Chemical Equilibria 2

Reading: Ch 14 sections 6 - 9   Homework: Chapter 14: 27*, 29*, 31, 33, 41, 43, 45, 51*, 55, 61*, 63, 67*, 69*

* = ‘important’ homework question

Review

A chemical equilibrium and its respective equilibrium expression are *quantitatively* related via the following generic expression:

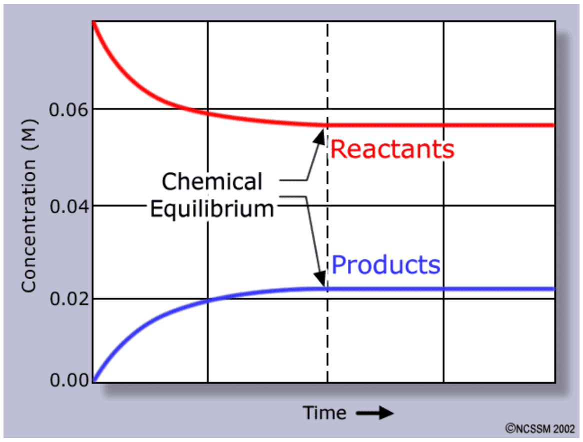
For: $aA + bB \Leftrightarrow cC + dD$

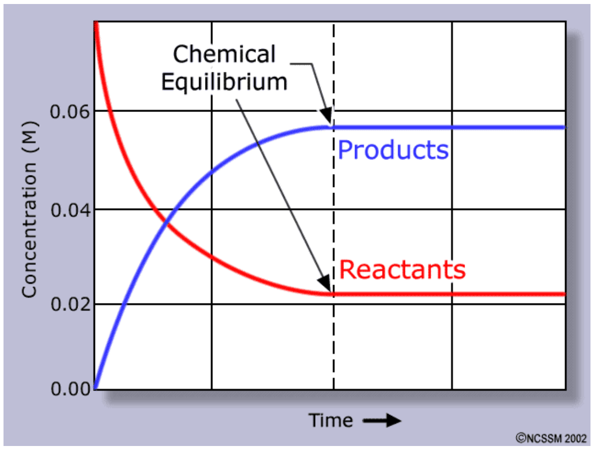
$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

If K is *large*, the equilibrium is said to lie to the *right*.

If K is *small*, the equilibrium is said to lie to the *left*.

Task: Analyze and discuss the following rate plots for chemical processes that attain measurable equilibria. Which equilibrium *lies to the right, to the left*?





Since the value of K is fixed for a specific temperature and pressure, the ratio of products to reactants is also fixed. Therefore:

A reaction mixture will approach the equilibrium position from either the reactants side (reactants in XS, ***forward reaction***) or the products side (products in XS, ***reverse reaction***). See slide and appendix table.

Notes

Reverse Reactions

Analogy Is the glass half full or half empty? There are two ways of looking at equilibrium too – *either* from the point of view of the formation of product(s) from reactants (L→R) *or* the formation of reactants from products (L←R).

Question: How are these two processes related?

For the Generic Equilibrium:

$$A \Leftrightarrow B \qquad K_{for} = \frac{[B]}{[A]}$$

Derivation

$$K_{rev} = \frac{[A]}{[B]}$$

Example:

$$HF\ (aq) \Leftrightarrow H^{+}\ (aq) + F^{-}\ (aq)\ ;\ K = 6.4 \times 10^{-4}$$

What is K_{rev}?

Do you think HF (aq) is a strong acid? Why?

More Equilibrium Math

If an equilibrium expression is multiplied by a constant value, its 'new' eq^{m} constant is the original value of K raised to the multiplying power

Example: Given:

$$HF\ (aq) \Leftrightarrow H^{+}\ (aq) + F^{-}\ (aq)\ ;\ K = 6.4 \times 10^{-4}$$

What is K for:

1. $2\ HF\ (aq) \Leftrightarrow 2\ H^{+}\ (aq) + 2\ F^{-}\ (aq)\ ;\ K =$

2. $\frac{1}{2}\ HF\ (aq) \Leftrightarrow \frac{1}{2}\ H^{+}\ (aq) + \frac{1}{2}\ F^{-}\ (aq)\ ;\ K =$

The eq^{m} constant for a net reaction made up from two or more steps is the product of the steps individual eq^{m} constants

i.e: *"Add reactions, multiply Ks"*

<u>Worked Example</u>: Given:

$2HF\ (aq) \Leftrightarrow 2H^{+}\ (aq) + 2F^{-}\ (aq)\ ;\ K_1 = 4.6 \times 10^{-7}$

and

$2\ H^{+}\ (aq) + C_2O_4{}^{2-}(aq) \Leftrightarrow H_2C_2O_4\ (aq)\ ;\ K_2 = 2.6 \times 10^{5}$

What is K for: $2HF\ (aq) + C_2O_4{}^{2-}(aq) \Leftrightarrow 2F^{-}\ (aq) + H_2C_2O_4\ (aq)$

Always add equations and multiply Ks first - just to see what you get

<u>Task</u>: What is K for: $CO\ (g) + 2\ H_2S\ (g) \Leftrightarrow CS_2\ (g) + H_2O(g) + H_2\ (g)$

Given: $CO\ (g) + 3\ H_2\ (g) \Leftrightarrow CH_4\ (g) + H_2O\ (g)\ ;\ K_1 = 3.92$
$CH_4\ (g) + 2\ H_2S\ (g) \Leftrightarrow CS_2\ (g) + 4\ H_2\ (g)\ ;\ K_2 = 3.3 \times 10^{4}$

The Equilibrium Constant K_p

For gas phase reactions it is easier to measure *partial pressures* of reactants and products. This will yield an equilibrium constant in terms of partial pressures *only*, K_p

K_p is related to the 'regular' equilibrium constant, K_c, (used for expressing molar concs. of reactants and products) by:

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

Where: R = molar gas constant (careful with units) = *or*
T = Temp. in Kelvin
$\Delta n = \Sigma$ (coeff gas products) - Σ(coeff gas reactants)

Math:

Example: What is K_p for: PCl_5 (g) ⇔ PCl_3 (g) + Cl_2 (g) at 191°C, given $K_c = 3.26 \times 10^{-2}$

The Reaction Quotient, Q_c

"An expression that has the same form as the eq^m constant (K_c), except that the conc values are not necessarily those at equilibrium"

For: $aA + bB \Leftrightarrow cC + dD$

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

Given the [conc] of all reactant(s) and product(s) under non-eq^m conditions, the direction of the reaction proceeds in order to establish eq^m can be found

Discussion: What does it really mean, in terms of the [reactants] and [products], when $Q_c > K_c$?

