

Chapter 14 CHEMICAL EQUILIBRIUM

Draft 9th ed Update

These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

The author is providing these notes as an addition to the students reading the text book and listening to the lecture. Although the author tries to keep errors to a minimum, the student is responsible for correcting any errors in these notes.

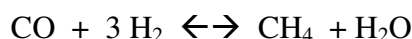
Chemical Equilibrium – Reversible Reactions

Coal Gasification $C_{\text{coal}} + H_2O_{\text{steam}} \rightarrow CO + H_2$ Starting Material for next reaction

Catalytic Methanation (gas phase) $CO + 3 H_2 \xrightarrow{\text{Cat}} CH_4 + H_2O$ To form Methane

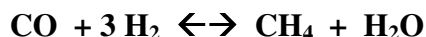
Steam Reforming $CH_4 + H_2O \rightarrow CO + 3 H_2$

These really establish a **Dynamic Equilibrium Reaction**: Both the forward and reverse reactions occur at the same rate or speed.



Chemical Equilibrium is the state reached by a reaction mixture when the rates of the forward and reverse reaction have become equal. Note: Both the forward and reverse reactions continue to occur, but they occur at the same rate. This is a Dynamic Process.

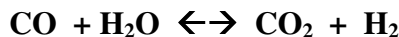
Example 14.1 Start with 1.000 mol of CO and 3.000 mol of Hydrogen. At equilibrium the mixture has 0.387 moles of water. What else is in the mixture?



| <u>Amount</u> | <u>CO</u> | + | <u>H₂</u> | \leftrightarrow | <u>CH₄</u> | + | <u>H₂O</u> |
|-----------------------|--------------|---|----------------------|-------------------|-----------------------|---|-----------------------|
| Starting | 1.000 | | 3.000 | | 0 | | 0 |
| Change | -x | | -3x | | +x | | +x |
| Equilibrium | 1.000 - x | | 3.000 - 3x | | x | | x = 0.387 |
| CO | = 1.000 - x | = | 1.000 - 0.387 | | | = | 0.613 moles |
| H₂O | = 3.000 - 3x | = | 3.000 - 3 * 0.387 | | | = | 1.839 moles |
| CH₄ | = x | | | | | = | 0.387 moles |

As A Check: The reaction starts with 1.000 mole of CO, 3.000 mole of H₂ = 4 moles of reactants. This would generate 1 mole of CH₄ and 1 mole of H₂O or 2 moles of products. We actually obtained 0.387 mole of CH₄ and 0.387 mole of H₂O or 0.774 moles of product. So this reaction is an equilibrium reaction and does not go to completion!

Exercise 14.1 Start with 1.00 mol of CO and 1.00 mol of water. At equilibrium the mixture has 0.43 mol of hydrogen. What else is in the mixture? **Class do – possible test question!**



Concept Check 14.1 A and B react to form C. When A decreases by x moles, C increases by x moles. When B decreases by x moles, C increases by 2x moles. What is the chemical equation? **Class do – possible test question!**

