Ch14 Chemical Equilibrium

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CHEMICAL EQUILIBRIUM

▲ If the rate at which people move from the first floor to the second equals the rate at which people move from the second floor to the first, the number of people on each floor remains constant and the two populations are in dynamic equilibrium.

Chemical Equilibrium The state reached when the concentrations of reactants and products remain constant over time

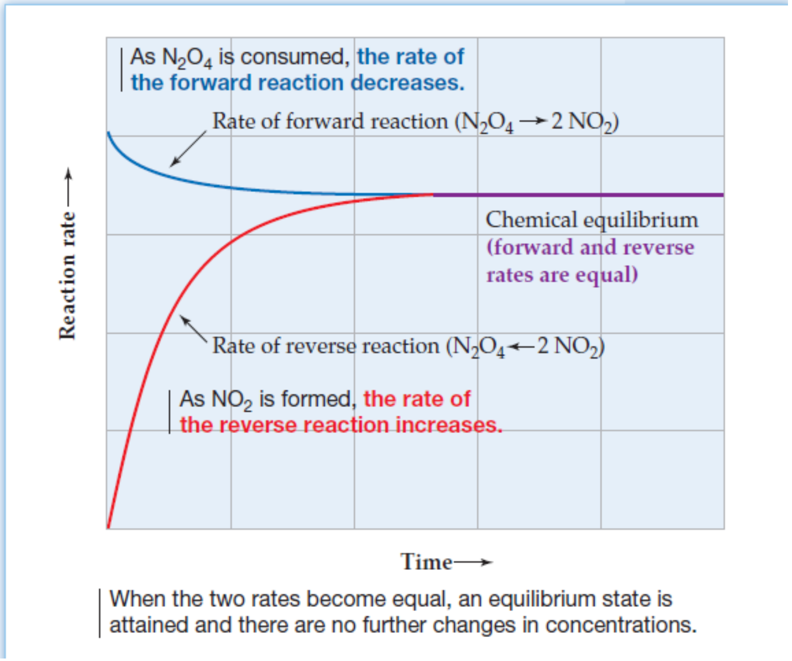
Chemical Equilibrium

Chemical Equilibrium:

When the rate of the forward reaction equals the rate of the reverse reaction and the concentration of products and reactants remains unchanged

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ Reaction occurs in both directions

Arrows going both directions (⇆) indicates equilibrium in a chemical equation



When the two rates become equal, an equilibrium state is attained and there are no further changes in concentrations.

Reversible Reactions:

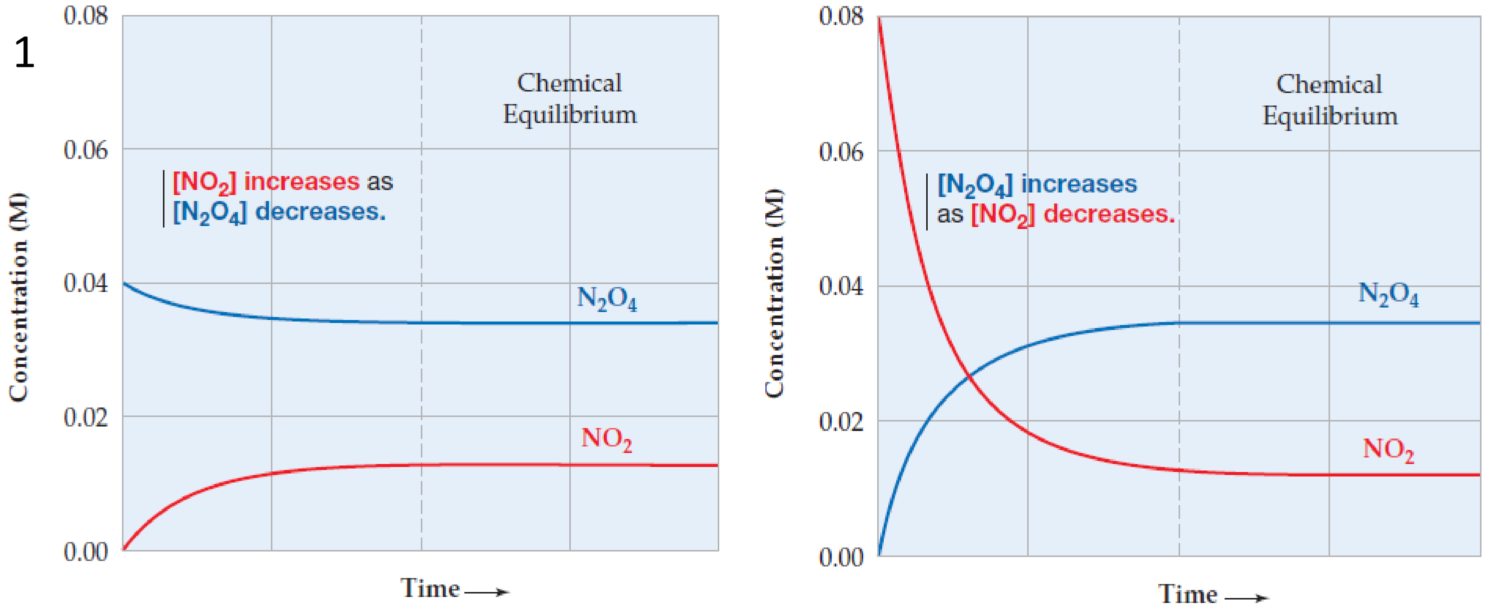
A chemical reaction in which the products can react to re-form the reactants

Eventually the rates are equal

TABLE 13.1 Concentration Data at 25 °C for the Reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

	Initial Concentrations (M)		Equilibrium Concentrations (M)		Equilibrium Constant Expression
Experiment	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$
1	0.0400	0.0000	0.0337	0.0125	4.64×10^{-3}
2	0.0000	0.0800	0.0337	0.0125	4.64×10^{-3}
3	0.0600	0.0000	0.0522	0.0156	4.66×10^{-3}
4	0.0000	0.0600	0.0246	0.0107	4.65×10^{-3}

Exp 1



Exp 2

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

The expression $[NO_2]^2/[N_2O_4]$ appears to be related to the balanced equation for the reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ in that the concentration of the product is in the numerator, raised to the power of its coefficient in the balanced equation, and the concentration of the reactant is in the denominator. Is there an analogous expression

Law of Mass Action

For the reaction, when $\text{Rate}_{\text{for}} = \text{Rate}_{\text{rev}}$

$$jA + kB \rightleftarrows lC + mD$$

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

Where K is the equilibrium constant

Writing an Equilibrium Expression

Write the equilibrium expression for the reaction:

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$

$$K = ???$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

Playing with Equilibrium Expressions

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

- The equilibrium expression for a reaction is the reciprocal for a reaction written in reverse

$$2NO(g) + O_2(g) \leftrightarrows 2NO_2(g)$$

$$K' = \frac{1}{K} = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

Playing with Equilibrium Expressions

$$2NO_2(g) \leftrightarrows 2NO(g) + O_2(g)$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

- When the balanced equation for a reaction is multiplied by a factor *n*, the equilibrium expression for the new reaction is the original expression, raised to the *nth* power.

