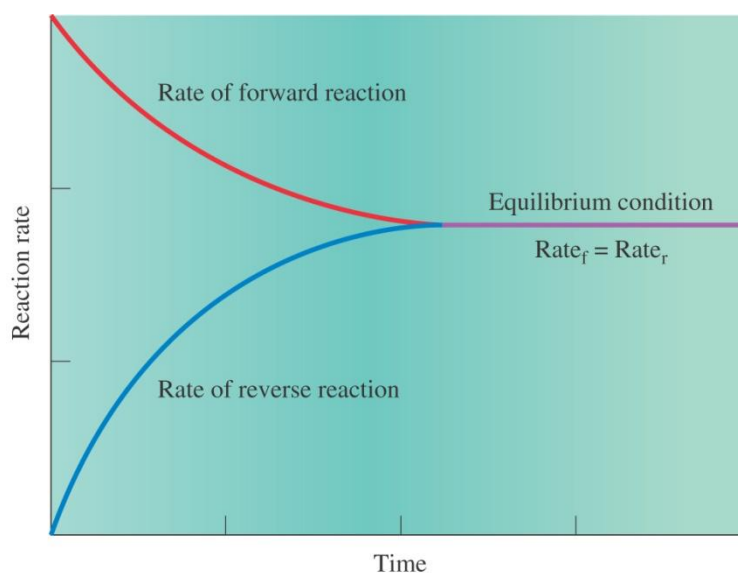


CHEMICAL EQUILIBRIUM

- 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	$A + B \xrightleftharpoons[\text{reverse}]{\text{forward}} C + D$ <p style="text-align: center; background-color: yellow;">RATE OF FORWARD REACTION = RATE OF REVERSE REACTION</p>	



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 \neq Concentration of products

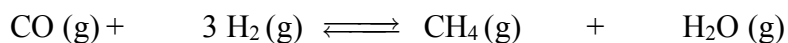
3. A Chemical Equilibrium is a Dynamic Equilibrium; both reactions (forward and reverse) are still going on
4. The Dynamic Equilibrium may be controlled (shifted to the right to favor products, or shifted to the left to favor reactants) by changing the conditions for the reaction.

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.**

COMPOSITION OF AN EQUILIBRIUM MIXTURE

- In an equilibrium mixture, the amount of one substance is determined experimentally and the amounts of the other substances are calculated.

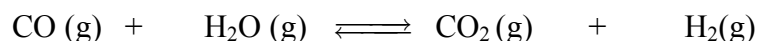
Example 1:


When 1.000 mol CO and 3.000 mol H₂ are placed in a 10.00 L vessel at 927 °C and allowed to come to equilibrium, the mixture is found to contain 0.387 mol H₂O. How many moles of each substance are present at equilibrium?

	CO (g) + 3 H ₂ (g) \rightleftharpoons CH ₄ (g) + H ₂ O (g)			
Initial	1.000	3.000	0	0
Δ	- 0.387	- 3(0.387)	+ 0.387	+ 0.387
Equilibrium	(1.000-0.387)	(3.000-1.161)	+0.387	+0.387
Equilibrium	0.613 mol	1.839 mol	0.387 mol	0.387 mol

Example 2:

Consider the following dynamic equilibrium:



Suppose you start with a gaseous mixture containing 1.00 mol of CO and 1.00 mol of H₂O.

When equilibrium is reached at 1000 °C, the mixture contains 0.43 mol H₂.

What is the molar composition of the equilibrium mixture?

	CO (g) + H ₂ O (g) \rightleftharpoons CO ₂ (g) + H ₂ (g)			
Initial	1.00 mol	1.00 mol	0	0
Δ	- x	- x	+ x	+ x
Equilibrium	(1.00-x)	(1.00-x)	+0.43	+0.43
Equilibrium	0.57 mol	0.57 mol	0.43 mol	0.43 mol

Example 3:

0.750 mol of N₂ and 2.250 mol of H₂ are placed into a reaction vessel at 450 °C and 10.0 atm.

