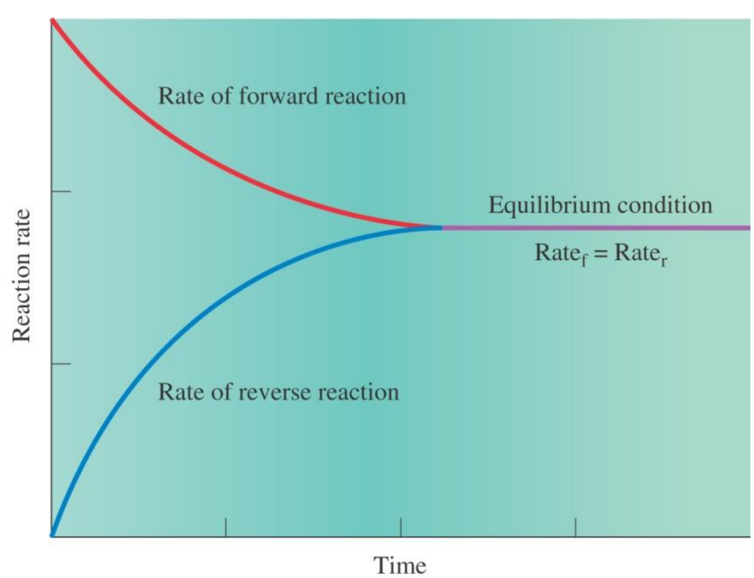
CHEMICAL EQUILIBRIUM

- Reactions that can go in both directions are called **reversible** reactions.
- These reactions seem to stop before they go to completion.
- When the rate of the forward and reverse reactions become equal, an **equilibrium** system is established.

Stepwise view to an equilibrium system

Step 1	A + B $\longrightarrow$ C + D Fast	No Reaction $\longleftarrow$ C + D
Step 2	A + B $\longrightarrow$ C + D Forward reaction slows down. There are fewer A and B molecules available.	A + B $\longleftarrow$ C + D Reverse reaction starts slowly at first. There are few C and D molecules available.
Step 3	A + B $\longrightarrow$ C + D Forward reaction slows down further as the number of A and B molecules decreases.	A + B $\longleftarrow$ C + D Reverse reaction speeds up as the number of C and D molecules increases.
Step 4	A + B $\underset{\text{reverse}}{\overset{\text{forward}}{\rightleftarrows}}$ C + D **RATE OF FORWARD REACTION = RATE OF REVERSE REACTION**	



CHEMICAL EQUILIBRIUM

Characteristics of a Chemical Equilibrium System:

1. A mixture of Reactants and Products is present

2. The composition of the reaction mixture no longer changes:

    - Concentration of reactants is constant

    - Concentration of products is constant

    NOTE: **Concentration of reactants ≠ Concentration of products**

3. A Chemical Equilibrium is a Dynamic Equilibrium; both reactions (forward and reverse) are still going on

4. The Dynamic Equilibrium may be controlled (shifted to the right to favor products, or shifted to the left to favor reactants) by changing the conditions for the reaction.

Definition of Chemical Equilibrium:

- A state reached by a reaction mixture when the **rate of forward reaction and the rate of reverse reactions become equal.**

THE EQUILIBRIUM CONSTANT

- Concentrations of reactants and products are not equal at equilibrium, but can be quantified by use of the ***equilibrium constant (K).***

- Consider the general chemical equation below:

$$aA + bB \rightleftharpoons cC + dD$$

where A and B are reactants and C and D are products, and a, b, c, and d represent the stoichiometric coefficients in the equation. The ***equilibrium constant*** for the reaction is defined by the expression below (also known as the ***law of mass action***):

Law of Mass Action

$$K = \frac{\overbrace{[C]^c[D]^d}^{\text{Products}}}{\underbrace{[A]^a[B]^b}_{\text{Reactants}}}$$

[C], [D] = molar concentrations (molarities) of the products at equilibrium

[A], [B] = molar concentrations (molarities) of the reactants at equilibrium

- When writing an equilibrium constant expression for a chemical equation, the balanced chemical equation is examined and the law of mass action is applied. For example, for the reaction shown below:

$$2\ N_2O_5\ (g) \rightleftharpoons 4\ NO_2\ (g) + O_2\ (g)$$

the equilibrium constant can be written as:

$$K = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

- Note that the coefficients of the chemical equation become the exponents in the expression of the equilibrium constant.

- The equilibrium constant expressed in terms of the concentration of the reactants and products is designated as K_c.

- It is common practice to write K <u>without</u> units.

THE EQUILIBRIUM CONSTANT

Examples:

1. Write the equilibrium constant expression for the equation shown below:

$$2\ NO_2\,(g) \quad + \quad 7\ H_2\,(g) \rightleftharpoons 2\ NH_3\,(g) \quad + \quad 4\ H_2O(g)$$

K_c =

2. Write the equilibrium constant expression for the combustion of propane:

$$C_3H_8\,(g) \quad + \quad 5\ O_2\,(g) \rightleftharpoons 3\ CO_2\,(g) \quad + \quad 4\ H_2O\,(g)$$

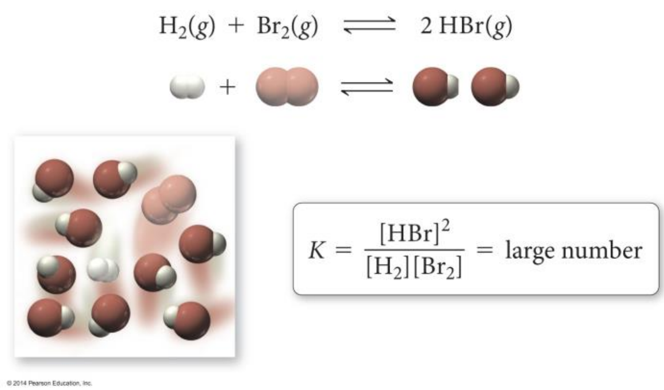
K_c =

SIGNIFICANCE OF THE EQUILIBRIUM CONSTANT

- The magnitude of the equilibrium constant indicates the extent to which the forward and reverse reactions take place.