When $Q_c > K_c$, reaction moves to ____________________

When $Q_c < K_c$, reaction moves to ____________________

When $Q_c = K_c$, reaction is ____________________

See appendix

Worked Example: A 10.0 L vessel contains 0.0015 mol. CO_2 (g) and 0.100 mol. CO (g). If:

$$CO_2\,(g) + C\,(s) \Leftrightarrow 2\,CO\,(g)\ ;\ K_c = 1.17$$

What will happen to the concentrations of the gasses present if a small amount of C (s) is added to the vessel?

Initial $[CO_2]$ =

Initial [CO] =

Q_c =

Q_c K_c, therefore:

Task: A 50.0 L vessel contains 1.00 mol. N_2 (g), 3.00 mol. H_2 (g) and 0.500 mol. NH_3 (g). If:

$$N_2\,(g) + 3\,H_2\,(g) \Leftrightarrow 2\,NH_3\,(g)\ ;\ K_c = 0.5 \text{ under rxn. conditions}$$

Will more or less NH_3 (g) be present when the system attains equilibrium?

ANS = Less

Le Châtelier's Principle

When a system in eq^{m} is disturbed by a change in [*conc*], *temperature or pressure*, the eq^{m} will shift to compensate for this change

"You push me, I push back" - John Rambo, noted physical chemist

Discussion:

For: A ⇔ B $K = \frac{[B]}{[A]}$ (A constant)

What, then, *must* happen if [B] is reduced by removing this chemical from the reaction mixture?

Answer:

1. Altering Concentration - Removing Products and/or Adding Reactants

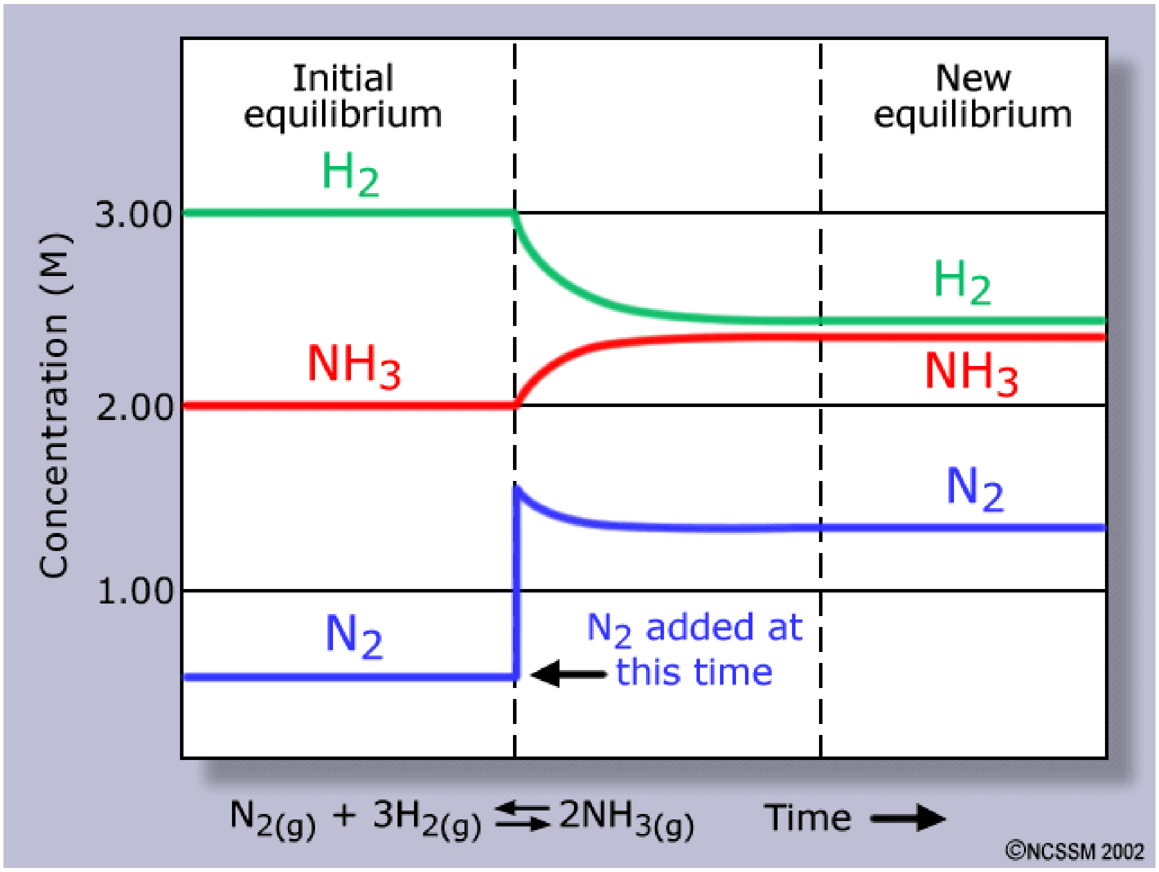
For: $N_2 (g) + 3 H_2 (g) \Leftrightarrow 2 NH_3 (g)$

What will happen to the position of the equilibrium if:

A. Some NH_3 (g) is removed from the reaction vessel (its partial pressure is reduced)

B. N_2 (g) and/or H_2 (g) is added to the reaction vessel

C. Some N_2 (g) is added to the reaction vessel (see slide)



Task: Predict the direction of reaction for:

$$CaCO_3\ (s) \Leftrightarrow CaO\ (s) + CO_2\ (g)$$

If the amount (pressure) of CO_2 (g) is increased

If the amount of $CaCO_3$ (s) is doubled

2. Changing Pressure and /or Temperature

Discussion: What exerts more pressure in a fixed volume container – 2 moles of gas or 4 moles of gas?