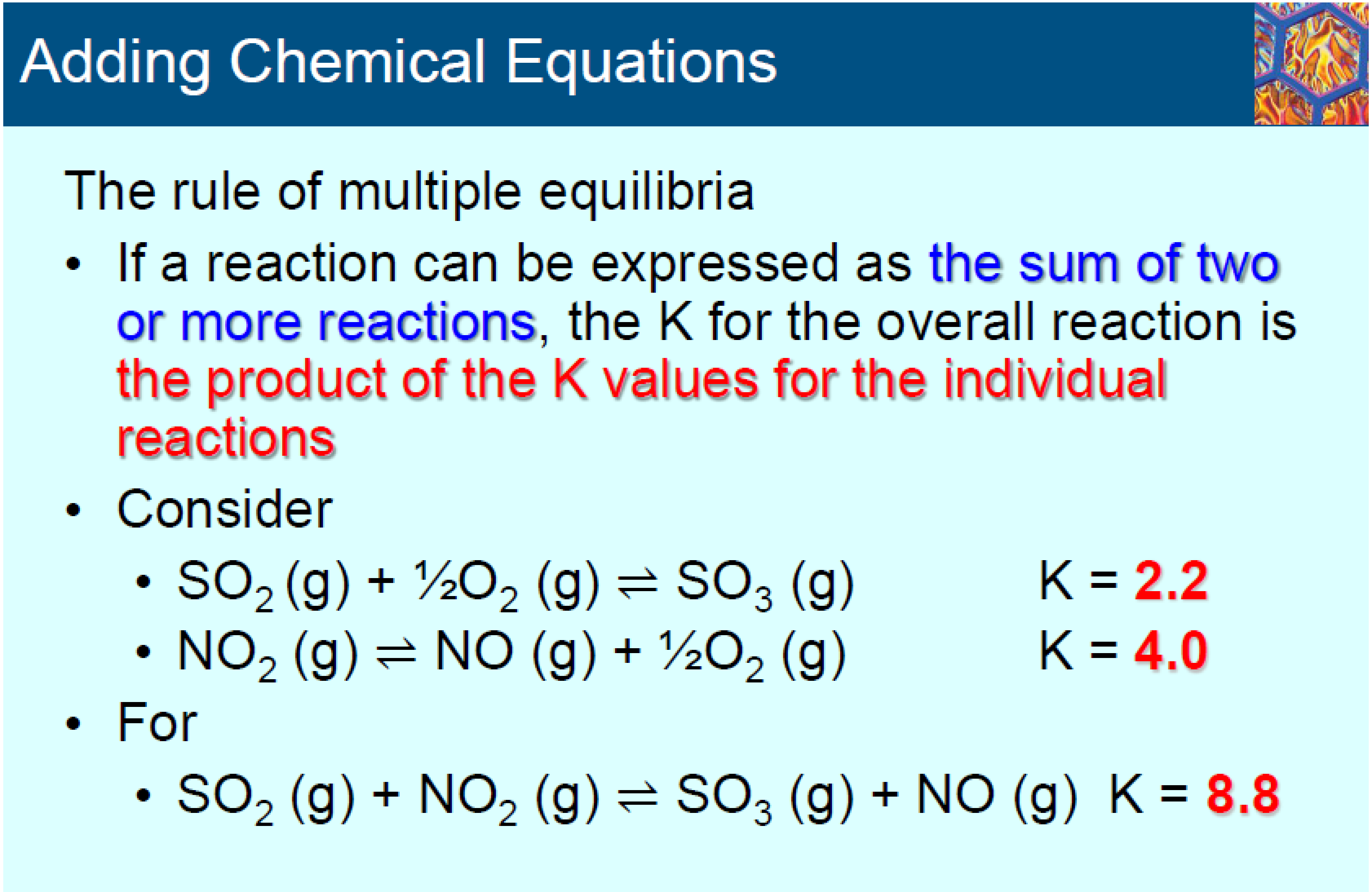
$$NO_2(g) \leftrightarrows NO(g) + \tfrac{1}{2}O_2(g)$$

$$K' = K^{\frac{1}{2}} = \frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]}$$

Playing with K

- If we multiply the equation by a constant, n
- $njA + nkB \rightleftharpoons nlC + nmD$
- Then the equilibrium constant is
- $$K' = \frac{[A]^{nj}[B]^{nk}}{[C]^{nl}[D]^{nm}} = \frac{([A]^{j}[B]^{k})^{n}}{([C]^{l}[D]^{m})^{n}} = K^{n}$$

Playing with K



Adding Chemical Equations

The rule of multiple equilibria

- If a reaction can be expressed as the sum of two or more reactions, the K for the overall reaction is the product of the K values for the individual reactions
- Consider
  - $SO_2\ (g) + \frac{1}{2}O_2\ (g) \rightleftharpoons SO_3\ (g)$ K = **2.2**
  - $NO_2\ (g) \rightleftharpoons NO\ (g) + \frac{1}{2}O_2\ (g)$ K = **4.0**
- For
  - $SO_2\ (g) + NO_2\ (g) \rightleftharpoons SO_3\ (g) + NO\ (g)$ K = **8.8**

Playing with K- Summary

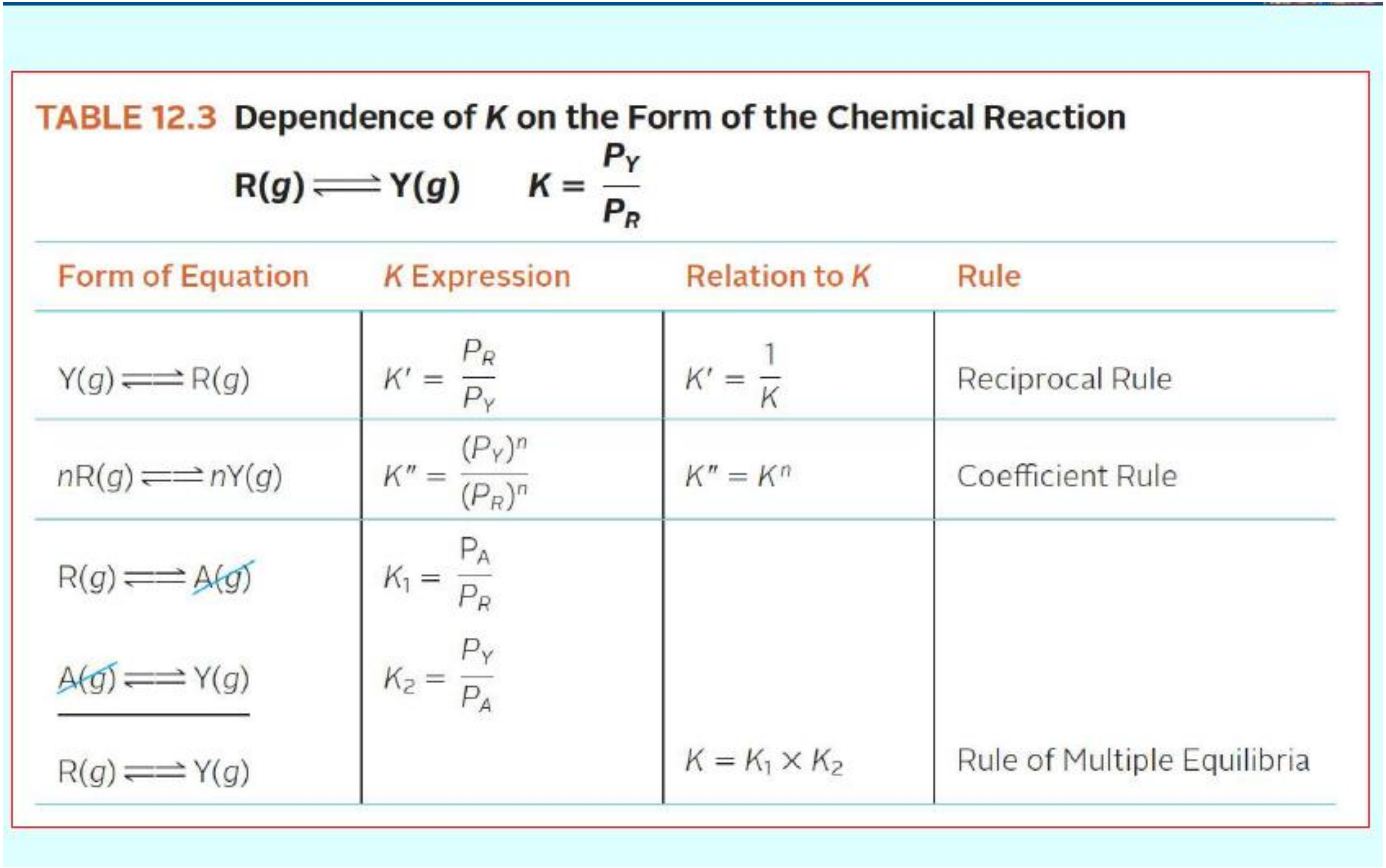


TABLE 12.3 Dependence of K on the Form of the Chemical Reaction

$$R(g) \rightleftharpoons Y(g) \qquad K = \frac{P_Y}{P_R}$$

Form of Equation	K Expression	Relation to K	Rule
$Y(g) \rightleftharpoons R(g)$	$K' = \frac{P_R}{P_Y}$	$K' = \frac{1}{K}$	Reciprocal Rule
$nR(g) \rightleftharpoons nY(g)$	$K'' = \frac{(P_Y)^n}{(P_R)^n}$	$K'' = K^n$	Coefficient Rule
$R(g) \rightleftharpoons \cancel{A(g)}$	$K_1 = \frac{P_A}{P_R}$		
$\cancel{A(g)} \rightleftharpoons Y(g)$	$K_2 = \frac{P_Y}{P_A}$		
$R(g) \rightleftharpoons Y(g)$		$K = K_1 \times K_2$	Rule of Multiple Equilibria

