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Chapter 12
Gaseous Chemical Equilibrium

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Chemical Equilibria

- For a gaseous chemical equilibrium, more than one gas is present:
  - aA (g) + bB (g) ⇌ cC (g) + dD (g)
  - To describe the state of this system, the partial pressures of all gases must be known
  - Using the Ideal Gas Law:

$$P_i = \frac{n_i RT}{V}$$

  - in a closed system, with fixed volume and temperature, the partial pressure of each species is proportional to the number of moles of that species

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Outline

1. N_2O_4-NO_2 equilibrium system
2. The equilibrium constant expression
3. Determination of K
4. Applications of the equilibrium constant
5. Effect of changes in conditions on an equilibrium system

Working with Chemical Equilibria

1. Writing the expression for the equilibrium constant
2. Calculating the equilibrium constant from experimental data
3. Using the equilibrium constant to predict the extent to which a reaction will take place
4. Using the equilibrium constant to predict the effect that disturbing a system in equilibrium will have

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Review of Liquid-Vapor Equilibrium

- In Chapter 9 we examined the equilibrium that is established between a liquid and a vapor, such as that for water
  - H_2O (l) ⇌ H_2O (g)
  - The state of the system can be described by stating the vapor pressure of water at the given temperature
  - The process is reversible
  - The forward and reverse processes take place at the same rate

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The N_2O_4-NO_2 Equilibrium

- N_2O_4 is colorless
- NO_2 is brown
- When N_2O_4 is sealed into a closed, evacuated container at 100 ° C, a reddish-brown color develops due to the decomposition to NO_2
  - N_2O_4 (g) ⇌ $2NO_2$ (g)
- As NO_2 builds up, it can react to form N_2O_4
  - The reverse reaction takes place
- An equilibrium is established where the rate of decomposition of N_2O_4 equals that of reaction of NO_2

Establishment of Equilibrium

- The rate of decomposition of N_2O_4 starts out fast but slows down as the pressure of N_2O_4 of drops
- The rate of reaction of NO_2 starts out slow but speeds up as the pressure of NO_2 builds up
- Once the rates of reaction are equal, equilibrium is established
  - No further pressure change of either gas unless the temperature or the volume of the container is changed
  - The concentrations (pressures) of the gases are independent of the direction from which equilibrium is approached
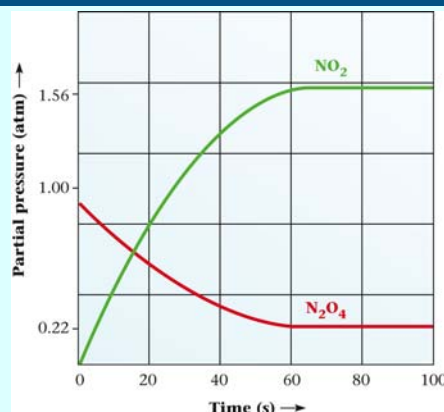
Figure 12.2 – Graphical Display of Equilibrium

Figure 12.1

Table 12.2

TABLE 12.2 Equilibrium Measurements in the N_2O_4–NO_2 System at 100°C

		Original Pressure (atm)	Equilibrium Pressure (atm)
Expt. 1	N_2O_4	1.00	0.22
	NO_2	0.00	1.56
Expt. 2	N_2O_4	0.00	0.07
	NO_2	1.00	0.86
Expt. 3	N_2O_4	1.00	0.42
	NO_2	1.00	2.16

Table 12.1 – Numeric Data on Equilibrium

TABLE 12.1 Establishment of Equilibrium in the System $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (at 100°C)

Time	0	20	40	60	80	100
$P_{N_2O_4}$ (atm)	1.00	0.60	0.35	0.22*	0.22	0.22
P_{NO_2} (atm)	0.00	0.80	1.30	1.56	1.56	1.56

*Boldface numbers are equilibrium pressures.