When an equilibrium involving gasses is stressed by altering the pressure, the equilibrium will shift to either increase (p↑) or decrease (p↓) the number of gasses species present

Thus:

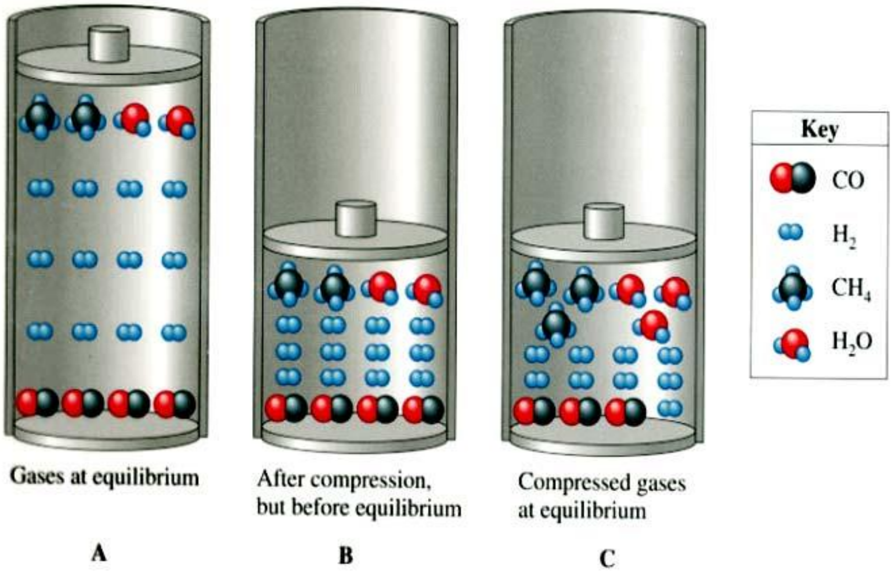
When the pressure is *increased*, the system will remove this stress by _______________ the moles of gaseous species present at equilibrium

When the pressure is *decreased*, the system will remove this stress by _______________ the moles of gaseous species present at equilibrium

Example: Consider the equilibrium:

$$CO\ (g)\ +\ 3\ H_2\ (g)\ \Leftrightarrow\ CH_4\ (g)\ +\ H_2O\ (g)$$

What would happen to the rxn. mixture if the vessel were compressed? (See below fig. for a microscopic view of what happens)



What would happen if the volume of the reaction vessel were doubled?

Examples: Can the amount of product(s) in the following reactions be increased by increasing the pressure inside the reaction vessel?

a. $CO_2\,(g) + H_2\,(g) \Leftrightarrow CO\,(g) + H_2O(g)$

b. $4\,CuO\,(s) \Leftrightarrow 2\,Cu_2O\,(s) + O_2\,(g)$

c. $2\,SO_2\,(g) + O_2\,(g) \Leftrightarrow 2\,SO_3\,(g)$

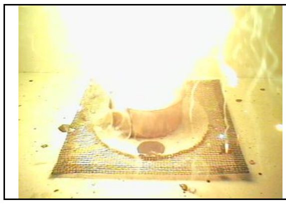
Temperature Effects

Aside: Recall from the 'Thermo' section of Chem. 101:

Discussion: what is an *exo*thermic reaction, what is an *endo*thermic reaction? Hint: think of the roots –(*ex*, *en*)

EXOthermic:

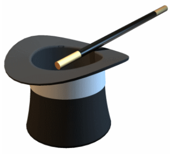
ENDOthermic:



Fact: The vast majority of all known reactions are *exo*thermic (heat is evolved). For example, *all* combustion reactions give out heat.

Type of reaction	Observation	Write heat where?	Sign of ΔH (enthalpy)
*Exo*thermic			**-VE**
*Endo*thermic			**+VE**

The amount of heat evolved (exothermic, -ve ΔH) or absorbed (endothermic, +ve ΔH) during a chemical process is expressed in the form of a thermochemical equation – like a regular balanced equation, but with the numerical value of ΔH included



Write 'heat' as a product (on the right) for exothermic reactions (vice versa for *endo*) – Le Châtelier's Principle can then be applied with regard to heating or cooling the reaction vessel

Example: Consider the following thermochemical process:

$$CO\ (g) + 3\ H_2\ (g) \Leftrightarrow CH_4\ (g) + H_2O\ (g)\ ;\ \Delta H = -206.2\ kJ/mol$$

What happens to the position of the equilibrium when the reaction vessel is:

a. Heated up:

b. Cooled down:

Another example: Is a high or low temperature favorable for the formation of CO (g) in the following process? Hint: Remember the previous trick.

$$CO_2\,(g) + C\,(s) \Leftrightarrow 2\,CO\,(g)\ ;\ \Delta H = +172\ kJ/mol$$

Choosing Optimal Reaction Conditions based on Le Châtelier’s Principle

Chemists typically want to maximize the formation of products from a chemical reaction. Therefore, choosing the ‘right’ conditions of P and T (according to Le Châtelier) will allow for the maximum possible yield of product(s)

Example: What conditions of temperature and pressure would maximize the formation of ammonia (NH_3) via the Haber process?

$$N_2\,(g) + 3\,H_2\,(g) \Leftrightarrow 2\,NH_3\,(g)\ ;\ \Delta H = -91.8\ kJ/mol$$

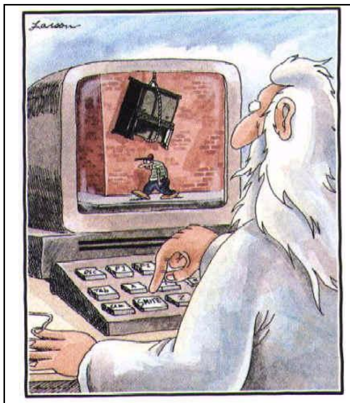
Temperature:	Increase temperature of vessel	OR	Decrease temperature of vessel
Pressure:	Increase pressure on vessel	OR	Decrease pressure on vessel

See appendix for figures

Another Example: What conditions of temperature and pressure would maximize the formation of CO (g) for:

$$2\ CO_2\ (g) \Leftrightarrow 2\ CO\ (g) + O_2\ (g)\ ;\ \Delta H = +556\ kJ/mol$$

Discussion: What happens to the rate of any *exo*thermic reaction when it is ‘optimized’ according to Le Châtelier’s Principle?



