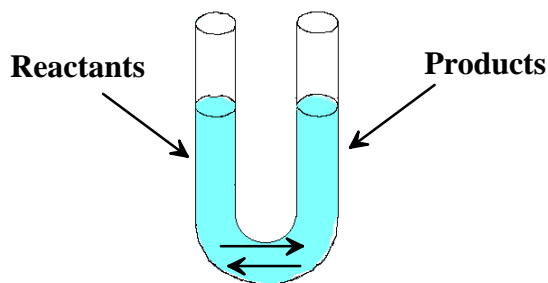


## Chemical Equilibrium-A Dynamic Equilibrium

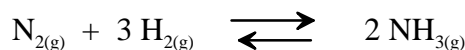
When compounds react, they eventually form a mixture of products and (unreacted) reactants, in a **dynamic equilibrium**.

Much like water in a U-shape tube, the water constantly mixes back and forth through the lower portion of the tube, as if the forward and reverse "reactions" were occurring at the same rate. This makes the system appear to be "static" (or, stationary), when in reality, it is "dynamic" (in constant motion).



Once the water seeks the proper level, that is, reaches equilibrium it continues to migrate back and forth across the "arrow" but at the same rate making it appear to be static.

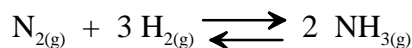
For example, The Haber process for producing ammonia from nitrogen and hydrogen gas does not go to completion, but instead reaches an equilibrium state where all three participants are present



**Chemical Equilibrium** is the state reached by a reaction mixture when the rates of the forward and reverse reactions have become equal.

### Example of Applying Stoichiometry to an Equilibrium Mixture

You place 1.000 mol  $\text{N}_2$  and 3.000 mol  $\text{H}_2$  into a reaction vessel at  $450^\circ\text{C}$ . and 10.0 atm. The reaction is:



What is the composition of the equilibrium mixture if you obtain 0.080 mol of  $\text{NH}_3$  from it?

### Solution

Using the information given in the problem, you set up the following table.

Amount (mol)	$\text{N}_{2(\text{g})}$	+	$3 \text{H}_{2(\text{g})}$	$\rightleftharpoons$	$2 \text{NH}_{3(\text{g})}$
Starting	1.000		3.000		0
Change	$-x$		$-3x$		$+2x$
Equilibrium	$1.000 - x$		$3.000 - 3x$		$2x = 0.080$ (or $x = 0.040$ )

The problem statement gives the equilibrium amount of  $\text{NH}_3$ . This tells you that  $2x$  is 0.080 mol ( $x = 0.040$ ). You calculate equilibrium amounts for other substances from the expressions given in the table, using this value of  $x$ .

$$\text{Equilibrium amount } \text{N}_2 = 1.000 - x = 1.000 - 0.040 = 0.960 \text{ mol } \text{N}_2$$

$$\text{Equilibrium amount } \text{H}_2 = 3.000 - 3x = 3.000 - (3 \times 0.040) = 2.880 \text{ mol } \text{H}_2$$

$$\text{Equilibrium amount } \text{NH}_3 = 2x = 0.080 \text{ mol } \text{NH}_3$$

## The Equilibrium Constant

Every equilibrium reaction has its own "balance" point under any given set of conditions. That is, the ratio of products produced to unreacted reactants remains constant under constant conditions of pressure and temperature.

Consider the reaction  $a A + b B \rightleftharpoons c C + d D$

where A,B,C, and D denote the reactants and products and a,b,c and d are the coefficients in the balanced chemical equation.