Equilibrium Expressions Involving Pressure

For the gas phase reaction:

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

$$K_P = \frac{{P_{NH_3}}^2}{(P_{N_2})({P_{H_2}}^3)}$$

$$P_{NH_3}, P_{N_2}, P_{H_2} \text{ are equilibrium partial pressures}$$

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

Equilibrium and Pressure – Kc and Kp

- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
- $$Kp = \frac{(P_{SO3})^2}{(P_{SO2})^2\ (P_{O2})}$$
- $$Kc = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]}$$

Equilibrium and Pressure – Kc and Kp

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

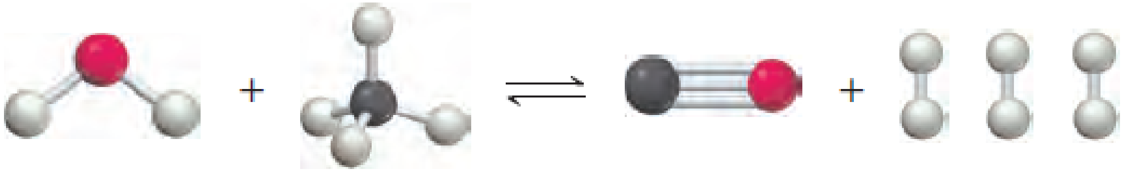
- $Kc = \dfrac{(P_{SO3}/RT)^2}{(P_{SO2}/RT)^2(P_{O2}/RT)}$
- $Kc = \dfrac{(P_{SO3})^2 \quad (1/RT)^2}{(P_{SO2})^2(P_{O2})\ (1/RT)^3}$
- $\underline{Kc} = Kp\ \dfrac{(1/RT)^2}{(1/RT)^3} = \underline{Kp\ RT}$

$$\Rightarrow Kp = kc\ (RT)^{-1}$$

RELATING THE EQUILIBRIUM CONSTANTS K_p AND K_c

Hydrogen is produced industrially by the steam–hydrocarbon re-forming process. The reaction that takes place in the first step of this process is

$$H_2O(g) + CH_4(g) \rightleftharpoons CO(g) + 3\,H_2(g)$$



(a) If $K_c = 3.8 \times 10^{-3}$ at 1000 K, what is the value of K_p at the same temperature?

(b) If $K_p = 6.1 \times 10^4$ at 1125 °C, what is the value of K_c at 1125 °C?

STRATEGY

To calculate K_p from K_c, or vice versa, use the equation $K_p = K_c(RT)^{\Delta n}$, where R must be in units of $(L \cdot atm)/(K \cdot mol)$, T is the temperature in kelvin, and Δn is the number of moles of gaseous products minus the number of moles of gaseous reactants.

SOLUTION

(a) For this reaction, $\Delta n = (1 + 3) - (1 + 1) = 2$. Therefore,

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^2 = (3.8 \times 10^{-3})[(0.082\,06)(1000)]^2 = 26$$

(b) Solving the equation $K_p = K_c(RT)^2$ for K_c gives

$$K_c = \frac{K_p}{(RT)^2} = \frac{6.1 \times 10^4}{[(0.082\,06)(1398)]^2} = 4.6$$

Note that the temperature in these equations is the absolute temperature; 1125 °C corresponds to 1125 + 273 = 1398 K.

Equilibrium Constant Expression

- For a reaction where
  - $aA\ (g) + bB\ (g) \rightleftharpoons cC\ (g) + dD\ (g)$
    - A, B, C, D all gases
    - a, b, c, d are the coefficients of the balanced equation
- K_p is the **equilibrium constant**

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

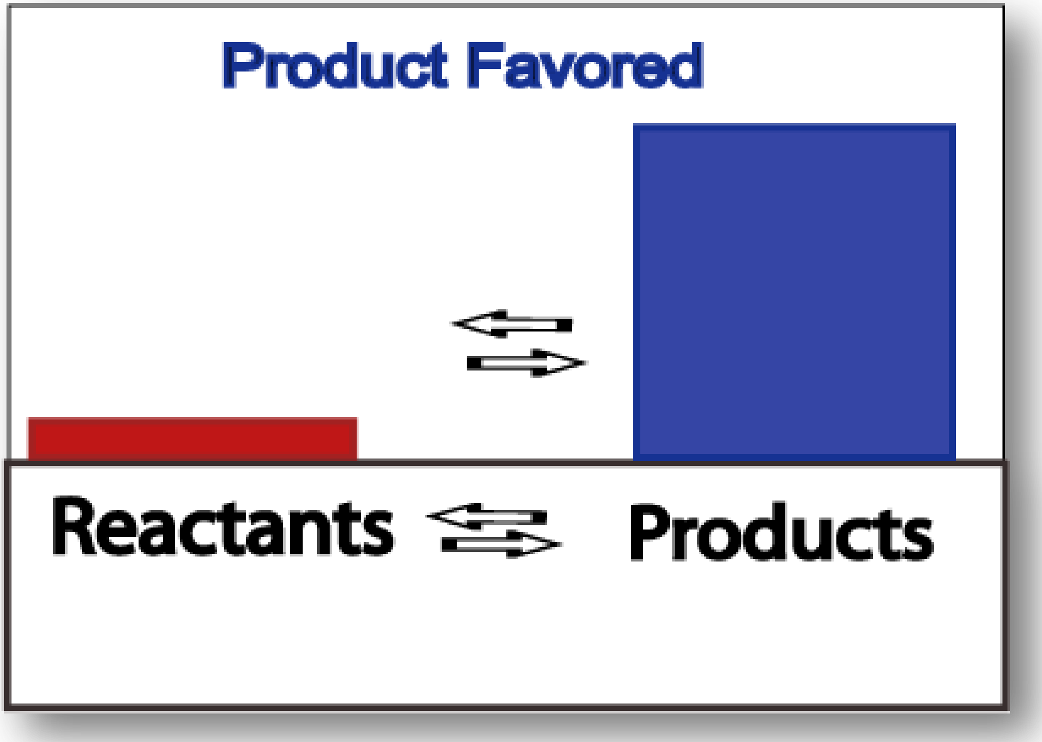
  - All partial pressures must be expressed in atm.
  - Product terms are in the numerator.
  - Reactant terms are in the denominator.
  - Coefficients of reactant and product are used as powers.
  - This K can be termed **K_p** (pressure equilibrium constant)

The units for K

- Are determined by the various powers and units of concentrations.
- They depend on the reaction.