K >>> 1:

$$H_2\,(g) + Br_2\,(g) \rightleftharpoons 2\,HBr\,(g) \qquad K_c = 1.9\text{x}10^{19} \text{ (at 25°C)}$$

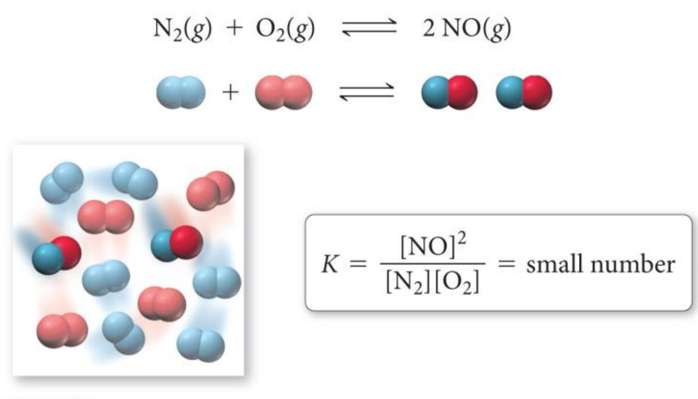


{amount of products at equilibrium} > {amount of reactants at equilibrium}

- ➢ **Products are favored at equilibrium**

K <<< 1:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \qquad K_c = 4.1\text{x}10^{-31} \text{ (at 25°C)}$$



{amount of products at equilibrium} < {amount of reactants at equilibrium}

- ➢ **Reactants are favored at equilibrium**

SIGNIFICANCE OF THE EQUILIBRIUM CONSTANT

K ≈ 1:

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

$$\left\{\begin{array}{c}\textbf{amount of}\\ \textbf{products at}\\ \textbf{equilibrium}\end{array}\right\} \approx \left\{\begin{array}{c}\textbf{amount of}\\ \textbf{reactants at}\\ \textbf{equilibrium}\end{array}\right\}$$

- **Neither reactants, nor products are predominant at equilibrium**

Summary:

- **K >> 1:** Forward reaction is favored; forward reaction proceeds essentially to completion.
- **K ≈ 1:** Neither direction is favored; forward reaction proceeds about halfway.
- **K<<1:** Reverse reaction is favored; forward reaction does not proceed very far.

Examples:

1. The equilibrium constant for the reaction A (g) $\rightleftharpoons$ B (g) is 10. A reaction mixture initially contains [A]=1.1 M and [B]= 0.0 M. Which statement below is true at equilibrium?

   a) The reaction mixture will contain [A]= 1.0 M and [B]= 0.1 M.

   b) The reaction mixture will contain [A]= 0.1 M and [B]= 1.0 M.

   c) The reaction mixture will contain equal concentrations of A and B.

MANIPULATING EQUILIBRIUM CONSTANTS

- If a chemical equation is modified in some way, then the equilibrium constant for the equation also changes because of the modification. Three common modifications are discussed below:

A) If an equation is reversed, then the equilibrium constant is inversed. For example, the equilibrium constant for the reaction below and its reverse can be written as shown:

$$A + 2\,B \rightleftharpoons 3C \qquad K_{forward} = \frac{[C]^3}{[A]\,[B]^2}$$

$$3\,C \rightleftharpoons A + 2B \qquad K_{reverse} = \frac{[A][B]^2}{[C]^3} = \frac{1}{K_{forward}}$$

B) If the coefficients in an equation are multiplied by a factor, then the equilibrium constant should also be multiplied by that factor. For example, consider the equilibrium below and when it is doubled:

$$A + 2\,B \rightleftharpoons 3C \qquad K = \frac{[C]^3}{[A]\,[B]^2}$$

$$2\,A + 4\,B \rightleftharpoons 6\,C \qquad K = \frac{[C]^6}{[A]^2\,[B]^4} = \left(\frac{[C]^3}{[A]\,[B]^2}\right)^2$$

<u>Examples:</u>

1. The reaction A (g) $\rightleftharpoons$ 2 B (g) has an equilibrium constant of K=0.010. What is the equilibrium constant for the reaction B (g) $\rightleftharpoons$ ½ A (g)?

   a) 1

   b) 10

   c) 100

   d) 0.0010

MANIPULATING EQUILIBRIUM CONSTANTS

C) If a given chemical equation can be obtained by taking the sum of other equations, the Equilibrium Constant for the overall equation equals the product of the equilibrium constants of the other equations.

$$\mathbf{K_{overall} = K_1K_2\ldots}$$

For example, the following equilibria occur at 1200K

$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$		$K_1 = 3.92$
$CH_4(g) + 2\,H_2S(g) \rightleftharpoons CS_2(g) + 4\,H_2(g)$		$K_2 = 3.3\text{x}10^4$
$CO(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + H_2O(g) + H_2(g)$		$K_3 = ???$

$$K_1 = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \qquad K_2 = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$$

$$K_1K_2 = \frac{[\cancel{CH_4}][H_2O]}{[CO][\cancel{H_2}]^3} \text{ x } \frac{[CS_2][H_2]^4}{[\cancel{CH_4}][H_2S]^2} = K_3$$

The equilibrium constant for an overall equation is equal to the product of the equilibrium constants of the individual equations.

$$\mathbf{K_3 = K_1 \text{ x } K_2}$$

Examples:

1. Predict the equilibrium constant for the first reaction shown below, given the two equilibrium constants given:

$CO_2(g) + 3\,H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$	$K_1 = ???$
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	$K_2 = 1.0\text{x}10^5$
$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$	$K_3 = 1.4\text{x}10^7$

GAS-PHASE EQUILIBRIA (K_P)

- **Gas-Phase Equilibria** refers to equilibrium systems where **all reactants and products** are **gases**.

- Concentrations of gases can be expressed in terms of partial pressures, since the concentration of a gas is proportional to its partial pressure.