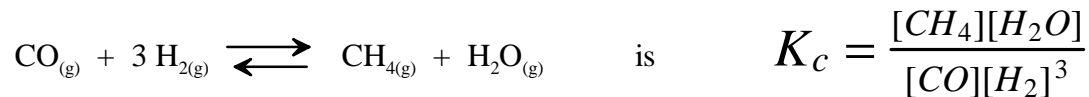
The **equilibrium-constant expression** for a reaction is *an expression obtained by multiplying the concentrations of products, dividing by the concentrations of reactants, and raising each concentration to a power equal to the coefficient in the chemical equation.*

The equilibrium constant,  $K_c$ , is the value obtained for the equilibrium-constant expression when equilibrium concentrations are substituted.

For the general reaction above, the equilibrium-constant expression would be 
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The **Law of Mass Action** is a relation that states that *the values of the equilibrium-constant expression  $K_c$  are constant for a particular reaction at a given temperature, whatever equilibrium concentrations are substituted.*

For example, the equilibrium-constant expression for the equation



## Equilibrium....from a Kinetics Standpoint

Consider the reaction  $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$

If we were to consider the Rate Laws outlined in the Kinetics chapter for the forward and reverse reactions, we would get:

$$\text{Rate}_{(\text{forward})} = k_f [\text{N}_2][\text{H}_2]^3$$

and

$$\text{Rate}_{(\text{reverse})} = k_r [\text{NH}_3]^2$$

At equilibrium, the rate of the forward and reverse reactions would be **equal**, therefore:

$$k_f [\text{N}_2][\text{H}_2]^3 = k_r [\text{NH}_3]^2$$

If we rearrange the equations to get both constants on one side of the equal sign, we get:

$$\frac{k_f}{k_r} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Therefore, we can identify the Equilibrium Constant,  $K_c$ , as  $\frac{k_f}{k_r}$

## Obtaining the Equilibrium Constant for a Reaction

Equilibrium concentrations for a reaction *must be determined experimentally* and then substituted into the equilibrium-constant expression in order to calculate  $K_c$ .

Consider the reaction

$$\text{CO}_{(g)} + 3 \text{H}_{2(g)} \rightleftharpoons \text{CH}_{4(g)} + \text{H}_2\text{O}_{(g)}$$

Suppose we started with initial concentrations of CO and H<sub>2</sub> of 0.100 M and 0.300 M respectively. When the reaction finally settled into equilibrium we determined the equilibrium concentrations to be as follows:

Reactants	Products
[CO] = 0.0613 M	[CH <sub>4</sub> ] = 0.0387 M
[H <sub>2</sub> ] = 0.1839 M	[H <sub>2</sub> O] = 0.0387 M

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

If we substitute the equilibrium concentrations, we get

$$K_c = \frac{(0.0387)(0.0387)}{(0.0613)(0.1839)^3} = 3.93$$

Note that regardless of what initial concentrations you begin with whether they be reactants or products, the Law of Mass Action dictates that the reaction *will always settle into an equilibrium where the equilibrium-constant expression will equal  $K_c$* .

For example, if we repeat the experiment on the previous page, only this time, we'll start with initial concentrations of **products**:

$$[\text{CH}_4]_{\text{init}} = 0.1000 \text{ M} \quad \text{and} \quad [\text{H}_2\text{O}]_{\text{init}} = 0.1000 \text{ M}$$

We find that with these initial conditions, as the reaction settles into equilibrium, the equilibrium concentrations are as follows.

Reactants	Products
[CO] = 0.0613 M	[CH <sub>4</sub> ] = 0.0387 M
[H <sub>2</sub> ] = 0.1839 M	[H <sub>2</sub> O] = 0.0387 M

Substituting these into the equilibrium-constant expression, we obtain the same result.

$$K_c = \frac{(0.0387)(0.0387)}{(0.0613)(0.1839)^3} = 3.93$$

**The notable thing here is that whether we start with reactants initially or products initially, the reaction will settle into the same equilibrium with the value of  $K_c$  remaining constant.**

## The Equilibrium Constant, $K_p$

In gas-phase equilibria, it is usually more convenient to express the equilibrium concentrations in terms of partial pressures rather than Molarities.

