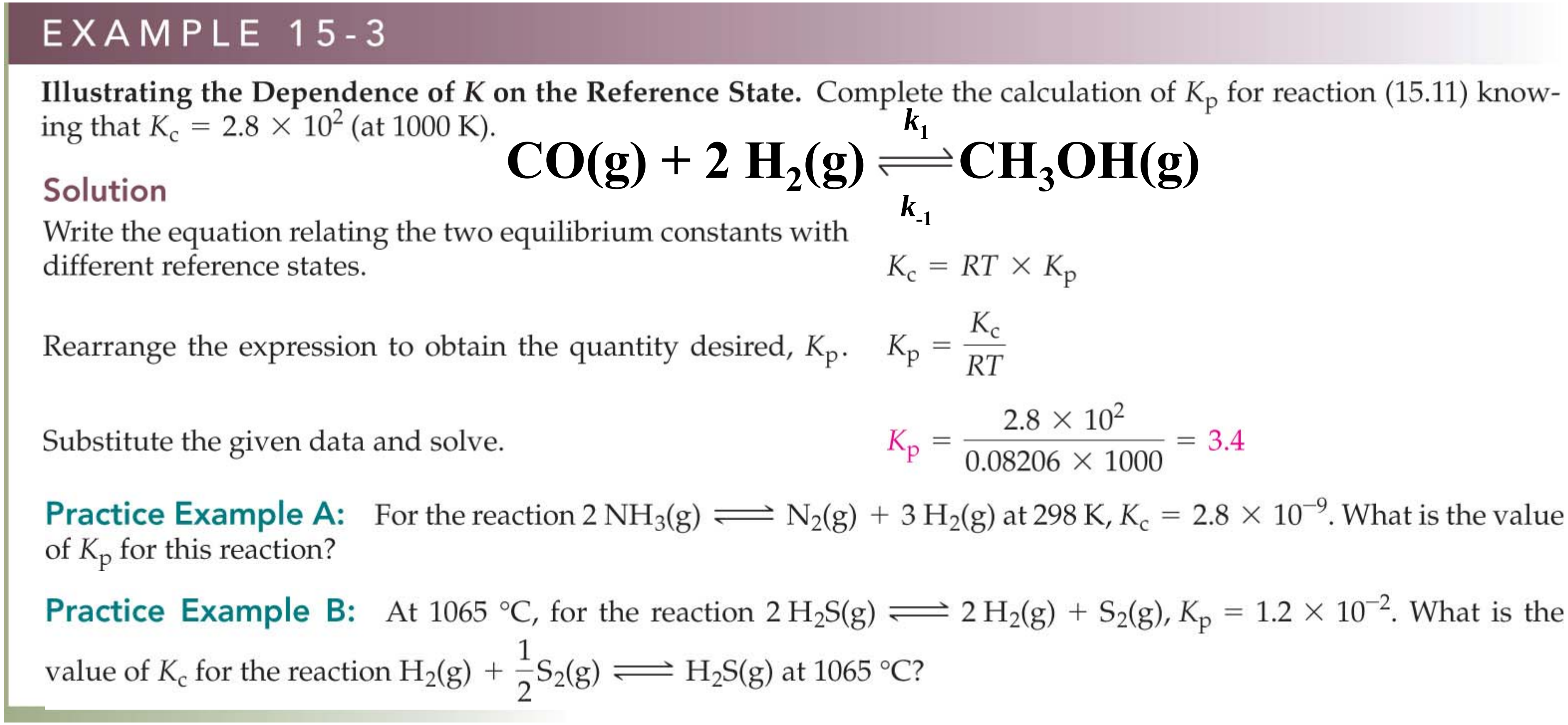
$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

Where $P^\circ = 1$ bar

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{P_{SO_3}}{RT}\right)^2}{\left(\frac{P_{SO_2}}{RT}\right)^2 \frac{P_{O_2}}{RT}} = \frac{P_{SO_3}^{\ 2}}{P_{SO_2}^{\ 2} P_{O_2}} RT$$

$$K_c = K_P(RT) \qquad K_P = K_c(RT)^{-1}$$

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



EXAMPLE 15-3

Illustrating the Dependence of K on the Reference State. Complete the calculation of K_p for reaction (15.11) knowing that $K_c = 2.8 \times 10^2$ (at 1000 K).

$$\mathrm{CO(g) + 2\,H_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3OH(g)}$$

Solution

Write the equation relating the two equilibrium constants with different reference states. $K_c = RT \times K_p$

Rearrange the expression to obtain the quantity desired, K_p. $K_p = \dfrac{K_c}{RT}$

Substitute the given data and solve. $K_p = \dfrac{2.8 \times 10^2}{0.08206 \times 1000} = 3.4$

Practice Example A: For the reaction $\mathrm{2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)}$ at 298 K, $K_c = 2.8 \times 10^{-9}$. What is the value of K_p for this reaction?

Practice Example B: At 1065 °C, for the reaction $\mathrm{2\,H_2S(g) \rightleftharpoons 2\,H_2(g) + S_2(g)}$, $K_p = 1.2 \times 10^{-2}$. What is the value of K_c for the reaction $\mathrm{H_2(g) + \frac{1}{2}S_2(g) \rightleftharpoons H_2S(g)}$ at 1065 °C?

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).**

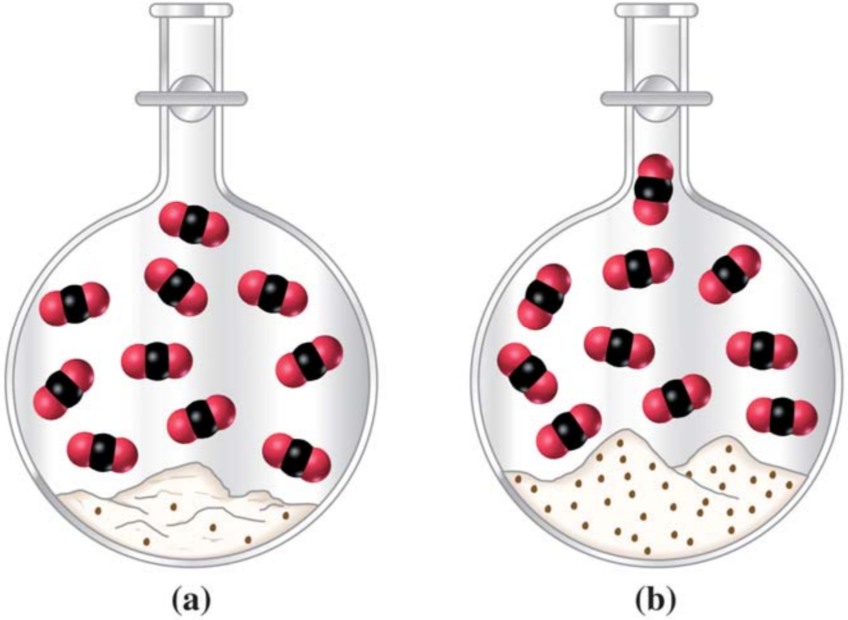
$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

$$K_c = \frac{[CO][H_2]}{[H_2O]^2} = \frac{P_{CO}P_{H_2}}{P_{H_2O}{}^2}(RT)^1$$

Burnt Lime

$$\mathbf{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$$

$$K_c = [CO_2] \qquad K_P = P_{CO_2}(RT)$$



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Equilibrium in the reaction
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(a) Decomposition of $CaCO_3(s)$ upon heating in a closed vessel yields a few granules of CaO (s), together with CO_2 which ultimately exerts its equilibrium partial pressure (and usually fairly quickly in this case). **(b)** Introduction of additional $CaCO_3(s)$ and/or more CaO (s) has no effect on the partial pressure of the $CO_2(g)$ which remains the same as in (a).

EXAMPLE 15-4

Writing Equilibrium Constant Expressions for Reactions Involving Pure Solids or Liquids. At equilibrium in the following reaction at 60 °C, the partial pressures of the gases are found to be $P_{HI} = 3.65 \times 10^{-3}$ atm and $P_{H_2S} = 9.96 \times 10^{-1}$ atm. What is the value of K_p for the reaction?

$$H_2S(g) + I_2(s) \rightleftharpoons 2\,HI(g) + S(s) \qquad K_p = ?$$

Solution

Write the equilibrium constant expression in terms of activities. Note that activities for the iodine and sulfur are not included, since the activity of a pure solid is 1.

$$K = \frac{(a_{HI})^2}{(a_{H_2S})}$$

Substitute partial pressures for the activities into the equilibrium constant expression.

$$K_p = \frac{(P_{HI})^2}{(P_{H_2S})}$$

Substitute the given equilibrium data into the equilibrium constant expression.

$$K_p = \frac{(3.65 \times 10^{-3})^2}{9.96 \times 10^{-1}} = 1.34 \times 10^{-5}$$

Practice Example A: Teeth are made principally from the mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, which can be dissolved in acidic solution such as that produced by bacteria in the mouth. The reaction that occurs is $Ca_5(PO_4)_3OH(s) + 4\,H^+(aq) \rightleftharpoons 5\,Ca^{2+}(aq) + 3\,HPO_4{}^{2-}(aq) + H_2O(l)$. Write the equilibrium constant expression K_c for this reaction.

Practice Example B: The steam–iron process is used to generate $H_2(g)$, mostly for use in hydrogenating oils. Iron metal and steam $[H_2O(g)]$ react to produce $Fe_3O_4(s)$ and $H_2(g)$. Write expressions for K_c and K_p for this reversible reaction. How are the values of K_c and K_p related to each other? Explain.

5-4 The Significance of the Magnitude of the Equilibrium Constant.

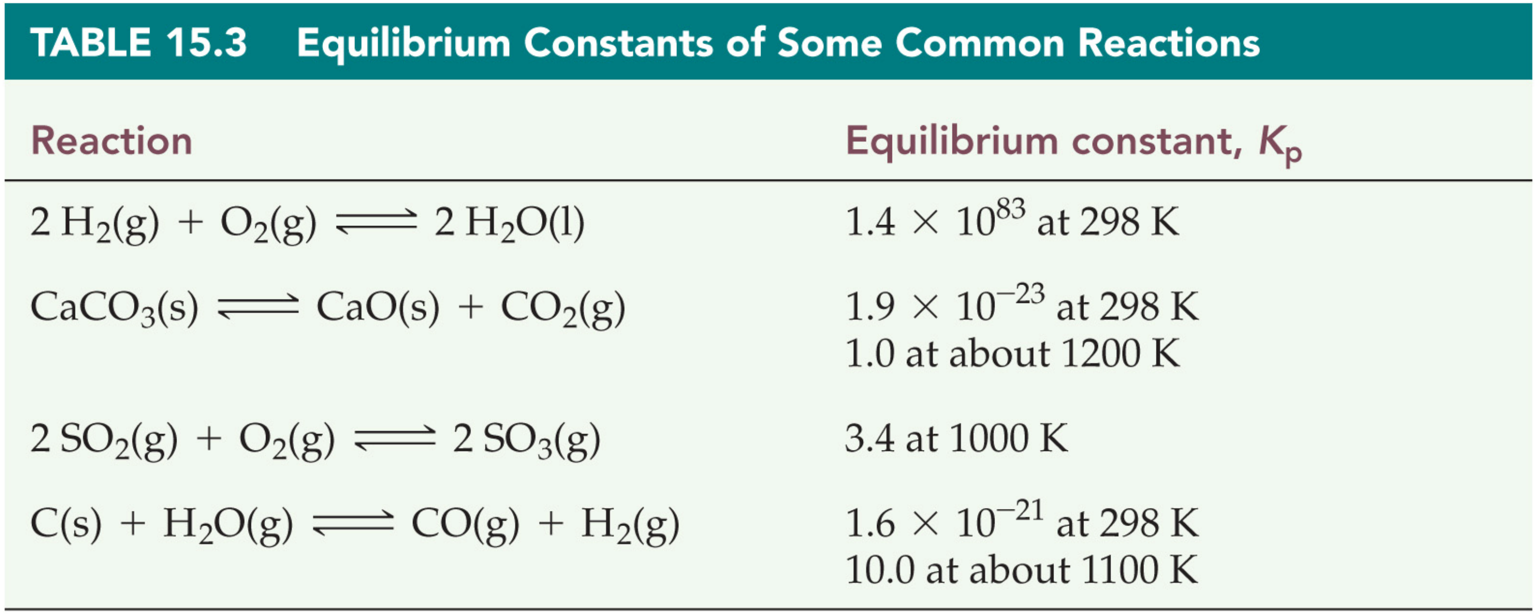


TABLE 15.3 Equilibrium Constants of Some Common Reactions

Reaction	Equilibrium constant, K_p
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(l)$	1.4×10^{83} at 298 K
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	1.9×10^{-23} at 298 K 1.0 at about 1200 K
$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$	3.4 at 1000 K
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	1.6×10^{-21} at 298 K 10.0 at about 1100 K