Common Ground

- What do the three experiments in Table 12.2 have in common?
  - The original pressures differ
  - A specific ratio of product to reactant is common to all three experiments
- The reaction quotient
  - We can define a ratio of product to reactant:

$$\frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

  - For all three experiments, the value of this quotient is 11

The Equilibrium Constant

- When we use the values for the pressure of each gas at equilibrium with the quotient we just defined, we arrive at the *equilibrium constant*
- The value of the equilibrium constant is *independent of the starting concentration or pressure* of the reactants and products
- The value of the equilibrium constant is *dependent on the temperature*

Changing the Chemical Reaction

- K depends on the equation written to describe the chemical reaction underlying the equilibrium
- Changing the reaction changes K
- The coefficient rule:
  - If the reaction is multiplied by a number, n, then K is raised to that power:
  - For n = 2 $\quad K = \dfrac{(P_{NO_2})^4}{(P_{N_2O_4})^2}$
    - $2N_2O_4 (g) \rightleftharpoons 4NO_2 (g)$
  - For n = ½ (i.e., divide the reaction by two):
    - $\frac{1}{2}N_2O_4 (g) \rightleftharpoons NO_2 (g)$ $\quad K = \dfrac{(P_{NO2})}{(P_{N_2O_4})^{\frac{1}{2}}}$

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 is the equilibrium constant

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

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

Changing the Chemical Reaction, (Cont'd)

- For the forward and reverse reactions, the K expressions are the reciprocals of each other (the reciprocal rule)
  - For $2NO_2 (g) \rightleftharpoons N_2O_4 (g)$,

$$K = \frac{(P_{N_2O_4})}{(P_{NO_2})^2}$$

Equilibrium Constant and Concentration

- For the same $aA (aq) + bB (aq) \rightleftharpoons cC (aq) + dD (aq)$
- *K_c is the concentration equilibrium constant*

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

- If Δn_g is the change in the number of moles of gas from left to right (i.e., n_g (product) – n_g (reactant)), then
- *K_p is the pressure equilibrium constant*

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

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
  - $SO_2 (g) + \frac{1}{2}O_2 (g) \rightleftharpoons SO_3 (g)$ $\quad$ K = 2.2
  - $NO_2 (g) \rightleftharpoons NO (g) + \frac{1}{2}O_2 (g)$ $\quad$ K = 4.0
- For
  - $SO_2 (g) + NO_2 (g) \rightleftharpoons SO_3 (g) + NO (g)$ K = 8.8

Table 12.3

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

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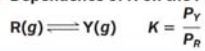
Form of Equation	K Expression	Relation to K	Rule
$Y(g) \rightleftharpoons R(g)$	$K' = \frac{P_R}{P_Y}$	$K' = \frac{1}{K}$	Reciprocal Rule
$nR(g) \rightleftharpoons nY(g)$	$K'' = \frac{(P_Y)^n}{(P_R)^n}$	$K'' = K^n$	Coefficient Rule
$R(g) \rightleftharpoons A(g)$	$K_1 = \frac{P_A}{P_R}$		
$A(g) \rightleftharpoons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

Example 12.1, (Cont'd)

(d)

STRATEGY

1. Start with two moles of NO, which is a product in Equation (1) but a reactant in the desired equation. Reverse Equation (1) and apply the reciprocal rule.
2. Focus on two moles of NO₂, which is the product in Equation (2) and in the desired equation. Change is unnecessary.
3. Add the two equations.
4. Apply the rule of multiple equilibria.

SOLUTION

1. Reverse Equation (1).
Apply reciprocal rule.
2. Keep Equation (2).
3. Overall equation
4. K

$$K = \left(\frac{1}{4.2 \times 10^{-31}}\right)(1.0 \times 10^{-18}) = 2.4 \times 10^{12}$$

Example 12.1

EXAMPLE 12.1 GRADED

Consider the air pollutants NO and NO₂, contributors to photochemical smog. Both can be formed by the reaction between atmospheric nitrogen and oxygen. At 25°C,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_1 = 4.2 \times 10^{-31} \qquad (1)$$
$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad K_2 = 1.0 \times 10^{-18} \qquad (2)$$

(a) Write the equilibrium constant expression for the formation of two moles of NO at 25°C.
(b) Calculate K for the formation of one mole of NO at 25°C.
(c) Calculate K for the decomposition of one mole of NO₂ at 25°C.
(d) Calculate K for the following reaction at 25°C:

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

(a) **SOLUTION**

K expression $\qquad K_1 = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$

(b) **STRATEGY**

1. Write the reaction for the formation of one mole of NO. Note that all the coefficients of the original equation are divided by two.
2. Find K. Apply the coefficient rule.