Constant at a given temperature

$$PV = nRT \qquad \frac{n}{V}\left(\frac{mol}{L}\right) = \frac{P}{RT}$$

$$\text{molar concentration of a gas} = \frac{n}{V} = P\left(\frac{1}{RT}\right)$$

- K_p is the equilibrium constant for a gaseous reaction expressed in terms of partial pressures.

- K_p has a value different from K_c

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

$$\Delta n = \left(\begin{array}{c}\text{sum of coefficients}\\ \text{of}\\ \text{gaseous products}\end{array}\right) - \left(\begin{array}{c}\text{sum of coefficients}\\ \text{of}\\ \text{gaseous reactants}\end{array}\right)$$

<u>Examples:</u>

1. The reaction shown below has $K_c = 3.92$ at 1200 K. Calculate K_p for this reaction at this temperature.

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

$\Delta n =$

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

2. K_p for the formation of NO at 25 °C is 2.2×10^{12}. What is the value of K_c at this temperature?

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

$\Delta n =$

$K_c =$

CLASSIFICATION OF CHEMICAL EQUILIBRIA

- Chemical Equilibria can be classified according to the physical state of the reactants and products present:

A) <u>Homogeneous Equilibrium</u>

An equilibrium that involves reactants and products in a single phase. For example:

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

B) <u>Heterogeneous Equilibrium</u>

An equilibrium involving reactants and products in more than one phase For example

$$3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$$

$$K_c = \frac{[H_2]^4}{[H_2O]^4}$$

<u>NOTE:</u> The concentrations of solids are omitted.

Reason: The concentration of a pure solid or pure liquid is a constant at a given temperature.

- Equilibrium Constant expression can be written with pure solids included:

$$K_c = \frac{[Fe_3O_4]\,[H_2]^4}{[Fe]^3\,[H_2O]^4}$$

By rearrangement:

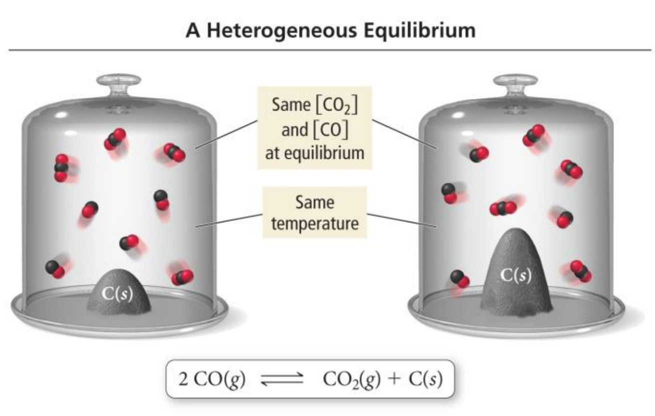
$$\underbrace{\frac{[Fe]^3}{[Fe_3O_4]}}_{\text{constant factors}} K_c = \underbrace{\frac{[H_2]^4}{[H_2O]^4}}_{\text{variable factors}}$$

$$K_c' = \frac{[Fe]^3}{[Fe_3O_4]} K_c = \frac{[H_2]^4}{[H_2O]^4}$$

- The concentrations of pure solids and liquids are incorporated in the value of K_c'.

- The concentration of solvent is also omitted from the expression of K_c for a homogeneous reaction (if constant).

- The equilibrium is not affected by pure solids, pure liquids, or solvents.



CLASSIFICATION OF CHEMICAL EQUILIBRIA

Examples:

Identify each of the following equilibriums as homogeneous or heterogeneous and write Kc expressions for each:

1. $FeO\ (s) + H_2\ (g) \rightleftharpoons Fe\ (s) + H_2O\ (g)$ ____________________

2. $CH_4\ (g) + 2\ H_2S\ (g) \rightleftharpoons CS_2\ (g) + 4\ H_2O\ (g)$ ____________________

3. $Ti\ (s) + 2\ Cl_2\ (g) \rightleftharpoons TiCl_4\ (l)$ ____________________

4. For which reaction below does $K_p = K_c$?

   a) $2\ Na_2O_2\ (s) + 2\ CO_2\ (g) \rightleftharpoons 2\ Na_2CO_3\ (s) + O_2\ (g)$

   b) $Fe_2O_3\ (s) + 3\ CO\ (g) \rightleftharpoons 2\ Fe\ (s) + 3\ CO_2\ (g)$

   c) $NH_4NO_3\ (s) \rightleftharpoons N_2O\ (g) + 2\ H_2O\ (g)$

CALCULATING K_C FOR REACTIONS

- The most direct way to obtain an experimental value for the equilibrium constant of a reaction is to measure the concentration of the reactants and products in a reaction mixture in equilibrium.

- For example, for the reaction shown below, suppose a mixture of H_2 and I_2 are allowed to come to equilibrium at 455 °C.

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

- If at equilibrium, the concentrations are $[H_2]$= 0.11 M, $[I_2]$ = 0.11 M and [HI] = 0.78 M, what is the value of the equilibrium constant at this temperature?

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(0.78)^2}{(0.11)(0.11)} = 5.0\text{x}10^1$$

- For any reaction, the ***equilibrium concentrations*** of the reactants and products depend on the initial concentrations, and commonly vary for each case. However, the equilibrium constant is always the same at a given temperature, regardless of the initial concentrations.

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	$\frac{(0.934)^2}{(0.033)(0.53)} = 50$

CALCULATING K_C FOR REACTIONS

- When equilibrium concentrations are not given, they can be determined from the initial concentrations and the stoichiometric relationships in the equation. For example, consider the simple reaction below:

$$A\ (g) \rightleftharpoons 2\ B\ (g)$$

- If a reaction mixture with an initial concentration of [A]= 1.00 M and [B] = 0.00 is allowed to come to equilibrium, and if the concentration of A at equilibrium equals 0.75 M, then the following information can be determined for this reaction.