A reaction is most likely to reach a state of equilibrium in which significant quantities of both reactants and products are present if the numerical value of K_c or K_p is neither vary large nor very small, roughly in the range of about 10^{-10} to 10^{10}.

15-5 The Reaction Quotient(商), *Q*: Predicting the Direction of Net Change.

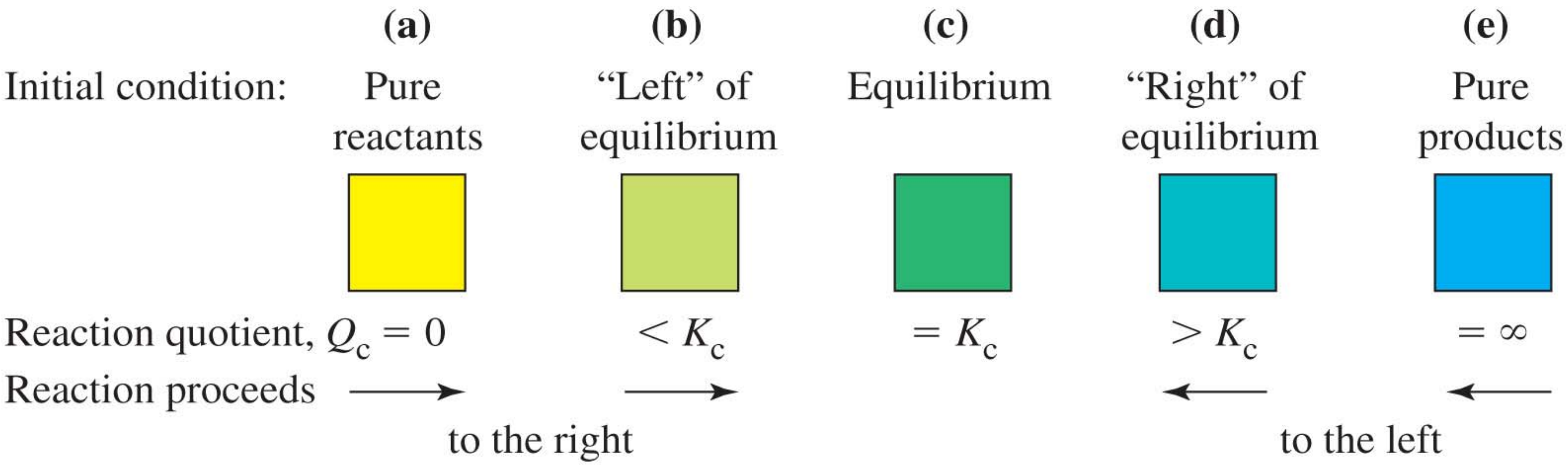
$$\mathrm{CO(g)} + 2\,\mathrm{H_2(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3OH(g)}$$

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

$$Q_c = \frac{[\mathrm{G}]_\mathrm{t}^{g}[\mathrm{H}]_\mathrm{t}^{h}}{[\mathrm{A}]_\mathrm{t}^{m}[\mathrm{B}]_\mathrm{t}^{n}}$$

At equilibrium $Q_c = K_\mathrm{c}$

Reaction Quotient



If $Q_c < K_c$, a net change occurs from left to right (the direction of the forward reaction).

If $Q_c > K_c$, a net change occurs from right to left (the direction of the reverse reaction).

If $Q_c = K_c$, *a reaction is at equilibrium*.

EXAMPLE 15-5

Predicting the Direction of a Net Chemical Change in Establishing Equilibrium. To increase the yield of $H_2(g)$ in the water–gas reaction—the reaction of C(s) and $H_2O(g)$ to form CO(g) and $H_2(g)$—a follow-up reaction called the "water–gas shift reaction" is generally used. In this reaction, some of the CO(g) of the water gas is replaced by $H_2(g)$.

$$\mathrm{CO(g)} + \mathrm{H_2O(g)} \rightleftharpoons \mathrm{CO_2(g)} + \mathrm{H_2(g)}$$

$K_c = 1.00$ at about 1100 K. The following amounts of substances are brought together and allowed to react at this temperature: 1.00 mol CO, 1.00 mol H_2O, 2.00 mol CO_2, and 2.00 mol H_2. Compared with their initial amounts, which of the substances will be present in a greater amount and which in a lesser amount when equilibrium is established?

Solution

Our task is to determine the direction of net change by evaluating Q_c. Write down the expression for Q_c.

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]}$$

Substitute concentrations into the expression for Q_c, by assuming an arbitrary volume V (which cancels out in the calculation).

$$Q_c = \frac{(2.00/V)(2.00/V)}{(1.00/V)(1.00/V)} = 4.00$$

Compare Q_c to K_c.

$$4.00 > 1.00$$

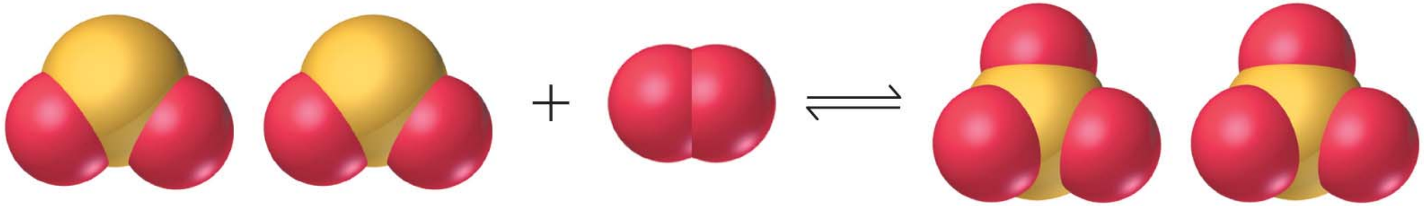
Because $Q_c > K_c$ (that is, $4.00 > 1.00$), a net change occurs to the *left*. When equilibrium is established, the amounts of CO and H_2O will be greater than the initial quantities and the amounts of CO_2 and H_2 will be less.

Practice Example A: In Example 15-5, equal masses of CO, H_2O, CO_2, and H_2 are mixed at a temperature of about 1100 K. When equilibrium is established, which substance(s) will show an increase in quantity and which will show a decrease compared with the initial quantities?

Practice Example B: For the reaction $\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)}$, $K_c = 0.0454$ at 261 °C. If a vessel is filled with these gases such that the initial partial pressures are $P_{\mathrm{PCl_3}} = 2.19$ atm, $P_{\mathrm{Cl_2}} = 0.88$ atm, $P_{\mathrm{PCl_5}} = 19.7$ atm, in which direction will a net change occur?

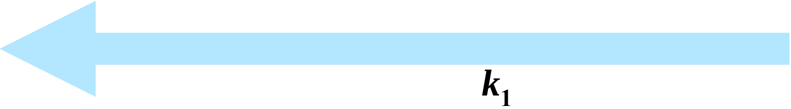
5-6 Altering Equilibrium Conditions: Le Châtelier’s Principle (勒夏特列原理)

- **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.**



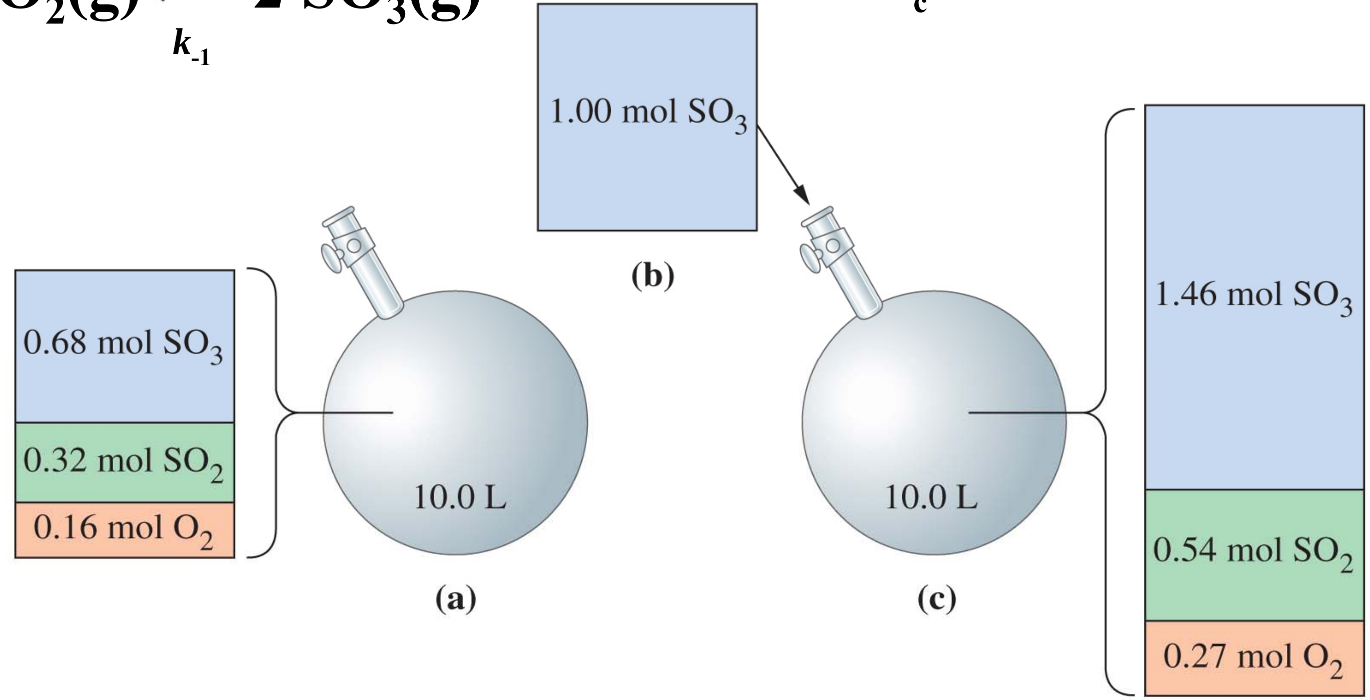
What happens if we add SO_3 to this equilibrium?