SOLUTION

1. Equation for the reaction $\quad \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$
2. K $\quad K = (K_1)^{1/2} = (4.2 \times 10^{-31})^{1/2} = 6.5 \times 10^{-16}$

continued

Heterogeneous Equilibria

- In mixed-phase systems, note that the liquids and solids present do not change with time
  - Pure solids and pure liquids **do not appear in equilibrium expressions**
  - The position of equilibrium is independent of the amount of solid or liquid, **as long as some is present in the reaction mixture**

Example 12.1, (Cont'd)

(c)

STRATEGY

1. Write the reaction for the decomposition of NO₂ and note that you are asked for the decomposition of *one* mole.
2. To arrive at the equation for the decomposition of one mole of NO₂, you switch sides (reciprocal rule) and multiply the coefficients by $\frac{1}{2}$ (coefficient rule).
3. Apply both rules.

SOLUTION

Equation for the reaction	$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \longrightarrow 2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g) \longrightarrow NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$
Reciprocal rule	$K' = 1/K_2$
Coefficient rule	$K = (K')^{1/2} = (1/K_2)^{1/2}$
K	$\left(\frac{1}{1.0 \times 10^{-18}}\right)^{1/2} = 1.0 \times 10^9$

Carbon-Dioxide-Hydrogen Equilibrium

- $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$ at 25°C
  - The equilibrium vapor pressure of water at 25°C is constant
  - Water is left out of the equilibrium expression since its pressure does not change

$$K = \frac{P_{CO}}{P_{CO_2} P_{H_2O}}$$

Table 12.4

TABLE 12.4 Equilibrium Constant Expressions for the Reaction
$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Mass $H_2O(l)$	8 g	6 g	4 g	2 g
P_{H_2O} (atm)	3×10^{-2}	3×10^{-2}	3×10^{-2}	3×10^{-2}
K_I	9×10^{-6}	9×10^{-6}	9×10^{-6}	9×10^{-6}
K_{II}	3×10^{-4}	3×10^{-4}	3×10^{-4}	3×10^{-4}

$$K_I = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} \qquad K_{II} = \frac{P_{CO}}{P_{CO_2} \times P_{H_2}}$$

Heterogeneous Equilibrium – I_2

Example 12.2

EXAMPLE 12.2

Write the expression for K for

(a) the reduction of black solid copper(II) oxide (1 mol) with hydrogen to form copper metal and steam.

(b) the reaction of one mole of steam with red-hot coke (carbon) to form a mixture of hydrogen and carbon monoxide, called water gas.

STRATEGY

1. Write a balanced chemical equation for the equilibrium system. Do not forget to include physical states.
2. Write the expression for K, leaving out pure solids and liquids.
3. Recall that gases are represented by their partial pressures.

SOLUTION

(a) Reaction $\quad CuO(s) + H_2(g) \rightleftharpoons Cu(s) + H_2O(g)$

K expression $\quad K = \dfrac{P_{H_2O}}{P_{H_2}}$

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

K expression $\quad K = \dfrac{(P_{H_2})(P_{CO})}{P_{H_2O}}$

Determination of K

- K can be evaluated numerically by experiment
- One of two sets of data will be used
  - Equilibrium pressures, which may be used directly to determine the value for K
  - Original pressures, which must be algebraically linked to the equilibrium pressure ultimately used to determine the value for K

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
  - $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$
  - $K = \dfrac{[Zn^{2+}]p_{H_2}}{[H^+]^2}$

Example 12.3

EXAMPLE 12.3

Ammonium chloride is sometimes used as a flux in soldering because it decomposes on heating:

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

The HCl formed removes oxide films from metals to be soldered. In a certain equilibrium system at 400°C, 22.6 g of NH_4Cl is present; the partial pressures of NH_3 and HCl are 2.5 atm and 4.8 atm, respectively. Calculate K at 400°C.