God at His computer

The Great Cosmic Joke – Kinetics v Equilibrium

Increasing the temperature of a reaction increases the rate at which reactants form. However, most reactions are exothermic, so the equilibrium is shifted in favor of reactant and higher temps. IE

You can either make less ‘stuff’ more quickly (high temp.) or more ‘stuff’ over a longer period of time (low temp) – you just can’t win!

Wrap up: Intro to the ICE method (will be covered in more detail in acid/base equilibria)

Worked Example (Lab question 4): The air pollutant NO (g) is produced in automobile engines from the high temperature reaction below. If the initial concentrations of N_2 (g) and O_2 (g) are both 1.40 M, what is the concentration of each reactant and product at equilibrium. K = 0.0017 at 2300 K.

$$N_2\,(g) + O_2\,(g) \Leftrightarrow 2\,NO\,(g)$$

"Equilibrium"

The following question was taken from a previous 102 quiz:

<u>Question 1 (6 points)</u>: Write equilibrium (K) expressions for the following:

1. $MgCO_3(s) \leftrightarrow MgO(s) + CO_2(g)$

2. $N_2(g) + O_2(g) \leftrightarrow 2NO(g)$

3. $Sn(s) + 2H^+(aq) \leftrightarrow Sn^{2+}(aq) + H_2(g)$

<u>Question 2 (5 points)</u>: The following equilibrium has a value of $K_p = 0.556$ at 700 K:

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

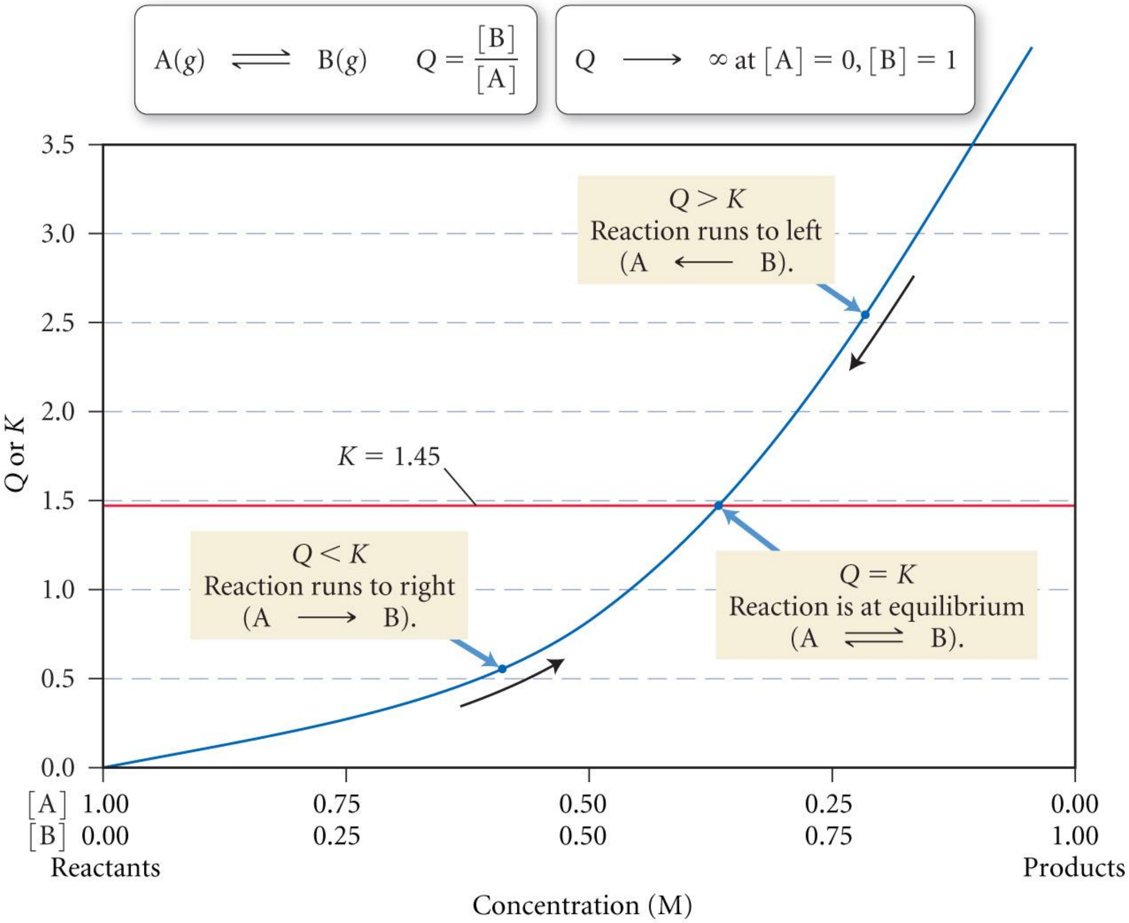
If the partial pressures of $SO_2(g)$ and $O_2(g)$ at equilibrium are 0.175 atm and 0.856 atm, respectively, what is the equilibrium partial pressure of $SO_3(g)$?