Le Châtelier's Principle



$$2\ SO_2(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\ SO_3(g)$$

$K_c = 2.8\times10^2$ at 1000K



Original equilibrium

$$Q = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_c$$

Following disturbance

$$Q > K_c$$

Effect of Condition Changes

- **Adding a gaseous reactant or product changes P_{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.**

$$K_c = \frac{[SO_3]}{[SO_2]^2[O_2]} = \frac{\left(\frac{n_{SO_3}}{V}\right)^2}{\left(\frac{n_{SO_2}}{V}\right)^2 \frac{n_{O_2}}{V}} = \frac{n_{SO_3}^{\ 2}}{n_{SO_2}^{\ 2}\, n_{O_2}}\ V$$

EXAMPLE 15-6

Applying Le Châtelier's Principle: Effect of Adding More of a Reactant to an Equilibrium Mixture. Predict the effect of adding more $H_2(g)$ to a constant-volume equilibrium mixture of N_2, H_2, and NH_3.

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

Solution

Increasing $[H_2]$ stimulates the forward reaction and a shift in the equilibrium condition to the right. However, only a portion of the added H_2 is consumed in this reaction. When equilibrium is reestablished, there will be more H_2 than was present originally, and also more NH_3, but the amount of N_2 will be *smaller*. Some of the original N_2 must be consumed in converting some of the added H_2 to NH_3.

Practice Example A: Given the reaction $2\,CO(g) + O_2(g) \rightleftharpoons 2\,CO_2(g)$, what is the effect of adding $O_2(g)$ to a constant-volume equilibrium mixture?

Practice Example B: Calcination of limestone (decomposition by heating), $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, is the commercial source of quicklime, $CaO(s)$. After this equilibrium has been established in a constant-temperature, constant-volume container, what is the effect on the equilibrium amounts of materials caused by *adding* some **(a)** $CaO(s)$; **(b)** $CO_2(g)$; **(c)** $CaCO_3(s)$?

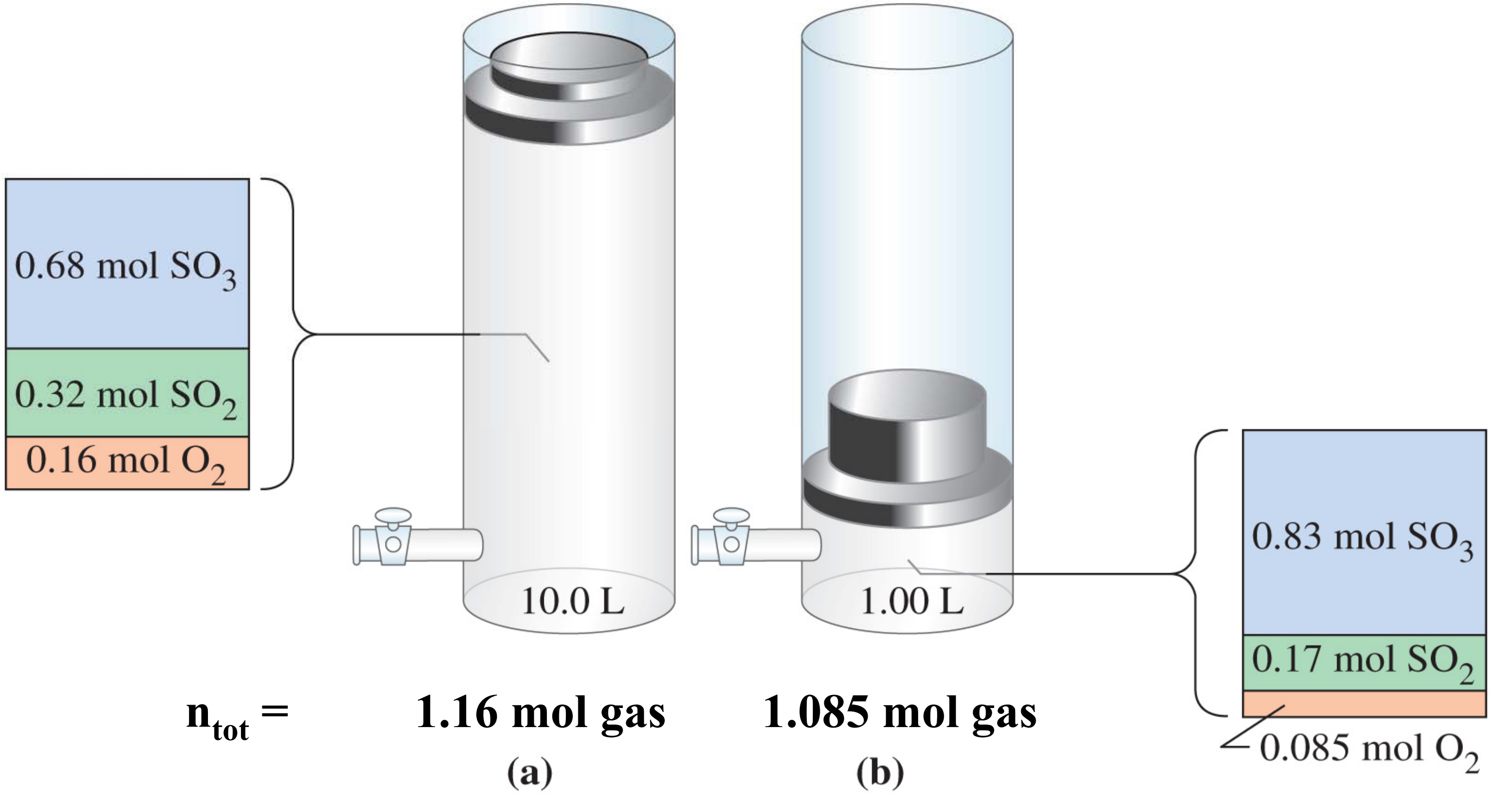
Effect of Change in Volume

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

$$= \frac{n_G^g \; n_H^h}{n_A^a \; n_B^a} V^{-\Delta n}$$

- **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

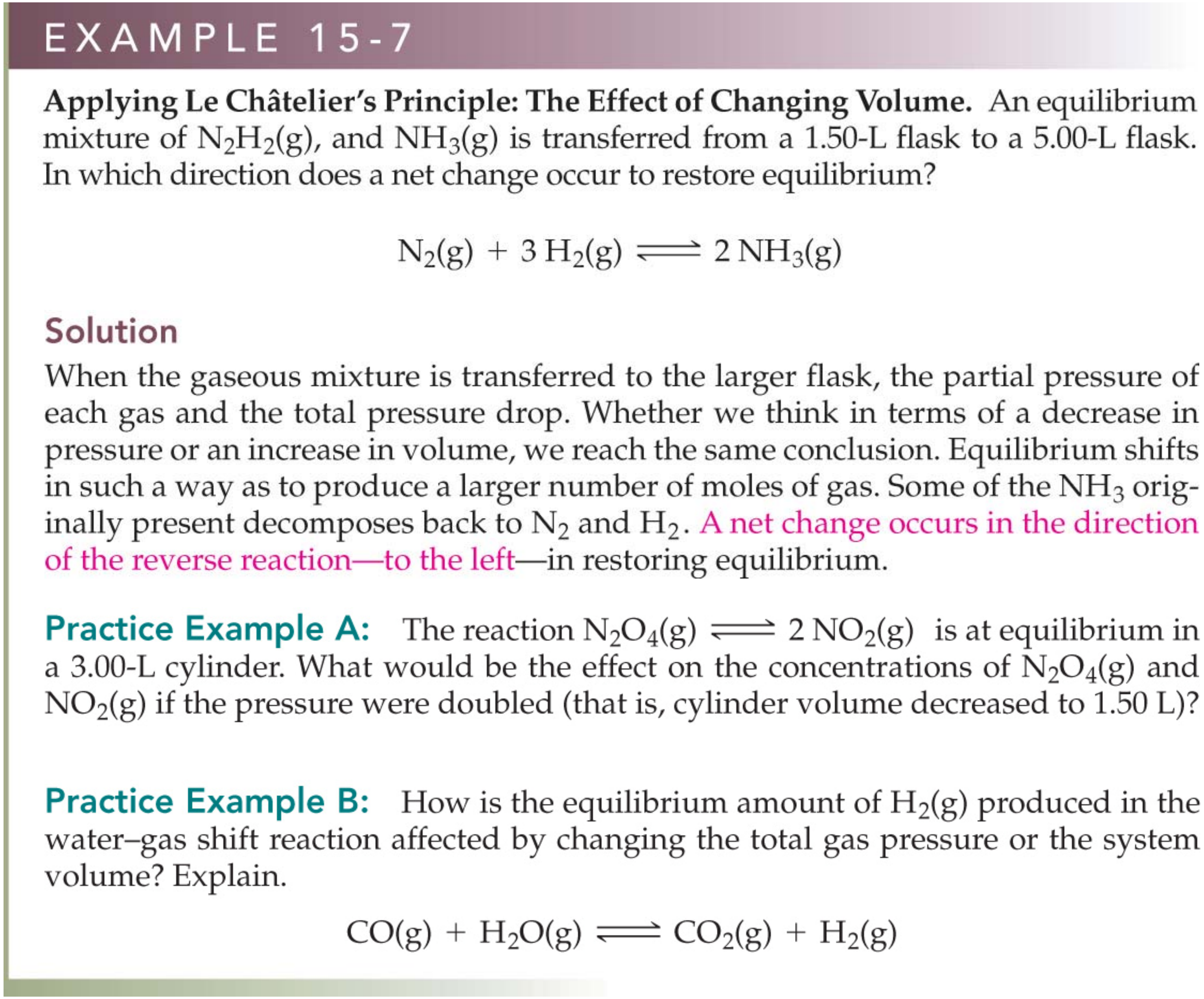


n_{tot} = 1.16 mol gas 1.085 mol gas

K_P = 415 338

Effect of pressure change on equilibrium in the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

An increase in external pressure causes a decrease in the reaction volume and a shift in equilibrium "to the right."



EXAMPLE 15-7

Applying Le Châtelier's Principle: The Effect of Changing Volume. An equilibrium mixture of $N_2H_2(g)$, and $NH_3(g)$ is transferred from a 1.50-L flask to a 5.00-L flask. In which direction does a net change occur to restore equilibrium?

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

Solution

When the gaseous mixture is transferred to the larger flask, the partial pressure of each gas and the total pressure drop. Whether we think in terms of a decrease in pressure or an increase in volume, we reach the same conclusion. Equilibrium shifts in such a way as to produce a larger number of moles of gas. Some of the NH_3 originally present decomposes back to N_2 and H_2. A net change occurs in the direction of the reverse reaction—to the left—in restoring equilibrium.

Practice Example A: The reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ is at equilibrium in a 3.00-L cylinder. What would be the effect on the concentrations of $N_2O_4(g)$ and $NO_2(g)$ if the pressure were doubled (that is, cylinder volume decreased to 1.50 L)?