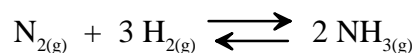
It should be noted that the partial pressure of a gas in a mixture (which is proportional to its mole fraction) is proportional to its Molarity concentration at a fixed temperature. You can see this by looking at the Ideal Gas Equation  $PV = nRT$  and solving for  $n/V$ , which is the molar concentration of the gas.

$$M_{gas} = \frac{n}{V} = \frac{p_{gas}}{RT}$$

In other words, the molar concentration of a gas equals its partial pressure divided by  $RT$  which is constant at a given temperature.

When you express an equilibrium-constant expression for a gas-phase reaction in terms of partial pressures, it is called  $K_p$ .

For example, consider again the equation for the formation of ammonia.



The equilibrium-constant expression in terms of partial pressures becomes;

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

In general, the numerical values for  $K_p$  and  $K_c$  are different.

## The Difference Between $K_p$ and $K_c$

These two constants differ whenever the total number of moles of gaseous products differ from the total number of gaseous reactants. This can be illustrated by using the Ideal Gas Equation to relate the partial pressure of a gas to the number of moles of gas present. That is,

$$p = \frac{nRT}{V}$$

If the sum of gaseous products differs from the number of gaseous reactants, then:  $K_p = K_c(RT)^{\Delta n}$

where  $\Delta n = \sum$  coefficients of gaseous products  $- \sum$  coefficients of gaseous reactants

### Example of $K_c$ vs. $K_p$

Consider the reaction  $2 SO_{2(g)} + O_{2(g)} \rightleftharpoons 2 SO_{3(g)}$

The  $K_c$  for this reaction is  $2.8 \times 10^2$  (at 1000 K). Calculate the  $K_p$  for the reaction.

### Solution

Since  $K_p = K_c(RT)^{\Delta n}$  and from the equation we see that  $\Delta n = -1$ , we can simply substitute the given reaction temperature and the value of  $R$  (0.08206 L-atm/mol-K) to obtain  $K_p$

$$K_p = 2.8 \times 10^2 (0.08206 \times 1000K)^{-1} = 3.4$$

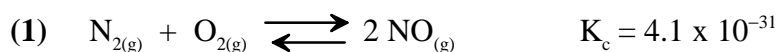
## Equilibrium Constant for the Sum of Reactions

Similar to the method of combining equations we saw in Chapter Six using Hess' Law, we can also combine equilibrium reactions whose  $K_c$  is known to obtain the  $K_c$  for the resultant sum.

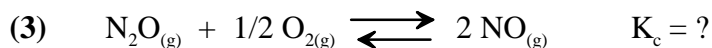
Just as in Hess' Law, when we reversed reactions or took multiples of them prior to adding them together, we had to manipulate the  $\Delta H$ 's to reflect what we had done. The rules are a bit different for the manipulation of  $K_c$ 's.

1. If you *reverse* an equation, *invert* the value of  $K_c$
2. If you *multiply* each of the coefficients in an equation by the same factor (2,3...), *raise* the equilibrium constant to the corresponding power (2,3...).
3. If you *divide* each of the coefficients in an equation by the same factor (2,3,...) *take the corresponding root* of the equilibrium constant (i.e., square root, cube root,...)
4. When you finally combine (that is, add) individual equations together, *multiply* their equilibrium constants for the net reaction.

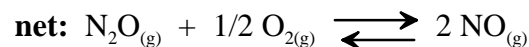
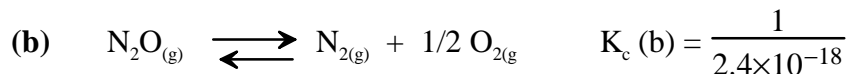
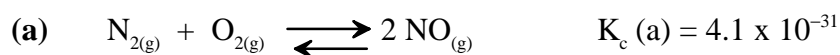
**For example**, Nitrogen and oxygen can combine to form either  $\text{NO}_{(g)}$  or  $\text{N}_2\text{O}_{(g)}$ .