ANALYSIS

Information given:	equation for the reaction at $T = 400°C$
	mass of NH_4Cl (22.6 g)
	partial pressures of NH_3 (2.5 atm) and HCl (4.8 atm)
Asked for:	K at 400°C

STRATEGY

1. Write the expression for K. Recall that pure liquids and solids are not included in the expression.
2. Substitute the partial pressures of the gases into the expression for K.

SOLUTION

K expression	$K = (P_{NH_3})(P_{HCl})$
K	$K = (2.5 \text{ atm})(4.8 \text{ atm}) = 12$

END POINT

Note that the mass of NH_4Cl is not relevant to the calculation because NH_4Cl is a solid and hence is not included in the expression for K.

Example 12.4

EXAMPLE 12.4

Consider the equilibrium system

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

Originally, a system contains only HI at a pressure of 1.00 atm at 520°C. The equilibrium partial pressure of H_2 is found to be 0.10 atm. Calculate

(a) P_{I_2} and P_{HI} at equilibrium   (b) K

(a)

ANALYSIS	
Information given:	initial pressure (P_o) for HI (1.00 atm) equilibrium pressure (P_{eq}) for H_2 (0.10 atm)
Information implied:	initial pressures (P_o) for H_2 and I_2
Asked for:	equilibrium partial pressures (P_{eq}) for I_2 and HI

Example 12.4, (Cont'd)

SOLUTION	
K	$K = \dfrac{(P_{H_2})(P_{I_2})}{(P_{HI})^2} = \dfrac{(0.10)(0.10)}{(0.80)^2} = 0.016$

END POINT

You should expect K to be rather small (0.016). Recall that at equilibrium, P_{H_2} is 0.10 atm, only one tenth of the original pressure of HI (1.00 atm).

Example 12.4, (Cont'd)

Example 12.4, (Cont'd)

(b)

ANALYSIS	
Information given:	from part (a): equilibrium pressures for HI (0.80 atm) and for I_2 (0.10 atm) equilibrium pressure (P_{eq}) for H_2 (0.10 atm)
Information implied:	K expression
Asked for:	equilibrium constant K at 520°C

STRATEGY

1. Write the equilibrium expression.
2. Substitute into the expression for K.

Fundamentals of Equilibrium Problems

- As a system approaches equilibrium, changes in partial pressures of reactants and products are related to each other through the coefficients of the balanced equation
  - The same holds for changes to molar amounts
  - The balanced equation is the key to setting up and solving equilibrium problems

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Applications of the Equilibrium Constant

- The magnitude of the equilibrium constant translates directly into the extent of reaction
  - Reactions are feasible as written only if K is large enough that an appreciable amount of product forms
  - Consider the reaction
    - $N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$
    - $K = 1 \times 10^{-30}$ at 25°C
    - This reaction does not proceed to any great extent at this temperature, so nitrogen and oxygen in air do not react appreciably at room temperature

Synthesis of Ammonia

- N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)
  - K = 6 X 10^5 at 25 ° C
  - When the reaction reaches equilibrium, mostly product (ammonia) is present

- Conclusions
  - If K is very small, the mixture contains mostly unreacted reactants at equilibrium
  - If K is large, the mixture contains mostly products at equilibrium

Table 12.5

TABLE 12.5 Approach to Equilibrium in the System A $\rightleftharpoons$ B for which K = 1.00

	Experiment 1*				Experiment 2*			
t	0	20	40	60	0	20	40	60
[B]	1.00	1.35	1.50	1.50	2.00	1.65	1.50	1.50
[A]	2.00	1.65	1.50	1.50	1.00	1.35	1.50	1.50
Q = [B]/[A]	0.500	0.818	1.00	1.00	2.00	1.22	1.00	1.00
	Q < K		Q = K		Q > K		Q = K	

*In both experiments, systems to the right of the broken line have reached equilibrium.