Practice Example B: How is the equilibrium amount of $H_2(g)$ produced in the water–gas shift reaction affected by changing the total gas pressure or the system volume? Explain.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

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.**

EXAMPLE 15-8

Applying Le Châtelier's Principle: Effect of Temperature on Equilibrium. Consider the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \qquad \Delta H^\circ = -197.8\text{ kJ}$$

Will the amount of $SO_3(g)$ formed from given amounts of $SO_2(g)$ and $O_2(g)$ be greater at high or low temperatures?

Solution

Raising the temperature favors the endothermic reaction, the *reverse* reaction. Lowering the temperature favors the forward (exothermic) reaction. Therefore, an equilibrium mixture would have a higher concentration of SO_3 at lower temperatures. The conversion of SO_2 to SO_3 is favored at *low* temperatures.

Practice Example A: The reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ has $\Delta H^\circ = +57.2$ kJ. Will the amount of $NO_2(g)$ formed from $N_2O_4(g)$ be greater at high or low temperatures?

Practice Example B: The enthalpy of formation of NH_3 is $\Delta H_f^\circ[NH_3(g)] = -46.11$ kJ/mol NH_3. Will the concentration of NH_3 in an equilibrium mixture with its elements be greater at 100 or at 300 °C? Explain.

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.**

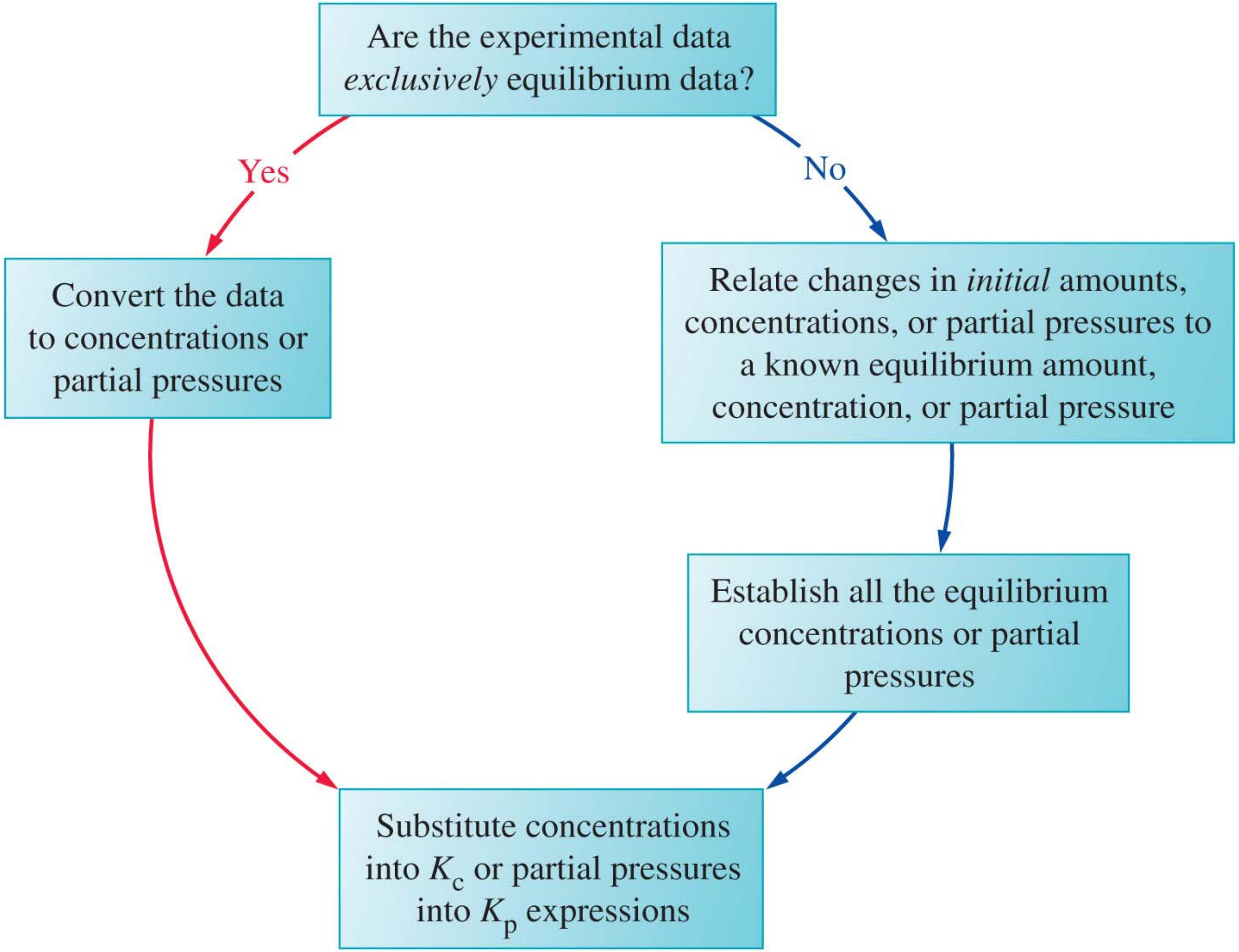
Sulfuric acid is produced from SO_3

$SO_3(g) + H_2O(l) \leftrightarrow H_2SO_4(aq)$

The catalyst used to speed up the conversion of SO_2 to SO_3 in the commercial production of sulfuric acid is $V_2O_5(s)$.

5-7 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.**



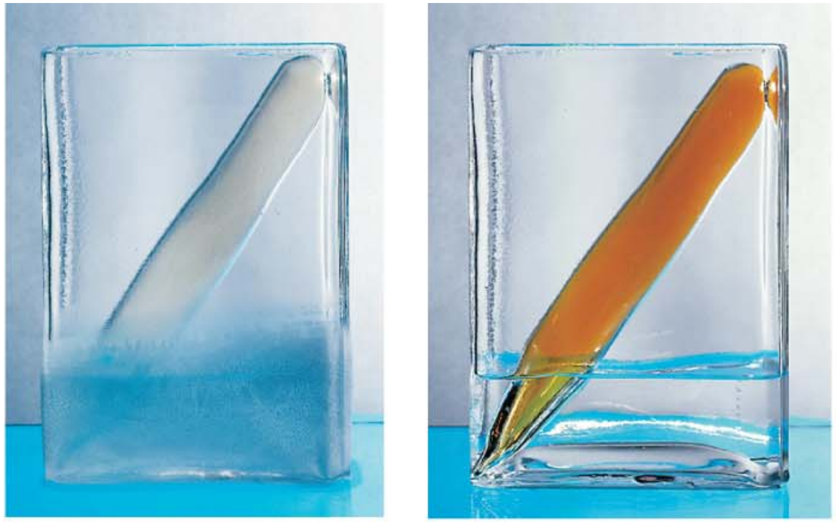
Determining K_c or K_p from experimental data

A schematic approach to determining the value of a given equilibrium constant

EXAMPLE 15-9

Determining a Value of K_c from the Equilibrium Quantities of Substances. Dinitrogen tetroxide, $N_2O_4(l)$, is an important component of rocket fuels—for example, as an oxidizer of liquid hydrazine in the Titan rocket. At 25 °C, N_2O_4 is a colorless gas that partially dissociates into NO_2, a red-brown gas. The color of an equilibrium mixture of these two gases depends on their relative proportions, which in turn depends on the temperature (Fig. 15-8).

Equilibrium is established in the reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ at 25 °C. The quantities of the two gases present in a 3.00-L vessel are 7.64 g N_2O_4 and 1.56 g NO_2. What is the value of K_c for this reaction?



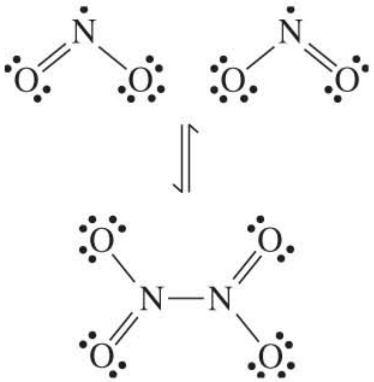
(a) (b)

FIGURE 15-8

The equilibrium $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

(a) At dry ice temperatures, N_2O_4 exists as a solid. The gas in equilibrium with the solid is mostly colorless N_2O_4, with only a trace of brown NO_2. **(b)** When warmed to room temperature and above, the N_2O_4 melts and vaporizes. The proportion of $NO_2(g)$ at equilibrium increases over that at low temperatures, and the equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$ has a red-brown color.

Titan rocket: 大力神式航天火箭助推器(代号)



The Lewis structures of N_2O_4 and $NO_2(g)$

Nitrogen dioxide is a free radical that combines exothermically to form dinitrogen tetroxide.

EXAMPLE 15-9 continued

Solution

Convert the mass of N_2O_4 to moles.

$$\text{mol } N_2O_4 = 7.64 \text{ g } N_2O_4 \times \frac{1 \text{ mol } N_2O_4}{92.01 \text{ g } N_2O_4} = 8.303 \times 10^{-2} \text{ mol}$$

Convert moles of N_2O_4 to mol/L.

$$[N_2O_4] = \frac{8.303 \times 10^{2} \text{ mol}}{3.00 \text{ L}} = 0.0277 \text{ M}$$

Convert the mass of NO_2 to moles.

$$\text{mol } NO_2 = 1.56 \text{ g } NO_2 \times \frac{1 \text{ mol } NO_2}{46.01 \text{ g } NO_2} = 3.391 \times 10^{-2} \text{ mol}$$

Convert moles of NO_2 to mol/L.

$$[NO_2] = \frac{3.391 \times 10^{-2}}{3.00 \text{ L}} = 0.0113 \text{ M}$$

Write the equilibrium constant expression, substitute the equilibrium concentrations, and solve for K_c.

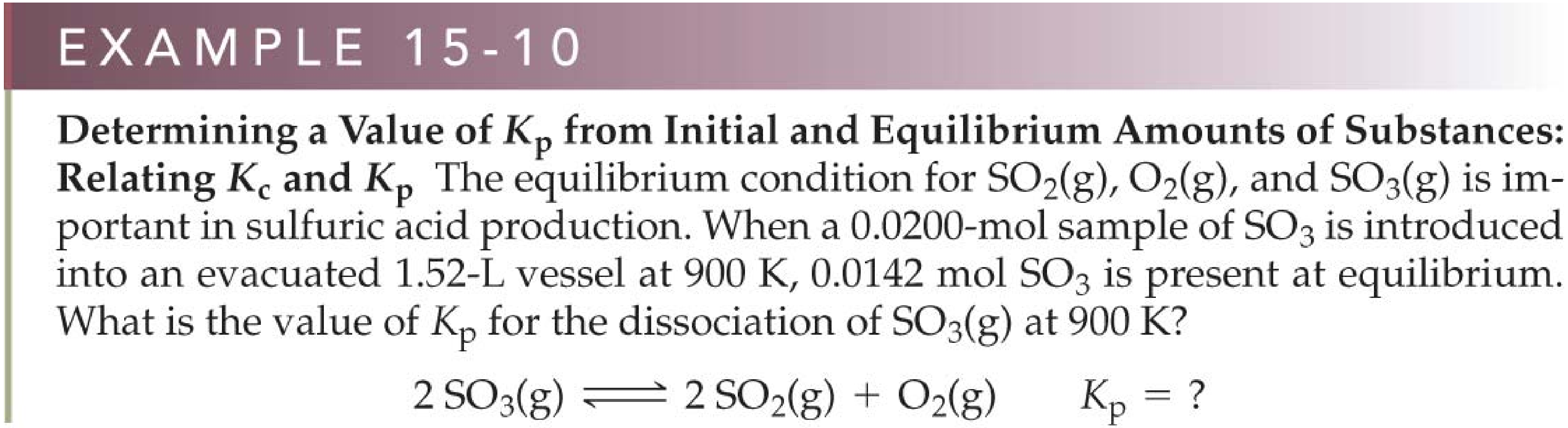
$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0113)^2}{(0.0277)} = 4.61 \times 10^{-3}$$

Practice Example A: Equilibrium is established in a 3.00-L flask at 1405 K for the reaction $2\,H_2S(g) \rightleftharpoons 2\,H_2(g) + S_2(g)$. At equilibrium, there is 0.11 mol $S_2(g)$, 0.22 mol $H_2(g)$, and 2.78 mol $H_2S(g)$. What is the value of K_c for this reaction?