Using these two equations, we can obtain the  $K_c$  for the formation of  $\text{NO}_{(g)}$  from  $\text{N}_2\text{O}_{(g)}$ .



To combine equations (1) and (2) above to obtain reaction (3), we need to *reverse* equation (2), and when we do, we must also take the *reciprocal* of its  $K_c$  value.



$$K_c(\text{net}) = K_c(a) \times K_c(b) = (4.1 \times 10^{-31})(1/(2.4 \times 10^{-18})) = 1.7 \times 10^{-13}$$

## Heterogeneous Equilibrium

A **homogeneous equilibrium** is an equilibrium that involves reactants and products in a *single phase*.

A **heterogeneous equilibrium** is one in which one or more of the reactants is in a *different phase*.

The equilibrium of a heterogeneous system is not affected by the amounts of pure solids or liquids present, as long as some of each is present. Therefore, the concentration of a pure solid or liquid present in a heterogeneous system is considered to be "1" and therefore do not appear in the equilibrium expression or have any effect on the equilibrium itself.

**Example** Consider the reaction  $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

The equilibrium expression contains terms for only the species in the homogeneous gas phase...H<sub>2</sub>O, CO, and H<sub>2</sub>.

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

## Using the Equilibrium Constant

### Qualitatively interpreting the Equilibrium Constant

If the value of the equilibrium constant is large, you immediately know that the products are favored at equilibrium. However, a small  $K_c$  would indicate that the reactants are favored at equilibrium.

If the  $K_c$  is neither large or small (around 1), neither reactants or products are strongly favored.

### Predicting the Direction of a Reaction

Consider a reaction mixture not at equilibrium. How could one predict the direction in which it will go, that is, toward products or toward reactants.

The **reaction quotient,  $Q_c$** , is an expression that has the same form as the equilibrium-constant expression but whose concentration values are not necessarily those at equilibrium.

For the general equation  $aA + bB \rightleftharpoons cC + dD$   $Q_c = \frac{[C]_i^c [D]_i^d}{[A]_i^a [B]_i^b}$

Then

**If  $Q_c > K_c$ , the reaction will go left...toward reactants**

**If  $Q_c < K_c$ , the reaction will go right...toward products**

**If  $Q_c = K_c$ , then the reaction is at equilibrium**

### Calculating Equilibrium Concentrations

Once you have determined the equilibrium constant for a reaction, you can use it to calculate the concentrations of substances in an equilibrium mixture using any set of initial concentrations.

## Le Chatelier's Principle

Obtaining the maximum amount of product from a reaction depends on the proper selection of reaction conditions. By changing the reaction conditions, one can increase or decrease the amount of products.

Le Chatelier's Principle states that *an equilibrium will shift under conditions of "stress" in such a way as to remove that stress*. This applied "stress" can be achieved in several ways.

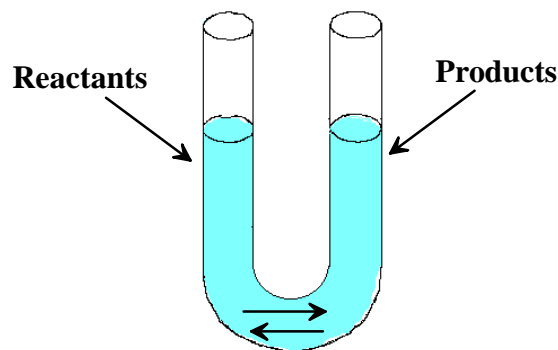
1. Changing the concentrations by removing products or adding more reactants to the reaction vessel.
2. Changing the partial pressure of gaseous reactants and products by changing the volume of the reaction vessel.
3. Changing the temperature.