Direction of Reaction; the Reaction Quotient, Q

- We can define a new quantity called the reaction quotient, Q
- Q has the same form as the equilibrium expression
  - Values for reactant and product need not be equilibrium pressures
- For aA (g) + bB (g) $\rightleftharpoons$ cC (g) + dD (g)

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

Q and the Direction of Reaction, (Cont'd)

- Comparing Q and K
  - When Q < K, the reaction proceeds from left to right
  - When Q > K, the reaction proceeds from right to left
  - When Q = K, the reaction is at equilibrium

Q and the Direction of Reaction

- When we start with only reactants
  - aA (g) + bB (g) $\rightleftharpoons$ cC (g) + dD (g)
    - P_C and P_D are 0, so Q = 0
- When we start with only products
  - P_A and P_B are 0, so Q $\rightarrow$ ∞
- Q can take any value from zero to infinity

Example 12.5

EXAMPLE 12.5

Consider the following system at 100°C:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K = 11$$

Predict the direction in which reaction will occur to reach equilibrium, starting with 0.10 mol of N_2O_4 and 0.20 mol of NO_2 in a 2.0-L container.

ANALYSIS	
Information given:	reaction and K at 100°C (11)
	initial amounts of N_2O_4 (0.10 mol) and NO_2 (0.20 mol)
	volume of the container (2.0 L)
Information implied:	R value
Asked for:	direction of the reaction

STRATEGY
1. Calculate the partial pressures of all species using the ideal gas law and stoichiometric ratios.
2. Write the expression for Q and find its value.
3. Compare Q with K to predict the direction of the reaction.

Example 12.5, (Cont'd)

SOLUTION

1. $P_{N_2O_4}$, P_{NO_2}

$$P = \frac{nRT}{V} = \frac{(0.10)(0.0821)(373)}{2.0} = 1.5 \text{ atm}$$

Since V and T are constant, n is proportional to P, and P can be obtained using the stoichiometric ratio of NO_2 and N_2O_4.

$$1.5 \text{ atm for } N_2O_4 \times \frac{2 \text{ mol } NO_2}{1 \text{ mol } N_2O_4} = 3.0 \text{ atm}$$

2. Q

$$Q = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(3.0)^2}{1.5} = 6.0$$

3. Direction

$Q(6.0) < K(11)$ The reaction proceeds from left to right ($\rightarrow$).

END POINT

When we say that the reaction proceeds from left to right or in the forward direction, we refer to the reaction as written. In this case, the partial pressure of NO_2 increases while that of N_2O_4 decreases until the system reaches equilibrium.

Example 12.6, (Cont'd)

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_o (atm)	1.00		1.00		0		0
ΔP (atm)	x		x		x		x
P_{eq} (atm)							

3. Direction of the reaction ($\rightarrow$)

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (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_o (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: $0.80 = \frac{x}{1.00 - x} \longrightarrow x = 0.44$

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

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Equilibrium Partial Pressures

- The equilibrium constant can be used to calculate the partial pressures of the species present at equilibrium
  1. Using the balanced equation, write the K expression
  2. Express the equilibrium partial pressures in terms of a single unknown.
      - Use the balanced equation to make the expression
  3. Substitute into the expression for K to find the unknown in (2)
  4. Calculate the equilibrium partial pressures using (3)

Example 12.6, (Cont'd)

(b)

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: $ax^2 + bx + c = 0 \longrightarrow 0.36 x^2 + 1.92 x - 1.28 = 0$

continued

Example 12.6

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

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

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

(a)

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)							

continued

Example 12.6, (Cont'd)

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

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

6. P_{eq} $P_{CO} = P_{H_2O} = x = 0.60$ atm

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

END POINT

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

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

Changes to Equilibrium Systems

- Several changes can disturb a system in equilibrium
  1. Adding or removing a gaseous reactant or product
  2. Compressing or expanding the system
  3. Changing the temperature