Practice Example B: Equilibrium is established at 25 °C in the reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$, $K_c = 4.61 \times 10^{-3}$. If $[NO_2] = 0.0236$ M in a 2.26-L flask, how many grams of N_2O_4 are also present?

Comments

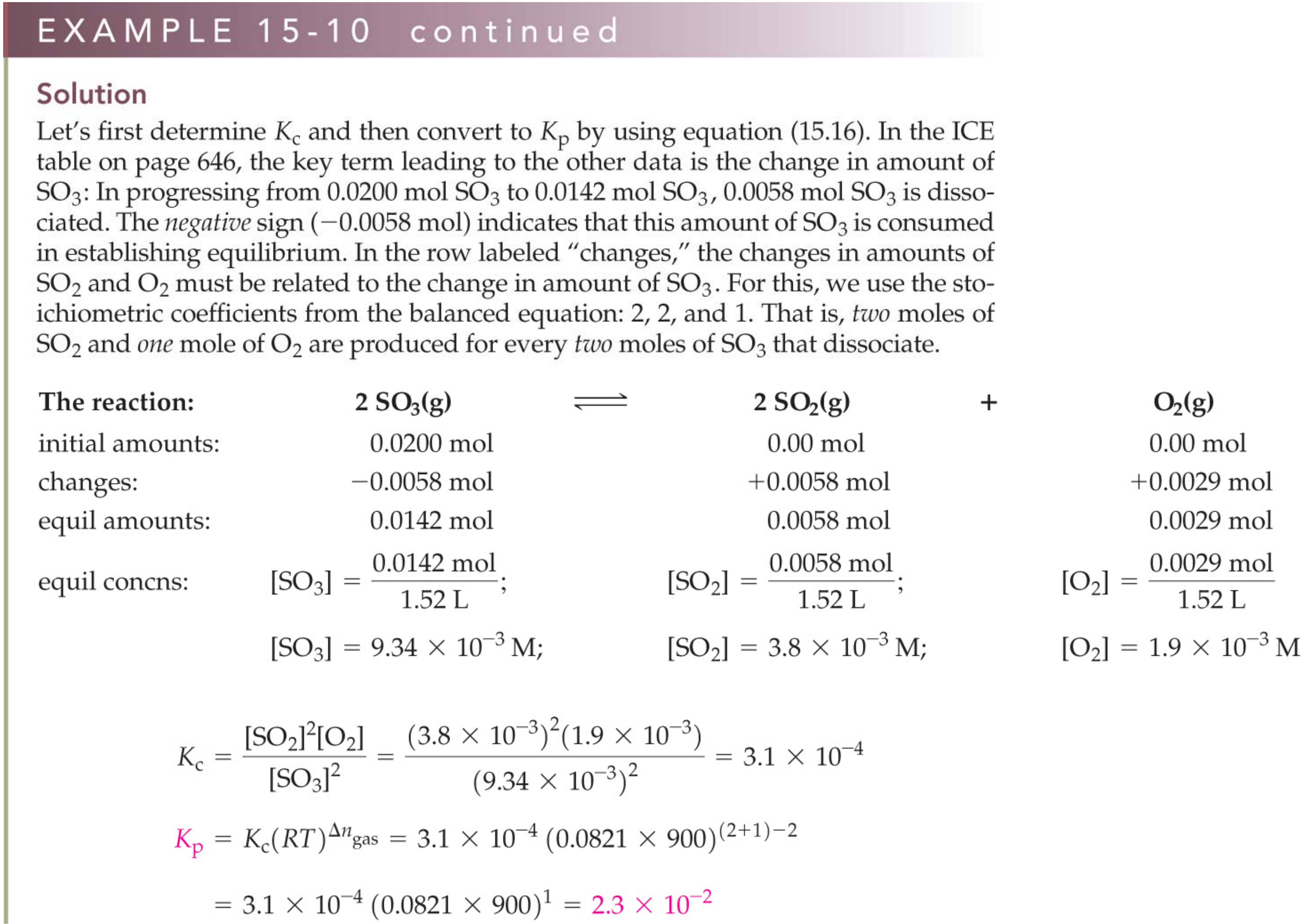
1. The quantities required in an equilibrium constant expression, K_c, are equilibrium *concentrations* in *moles per liter*, not simply equilibrium amounts in moles or masses in grams. You will find it helpful to organize all the equilibrium data and carefully label each item.



EXAMPLE 15-10

Determining a Value of K_p from Initial and Equilibrium Amounts of Substances: Relating K_c and K_p The equilibrium condition for $SO_2(g)$, $O_2(g)$, and $SO_3(g)$ is important in sulfuric acid production. When a 0.0200-mol sample of SO_3 is introduced into an evacuated 1.52-L vessel at 900 K, 0.0142 mol SO_3 is present at equilibrium. What is the value of K_p for the dissociation of $SO_3(g)$ at 900 K?

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \qquad K_p = ?$$



EXAMPLE 15-10 continued

Solution

Let's first determine K_c and then convert to K_p by using equation (15.16). In the ICE table on page 646, the key term leading to the other data is the change in amount of SO_3: In progressing from 0.0200 mol SO_3 to 0.0142 mol SO_3, 0.0058 mol SO_3 is dissociated. The *negative* sign (−0.0058 mol) indicates that this amount of SO_3 is consumed in establishing equilibrium. In the row labeled "changes," the changes in amounts of SO_2 and O_2 must be related to the change in amount of SO_3. For this, we use the stoichiometric coefficients from the balanced equation: 2, 2, and 1. That is, *two* moles of SO_2 and *one* mole of O_2 are produced for every *two* moles of SO_3 that dissociate.

The reaction:	$2\,SO_3(g)$	$\rightleftharpoons$	$2\,SO_2(g)$	+	$O_2(g)$
initial amounts:	0.0200 mol		0.00 mol		0.00 mol
changes:	−0.0058 mol		+0.0058 mol		+0.0029 mol
equil amounts:	0.0142 mol		0.0058 mol		0.0029 mol
equil concns:	$[SO_3] = \dfrac{0.0142\text{ mol}}{1.52\text{ L}}$;		$[SO_2] = \dfrac{0.0058\text{ mol}}{1.52\text{ L}}$;		$[O_2] = \dfrac{0.0029\text{ mol}}{1.52\text{ L}}$
	$[SO_3] = 9.34 \times 10^{-3}$ M;		$[SO_2] = 3.8 \times 10^{-3}$ M;		$[O_2] = 1.9 \times 10^{-3}$ M

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(3.8 \times 10^{-3})^2(1.9 \times 10^{-3})}{(9.34 \times 10^{-3})^2} = 3.1 \times 10^{-4}$$

$$K_p = K_c(RT)^{\Delta n_{\text{gas}}} = 3.1 \times 10^{-4}\,(0.0821 \times 900)^{(2+1)-2}$$

$$= 3.1 \times 10^{-4}\,(0.0821 \times 900)^1 = 2.3 \times 10^{-2}$$

EXAMPLE 15-10 continued

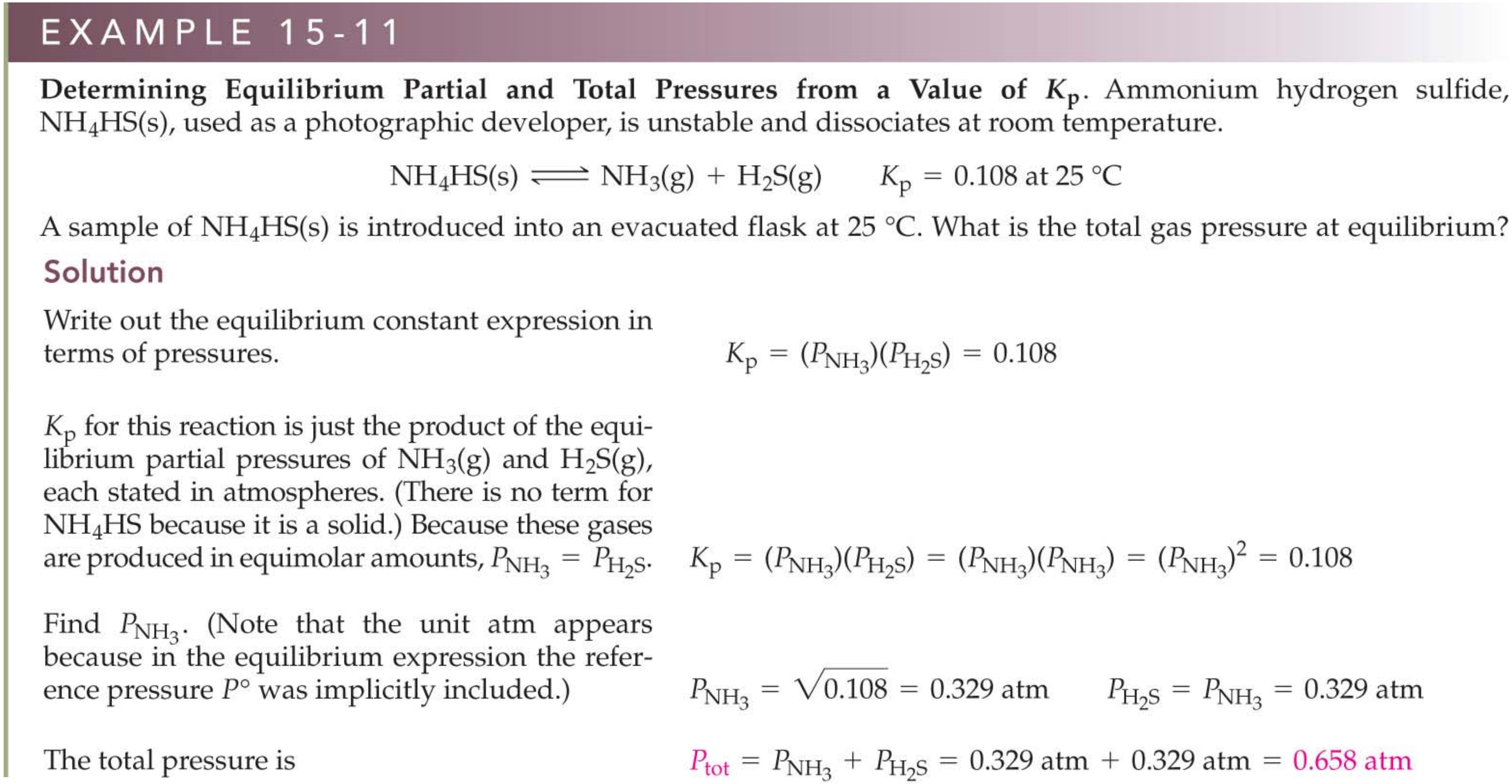
Practice Example A: A 5.00-L evacuated flask is filled with 1.86 mol NOBr. At equilibrium at 25 °C, there is 0.082 mol of Br_2 present. Determine K_c and K_p for the reaction $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$.