Product Favored Equilibrium

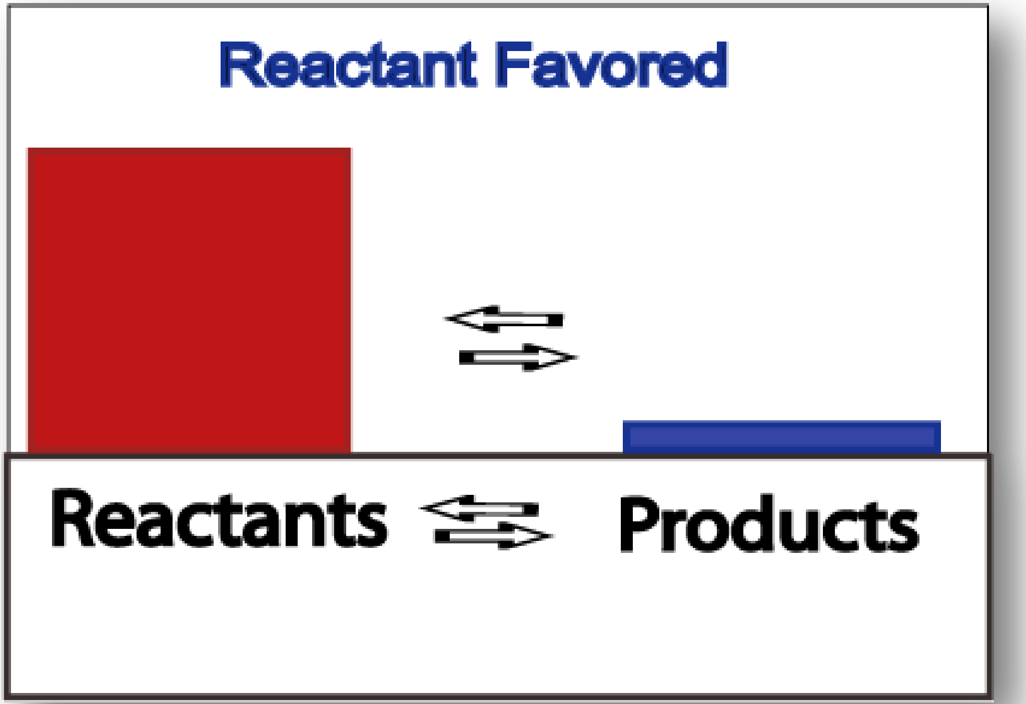
Large values for K signify the reaction is “product favored”



When equilibrium is achieved, most reactant has been converted to product

Reactant Favored Equilibrium

Small values for *K* signify the reaction is “reactant favored”



When equilibrium is achieved, very little reactant has been converted to product

Solving for Equilibrium Concentration

Consider this reaction at some temperature:

$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$ $K = 2.0$

Assume you start with 8 molecules of H_2O and 6 molecules of CO. How many molecules of H_2O, CO, H_2, and CO_2 are present at equilibrium?

Here, we learn about **"ICE"** – the most important problem solving technique in the second semester. You will use it for the next 4 chapters!

Solving for Equilibrium Concentration

$H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$ $K = 2.0$

Step #1: We write the law of mass action for the reaction:

$$2.0 = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

Solving for Equilibrium Concentration

Step #2: We "ICE" the problem, beginning with the Initial concentrations

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

Initial:	8	6	0	0
Change:	-x	-x	+x	+x
Equilibrium:	8-x	6-x	x	x

Solving for Equilibrium Concentration

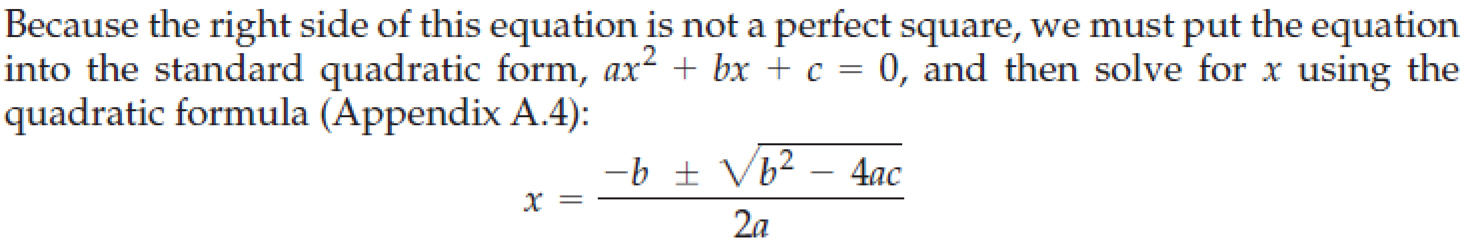
Step #3: We plug equilibrium concentrations into our equilibrium expression, and solve for x

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

Equilibrium:	**8-x**	**6-x**	**x**	**x**

$$2.0 = \frac{(x)(x)}{(8-x)(6-x)}$$

$$\boxed{x = 4}$$



Because the right side of this equation is not a perfect square, we must put the equation into the standard quadratic form, $ax^2 + bx + c = 0$, and then solve for x using the quadratic formula (Appendix A.4):

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solving for Equilibrium Concentration

Step #4: Substitute x into our equilibrium concentrations to find the actual concentrations

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

Equilibrium:	**8-x**	**6-x**	**x**	**x**

$$x = 4$$

Equilibrium:	**8-4=4**	**6-4=2**	**4**	**4**

Example 14.5 Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:

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

A reaction mixture at 780 ° C initially contains [CO] = 0.500 M and $[H_2]$ = 1.00 M. At equilibrium, the CO concentration is found to be 0.15 M. What is the value of the equilibrium constant?

	[CO]	$[H_2]$	$[CH_3OH]$
Initial	0.500	1.00	0.00
Change			
Equil	0.15		

	[CO]	$[H_2]$	$[CH_3OH]$
Initial	0.500	1.00	0.00
Change	−0.35	−0.70	+0.35
Equil	0.15		

$$\begin{aligned} K_c &= \frac{[CH_3OH]}{[CO][H_2]^2} \\ &= \frac{0.35}{(0.15)(0.30)^2} \\ &= 26 \end{aligned}$$

Example 14.6 Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g)$$

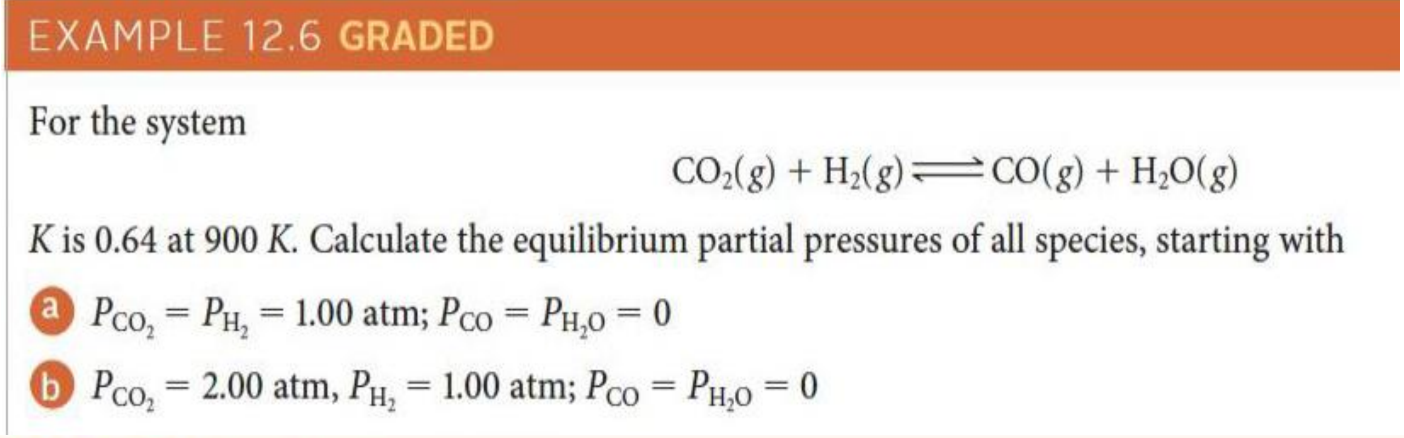
A reaction mixture at 1700 ° C initially contains $[CH_4] = 0.115$ M. At equilibrium, the mixture contains $[C_2H_2] = 0.035$ M. What is the value of the equilibrium constant?