	[A]	[B]
Initial	1.00	0.00
Change	−0.25	+0.50
Equilibrium	0.75	0.50

- The equilibrium constant for this reaction can then be calculated as shown below:

$$K_c = \frac{[B]^2}{[A]} = \frac{(0.50)^2}{(0.75)} = 0.33$$

- For any reaction, the ICE table (shown above) can be used to determine the equilibrium concentrations of reactants and products from the initial concentrations given.

Examples:

1. When 2.00 mole each of H_2 and I_2 are mixed in a 1.00-L flask and allowed to come to equilibrium, 3.5 mol of HI is produced. What is the value of the equilibrium constant for this reaction?

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

Examples (cont'd):

2. Consider the reaction below. 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?

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

Initial	0.500	1.00	0.00
Δ			
Equilibrium	0.15		

$K_c = \dfrac{\qquad\qquad}{\qquad\qquad} =$

3. Consider the reaction below. 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?

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

Initial	0.115	0.00	0.00
Δ			
Equilibrium		0.035	

$K_c = \dfrac{\qquad\qquad}{\qquad\qquad} =$

Examples (cont'd):

4. Consider the reaction shown below. A reaction mixture is made containing an initial [SO_2Cl_2] of 0.020 M. At equilibrium, [Cl_2] = 1.2×10^{-2} M. Calculate the value of the equilibrium constant (K_c).

$$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$$

	SO_2Cl_2 (g) $\rightleftharpoons$	SO_2 (g) +	Cl_2 (g)
Initial			
Δ			
Equilibrium			

K_c =

5. A sample of SO_3 is placed in an evacuated sealed container and heated to 600 K. The following equilibrium is established:

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

The total pressure in the system at equilibrium is found to be 3.0 atm and the mole fraction of O_2 is 0.12. Determine K_p for this equilibrium.

PREDICTING THE DIRECTION OF CHANGE

- When the reactants in a chemical reaction mix, they generally form products, and the reaction is said to proceed in the forward direction. The amount of products formed depends on the magnitude of the equilibrium constant.

- What direction would the reaction proceed if the initial reaction mixture contains both reactants and products? To gauge the progress of a reaction relative to equilibrium, a quantity called the ***reaction quotient*** is used.

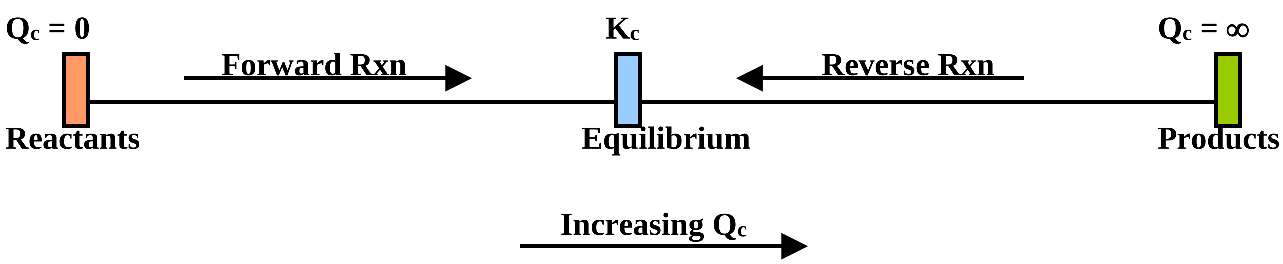
- The ***reaction quotient (Q_c)*** has the same definition as the equilibrium constant, except that the concentrations are not at equilibrium. Therefore, for the general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the reaction quotient is:

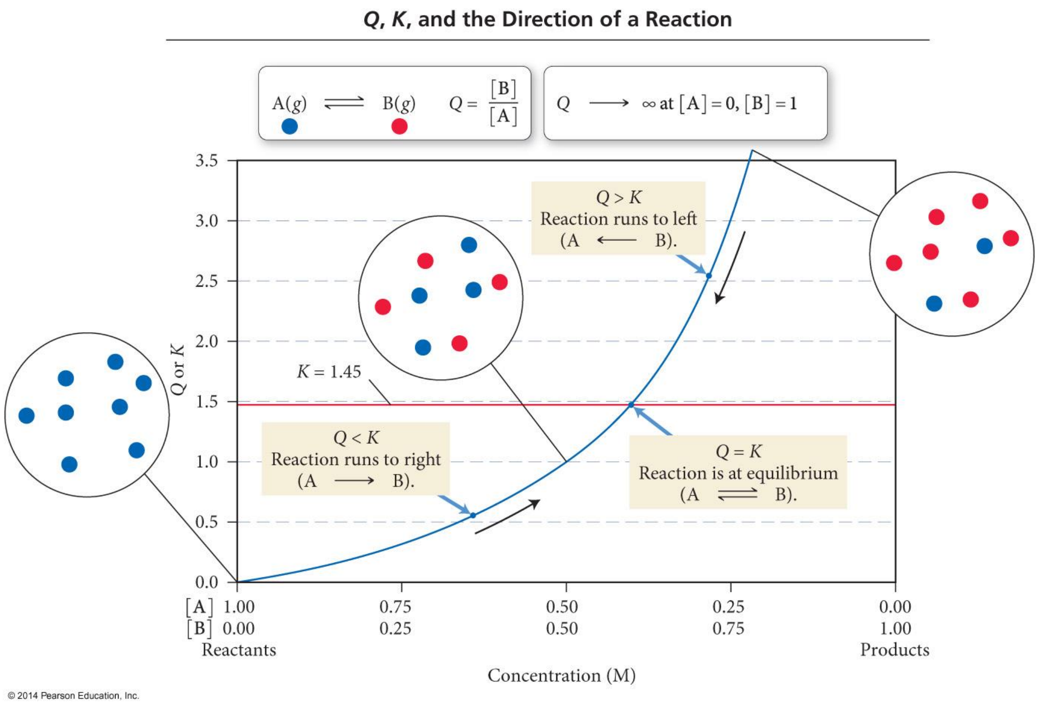
$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

- The reaction quotient is useful because the value of Q relative to K is a measure of the progress of reaction towards equilibrium. At equilibrium, the reaction quotient (Q) is equivalent to the equilibrium constant (K).