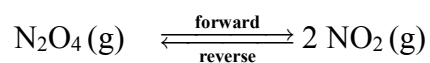


What is the composition of the equilibrium mixture if you obtain 0.060 mol of NH₃ from it?

	N ₂ (g) + 3 H ₂ (g) \rightleftharpoons 2 NH ₃ (g)		
Initial			
Δ			
Equilibrium			
Equilibrium			

THE EQUILIBRIUM CONSTANT

- Consider the following equilibrium system:



NOTE: Both forward and reverse reactions are elementary reactions.

At Equilibrium:

$$\begin{aligned} \text{Rate (forward reaction)} &= \text{Rate (reverse reaction)} \\ k_f[\text{N}_2\text{O}_4] &= k_r[\text{NO}_2]^2 \end{aligned}$$

$$\frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \text{constant}$$

$$\frac{k_f}{k_r} = \mathbf{K_c} = \text{equilibrium constant}$$

↑
implies molar concentration



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

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

- This relationship was postulated by two chemists in 1864 and called the **law of mass action**.

EQUILIBRIUM CONSTANT

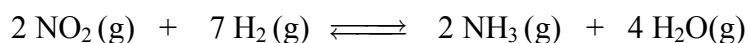
- The Equilibrium Constant, K_c , is a constant for a particular reaction at a given temperature.

NOTE:

1. If the overall reaction occurs by a multi-step mechanism, one can show that K_c for the overall reaction equals a product of ratios of the individual rate constants.
2. It is common practice to write K_c without units

Example 1:

Write the equilibrium constant expression for the equation shown below:



$$K_c =$$

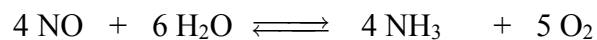
Example 2:

The Equilibrium Constant for a reaction is:

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

What is the Equilibrium Constant expression when the equation for this reaction is halved and then reversed?

Original Equation:

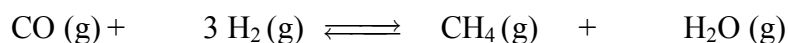


Halved and Reversed:

$$K_c =$$

CALCULATING K_c FOR REACTIONS

- Molar concentrations (molarities) of products and reactants at equilibrium must be substituted in the expression of K_c

Example 1:

When 1.00 mol CO and 3.00 mol H_2 are placed in a 10.0 L vessel at 927°C and allowed to come to equilibrium, the mixture is found to contain 0.387 mol H_2O . Calculate the equilibrium constant for this reaction.

	$\text{CO (g)} + 3 \text{H}_2 \text{(g)} \rightleftharpoons \text{CH}_4 \text{(g)} + \text{H}_2\text{O (g)}$			
Initial	1.00 mol	3.00 mol	0	0
Δ	- 0.387	- 1.16	+ 0.387	+ 0.387
Equilibrium	0.613 mol	1.84 mol	0.387 mol	0.387 mol

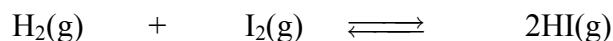
	<u>Equilibrium amounts:</u>	<u>Equilibrium Concentrations(M)</u>
CO:	0.613 mol	$0.613 \text{ mol}/10.00 \text{ L} = 0.0613 \text{ M}$
H₂ :	1.84 mol	$1.84 \text{ mol}/10.00 \text{ L} = 0.184 \text{ M}$
CH₄:	0.387 mol	$0.387 \text{ mol}/10.00 \text{ L} = 0.0387 \text{ M}$
H₂O:	0.387 mol	$0.387 \text{ mol}/10.00 \text{ L} = 0.0387 \text{ M}$

$$K_c = \frac{[\text{H}_2\text{O}][\text{CH}_4]}{[\text{CO}][\text{H}_2]^3} = \frac{(0.387 \text{ M})(0.387 \text{ M})}{(0.0613 \text{ M})(0.184 \text{ M})^3} = 3.93$$

Example 2:

An 8.00 L reaction vessel at 491°C contained 0.650 mol H_2 , 0.275 mol I_2 and 3.00 mol HI. Assuming that the substances are at equilibrium, find the value of K_c at 491°C .