N_2O_4 (g) $\rightleftharpoons$ 2NO_2 (g)
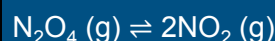
- **Adding N_2O_4** will cause a shift from *left to right*
- **Adding NO_2** will cause a shift from *right to left*
- **Removing N_2O_4** will cause a shift from *right to left*
- **Removing NO_2** will cause a shift from *left to right*
- It is possible to use K to calculate the extent to which the shift occurs when a reactant or product is added or removed

LeChâtelier's Principle

- Henri LeChâtelier (1850-1936)
- If a system at equilibrium is disturbed by a change in concentration, pressure, or temperature, the system will, if possible, shift to partially counteract the change and restore equilibrium

Example 12.7

EXAMPLE 12.7

In Example 12.4 you found that the HI–H_2–I_2 system is in equilibrium at 520°C when P_{HI} = 0.80 atm and P_{H_2} = P_{I_2} = 0.10 atm. Suppose enough HI is added to raise its pressure temporarily to 1.00 atm. When equilibrium is restored, what are P_{HI}, P_{H_2}, and P_{I_2}?

ANALYSIS	
Information given:	equilibrium pressures for HI (0.80 atm), I_2 (0.10 atm), and H_2 (0.10 atm) from Example 12.4
	K (0.016)
	equilibrium disturbed by adding HI (now 1.00 atm)
Information implied:	direction of the reaction
Asked for:	equilibrium pressures when equilibrium is reestablished

STRATEGY

1. Create a table. Note that the equilibrium partial pressures now become initial pressures for HI and I_2. P_o for HI is now 1.00 atm.
2. Since HI is added, the reaction goes in the direction of using up the HI, thus to the right.
3. Write the K expression and solve for x.
4. Substitute the value for x into the equilibrium pressures for all species.

Adding or Removing a Gas

- If a chemical equilibrium is disturbed by *adding* a gas (reactant or product), the system will *shift in the direction that consumes the added species*.
- If a chemical equilibrium is disturbed by *removing* a gas (reactant or product), the system will *shift in the direction that restores part of the added species*.

Example 12.7, (Cont'd)

SOLUTION				
Table		2HI(g) $\rightleftharpoons$	H_2(g) +	I_2(g)
	P_o (atm)	1.00	0.10	0.10
	ΔP (atm)	$-2x$	$+x$	$+x$
	P_{eq} (atm)	$1.00 - 2x$	$0.10 + x$	$0.10 + x$
K expression	$K = 0.016 = \dfrac{(P_{H_2})(P_{I_2})}{(P_{HI})^2} = \dfrac{(0.10 + x)(0.10 + x)}{(1.00 - 2x)^2} = \dfrac{(0.10 + x)^2}{(1.00 - 2x)^2}$			
x	Take the square root of both sides: $0.13 = \dfrac{(0.10 + x)}{(1.00 - 2x)} \longrightarrow x = 0.024$ atm			
Equilibrium pressures	$P_{I_2} = P_{H_2} = 0.10 + 0.024 = 0.12$ atm; $\qquad P_{HI} = 1.00 - 2(0.024) = 0.95$ atm			

continued

Example 12.7, (Cont'd)

END POINT

Note that the equilibrium partial pressure of HI is intermediate between its value before equilibrium was established (0.80 atm) and that immediately afterward (1.00 atm). This is exactly what LeChâtelier's principle predicts: part of the added HI is consumed to reestablish equilibrium!

Table 12.6

TABLE 12.6 Effect of Compression on the Equilibrium System
$$N_2O_4(g) \rightleftharpoons 2NO_2(g); \; K = 11 \text{ at } 100°C$$

P_{tot} (atm)	n_{NO_2}	$n_{N_2O_4}$	n_{tot}
1.0	0.92	0.08	1.00
2.0	0.82	0.13	0.95
5.0	0.64	0.22	0.86
10.0	0.50	0.29	0.79

Volume Changes

- Consider again the equilibrium
  - N_2O_4 (g) $\rightleftharpoons$ 2NO$_2$ (g)
- Reducing the volume will increase the pressure
  - Recall that P = nRT/V
    - Pressure and volume are inversely related
    - As V becomes smaller, P becomes larger
- Now consider the system response
  - By shifting to the left, two moles of gas are consumed and one is produced
    - The pressure is reduced by shifting to the left, so the stress is counteracted