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.115	0.00	0.00
Change			
Equil		0.035	

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.115	0.00	0.00
Change	−0.070	+0.035	+0.105
Equil		0.035	

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} = \frac{(0.035)(0.105)^3}{(0.045)^2} = 0.020$$



EXAMPLE 12.6 **GRADED**

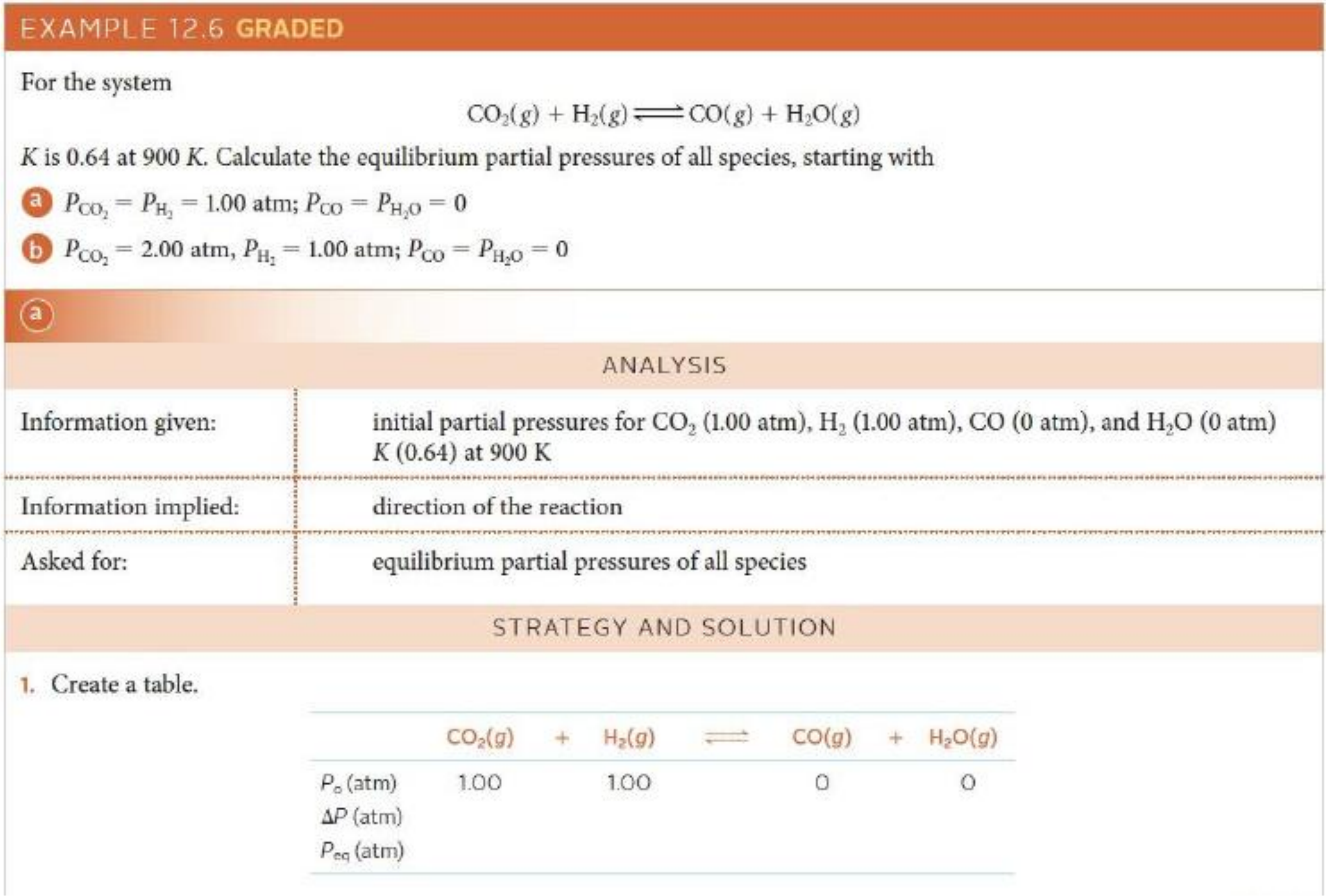
For the system

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

K is 0.64 at 900 K. Calculate the equilibrium partial pressures of all species, starting with

ⓐ $P_{CO_2} = P_{H_2} = 1.00$ atm; $P_{CO} = P_{H_2O} = 0$

ⓑ $P_{CO_2} = 2.00$ atm, $P_{H_2} = 1.00$ atm; $P_{CO} = P_{H_2O} = 0$



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ⓑ $P_{CO_2} = 2.00$ atm, $P_{H_2} = 1.00$ atm; $P_{CO} = P_{H_2O} = 0$

ⓐ

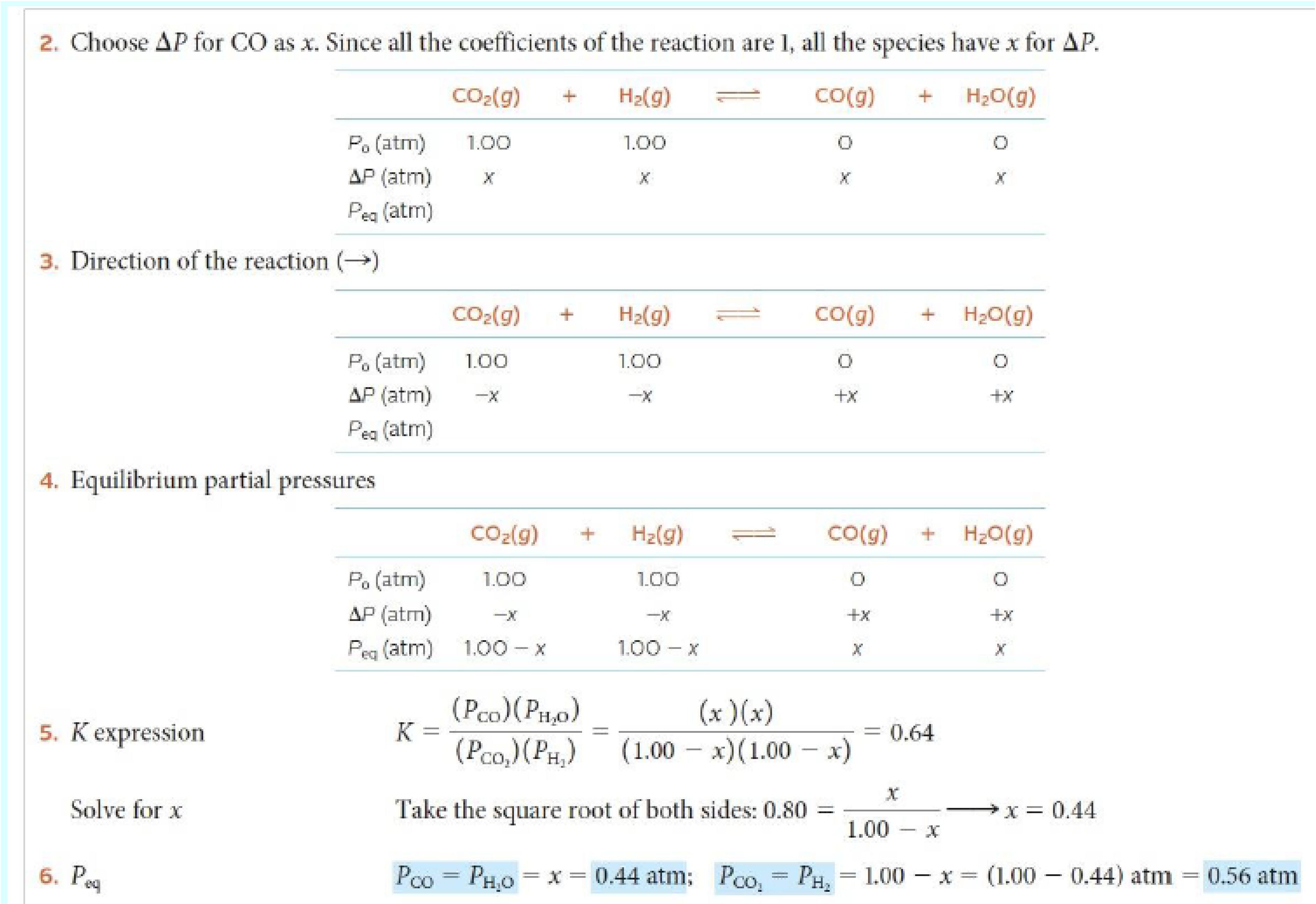
ANALYSIS

Information given:	initial partial pressures for CO_2 (1.00 atm), H_2 (1.00 atm), CO (0 atm), and H_2O (0 atm) K (0.64) at 900 K
Information implied:	direction of the reaction
Asked for:	equilibrium partial pressures of all species