The equilibrium is:



Moles at Equilibrium:	0.650	0.275	3.00
Molarities at Equilibrium: (moles/L)	$\frac{0.650 \text{ moles}}{8.00 \text{ L}}$	$\frac{0.275 \text{ moles}}{8.00 \text{ L}}$	$\frac{3.00 \text{ moles}}{8.00 \text{ L}}$

Molarities at Equilibrium: **0.08125 M** **0.03438 M** **0.375 M**

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.375 \text{ M})^2}{(0.08125 \text{ M})(0.03438 \text{ M})} = 50.3$$

Example 3:

H₂S, a colorless gas dissociates on heating: $2 \text{H}_2\text{S} \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$

When 0.100 mol of H₂S was put in a 10.0 L vessel and heated to 1132 °C, it gave an equilibrium mixture containing 0.0285 mol H₂. What is the value of K_c at this temperature?

Note: It is convenient to express equilibrium amounts of reactants and products in molar concentrations (molarities in mol/L)

Molarity of H₂S =

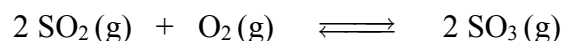
Molarity of H₂ =

	$2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$		
Initial			
Δ			
Equilibrium			
Equilibrium			

K_c =

Example 4:

In the contact process, sulfuric acid is manufactured by first oxidizing SO₂ to SO₃, which is then reacted with water. The reaction of SO₂ with O₂ is:



A 2.00 L flask was filled with 0.0400 mol SO₂ and 0.0200 mol O₂. At equilibrium, at 900 K, the flask contained 0.0296 mol SO₃. Obtain the value of K_c.

Molarity of SO₂ =

Molarity of O₂ =

	$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$		
Initial			
Δ			
Equilibrium			
Equilibrium			

K_c =

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.

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

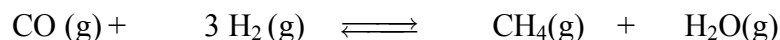
$$\text{molar concentration of a gas} = \frac{n}{V} = P \left(\frac{1}{RT} \right)$$

**Constant at
a given
temperature**

- 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

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

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

Example 1:

$$K_p = \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{CO}} P_{\text{H}_2}^3}$$

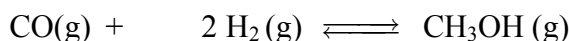
$$K_c = 3.92 \quad (\text{at } 1200\text{K})$$

$$\Delta n = (1+1) - (1+3) = -2$$

$$K_p = K_c(RT)^{\Delta n} = 3.92 [(0.0821)(1200)]^{-2} = 4.04 \times 10^{-4}$$

Example 2:

The equilibrium constant K_c equals 10.5 for the following reaction at 227 °C.



What is the value of K_p at this temperature?

$$\Delta n =$$

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

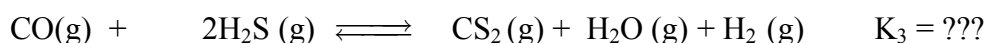
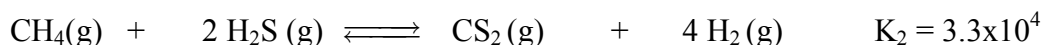
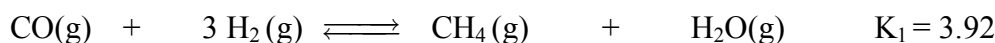
OTHER EQUILIBRIUM CONSTANT

- 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.

$$K_{\text{overall}} = K_1 K_2 \dots$$

Example 1:

The following equilibria occur at 1200K



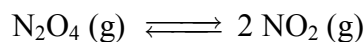
$$K_1 = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \quad K_2 = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$$

$$K_1 K_2 = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \times \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2} = K_3$$