PREDICTING THE DIRECTION OF CHANGE

- Shown below is a plot of Q as a function of the concentrations of A and B for the simple reaction A(g) $\rightleftarrows$ B (g), which has an equilibrium constant of K = 1.45.



- The three conditions highlighted above are represented by the 3 data points shown below:

Q	K	Predicted Direction of Reaction
0.55	1.45	To the right (toward products)
2.55	1.45	To the left (toward reactants)
1.45	1.45	No change (at equilibrium)

- The reaction quotient (Q) relative to the equilibrium constant (K) is a measure of the progress of the reaction toward equilibrium, and can be summarized as:
  - When: $\mathbf{Q_c > K_c}$ Reaction proceeds the left (towards the reactants)
  - When: $\mathbf{Q_c < K_c}$ Reaction proceeds to the right (towards the products)
  - When: $\mathbf{Q_c = K_c}$ Reaction mixture is at equilibrium

PREDICTING THE DIRECTION OF CHANGE

Examples:

1. The following reaction has an equilibrium constant, K_c, equal to 3.59 at 900 °C, and the following composition of reaction mixture:

$$\begin{array}{ccccccc} CH_4\,(g) & + & 2\,H_2S\,(g) & \rightleftharpoons & CS_2\,(g) & + & 4\,H_2\,(g) \\ 1.26\text{ M} & & 1.32\text{ M} & & 1.43\text{ M} & & 1.12\text{ M} \end{array}$$

(a) Is the reaction mixture at equilibrium?

$$Q_c = \frac{[H_2]^4[CS_2]}{[CH_4][H_2S]^2} =$$

(b) If not at equilibrium, in which direction will the reaction go to reach equilibrium?

2. Nitrogen dioxide dimerizes according to the reaction:

$$2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g) \qquad K_p = 6.7 \text{ at } 298 \text{ K}$$

A 2.25-L container contains 0.055 mol of NO_2 and 0.082 mol of N_2O_4 at 298 K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

CALCULATING EQUILIBRIUM CONCENTRATIONS

- We can use equilibrium constant to calculate the equilibrium concentration of all the substances in the mixture.
- At times, the equilibrium concentration of one substance is determined from equilibrium constant and the equilibrium concentration of the other substances.

Examples:

1. Nitric oxide, NO, is formed in automobile exhaust by the reaction of N_2 and O_2 (from air):

$$N_2\,(g) \;+\; O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

K_c for this reaction equals 0.0025 at 2127 °C. If an equilibrium mixture at 2127 °C contains 0.023 mol N_2 and 0.031 mol O_2 per liter, what is the equilibrium concentration of NO?

$$K_c = \frac{[NO]^2}{[N_2][O_2]} \qquad [NO]^2 = K_c\,[N_2][O_2]$$

$$[NO] = \sqrt{K_c\,[N_2][O_2]} = \sqrt{(0.0025)(0.023)(0.031)} = 1.3\text{x}10^{-3}\ M$$

2. The equilibrium shown below has a K_p value of $1.45\text{x}10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases at this temperature, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this mixture?

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

$K_p =$

CALCULATING EQUILIBRIUM CONCENTRATIONS

- At times, the equilibrium concentrations of all substances are determined from equilibrium constant and the initial concentration of the reactants. When solving these problems, we use an ICE table with the known initial concentrations and then represent the unknown changes with the variable x.

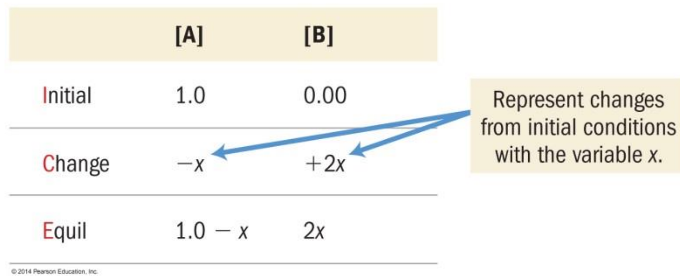
- For example, consider the simple reaction below:

$$A\ (g) \rightleftharpoons 2\ B\ (g)$$

- If a reaction mixture with an initial concentration of [A]= 1.00 M and [B] = 0.00 is allowed to come to equilibrium, and the equilibrium constant (K) is found to be 0.33, the equilibrium concentration of each substance can be found as shown below:

- The equilibrium concentration of each substance can then be found by setting up the equilibrium constant expression and solving for x.

- Examples below show some of the variations for this type of problems.



Examples:

1. For the reaction shown below, initially a mixture contains $[N_2]$ = 0.200 M and $[O_2]$ = 0.200 M. Find the equilibrium concentration of the reactants and products in this reaction.

$$N_2\ (g) + O_2\ (g) \rightleftharpoons 2\ NO\ (g) \qquad K_c = 0.10 \text{ at } 2000\ °C$$

	N_2 (g) +	O_2 (g) $\rightleftharpoons$	2 NO (g)
Initial	0.200	0.200	0.00
Δ	-x	–x	+2x
Equilibrium	0.200–x	0.200–x	2x

$$K_c = 0.10 = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(0.200\text{-}x)(0.200\text{-}x)}$$

Taking square roots of both sides: $0.316 = \dfrac{2x}{(0.200\text{-}x)}$

Simplifying: $(0.316)(0.200) - 0.316\ x = 2x$

Rearranging & solving for x: $0.063 = 2.316\ x$ **x = 0.027 M**

Equilibrium concentrations are:

$[O_2]$ = $[N_2]$ = 0.200 – x = 0.200 – 0.027= <u>**0.173 M**</u>

[NO] = 2x = 2 x 0.027 M = <u>**0.054 M**</u>

Examples:

2. Ammonium hydrogen sulfide decomposes at room temperature as shown below:

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

A sample of ammonium hydrogen sulfide is placed in a flask at 25°C. After equilibrium has been reached, what is the total pressure of the flask? (Note: solids have no pressure)

$K_p = 0.108 =$

3. At relatively high temperatures, the following reaction can be used to produce methyl alcohol:

$$CO\ (g) + 2\ H_2\ (g) \rightleftharpoons CH_3OH\ (l) \qquad K_c = 13.5$$

If the concentration of CO at equilibrium were found to be 0.010 M, what would be the equilibrium concentration of H_2?