Practice Example B: 0.100 mol SO_2 and 0.100 mol O_2 are introduced into an evacuated 1.52-L flask at 900 K. When equilibrium is reached, the amount of SO_3 found is 0.0916 mol. Use these data to determine K_p for the reaction $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$.

Comments

2. The chemical equation for a reversible reaction serves both to establish the form of the equilibrium constant expression and to provide the conversion factors (stoichiometric factors) to relate the equilibrium quantity of one species to equilibrium quantities of the others.

3. For equilibria involving gases, you can use either K_c or K_p. In general, if the data given involve amounts of substances and volumes, it is easier to work with K_c. If data are given as partial pressures, then work with K_p. Whether working with K_c or K_p or the relationship between them, you must always base these expressions on the given chemical equation, not on equations you may have used in other situations.



EXAMPLE 15-11

Determining Equilibrium Partial and Total Pressures from a Value of K_p. Ammonium hydrogen sulfide, $NH_4HS(s)$, used as a photographic developer, is unstable and dissociates at room temperature.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad K_p = 0.108 \text{ at } 25\ °C$$

A sample of $NH_4HS(s)$ is introduced into an evacuated flask at 25 °C. What is the total gas pressure at equilibrium?

Solution

Write out the equilibrium constant expression in terms of pressures.

$$K_p = (P_{NH_3})(P_{H_2S}) = 0.108$$

K_p for this reaction is just the product of the equilibrium partial pressures of $NH_3(g)$ and $H_2S(g)$, each stated in atmospheres. (There is no term for NH_4HS because it is a solid.) Because these gases are produced in equimolar amounts, $P_{NH_3} = P_{H_2S}$.

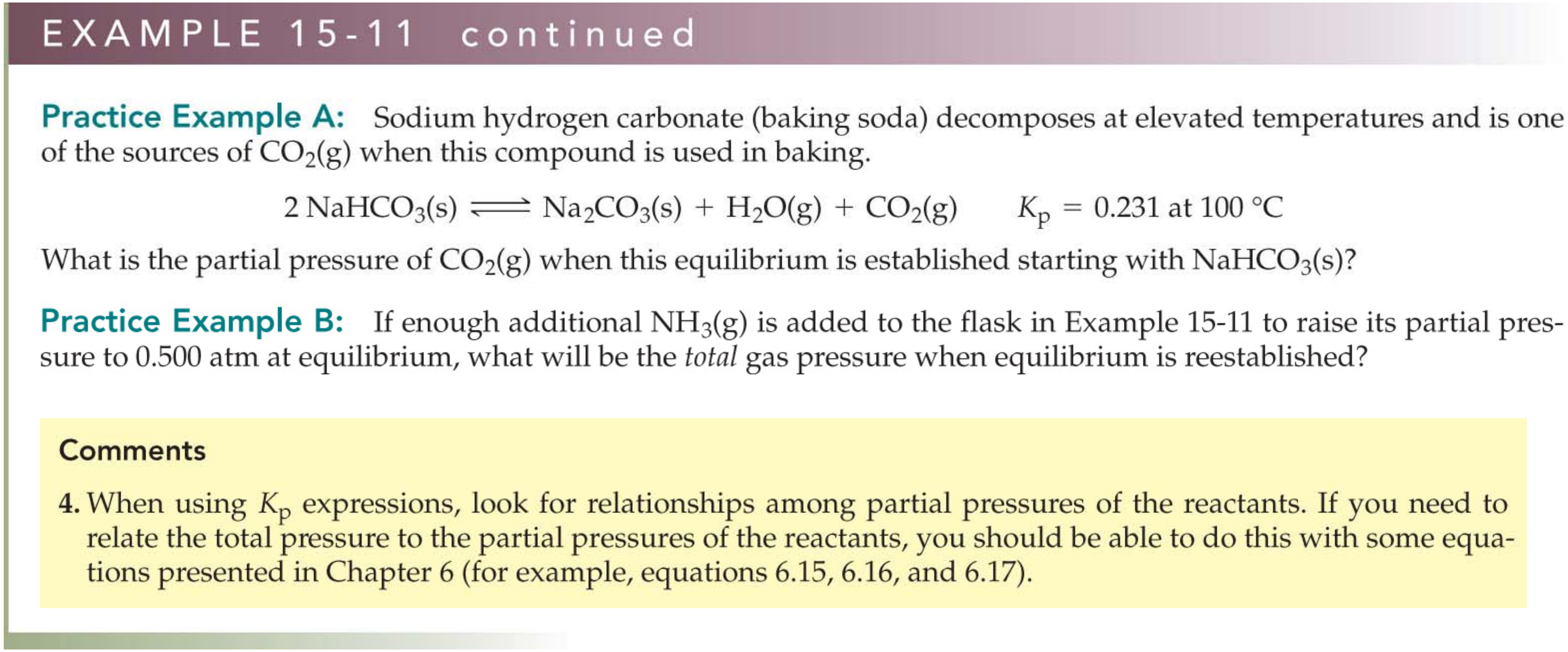
$$K_p = (P_{NH_3})(P_{H_2S}) = (P_{NH_3})(P_{NH_3}) = (P_{NH_3})^2 = 0.108$$

Find P_{NH_3}. (Note that the unit atm appears because in the equilibrium expression the reference pressure $P°$ was implicitly included.)

$$P_{NH_3} = \sqrt{0.108} = 0.329 \text{ atm} \qquad P_{H_2S} = P_{NH_3} = 0.329 \text{ atm}$$

The total pressure is

$$P_{tot} = P_{NH_3} + P_{H_2S} = 0.329 \text{ atm} + 0.329 \text{ atm} = 0.658 \text{ atm}$$



EXAMPLE 15-11 continued

Practice Example A: Sodium hydrogen carbonate (baking soda) decomposes at elevated temperatures and is one of the sources of $CO_2(g)$ when this compound is used in baking.

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g) \qquad K_p = 0.231 \text{ at } 100\ °C$$

What is the partial pressure of $CO_2(g)$ when this equilibrium is established starting with $NaHCO_3(s)$?

Practice Example B: If enough additional $NH_3(g)$ is added to the flask in Example 15-11 to raise its partial pressure to 0.500 atm at equilibrium, what will be the *total* gas pressure when equilibrium is reestablished?

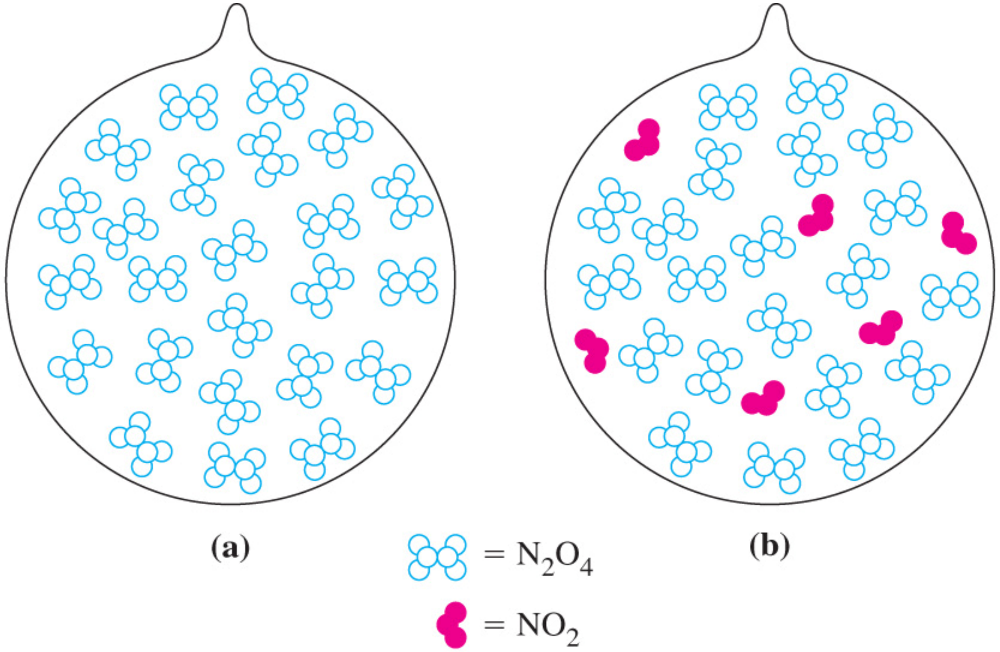
Comments

4. When using K_p expressions, look for relationships among partial pressures of the reactants. If you need to relate the total pressure to the partial pressures of the reactants, you should be able to do this with some equations presented in Chapter 6 (for example, equations 6.15, 6.16, and 6.17).

EXAMPLE 15-12

Calculating Equilibrium Concentrations from Initial Conditions. A 0.0240-mol sample of $N_2O_4(g)$ is allowed to come to equilibrium with $NO_2(g)$ in a 0.372-L flask at 25 °C. Calculate the amount of N_2O_4 present at equilibrium (Fig. 15-10).