TABLE 14.1 Initial and Equilibrium Concentrations for the Reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ at 445 °C

Initial Concentrations			Equilibrium Concentrations			Equilibrium Constant
$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\frac{0.78^2}{(0.11)(0.11)} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\frac{0.39^2}{(0.055)(0.055)} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\frac{1.17^2}{(0.165)(0.165)} = 50$
1.0	0.50	0.0	0.53	0.033	0.934	$\frac{0.934^2}{(0.53)(0.033)} = 50$
0.50	1.0	0.0	0.033	0.53	0.934	$\frac{0.934^2}{(0.033)(0.53)} = 50$

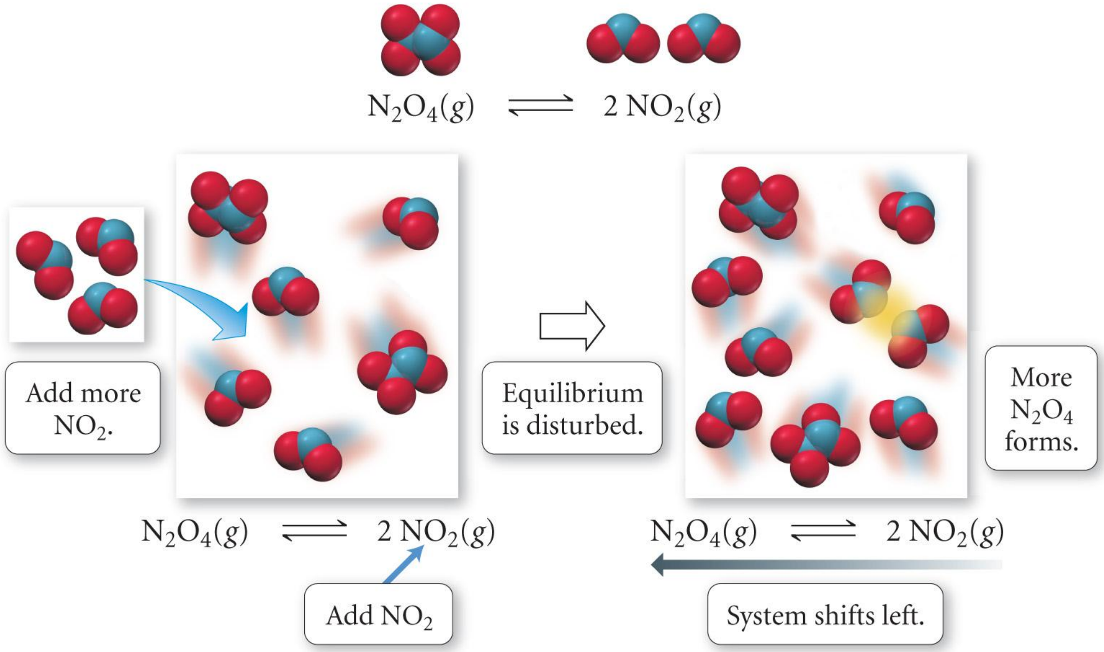
Copyright © 2008 Pearson Prentice Hall, Inc.

Q, *K*, and the Direction of a Reaction



Copyright © 2008 Pearson Prentice Hall, Inc.

Le Châtelier's Principle: Changing Concentration



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

Add more NO_2.

Equilibrium is disturbed.

More N_2O_4 forms.