CALCULATIONS INVOLVING QUADRATIC EQUATIONS

- Some of the problems involving equilibrium require use of the quadratic equation in order to determine the unknown variable. The example below shows one such problem.

Examples:

1. PCl_5 decomposes when heated: $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

   If the initial concentration of PCl_5 is 1.00 M, what is the equilibrium composition of the gaseous mixture at 160 °C? K_c at 160 °C is 0.0211

	PCl_5 (g) $\rightleftharpoons$	PCl_3 (g) +	Cl_2 (g)
Initial	1.00 M	0	0
Δ	–x	+x	+x
Equilibrium	1.00–x	x	x

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)(x)}{(1.00-x)} = 0.0211$$

$$(0.0211)(1.00 - x) = x^2 \qquad\qquad 0.0211 - 0.0211\,x = x^2$$

$$\boxed{\mathbf{x^2 + 0.0211\,x - 0.0211 = 0}}$$ **Quadratic Equation**

$$\mathbf{ax^2 + bx + c = 0} \qquad \mathbf{x_1, x_2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}$$

$$x^2 + 0.0211\,x - 0.0211 = 0$$

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(-0.0211)}}{2} = \frac{-0.0211 \pm 0.2913}{2}$$

- In theory: There are two mathematical solutions
- In practice: Only one solution makes physical sense

$$x_1 = \frac{-0.0211 + 0.2913}{2} = 0.1351 \qquad\qquad x_2 = \frac{-0.0211 - 0.2913}{2} = -\,0.1562$$

correct

reject
(concentration cannot be negative)

Equilibrium Concentrations are:

$[PCl_5]$ = 1.00 M – x = 1.00 M - 0.1351 M = 0.86 M
$[PCl_3]$ = $[Cl_2]$ = x = 0.135 M

LE CHATELIER'S PRINCIPLE

- The **effect of changes on the equilibrium** can be predicted using the **Le Chatelier's principle**.

- Le Chatelier's principle states that:
  "If a stress is applied to a system at equilibrium, the system will respond in such a way as to relieve the stress and restore a new equilibrium under a new set of conditions".

- Note sequence of events:
  1. Stress applied
  2. Equilibrium system response (equilibrium shift)
  3. New equilibrium

- Stress is a change in any of the following:
  A) Concentration of Reactants or Products
  B) Pressure
  C) Temperature

A) Effect of Concentration Change on Equilibrium
(Adding or Removing Reactants or Products)

Consider:

$$A + B \rightleftharpoons C + D$$

Stress: B increased to B*

Response:

- ➢ Forward reaction speeds up
- ➢ Equilibrium shifts to the right
- ➢ Products are favored

New Equil.:

$$A' + B' \rightleftharpoons C' + D'$$

A'	B'	C'	D'
decreased	increased	increased	increased
A' < A	B<B'<B*	C'>C	D'>D

EFFECT OF CONCENTRATION CHANGE ON EQUILIBRIUM

In General:

- **Adding Reagent**
  - Equilibrium always shifts in the direction that tends to **reduce** the concentration of the added reacting species.
  - When concentration of **reactant is increased** equilibrium **shifts forward** ($Q < K$).
  - When concentration of **product is increased** equilibrium **shifts reverse** ($Q > K$).
- **Removing Reagent**
  - Equilibrium always shifts in the direction that tends to **increase** the concentration of the removed reacting species.
  - When concentration of **reactant is decreased** equilibrium **shifts reverse** ($Q > K$).
  - When concentration of **product is decreased** equilibrium **shifts forward** ($Q < K$).

Example 1:

	H_2 (g)	+	I_2 (g)	$\rightleftharpoons$	2 HI (g)	(700K)
Starting conc's	1.00 M		1.00 M		0	
Change:	–0.79 M		–0.79 M		+ 1.58 M	
Equil Conc's:	0.21 M		0.21 M		1.58 M	
Stress:			**+ 0.20 M**			

Response: - Equilibrium shifts forward to use up added reactant

	H_2 (g)	+	I_2 (g)	$\rightleftharpoons$	2 HI (g)	(700K)
New Equil. Conc's:	**0.15 M**		**0.35 M**		**1. 70 M**	

0.21M<0.35 M<0.41 M

Example 2:

$$Cl_2\,(g) + 2\,H_2O\,(l) \rightleftharpoons HOCl\,(aq) + H_3O^+\,(aq) + Cl^-\,(aq)$$

Reagent Species	Change in concentration	Equilibrium Shift
Cl_2	increase	
Cl_2	decrease	
H_2O	increase	
H_2O	decrease	
HOCl	increase	
HOCl	decrease	
Cl^-	increase	
Cl^-	decrease	

Example 3:

	CO (g)	+	3 H_2 (g) ⇌	CH_4 (g)	+	H_2O (g)
Molar Equil. Composition:	0.613 mol		1.839 mol	0.387 mol		0.387 mol

What changes in the amount of reagents would produce more CH_4?