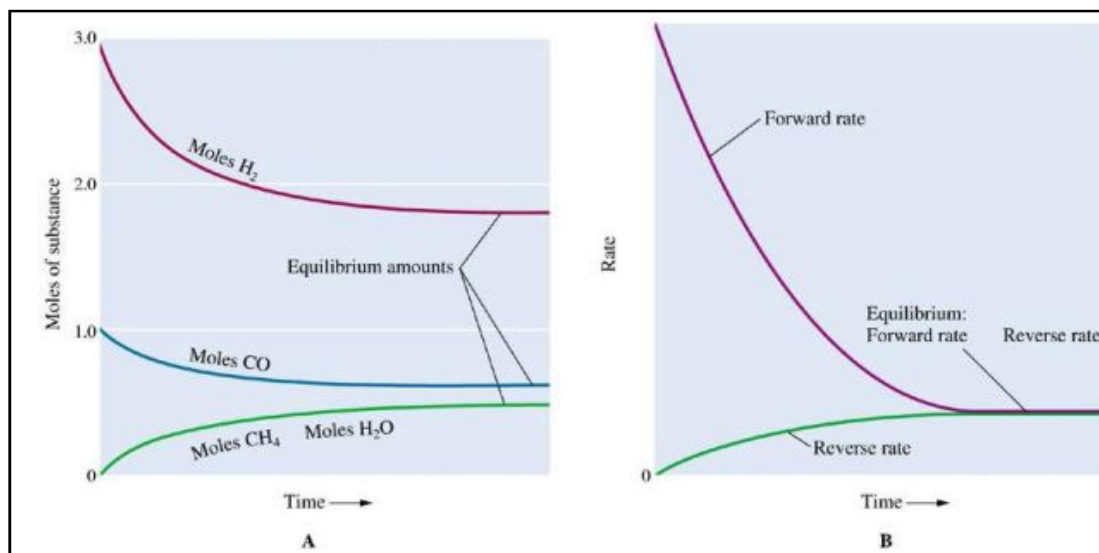


Figure 14.3: Graph shows the Moles of H₂ and CO as they decrease with time and CH₄ as it starts at zero and then increases to equilibrium. B shows the change in rates of reaction. The forward reaction is fast at first, the reverse is zero at first.

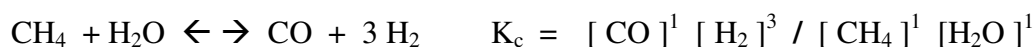
The Equilibrium Constant:

Equilibrium Constant Expression: $aA + bB \leftrightarrow cC + dD$

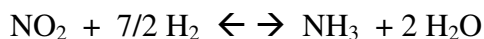
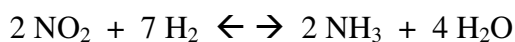
Equilibrium Constant $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ [] = Molar Conc = moles / L = Molarity = M

Law of Mass Action: the values of an equilibrium constant expression K_c are constant of a particular reaction at a given temperature no matter what equilibrium concentrations are substituted.

Example 14.2 Write the Equilibrium Constant Expressions for the following:



Exercise 14.2 Write the Equilibrium Constant Expressions for the following:



Class do – possible test question!

Equilibrium: $\text{N}_2\text{O}_4 \leftarrow k_R \quad k_F \rightarrow 2 \text{NO}_2$ k_F = rate of forward reaction, k_R = rate of reverse

At the start, there is only N_2O_4 . As the reaction proceeds, NO_2 is formed and reverse reaction starts.

Eventually, the rate of the forward reaction equals the rate of the reverse reaction. This is called **equilibrium**.

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

At Equilibrium: Rate of forward reaction * Concentration of reactants =
Rate of reverse reaction * Concentration of products

$$k_F * [\text{N}_2\text{O}_4] = k_R [\text{NO}_2]^2$$

Experiment 1 $\text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ What is K_c in a 10.00 Liter Reactor

CO = 0.613 mol H₂ = 1.839 mol CH₄ = 0.387 mol H₂O = 0.387 mol

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = \frac{[\text{CH}_4]^1 [\text{H}_2\text{O}]^1}{[\text{CO}]^1 [\text{H}_2]^3} = \frac{[0.387 \text{ mol} / 10.00 \text{ L}] [0.387 \text{ mol} / 10.00 \text{ L}]}{[0.613 \text{ mol} / 10.00 \text{ L}] [1.839 \text{ mol} / 10.00 \text{ L}]^3} = \mathbf{3.93}$$

Experiment 2 in a 10.00 Liter Reactor

CO = 1.522 mol H₂ = 1.566 mol CH₄ = 0.478 mol H₂O = 0.478 mol

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = \frac{[\text{CH}_4]^1 [\text{H}_2\text{O}]^1}{[\text{CO}]^1 [\text{H}_2]^3} = \frac{[0.478 \text{ mol} / 10.00 \text{ L}] [0.478 \text{ mol} / 10.00 \text{ L}]}{[1.522 \text{ mol} / 10.00 \text{ L}] [1.566 \text{ mol} / 10.00 \text{ L}]^3} =$$

$$= \frac{(0.0478) * (0.0478)}{(0.0613) * (0.1839)^3} = \mathbf{3.91}$$

Note above, the different concentrations of components, but K_c are equivalent!