### Removing Products or Adding Reactants.

Let's refer back to the illustration of the U-tube in the first section of this chapter

It's a simple concept to see that if we were to remove products (analogous to dipping water out of the right side of the tube) the reaction would shift to the right until equilibrium was re-established.

Likewise, if more reactant is added (analogous to pouring more water in the left side of the tube) the reaction would also shift to the right..again until equilibrium is re-established.



Conversely, if more product were to be added, or reactants removed, the reaction would shift to the left until equilibrium is re-established.

### Effects of Pressure Change

A pressure change obtained by changing the volume of the reaction vessel can affect the yield of products in a gaseous reaction **only if the reaction involves a change in the total moles of gas present**.

If the products in a gaseous reaction contain *fewer moles of gas* than the reactants, then it is logical that they would require less space. So *reducing the volume of the reaction vessel would favor the products*.

Conversely, if the reactants require less volume (that is, fewer moles of gas on the left side of the arrows) then *decreasing the volume of the reaction vessel would shift the equilibrium to the left*.

**So literally, "squeezing" the reaction will cause a shift in the equilibrium toward the fewer moles of gas.**

It's a simple step, then, to see that reducing the pressure in the reaction vessel by increasing its volume would have the opposite effect.

In the event that the number of moles of gaseous products equals the number of moles of gaseous reactants...vessel volume will have **no effect** on the position of the equilibrium.

## Effect of Temperature Change

Temperature has a significant effect on most reactions. Reaction rates generally increase with an increase in temperature, consequently, equilibrium is established sooner.

In addition, **equilibrium constants vary with temperature.**

If we look at heat as if it were a *product in exothermic reactions*...and a *reactant in endothermic reactions*, we can see that increasing the temperature of a reaction is analogous to adding more product (in the case of exothermic) or adding more reactant (in the case of endothermic).

This ultimately has the same effect as if this added heat were a physical substance.

For example, consider the following generic exothermic reaction.



Increasing the temperature would be *analogous to adding more product*, consequently the equilibrium would now shift to the left. Since HEAT does not appear in the equilibrium-constant expression for this reaction, but the equilibrium concentrations have increased for the reactants and decreased for the products....this would result in a smaller value for  $K_c$ .

For an endothermic reaction, the opposite is true.



Increasing the temperature in this case would cause the equilibrium position to *shift toward the products*. This would result in a larger value for  $K_c$  at higher temperatures for endothermic reactions.

So, in summary

**For an endothermic reaction ( $\Delta H$  positive), the amounts of product are increased at equilibrium by an increase in temperature ( $K_c$  is larger at higher T).**

**For an exothermic reaction ( $\Delta H$  negative), the amounts of reactants are increased by an increase in temperature ( $K_c$  is smaller at higher T)**

## Effect of a Catalyst

A catalyst is a substance that increases the rate of a reaction but is not consumed by it.

It is important to understand that a *catalyst* has *no effect* on the equilibrium composition of a reaction mixture. A catalyst merely speeds up the attainment of equilibrium.

Although a catalyst cannot affect the composition at true equilibrium, in some cases it can affect the product in a reaction because it affects the rate of one reaction out of several possible reactions.

**CHEM 2****Chapter 14 Assignments**

**The following problems will be collected at the first exam.**

Review Questions: 4,6,7,8,10

Problems: 15,21,25,29,31,39,41,45,47,51,55,61,63,65,67,79,81,87,91,95,101,105

**Exam Review Topics****terms**

Chemical Equilibrium  
Equilibrium-constant Expression  
Equilibrium Constant  
Law of Mass Action  
Homogeneous Equilibrium  
Heterogeneous Equilibrium  
Reaction Quotient  
Le Chatelier's Principle

**skills/operations**

Applying Stoichiometry to an Equilibrium Mixture  
Writing Equilibrium-constant Expressions  
Obtaining an Equilibrium Constant from Molarities  
Using the Reaction Quotient  
Solving Equilibrium Problems  
Applying Le Chatelier's Principle