- increase amount of CO or H_2
- remove CH_4 or H_2O

- Most practical and least expensive solution is to remove H_2O (cool reaction mixture to condense water vapor)

	CO (g)	+	3 H_2 (g) ⇌	CH_4 (g)	+	H_2O (g)
Molar Equil. Composition:	0.613 mol		1.839 mol	0.387 mol		0.387 mol

Stress: **– 0.387 mol**

Response: Equilibrium shifts ⟶

New Equilibrium Composition:

	CO (g)	H_2 (g)	CH_4 (g)	H_2O (g)
	0.491 mol decreased	1.473 mol decreased	0.509 mol increased	0.122 mol decreased

- Equilibrium shift can also be predicted from an evaluation of Q_c (Reaction Quotient)

EFFECT OF PRESSURE CHANGE ON EQUILIBRIUM

- A change in pressure has an effect on equilibrium only when the following two conditions exist:

    1. At least one of the reacting species (reactant or product) is a gas.
    2. Total number of moles of gaseous reactants $\neq$ Total number of moles of gaseous products

- The Pressure of a gas may be:
    - increased by decreasing the volume, at constant temperature (achieved by decreasing the size of the reaction vessel)
    - decreased by increasing the volume, at constant temperature (achieved by increasing the size of the reaction vessel)

- To predict the equilibrium shift caused by a change in pressure, consider the following:

The effect of **increasing the pressure** (decreasing the volume) of the equilibrium system	=	**Increasing the concentration** of gaseous reacting species (reactants and products)

Examples:

1. Complete the table for the reaction shown below:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Stress	Pressure Change	Direction of Equilibrium shift	Amounts of Reacting Species		
			$CaCO_3$	CaO	CO_2
Decrease in volume					
Increase in volume					

EFFECT OF PRESSURE CHANGE ON EQUILIBRIUM

Examples (cont'd):

2. Complete the table for the reaction shown below:

$$\underbrace{N_2 (g) \quad + \quad 3\ H_2 (g)}_{\textbf{4 moles}} \quad \rightleftarrows \quad \underbrace{2\ NH_3 (g)}_{\textbf{2 moles}}$$

Stress	Pressure Change	Direction of Equilibrium shift	Amounts of Reacting Species		
			N_2	H_2	NH_3
Decrease in volume					
Increase in volume					

3. Complete the table for the reaction shown below:

$$C (s) \quad + \quad CO_2 (g) \quad \rightleftarrows \quad 2\ CO (g)$$

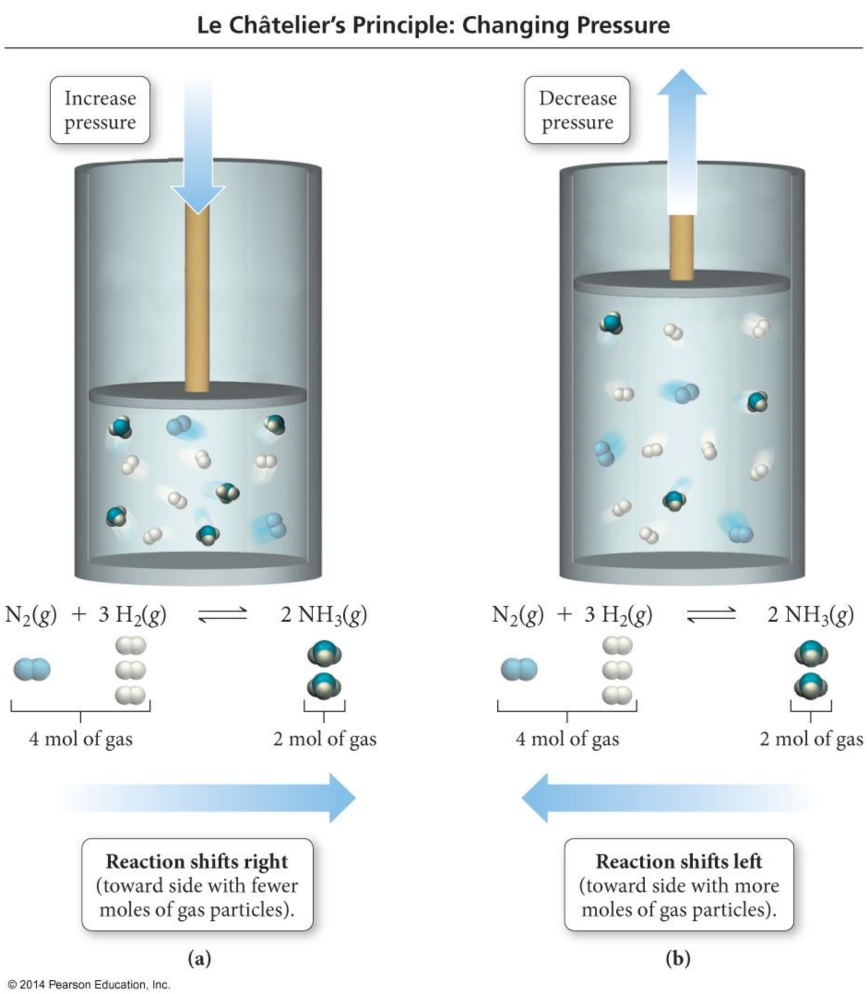
Stress	Pressure Change	Direction of Equilibrium shift	Amounts of Reacting Species		
			C	CO_2	CO
Decrease in volume					
Increase in volume					

EFFECT OF PRESSURE CHANGE ON EQUILIBRIUM

CONCLUSIONS:
At constant temperature:

- If the pressure is increased (volume is decreased), the reaction shifts in the direction of fewer moles of gas.

- If the pressure is decreased (Volume is increased), the reaction shifts in the direction of more moles of gas.



EFFECT OF TEMPERATURE CHANGE ON EQUILIBRIUM

- According to Le Chatelier's principle, if the temperature of a system at equilibrium is changed, then the system will shift in a direction to counter that change. Therefore, if the temperature is increased, the reaction will shift in the direction that tends to decrease the temperature and vice versa.