Exercise 14.3 1.00 mol of CO and 1.00 mol of H₂O react at 1000 °C and at equilibrium in a 10.0 L reactor produces 0.57 mol of CO, 0.57 mol H₂O, 0.43 mol CO₂ and 0.43 mol H₂. Write the balanced equilibrium chemical equation and calculate the value of K_c ? **Class do – possible test question!**

Example 14.3 HI decomposes by: $2 \text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$

The amount of I₂ is determined by measuring its absorption in the Visible Spectrum. Starting with 4.00 mol of HI in a 5.00 L container at 458 °C. At equilibrium there was 0.442 mol of I₂. What is K_c ?

HI = 4.00 mole / 5.00 L = 0.800 Molar (M)

I₂ = 0.442 mole / 5.00 L = 0.0884 Molar (M)

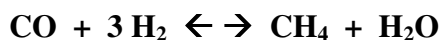
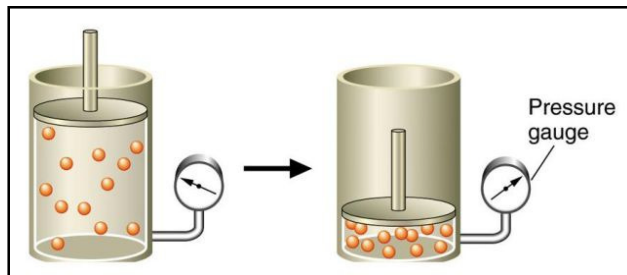
| | | | | |
|--------------------|-------------|------------|------------------------|----------------------|
| | 2 HI | ← → | H₂ + | I₂ |
| Starting | 0.800 M | | 0 | 0 |
| Change | - 2x | | x | x |
| Equilibrium | 0.800 - 2x | | x | x = 0.0884 |
| Answer | 0.623 M | | 0.0884 M | 0.0884 M |

$$K_c = [\text{H}_2] [\text{I}_2] / [\text{HI}]^2 = (0.0884 \text{ M}) (0.0884 \text{ M}) / (0.623 \text{ M})^2 = \mathbf{0.0201}$$

Exercise 14.4 H_2S decomposes by: $2 \text{H}_2\text{S} \rightleftharpoons 2 \text{H}_2 + \text{S}_2$ Starting with 0.100 mol of H_2S in a 10.0 L container at 1132 °C at equilibrium gave 0.0285 mol of H_2 . What is K_c ? **Class do, possible test quest!**

Partial Pressure Equilibrium Constant K_p Remember $PV = nRT$?

Well, you can do equilibrium reactions based on partial pressure instead of concentration. At a higher pressure, there is a higher concentration of reactants:



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

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

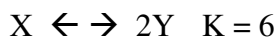
where Δn = the sum of the coefficients of gas products minus the sum of coefficients of gas reactants.

For above reaction $\Delta n = 2 - 4 = -2$. From Experiment 1 and 2 above $K_c = 3.92$

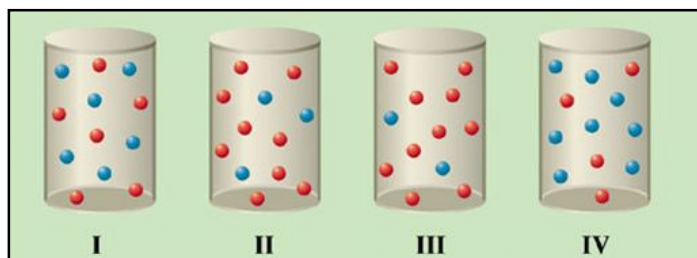
$$K_p = K_c (RT)^{\Delta n} = 3.92 * (0.0821 \text{ L atm / Mol } ^\circ\text{K} * 1200 ^\circ\text{K})^{-2} = 4.04 \times 10^{-4}$$