STRATEGY AND SOLUTION

1. Create a table.

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	1.00		1.00		0		0
ΔP (atm)							
P_{eq} (atm)							



2. Choose ΔP for CO as x. Since all the coefficients of the reaction are 1, all the species have x for ΔP.

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_0 (atm)	1.00		1.00		0		0
ΔP (atm)	x		x		x		x
P_{eq} (atm)							

3. Direction of the reaction (→)

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_0 (atm)	1.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)							

4. Equilibrium partial pressures

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_0 (atm)	1.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)	$1.00 - x$		$1.00 - x$		x		x

5. K expression

$$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(x)(x)}{(1.00 - x)(1.00 - x)} = 0.64$$

Solve for x

Take the square root of both sides: $0.80 = \dfrac{x}{1.00 - x} \longrightarrow x = 0.44$

6. P_{eq}

$P_{CO} = P_{H_2O} = x = 0.44$ atm; $P_{CO_2} = P_{H_2} = 1.00 - x = (1.00 - 0.44)$ atm $= 0.56$ atm

ⓑ

ANALYSIS

Information given:	initial partial pressures for CO_2 (2.00 atm), H_2 (1.00 atm), CO (0 atm), and H_2O (0 atm) K (0.64) at 900 K
Information implied:	direction of the reaction
Asked for:	equilibrium partial pressures of all species

STRATEGY AND SOLUTION

1–4. The first four steps (shown in detail in part (a)) of the pathway give the following table:

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	2.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)	$2.00 - x$		$1.00 - x$		x		x

5. K expression

$$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(x)(x)}{(2.00 - x)(1.00 - x)} = 0.64$$

It is not useful to take the square root of both sides, so rearrange the equation to the standard form for using the quadratic equation: $ax^2 + bx + c = 0 \longrightarrow 0.36\,x^2 + 1.92\,x - 1.28 = 0$

Apply the quadratic formula: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a} \longrightarrow x = 0.60$ or -5.93

0.60 atm is plausible; −5.93 atm would imply a negative partial pressure.

6. P_{eq}

$$P_{CO} = P_{H_2O} = x = 0.60 \text{ atm}$$

$$P_{CO_2} = 2.00 - 0.60 = 1.40 \text{ atm} \qquad P_{H_2} = 1.00 - 0.60 = 0.40 \text{ atm}$$

END POINT

Check your algebra by substituting the equilibrium partial pressures back into the expression for K.

$$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(0.60)(0.60)}{(1.40)(0.40)} = 0.64 \qquad \text{Voila!}$$

Homogeneous Equilibria

- So far every example dealt with reactants and products where all were in the same phase.
- We can use K in terms of either concentration or pressure.
- Units depend on reaction.

Heterogeneous Equilibria

- If the reaction involves pure solids or pure liquids the concentration of the solid or the liquid doesn’t change.
- As long as they are not used up they are not used up we can leave them out of the equilibrium expression.
- For example

For Example

- $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$
- $K = \frac{[HI]^2}{[H_2][I_2]}$
- But the concentration of I_2 does not change- fro example $[H_2O]=15.6$ M
- Combining $[I_2]$ into Kc , then

$$K[I_2] = \boxed{\frac{[HI]^2}{[H_2]} = \text{new } K'}$$

HETEROGENEOUS EQUILIBRIA

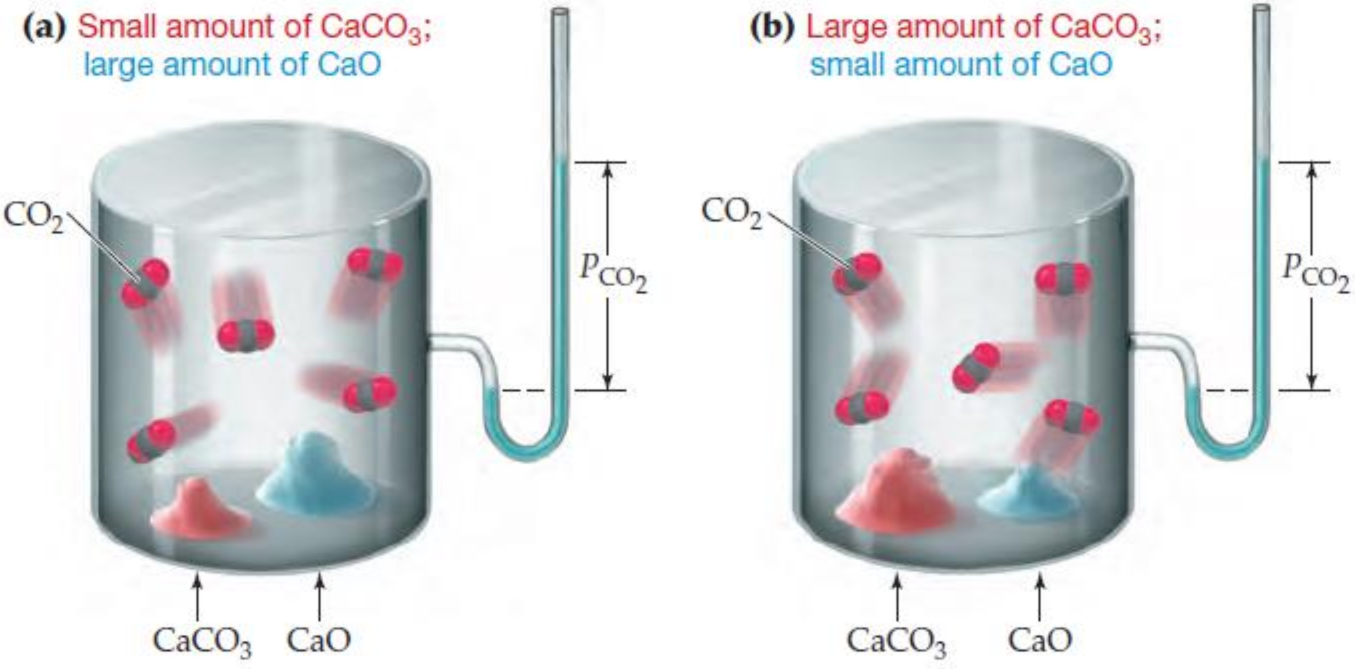
$$\underset{\text{Limestone}}{CaCO_3(s)} \rightleftharpoons \underset{\text{Lime}}{CaO(s)} + CO_2(g)$$

$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

The analogous equilibrium equation in terms of pressure is $K_p = P_{CO_2}$ where P_{CO_2} is the equilibrium pressure of CO_2 in atmospheres:

$$K_c = [CO_2] \qquad K_p = P_{CO_2}$$

$$Kp=Kc(RT)^1$$


(a) Small amount of $CaCO_3$; large amount of CaO

(b) Large amount of $CaCO_3$; small amount of CaO

At the same temperature, the equilibrium pressure of CO_2 is the same in (**a**) and (**b**), independent of how much solid $CaCO_3$ and CaO is present.

WRITING EQUILIBRIUM EQUATIONS FOR HETEROGENEOUS EQUILIBRIA

Write the equilibrium equation for each of the following reactions:

(a) $CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$

(b) $Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{\;2+}(aq)$

STRATEGY

Write the usual equilibrium constant expressions but omit the pure solid carbon in part (a) and the pure liquid mercury in part (b) because the ratio of their concentrations to their concentrations in the standard state is equal to 1.

SOLUTION

(a) $K_c = \dfrac{[CO]^2}{[CO_2]}$

Alternatively, because CO and CO_2 are gases, the equilibrium equation can be written using partial pressures:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}}$$

The relationship between K_p and K_c is $K_p = K_c(RT)^{\Delta n} = K_c(RT)$, because $\Delta n = 2 - 1 = 1$.