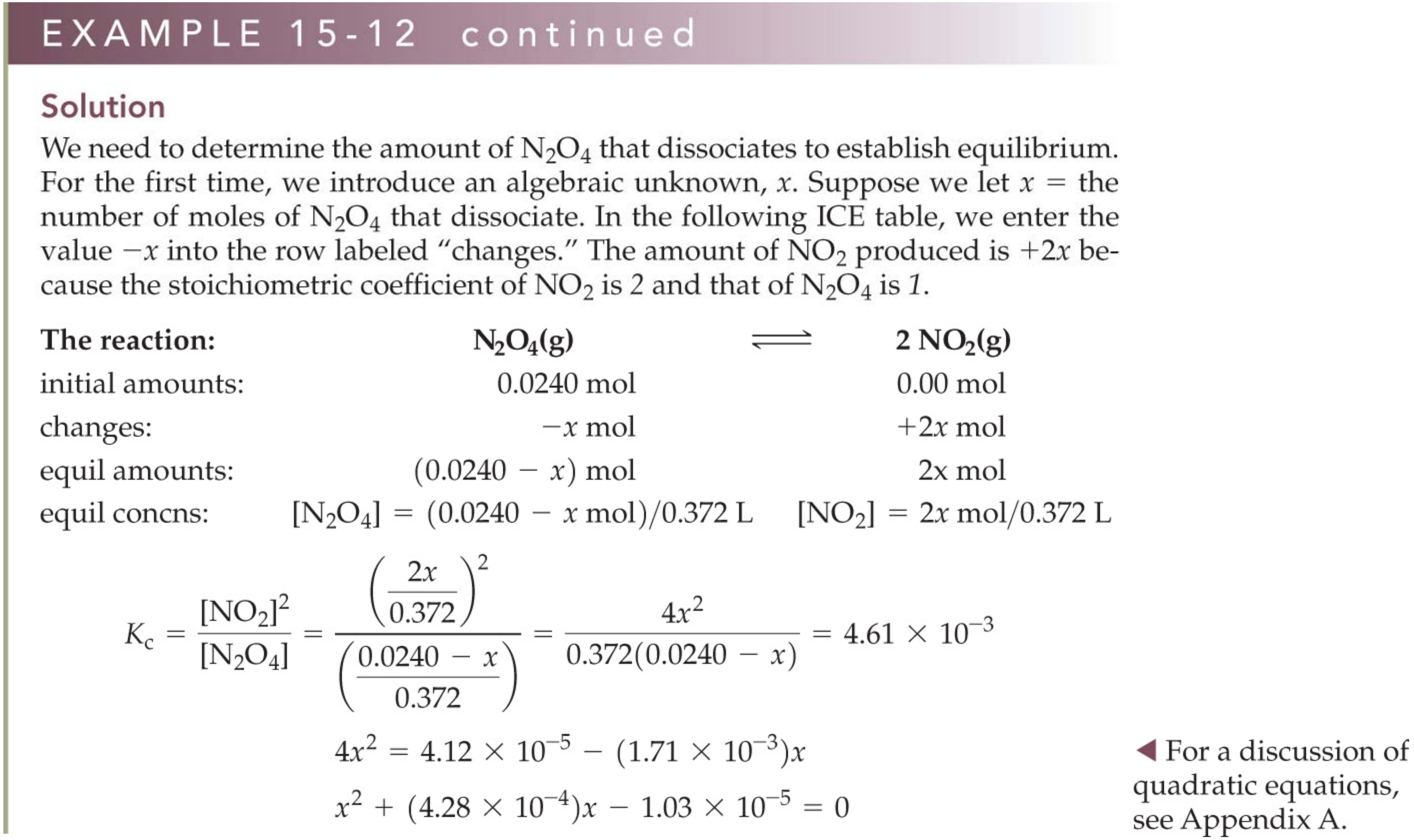
$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad K_c = 4.61 \times 10^3 \text{ at } 25\ °C$$



▲ **FIGURE 15-10**
Equilibrium in the reaction

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

at 25 °C—Example 15-12 illustrated
Each "molecule" illustrated represents 0.001 mol. **(a)** Initially, the bulb contains 0.024 mol N_2O_4, represented by 24 "molecules." **(b)** At equilibrium, some "molecules" of N_2O_4 have dissociated to NO_2. The 21 "molecules" of N_2O_4 and 6 of NO_2 correspond to 0.021 mol N_2O_4 and 0.006 mol NO_2 at equilibrium.



EXAMPLE 15-12 continued

Solution

We need to determine the amount of N_2O_4 that dissociates to establish equilibrium. For the first time, we introduce an algebraic unknown, x. Suppose we let x = the number of moles of N_2O_4 that dissociate. In the following ICE table, we enter the value $-x$ into the row labeled "changes." The amount of NO_2 produced is $+2x$ because the stoichiometric coefficient of NO_2 is *2* and that of N_2O_4 is *1*.

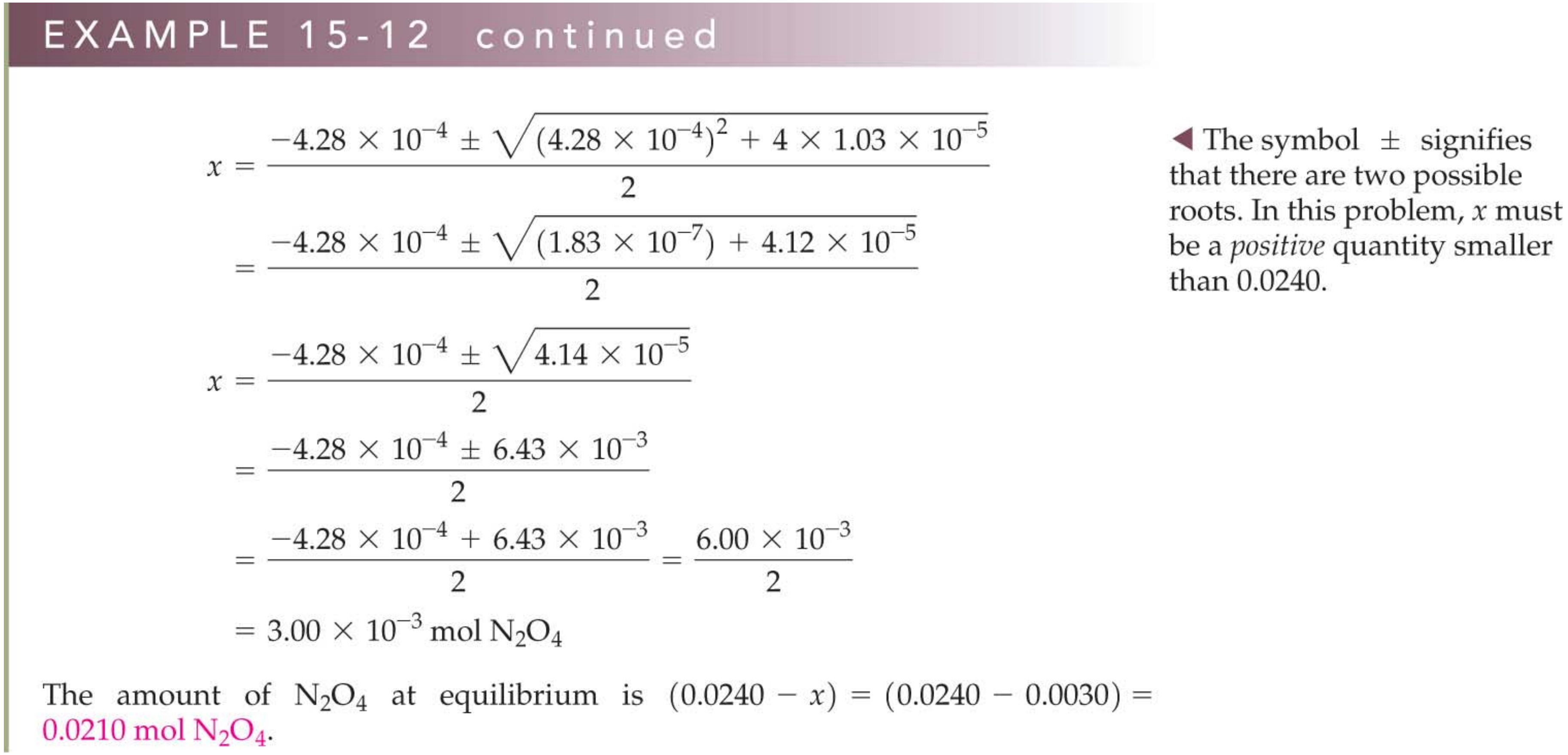
The reaction:	**$N_2O_4(g)$**	$\rightleftharpoons$	**$2\ NO_2(g)$**
initial amounts:	0.0240 mol		0.00 mol
changes:	$-x$ mol		$+2x$ mol
equil amounts:	$(0.0240 - x)$ mol		2x mol
equil concns:	$[N_2O_4] = (0.0240 - x \text{ mol})/0.372 \text{ L}$		$[NO_2] = 2x \text{ mol}/0.372 \text{ L}$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\dfrac{2x}{0.372}\right)^2}{\left(\dfrac{0.0240 - x}{0.372}\right)} = \frac{4x^2}{0.372(0.0240 - x)} = 4.61 \times 10^{-3}$$

$$4x^2 = 4.12 \times 10^{-5} - (1.71 \times 10^{-3})x$$

$$x^2 + (4.28 \times 10^{-4})x - 1.03 \times 10^{-5} = 0$$

◀ For a discussion of quadratic equations, see Appendix A.



EXAMPLE 15-12 continued

$$x = \frac{-4.28 \times 10^{-4} \pm \sqrt{(4.28 \times 10^{-4})^2 + 4 \times 1.03 \times 10^{-5}}}{2}$$

$$= \frac{-4.28 \times 10^{-4} \pm \sqrt{(1.83 \times 10^{-7}) + 4.12 \times 10^{-5}}}{2}$$

$$x = \frac{-4.28 \times 10^{-4} \pm \sqrt{4.14 \times 10^{-5}}}{2}$$

$$= \frac{-4.28 \times 10^{-4} \pm 6.43 \times 10^{-3}}{2}$$

$$= \frac{-4.28 \times 10^{-4} + 6.43 \times 10^{-3}}{2} = \frac{6.00 \times 10^{-3}}{2}$$

$$= 3.00 \times 10^{-3} \text{ mol } N_2O_4$$

◀ The symbol ± signifies that there are two possible roots. In this problem, x must be a *positive* quantity smaller than 0.0240.

The amount of N_2O_4 at equilibrium is $(0.0240 - x) = (0.0240 - 0.0030) =$ 0.0210 mol N_2O_4.

EXAMPLE 15-12 continued

Practice Example A: If 0.150 mol $H_2(g)$ and 0.200 mol $I_2(g)$ are introduced into a 15.0-L flask at 445 °C and allowed to come to equilibrium, how many moles of HI(g) will be present?

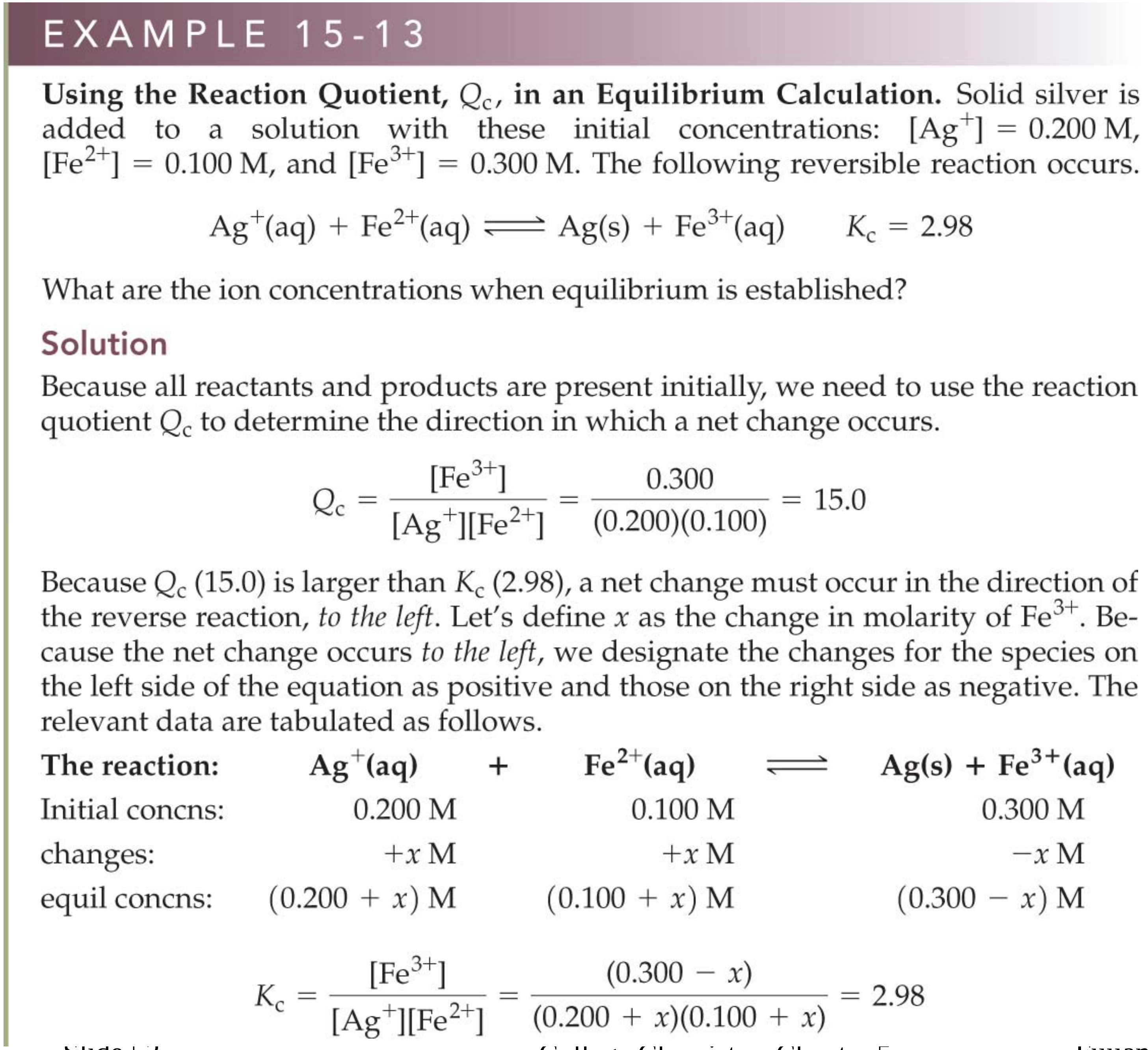
$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \qquad K_c = 50.2 \text{ at } 445\,^\circ\text{C}$$