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

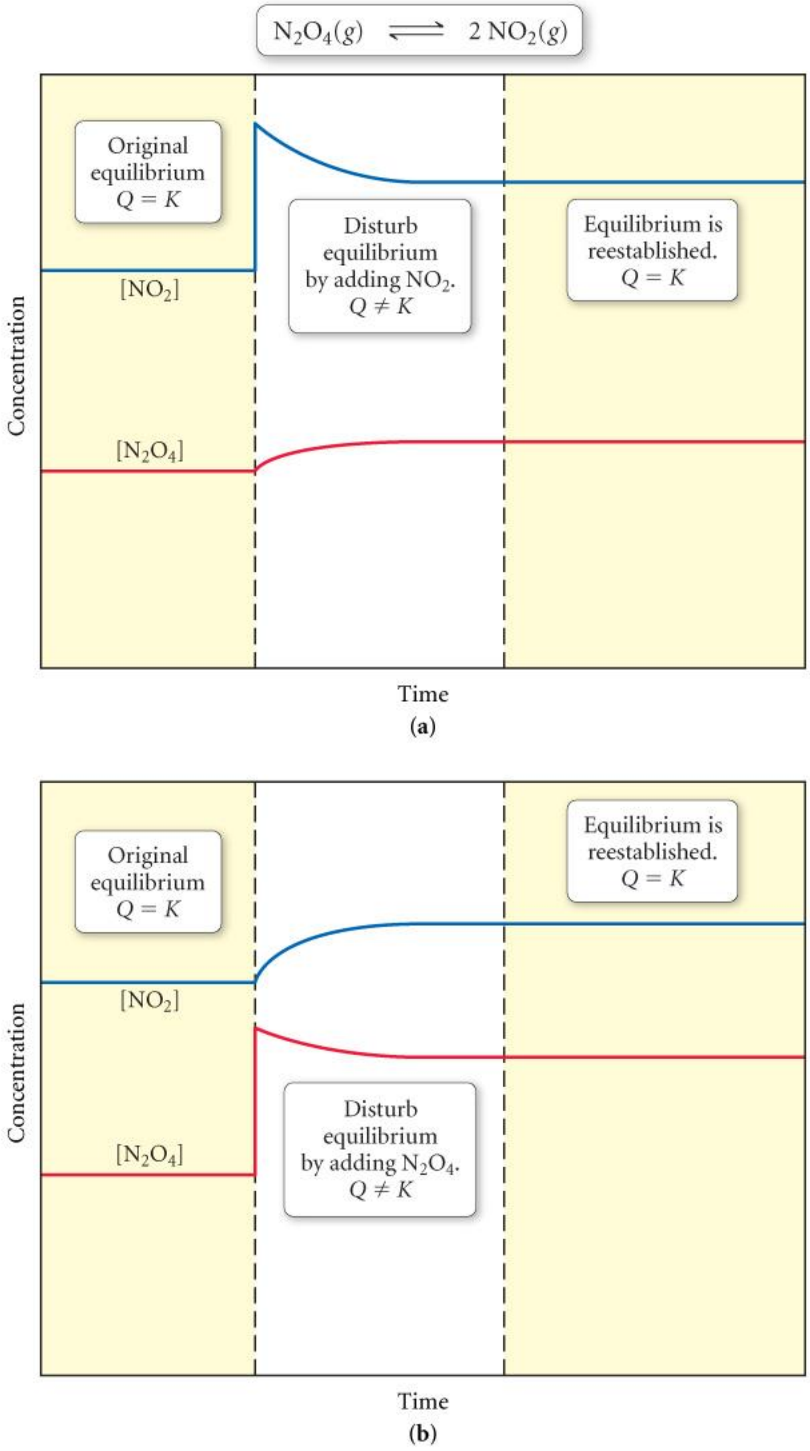
Add NO_2

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

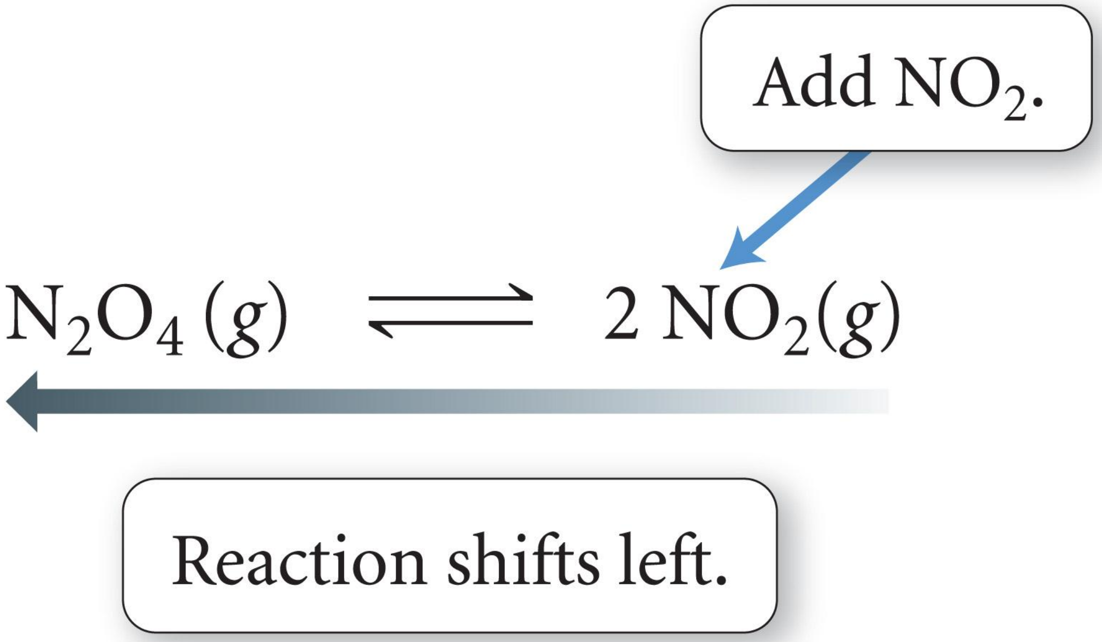
System shifts left.

Copyright © 2008 Pearson Prentice Hall, Inc.

Le Châtelier's Principle: Graphical Representation



Copyright © 2008 Pearson Prentice Hall, Inc.

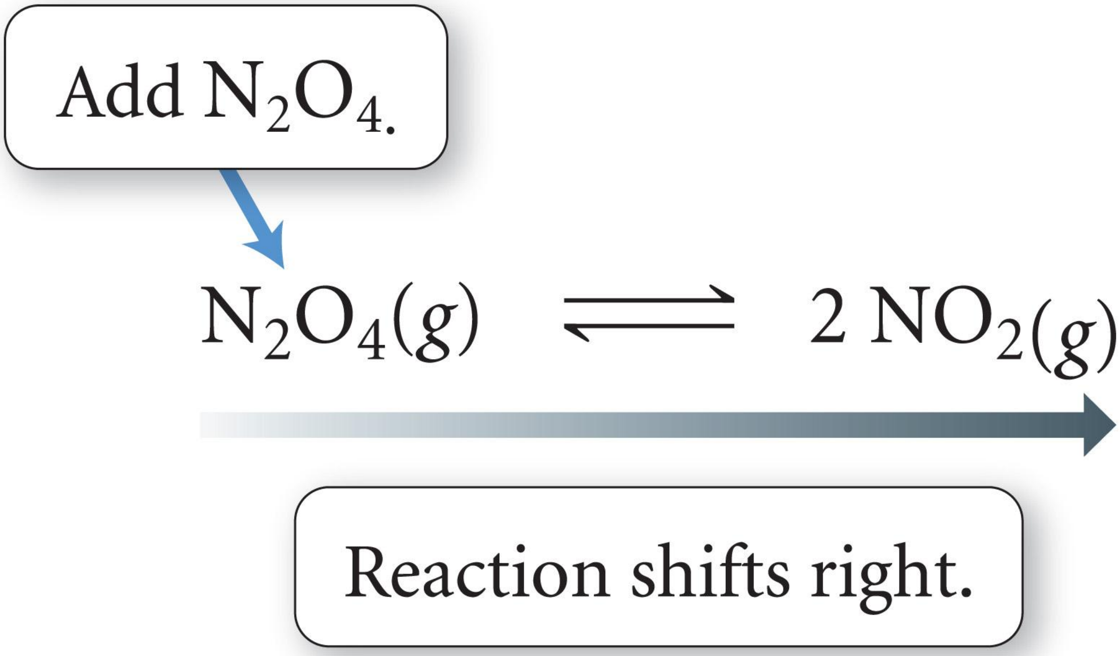


Add NO_2.

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

Reaction shifts left.

Copyright © 2008 Pearson Prentice Hall, Inc.