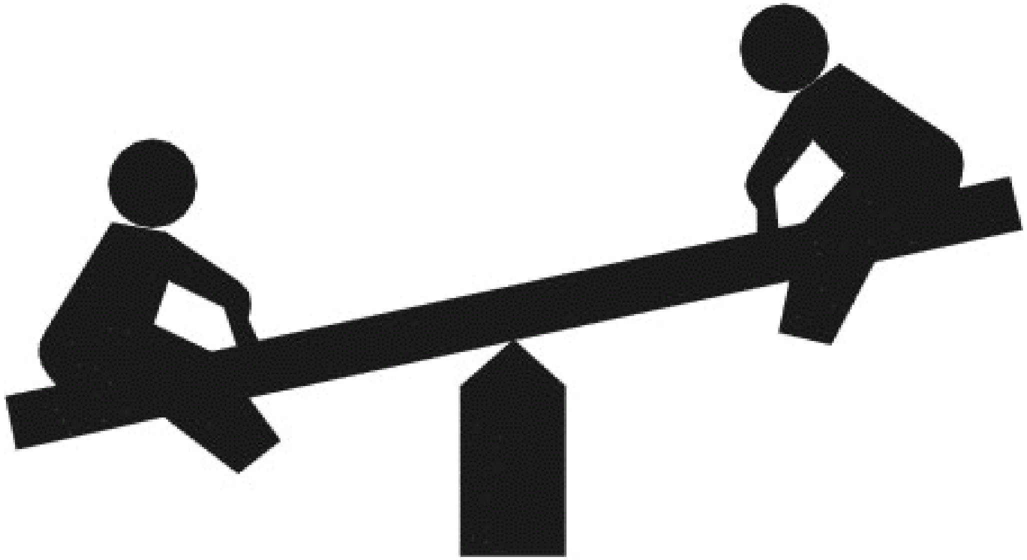
(b) $K_c = \dfrac{[Hg_2^{\;2+}]}{[Hg^{2+}]}$

In this case, it's not appropriate to write an expression for K_p because none of the reactants and products is a gas.

Recap

- In the equilibrium expression, always include
  - Partial pressures for gases, raised to the coefficient of each
  - Molar concentrations for aqueous species (molecules or ions), raised to the coefficient of each
- Always exclude
  - Terms for pure liquids and pure solids
  - $Zn\ (s) + 2H^{+}\ (aq) \leftrightarrows Zn^{2+}\ (aq) + H_2\ (g)$
  - $K = \frac{[Zn^{2+}]p_{H_2}}{[H^{+}]^{2}}$

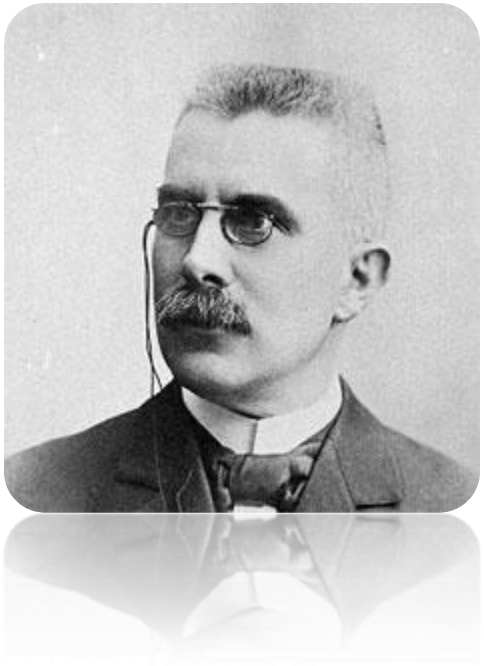
Le Chatelier’s Principle



LeChatelier’s Principle

When a system at equilibrium is placed under stress, the system will undergo a change in such a way as to relieve that stress and restore a state of equilibrium.

Henry Le Chatelier



Please see the link below :

http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/flash.mhtml

Le Chatelier Translated:

When you take something away from a system at equilibrium, the system shifts in such a way as to replace some what you've taken away.

When you add something to a system at equilibrium, the system shifts in such a way as to use up some of what you've added.

FACTORS THAT ALTER THE COMPOSITION OF AN EQUILIBRIUM MIXTURE: LE CHÂTELIER'S PRINCIPLE

Several factors can be exploited to alter the composition of an equilibrium mixture:

- The concentration of reactants or products can be changed.
- The pressure and volume can be changed.
- The temperature can be changed.

Case 1

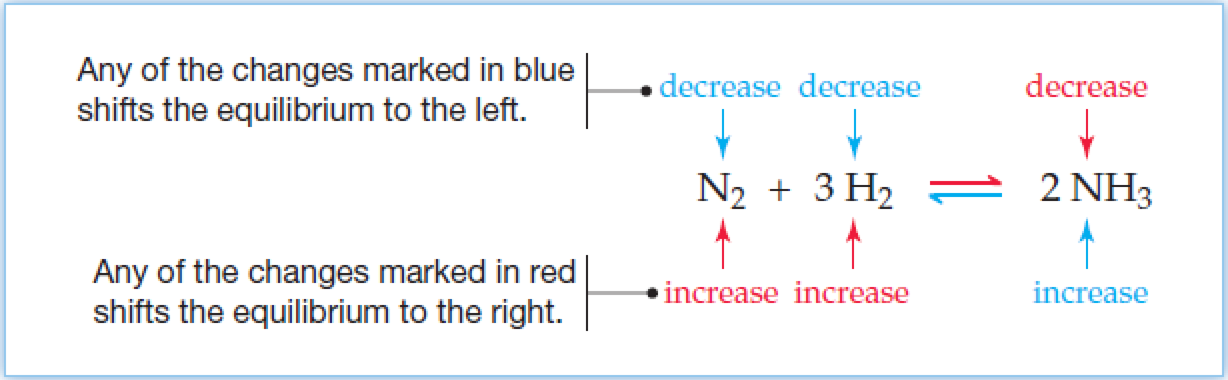


Figure 13.9

Effect of concentration changes on the equilibrium $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$. An increase in the N_2 or H_2 concentration or a decrease in the NH_3 concentration shifts the equilibrium from left to right. A decrease in the N_2 or H_2 concentration or an increase in the NH_3 concentration shifts the equilibrium from right to left.

Case 2

$$\mathrm{Fe^{3+}}(aq) + \mathrm{SCN^-}(aq) \rightleftharpoons \mathrm{FeNCS^{2+}}(aq)$$

Pale yellow Colorless Red

(a) Original solution: Fe^{3+}(pale yellow), SCN^-(colorless), and $FeNCS^{2+}$(red).

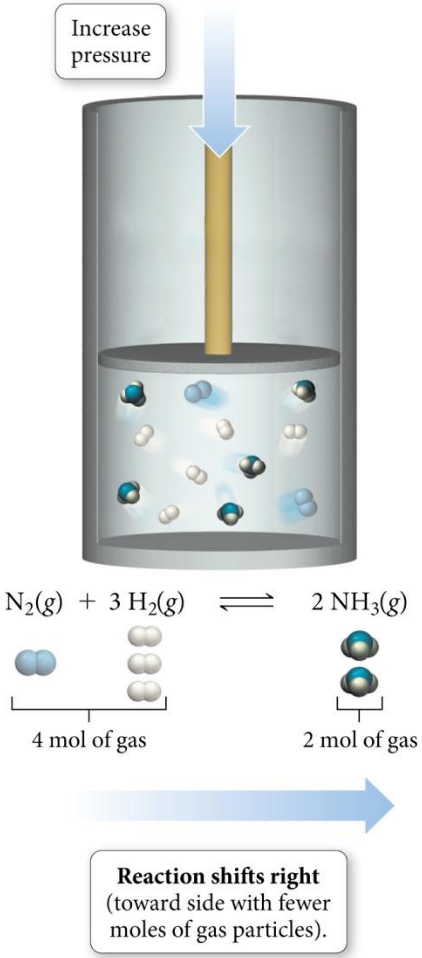
(b) After adding $FeCl_3$ to **(a)**: $[FeNCS^{2+}]$ increases.

(c) After adding KSCN to **(a)**: $[FeNCS^{2+}]$ increases.