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

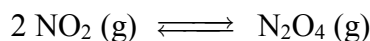
$$K_3 = K_1 \times K_2$$

- Because an equilibrium can be approached from either direction, the direction in which we write the chemical equation is arbitrary. For example, for the reaction shown below:



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \quad (\text{at } 100^\circ\text{C})$$

- When considering the equilibrium in the reverse direction:



$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100^\circ\text{C})$$

$$K_{\text{fwd}} = 1/K_{\text{rev}}$$

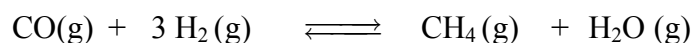
CLASSIFICATION OF CHEMICAL EQUILIBRIA

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

I. Homogeneous Equilibrium

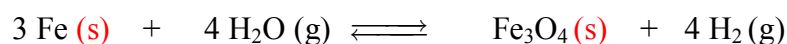
An equilibrium that involves reactants and products in a single phase.

Example: Catalytic methanation:


II. Heterogeneous Equilibrium

An equilibrium involving reactants and products in more than one phase

Example:



$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

NOTE: 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:

$$K_c = \frac{[\text{Fe}_3\text{O}_4] [\text{H}_2]^4}{[\text{Fe}]^3 [\text{H}_2\text{O}]^4} \quad \text{By rearrangement:} \quad \frac{[\text{Fe}]^3}{[\text{Fe}_3\text{O}_4]} K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

\uparrow
**constant
factors**

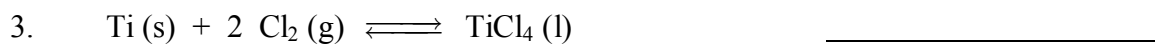
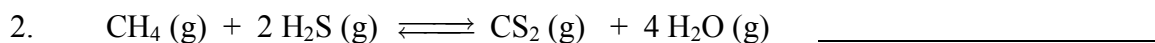
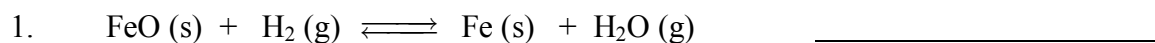
\uparrow
**variable
factors**

$$K'_c = \frac{[\text{Fe}]^3}{[\text{Fe}_3\text{O}_4]} K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

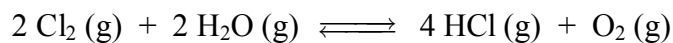
- The concentrations of pure solids and liquids are incorporated in the value of K'_c .
- The concentration of solvent is also omitted from the expression of K_c for a homogeneous reaction (if constant).
- The equilibrium is not affected by pure solids, pure liquids, or solvents.**

Examples:

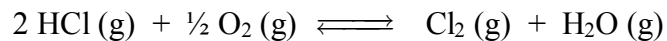
Identify each of the following equilibria as homogeneous or heterogeneous and write Kc expressions for each:



4. Given the equilibrium shown below, for which $K_p = 0.0752$ at 480°C :



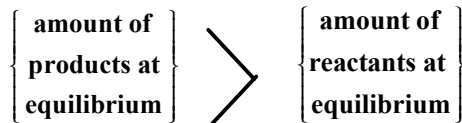
What is the value of K_p for the reaction shown below:



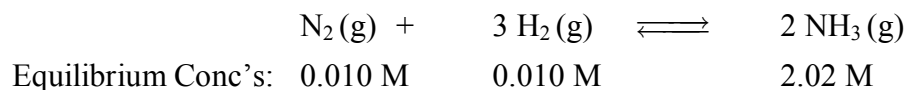
MEANING OF THE EQUILIBRIUM CONSTANT

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

$K_c \gg \gg 1$

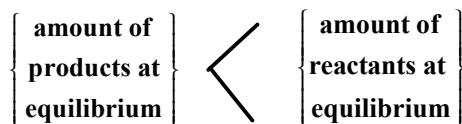


➤ **Products are favored at equilibrium**

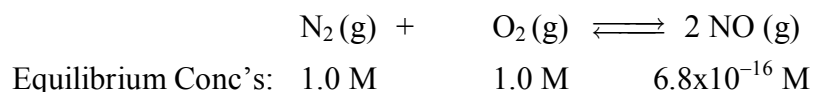


$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2.02 \text{ M})^2}{(0.010 \text{ M})(0.010 \text{ M})^2} = 4.1 \times 10^8$$