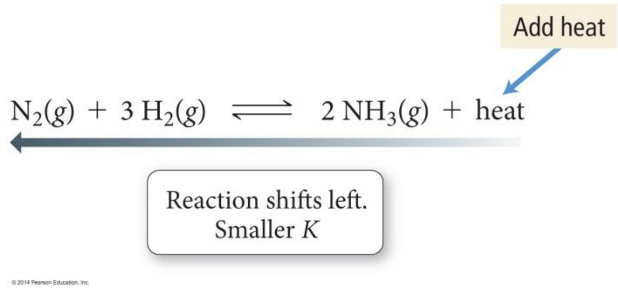
- Recall that exothermic reactions (–ΔH) emit heat. Therefore, heat can be represent heat as a product:

$$\text{Exothermic reaction:} \quad A + B \rightleftharpoons C + D + \text{heat}$$

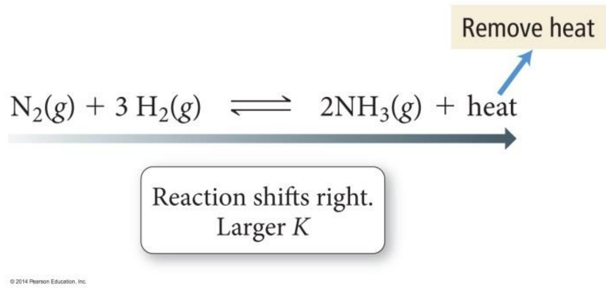
- Similarly, since endothermic reactions (+ΔH) absorb heat, we can be represent heat as a reactant:

$$\text{Endothermic reaction:} \quad A + B + \text{heat} \rightleftharpoons C + D$$

- At constant pressure, raising the temperature of an exothermic reaction–thought of as adding heat–shifts the reaction to the left (similar to adding products). For example:

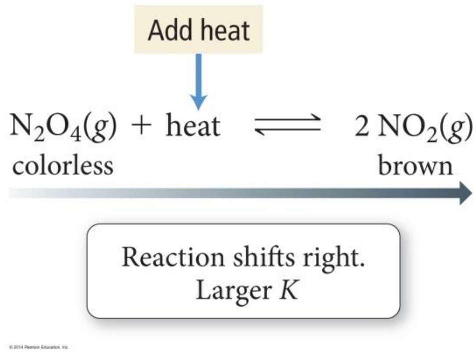


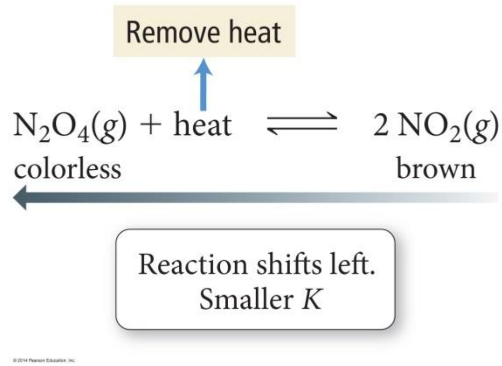
- Conversely, lowering the temperature of an exothermic reaction–thought of as removing heat–shifts the reaction to the right (similar to removing products). For example:



EFFECT OF TEMPERATURE CHANGE ON EQUILIBRIUM

- In contrast, raising the temperature of an endothermic reaction–thought of as adding heat–shifts the reaction to the right to absorb the heat. On the other hand, lowering the temperature–thought of as removing heat–shifts the reaction to the left.





<u>Summary of Effect of Temperature on Equilibrium:</u>

In an exothermic reaction (heat is a product):

- ➢ Increasing temperature causes reaction to shift left, decreasing equilibrium constant.
- ➢ Decreasing temperature causes reaction to shift right, increasing equilibrium constant.

In an endothermic reaction (heat is a reactant):

- ➢ Increasing temperature causes reaction to shift right, increasing equilibrium constant.
- ➢ Decreasing temperature causes reaction to shift left, decreasing equilibrium constant.

<u>Examples:</u>

1. Complete the table below for the reaction of formation of NH_3 from N_2 and H_2 gases:

$$N_2\,(g) \quad + \quad 3\,H_2\,(g) \quad \rightleftharpoons \quad 2\,NH_3\,(g) \qquad \Delta H = -91.8\text{ kJ}$$

Stress	**Equilibrium Shift**	**Amounts of Reacting Species**			**K_c**
		N_2	**H_2**	**NH_3**	
Increase in temp. (Heat added)					
Decrease in temp. (Heat removed)					

<u>Examples (cont'd):</u>

2. Coal can be used to generate hydrogen gas by the endothermic reaction shown below:

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

If this reaction mixture is at equilibrium, predict how each change below will affect the production of hydrogen gas:

a) adding more C to the reaction mixture
b) adding more H_2O to the reaction mixture
c) raising the temperature of the reaction mixture
d) decreasing the volume of the reaction mixture
e) adding a catalyst to the reaction mixture

3. Consider the reaction shown below:

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

A reaction mixture at equilibrium at 175 K contains P_{H2} = 0.958 atm, P_{I2} = 0.877 atm, and P_{HI} = 0.020 atm. A second reaction mixture at the same temperature contains P_{H2} = P_{I2} = 0.621 atm and P_{HI} = 0.101 atm.
a) Is the second reaction at equilibrium?
b) If not, what will be the partial pressure of HI when the reaction reaches equilibrium at 175 K?

Answers to In-Chapter Problems:

Page	*Example No.*	*Answer*
4	1	$K_c = \dfrac{[NH_3]^2[H_2O]^4}{[NO_2]^2[H_2]^7}$
	2	$K_c = \dfrac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$
6	1	b
7	1	b
8	1	$1.4x10^2$
9	1	$4.04x10^{-4}$
	2	$5.4x10^{13}$
11	1	heterogeneous; $K_c = \dfrac{[H_2O]}{[H_2]}$
	2	homogeneous; $K_c = \dfrac{[CS_2][H_2O]^4}{[CH_4][H_2S]^2}$
	3	heterogeneous; $K_c = \dfrac{1}{[Cl_2]^2}$
	4	b
13	1	196
14	2	26
	3	0.020
15	4	$1.8x10^{-2}$
	5	$5.1x10^{-2}$
18	1	a) Reaction is not at equilibrium b) Reaction will proceed to the right (forward)
	2	a) Reaction is not at equilibrium b) Reaction will proceed to the right (forward)
19	2	$P_{NH3} = 2.24x10^{-3}$ atm
21	2	$P_{total} = 0.658$ atm
	3	$[H_2] = 2.72$ M
31	2	a) no effect c) increases e) no effect b) increases d) decreases
	3	$P_{HI} = 0.0144$ atm