Practice Example B: Suppose the equilibrium mixture of Example 15-12 is transferred to a 10.0-L flask. **(a)** Will the equilibrium amount of N_2O_4 increase or decrease? Explain. **(b)** Calculate the number of moles of N_2O_4 in the new equilibrium condition.

Comments

5. When you need to introduce an algebraic unknown, x, into an equilibrium calculation, follow these steps.

- Introduce x into the ICE setup in the row labeled "changes."
- Decide which change to label as x, that is, the amount of a reactant consumed or of a product formed. Usually, we base this on the species that has the smallest stoichiometric coefficient in the balanced chemical equation.
- Use stoichiometric factors to relate the other changes to x (that is, $2x$, $3x, \ldots$).
- Consider that equilibrium amounts = intial amounts + "changes." (If you have assigned the correct signs to the changes, equilibrium amounts will also be correct.)
- After substitutions have been made into the equilibrium constant expression, the equation will often be a quadratic equation in x, which you can solve by the quadratic formula. Occasionally you may encounter a higher-degree equation. Appendix A-3 outlines a straightforward method of dealing with these.



EXAMPLE 15-13

Using the Reaction Quotient, Q_c, in an Equilibrium Calculation. Solid silver is added to a solution with these initial concentrations: $[Ag^+] = 0.200$ M, $[Fe^{2+}] = 0.100$ M, and $[Fe^{3+}] = 0.300$ M. The following reversible reaction occurs.

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq) \qquad K_c = 2.98$$

What are the ion concentrations when equilibrium is established?

Solution

Because all reactants and products are present initially, we need to use the reaction quotient Q_c to determine the direction in which a net change occurs.

$$Q_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{0.300}{(0.200)(0.100)} = 15.0$$

Because Q_c (15.0) is larger than K_c (2.98), a net change must occur in the direction of the reverse reaction, *to the left*. Let's define x as the change in molarity of Fe^{3+}. Because the net change occurs *to the left*, we designate the changes for the species on the left side of the equation as positive and those on the right side as negative. The relevant data are tabulated as follows.

The reaction:	**$Ag^+(aq)$**	**+**	**$Fe^{2+}(aq)$**	**$\rightleftharpoons$**	**$Ag(s) + Fe^{3+}(aq)$**
Initial concns:	0.200 M		0.100 M		0.300 M
changes:	$+x$ M		$+x$ M		$-x$ M
equil concns:	$(0.200 + x)$ M		$(0.100 + x)$ M		$(0.300 - x)$ M

$$K_c = \frac{[Fe^{3+}]}{[Ag^+][Fe^{2+}]} = \frac{(0.300 - x)}{(0.200 + x)(0.100 + x)} = 2.98$$

EXAMPLE 15-13 continued

This equation, which is solved in Appendix A-3, is a quadratic equation for which the acceptable root is $x = 0.11$. To obtain the equilibrium concentrations, we substitute this value of x into the terms shown in the table of data.

$$[\mathrm{Ag}^+]_{\mathrm{equil}} = 0.200 + 0.11 = 0.31\ \mathrm{M}$$

$$[\mathrm{Fe}^{2+}]_{\mathrm{equil}} = 0.100 + 0.11 = 0.21\ \mathrm{M}$$

$$[\mathrm{Fe}^{3+}]_{\mathrm{equil}} = 0.300 - 0.11 = 0.19\ \mathrm{M}$$

CHECK: If we have done the calculation correctly, we should obtain a value very close to that given for K_c when we substitute the *calculated* equilibrium concentrations into the reaction quotient, Q_c. We do.

$$Q_c = \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Ag}^+][\mathrm{Fe}^{2+}]} = \frac{(0.19)}{(0.31)(0.21)} = 2.9 \qquad (K_c = 2.98)$$

Practice Example A: Excess Ag(s) is added to 1.20 M Fe^{3+}(aq). Given that

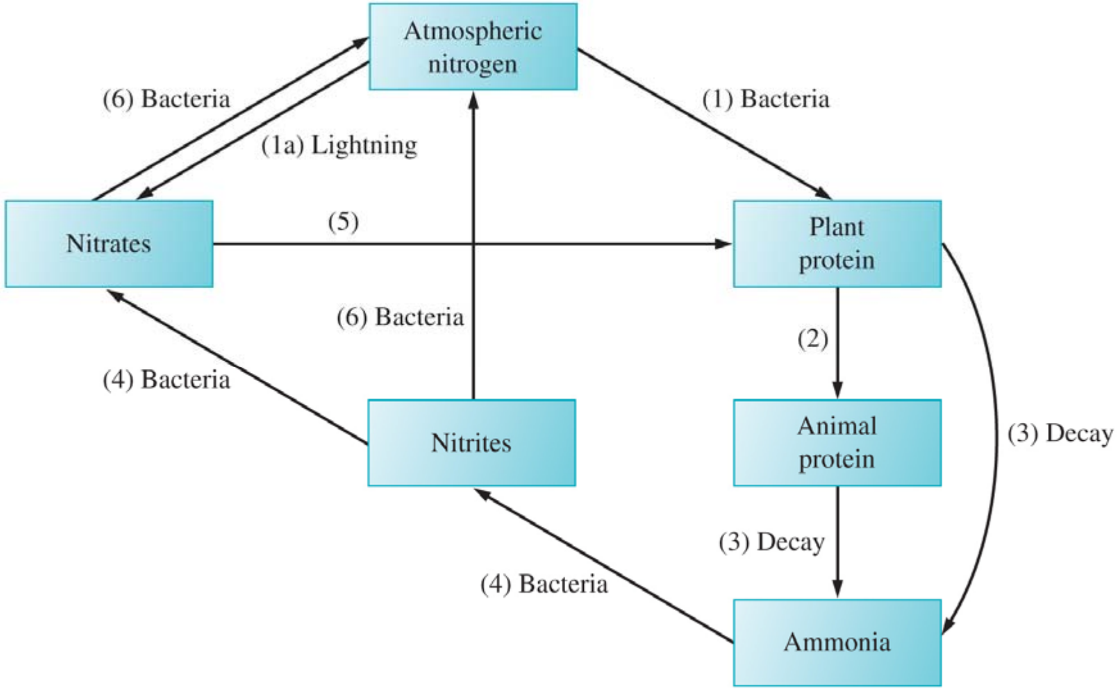
$$\mathrm{Ag}^+(\mathrm{aq}) + \mathrm{Fe}^{2+}(\mathrm{aq}) \rightleftharpoons \mathrm{Ag}(\mathrm{s}) + \mathrm{Fe}^{3+}(\mathrm{aq}) \qquad K_c = 2.98$$

what are the equilibrium concentrations of the species in solution?

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

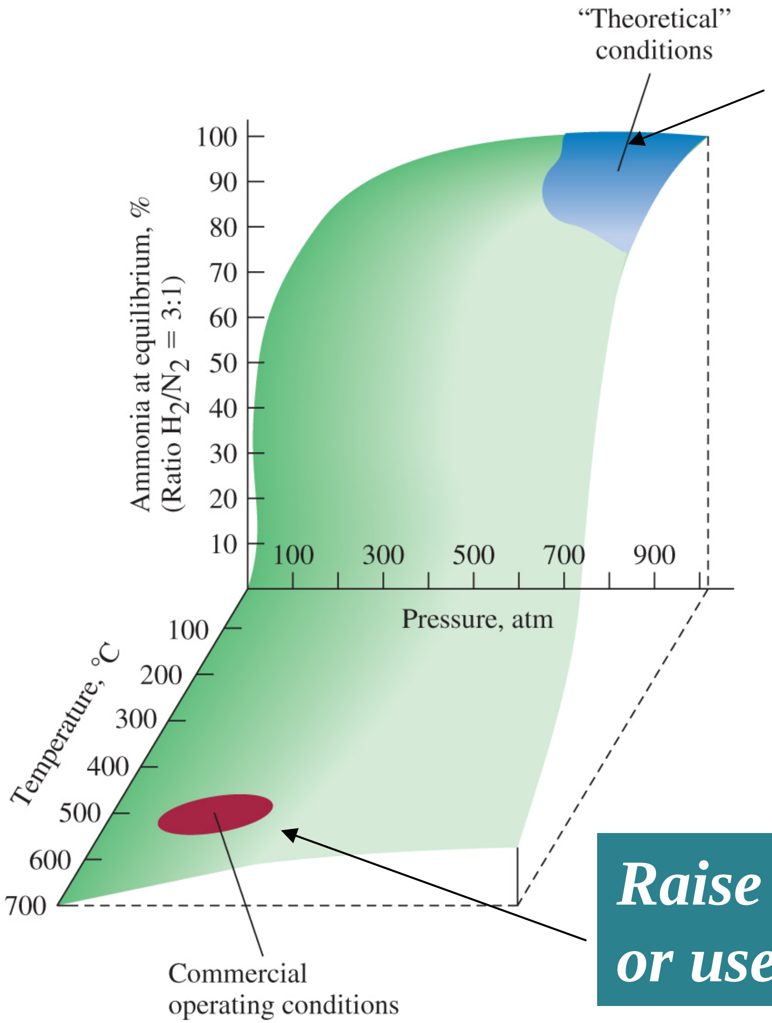
$$N_2(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO(g)$$

$K_P = 4.7\ 10^{-31}$ at 298K and
1.3×10^{-4} at 1800K



Use of liquid ammonia as a fertilizer, by direct inject into the soil.

Synthesis of Ammonia



high pressures
low temperatures

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

Raise the temperature or use a catalyst.

Summary

- Dynamic equilibrium and equilibrium constand, Kp,Kc
- Le Chatelier’s principle
- The reaction quotient. Qc and Qp.
- Quantitative equilibium calculation

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.