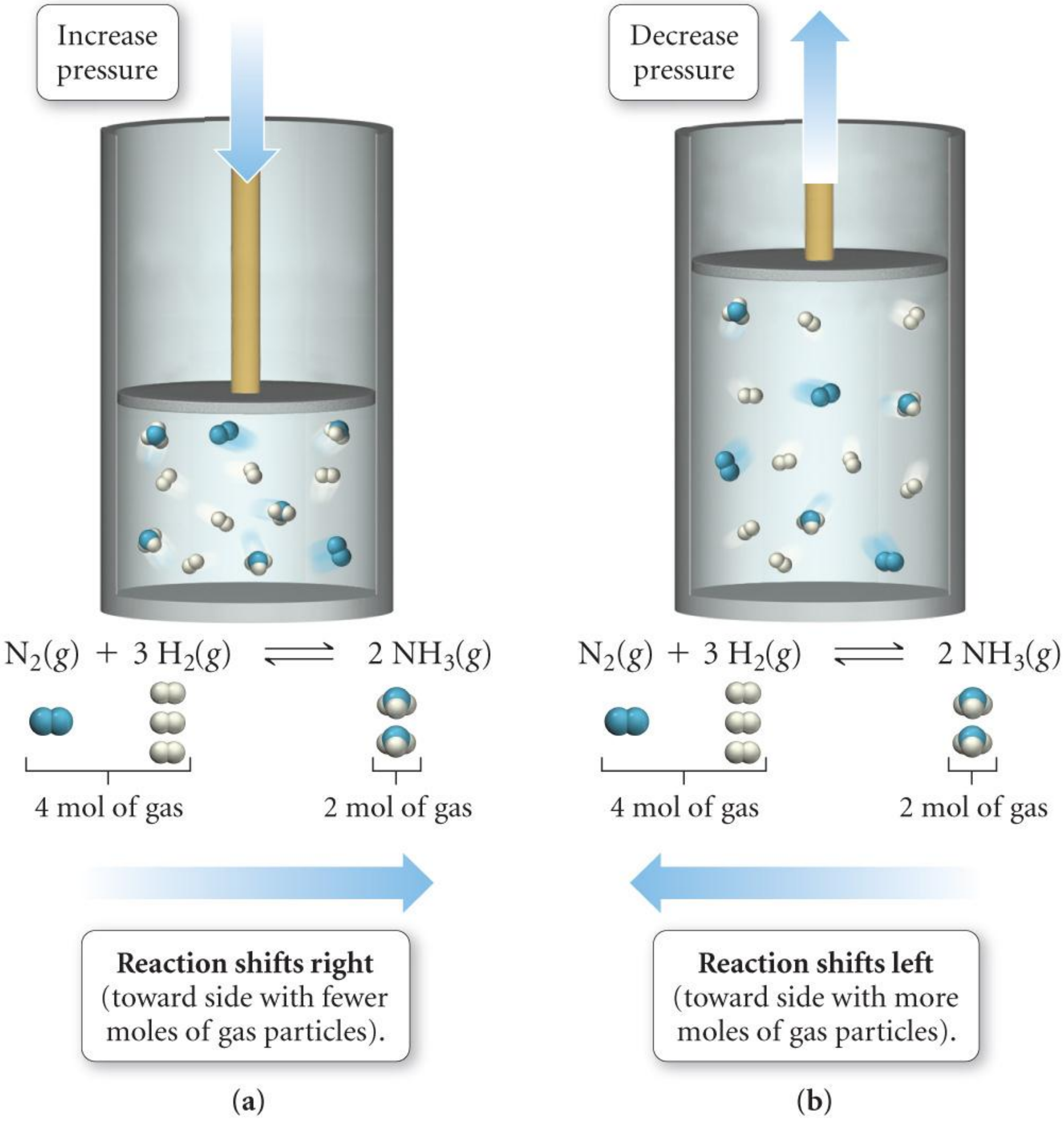
Add N_2O_4.

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

Reaction shifts right.

Copyright © 2008 Pearson Prentice Hall, Inc.

Le Châtelier's Principle: Changing Pressure



Copyright © 2008 Pearson Prentice Hall, Inc.

Add heat

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

Reaction shifts left.
Smaller K

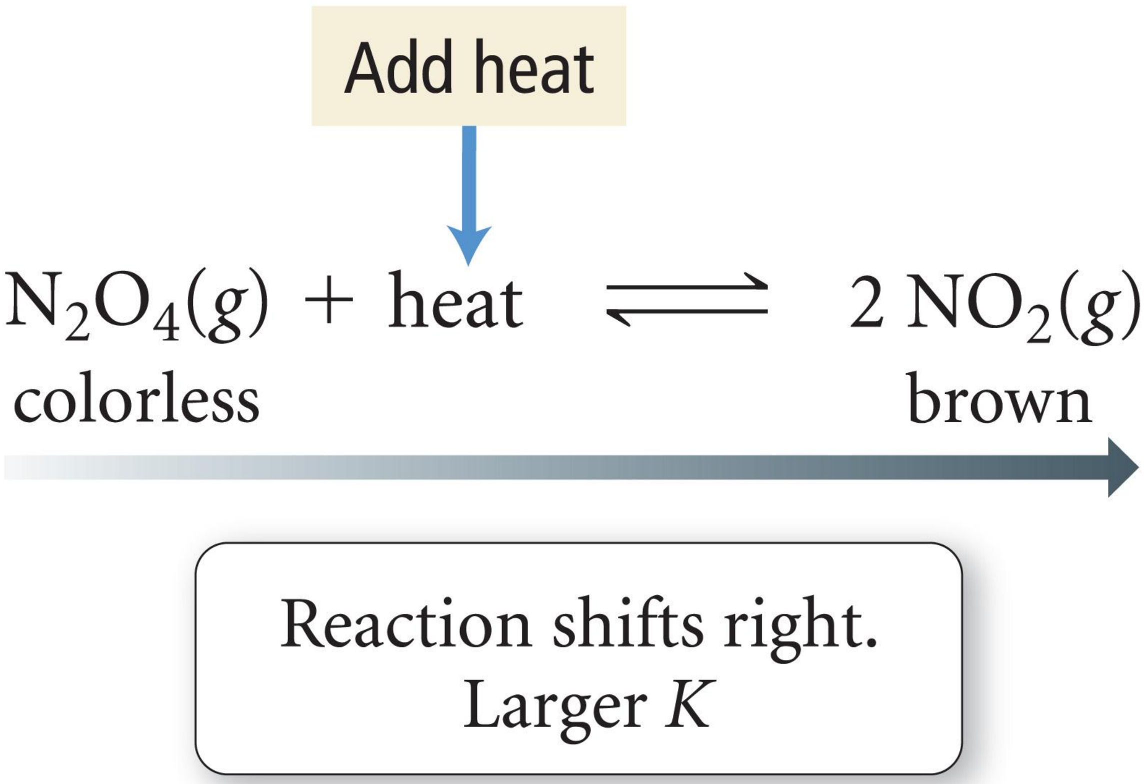
Copyright © 2008 Pearson Prentice Hall, Inc.