$K_c \ll \ll 1$



➤ **Reactants are favored at equilibrium**

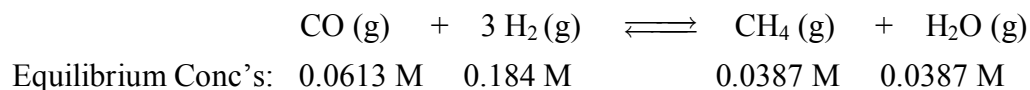


$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(6.8 \times 10^{-16} \text{ M})^2}{(1.0 \text{ M})(1.0 \text{ M})} = 4.6 \times 10^{-31}$$

$K_c \approx 1$ (0.5 – 10)



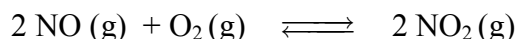
➤ **Neither reactants, nor products are predominant**



$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{(0.0387 \text{ M})(0.0387 \text{ M})}{(0.0613 \text{ M})(0.184 \text{ M})^3} = 3.93$$

Example 1:

The Equilibrium Constant for the reaction below equals 4.0×10^{13} at 25°C .

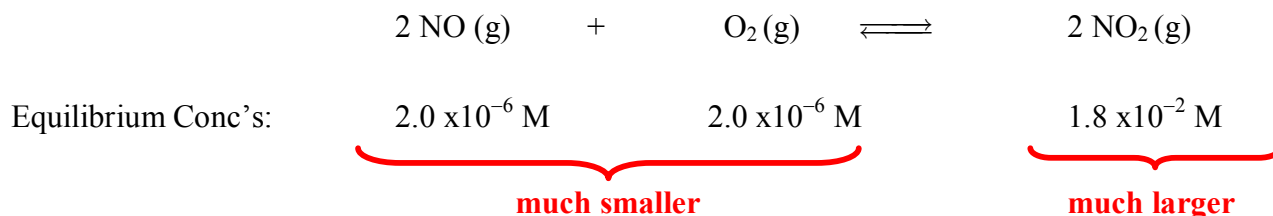


(a) Does the equilibrium mixture contain predominantly reactants or products?

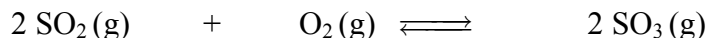
(b) If $[\text{NO}] = [\text{O}_2] = 2.0 \times 10^{-6} \text{ M}$ at equilibrium, what is the equilibrium concentration of $[\text{NO}_2]$?

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} \quad [\text{NO}_2]^2 = K_c [\text{NO}]^2[\text{O}_2]$$

$$[\text{NO}_2]^2 = \sqrt{K_c [\text{NO}]^2[\text{O}_2]} = \sqrt{(4.0 \times 10^{13})(2.0 \times 10^{-6})^2(2.0 \times 10^{-6})} = 1.8 \times 10^{-2} \text{ M}$$

**Example 2:**

Sulfur dioxide reacts with oxygen at 25°C to reach equilibrium. K_c for this reaction at this temperature is 8.0×10^{35} .

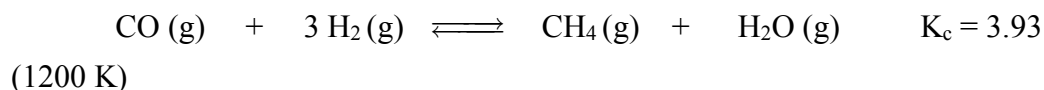


a) From the magnitude of K_c , which reaction is favored (forward or reverse) when equilibrium is established?

b) If an equilibrium mixture is 1.0 M SO_3 and has equal concentrations of SO_2 and O_2 , what is the concentration of SO_2 in the mixture? Does this result agree with what you expect from the magnitude of K_c ?