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Pressure Changes

- When a system is compressed, the ***total pressure increases***, causing the system to shift in the direction that decreases the total number of moles of gas
- When a system is expanded, the ***total pressure decreases***, causing the system to shift in the direction that increases the total number of moles of gas
- If the total number of moles of gas is the same on both sides of the equation, pressure change will have a small or negligible effect on the equilibrium
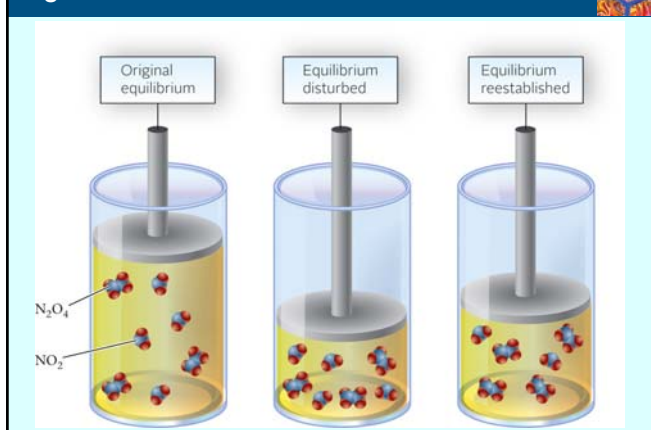

Figure 12.3

Table 12.7

TABLE 12.7 Effect of Pressure on the Position of Gaseous Equilibria

System	Δn_{gas}*	P_{tot} Increases	P_{tot} Decreases
1. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	+1	←	→
2. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$	$-\frac{1}{2}$	→	←
3. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	−2	→	←
4. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	+1	←	→
5. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	0	0	0

*Δn_{gas} is the change in the number of moles of gas as the forward reaction occurs.

Changes in Temperature

- In increase in temperature favors the endothermic reaction
  - N_2O_4 (g) $\rightleftharpoons$ 2NO_2 (g) $\Delta H°$ = +57.2 kJ
    - Increasing the temperature favors the formation of NO_2
  - N_2 (g) + 3H_2 (g) $\rightleftharpoons$ 2NH_3 (g) $\Delta H°$ = -92.2 kJ
    - Increasing the temperature favors the formation of N_2 and H_2
    - The *reverse reaction is endothermic*

Applying the van't Hoff Equation

- N_2 (g) + 3H_2 (g) $\rightleftharpoons$ 2NH_3 (g) $\Delta H°$ = -92.2 kJ
  - K = 6 X 10^5 at 25 ° C
  - Calculate K at 100 ° C
    - Convert temperatures to Kelvin and $\Delta H°$ to J
    - K at 100 ° C = 4 X 10^2
    - Note that K becomes smaller as T increases because of the negative enthalpy change
    - For reactions with positive $\Delta H°$, K increases with temperature

Figure 12.4: The N_2O_4-NO_2 Equilibrium System

Example 12.8

Two-Point Equilibrium Constant Equation

- van't Hoff Equation

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H°}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

- Same form as the Clausius-Clapeyron and Arrehius rate-constant equations
- K_2 and K_1 are equilibrium constants corresponding to T_2 and T_2
- $\Delta H°$ is the enthalpy change for the reaction

Final Notes

- We have examined three changes in conditions:
  1. Adding or removing a gas
  2. Compressing or expanding the system
  3. Changing the temperature

- The *only way to change the equilibrium constant* is to *change the temperature* at which the reaction takes place.

Key Concepts

1. Relate the expression for K to the corresponding equation for the chemical reaction
2. Calculate K knowing
   - appropriate K values for other reactions
   - all the equilibrium partial pressures
   - all the original and one equilibrium partial pressure
3. Use the value of K to determine
   - the direction of the reaction
   - equilibrium partial pressures of all species
4. Use LeChâtelier's principle to determine what will happen when the conditions on an equilibrium system are changed