Remove heat

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$$

Rection shifts right.
Larger K

Copyright © 2008 Pearson Prentice Hall, Inc.



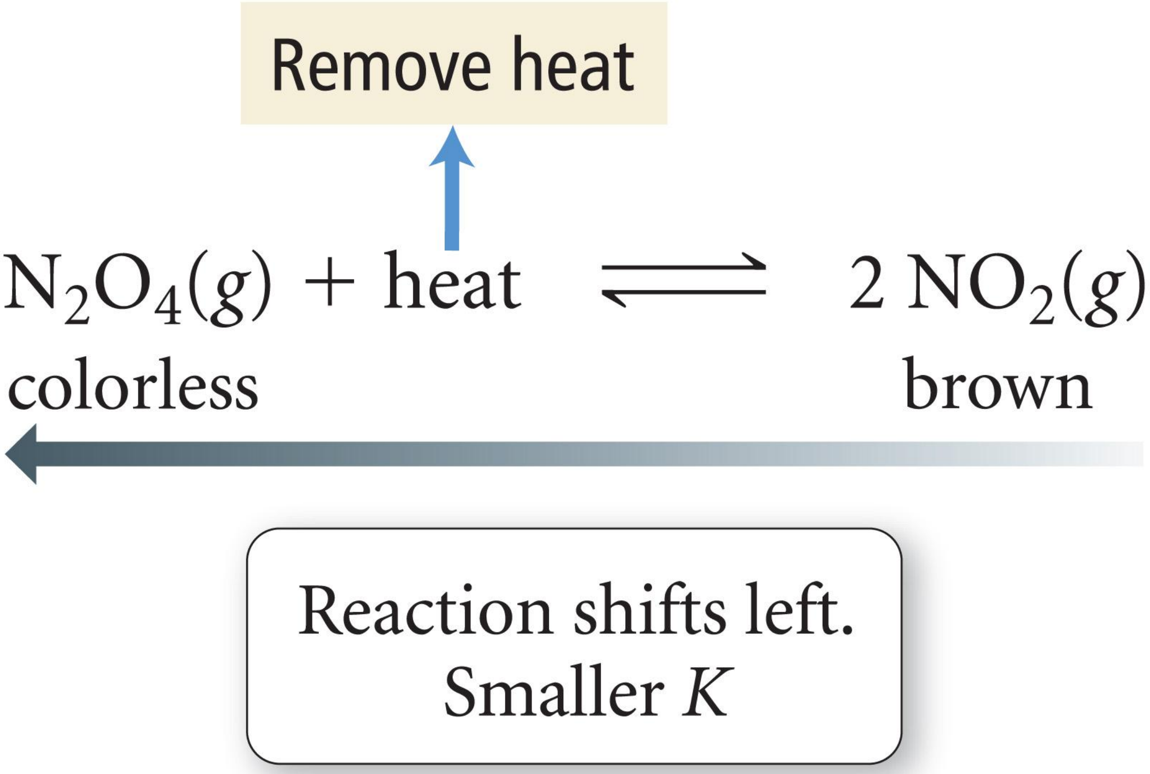
Add heat

$$N_2O_4(g) + \text{heat} \rightleftharpoons 2\,NO_2(g)$$

colorless brown

Reaction shifts right.
Larger *K*

Copyright © 2008 Pearson Prentice Hall, Inc.



Remove heat

$$N_2O_4(g) + \text{heat} \rightleftharpoons 2\,NO_2(g)$$

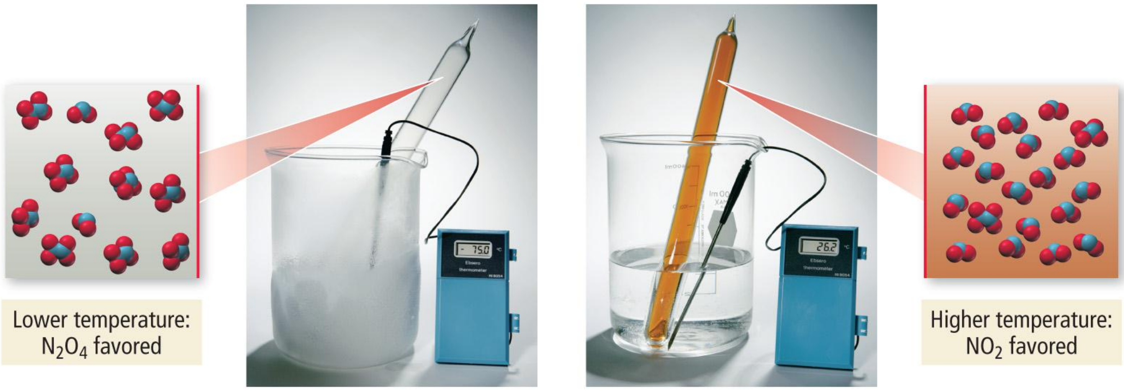
colorless brown

Reaction shifts left.
Smaller *K*

Copyright © 2008 Pearson Prentice Hall, Inc.

Le Châtelier's Principle: Changing Temperature

$$\underset{\text{colorless}}{N_2O_4(g)} + \text{heat} \rightleftharpoons \underset{\text{brown}}{2\,NO_2(g)}$$



Copyright © 2008 Pearson Prentice Hall, Inc.