PREDICTING THE DIRECTION OF REACTION

- Consider the following reaction and the following composition of gas mixture present.



Composition of gas mixture:
(NOT AT EQUIL)

0.0200 M	0.0200 M	0.00100 M	0.00100 M
-----------------	-----------------	------------------	------------------

At 1200K and in the presence of a catalyst, what would be more likely ?

1. Would forward reaction be favored? (would products be favored?)

OR

2. Would reverse reaction be favored? (would reactants be favored?)

- To answer this, a new quantity is introduced:

$Q_c = \text{the Reaction Quotient}$

= has the same form as K_c but the concentrations used to calculate its value are not equilibrium concentrations.

$$Q_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{(1.00 \times 10^{-3} \text{ M})(1.00 \times 10^{-3} \text{ M})}{(2.00 \times 10^{-2} \text{ M})(2.00 \times 10^{-2} \text{ M})^3} = 6.25$$

$$Q_c = 6.25$$

$$K_c = 3.92$$

should decrease to

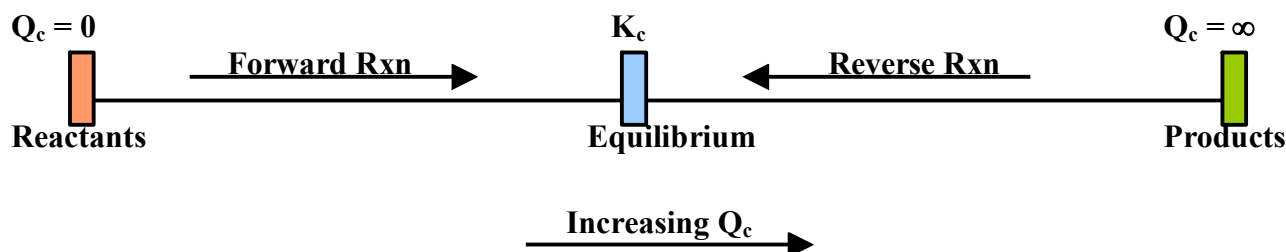
- For the reaction mixture to reach equilibrium: Q_c → 3.92

Q_c decreases if:

- $[\text{CH}_4]$, $[\text{H}_2\text{O}]$ decreases
- $[\text{CO}]$, $[\text{H}_2]$ increases

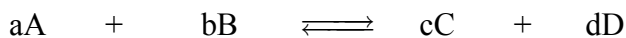


- The reaction goes to the left
- Reverse reaction is favored
- Formation of reactants is favored



PREDICTING THE DIRECTION OF REACTION

- In General: For a reaction mixture that is NOT AT EQUILIBRIUM :

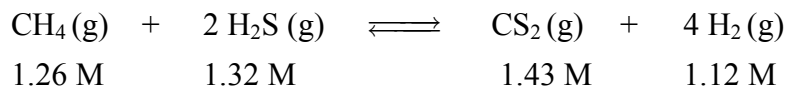


$$Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \text{Compare: } Q_c \text{ to } K_c$$

- If: $Q_c > K_c$ - Reaction will go the left (←)
- If: $Q_c < K_c$ - Reaction will go to the right (→)
- If: $Q_c = K_c$ - Reaction mixture is at equilibrium (↔)

Examples:

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



(a) Is the reaction mixture at equilibrium?

$$Q_c = \frac{[\text{H}_2]^4 [\text{CS}_2]}{[\text{CH}_4] [\text{H}_2\text{S}]^2} = \frac{(1.12 \text{ M})^4 (1.43 \text{ M})}{(1.26 \text{ M})(1.32 \text{ M})^2} = 1.02$$

$$Q_c = 1.02 \qquad K_c = 3.59 \qquad Q_c \neq K_c \qquad \text{Not at equilibrium}$$

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

$$Q_c < K_c$$

- Reaction will go to the right
- Forward reaction is favored
- Formation of products is favored