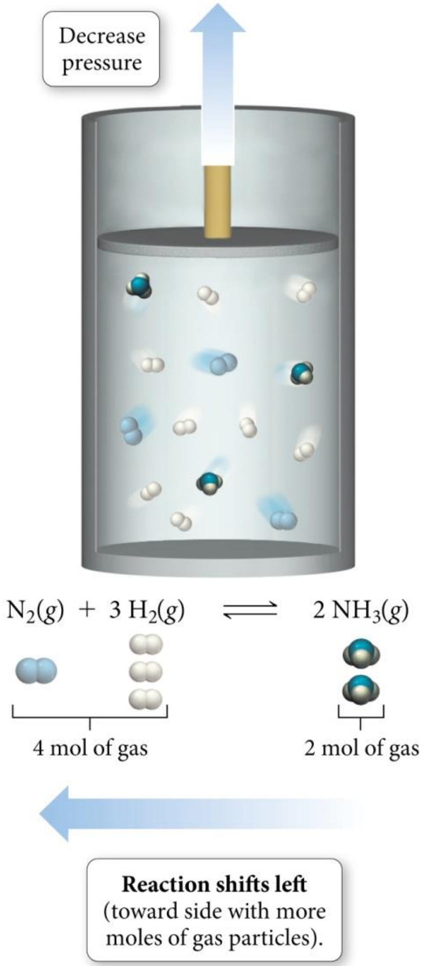
Figure 13.10

Color changes produced by adding various reagents to an equilibrium mixture of Fe^{3+} (pale yellow), SCN^- (colorless), and $FeNCS^{2+}$ (red).

The Effect of Volume Changes on Equilibrium



When the pressure is decreased by increasing the volume, the position of equilibrium shifts toward the side with the greater number of molecules—the reactant side.



Case 4

ALTERING AN EQUILIBRIUM MIXTURE: CHANGES IN TEMPERATURE

$$\underset{\text{Colorless}}{N_2O_4(g)} + 55.3\ \text{kJ} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2(g)} \qquad \Delta H^\circ = +55.3\ \text{kJ}$$

In general, the temperature dependence of an equilibrium constant depends on the sign of ΔH° for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH°) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH°) increases as the temperature increases.

$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$; $\Delta H > 0$

K_c increases as

$\longrightarrow$

T increases

The darker **brown** color of the sample at the highest temperature indicates that the equilibrium $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ shifts from reactants to products with increasing temperature, as expected for an endothermic reaction.

APPLYING LE CHÂTELIER'S PRINCIPLE TO TEMPERATURE CHANGES

In the first step of the Ostwald process for the synthesis of nitric acid, ammonia is oxidized to nitric oxide by the reaction

$$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g) \qquad \Delta H^\circ = -901.2\ \text{kJ}$$

How does the equilibrium amount of NO vary with an increase in temperature?

STRATEGY

Le Châtelier's principle predicts that the stress of added heat when the temperature is increased will be relieved by net reaction in the direction that absorbs the heat. It's helpful to include the heat in the balanced equation—on the reactant side if the reaction is endothermic, or on the product side if the reaction is exothermic.

SOLUTION

Because the oxidation of ammonia is exothermic, we include the heat (901.2 kJ) on the product side:

$$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g) + 901.2\ \text{kJ}$$

The stress of added heat when the temperature is increased will be relieved by net reaction from products to reactants, which absorbs the added heat. The equilibrium will therefore shift to the reactant side (K_c will decrease) with an increase in temperature. Consequently, the equilibrium mixture will contain less NO at higher temperatures.

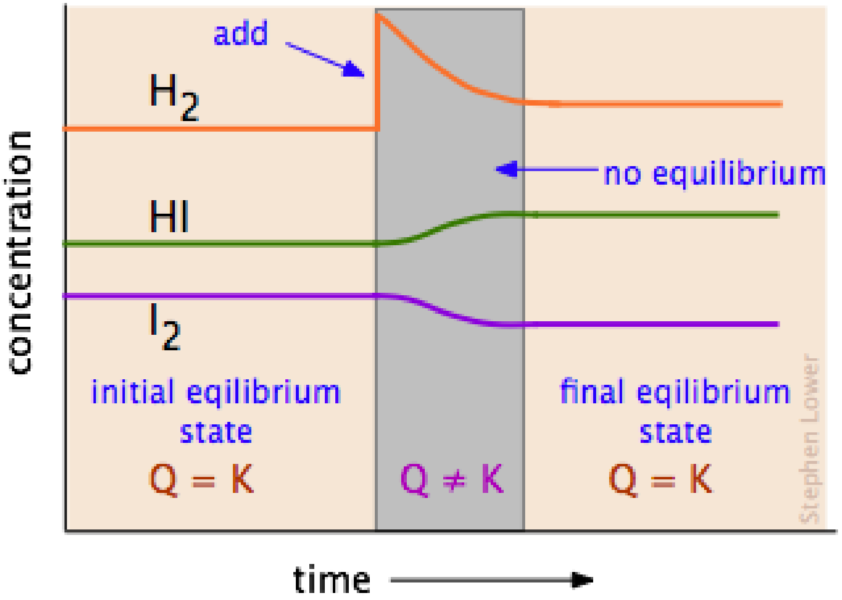
←

The Reaction Quotient

For some time, t, when the system is not at equilibrium, the reaction quotient, Q takes the place of K, the equilibrium constant, in the law of mass action.

$$jA + kB \leftrightarrows lC + mD$$

$$Q = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

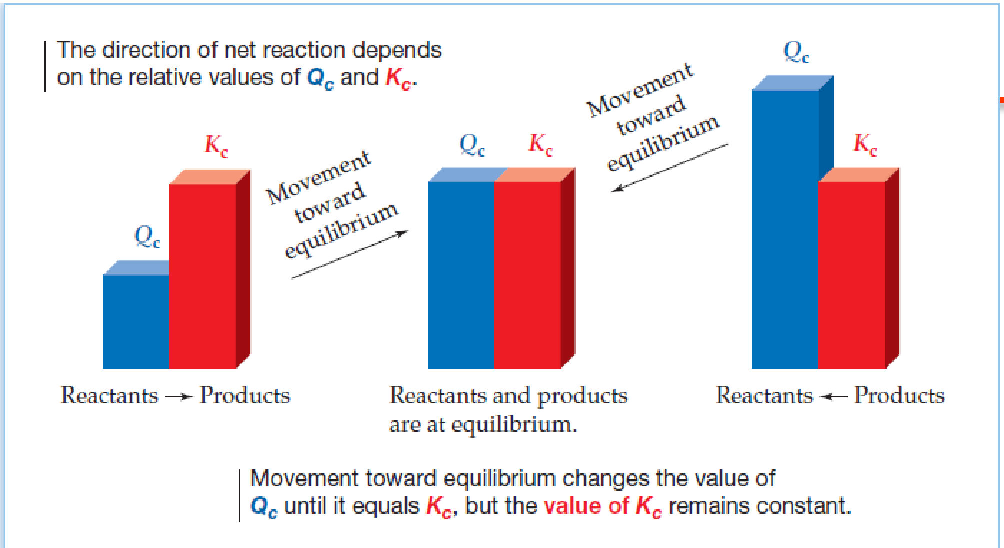


Significance of the Reaction Quotient

- If $Q = K$, the system is at equilibrium

- If $Q > K$, the system shifts to the left, consuming products and forming reactants until equilibrium is achieved

- If $Q < K$, the system shifts to the right, consuming reactants and forming products until equilibrium is achieved



The direction of net reaction depends on the relative values of Q_c and K_c.

Movement toward equilibrium changes the value of Q_c until it equals K_c, but the value of K_c remains constant.

Compare Q and K to predict the reaction Direction

$N_2O_{4\,(g)} \rightleftarrows 2\,NO_{2\,(g)}$ K_{eq} = 11 atm (T = 373 K)

mix 0.2 mol of N_2O_4 with 0.2 mol of NO_2 in a 4.0 L flask at 100°C.

$Q = (P_{NO2})^2 / P_{N2O4}$

First find P_{NO2} and P_{N2O4} using PV = nRT
$P_{NO2} = P_{N2O4}$ = (0.20 mol)(0.0821 L atm/mol K)(373 K)/(4.0 L) = 1.5 atm

$Q = (1.5\text{ atm})^2/1.5\text{ atm} = 1.5\text{ atm} < 11\text{ atm}$

Q < K, so the reaction will proceed in the forward direction,

$N_2O_{4\,(g)} \text{-->} 2\,NO_{2\,(g)}$ until it reaches equilibrium.