Exercise 14.5 $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ $K_c = 3.26 \times 10^{-2}$ at 191 °C. What is K_p ? **Class do possible test quest**

Concept Check 14.2 For the following reactions with the given equilibrium constants



Match each reaction above with the picture below and identify the color to reactant / product.



| | I | II | III | IV |
|--------------|---|----|-----|----|
| Red: | 6 | 9 | 10 | 4 |
| Blue: | 6 | 3 | 2 | 8 |

To answer this question, find the relationship between the two species present using the equilibrium constant expression and its value.

For the first reaction: $A(g) \rightleftharpoons B(g)$, with $K = 2$, this becomes

$K = 2 = \frac{[B]}{[A]}$ This reduces to $[B] = 2[A]$. This corresponds to the container that has twice as many

balls of one color than the other color, namely container IV. Here, the blue molecules are B (eight of them), and the red molecules are A (four of them).

For the second reaction, $X(g) \rightleftharpoons 2 Y(g)$, with $K = 6$, this becomes

$K = 6 = \frac{[Y]^2}{[X]}$ This reduces to $[Y]^2 = 6[X]$. This corresponds to container I, where there are six of each

color molecule. Since there are the same numbers of each molecule, you cannot determine which color corresponds to which molecule.

For the third reaction, $2 C(g) \rightleftharpoons D(g)$, with $K = 1$, this becomes

$K = 1 = \frac{[D]}{[C]^2}$ This reduces to $[C]^2 = [D]$. This corresponds to container II. The red balls (nine of them)

correspond to molecule D, and the blue balls (three of them) correspond to molecule C.

Heterogeneous / Homogeneous Equilibria:

Homogeneous Equilibrium involves reactants and products in a single phase.

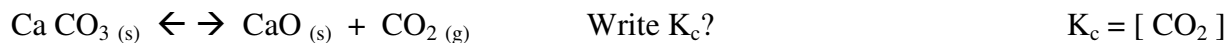
e.g. Cat Methanation above.

Heterogeneous Equilibrium involves reactants and products in more than one phase.

e.g. Iron and steam involves solid and gas phases: $3 Fe_{(s)} + 4 H_2O_{(g)} \rightleftharpoons Fe_3O_4_{(s)} + 4 H_2_{(g)}$

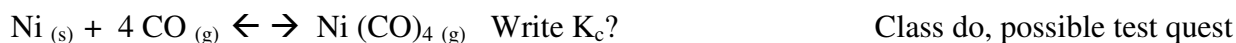
Equilibrium expressions omit pure solids and liquids [sometimes]: $K_c = [H_2]^4 / [H_2O]^4$

Example 14.4 Calcium Oxide is prepared from heating Calcium Carbonate:



Write K_c for liquid water in equilibrium with water vapor: $H_2O (l) \rightleftharpoons H_2O (g) \quad K_c = [H_2O (g)]$

Exercise 14.6 Nickel is purified by passing CO over it and condensing the Nickel Carbonyl:



Using the Equilibrium Constant:

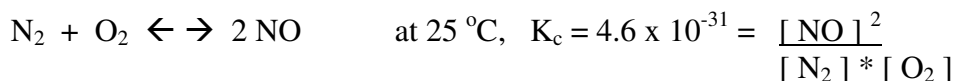
1. Qualitative interpreting the equilibrium constant

If K_c or K_p is large, the products are favored: Reactants \rightleftharpoons Products $K = \frac{[\text{Products}]}{[\text{Reactants}]}$

$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$ at $25^\circ C$, $K_c = 4.1 \times 10^8$. The products are 4.1×10^8 more concentrated.

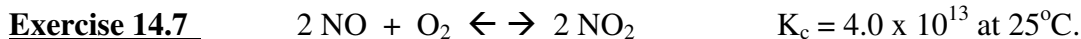
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

If K_c or K_p is small, the reactants are favored:



Assume $[N]$ and $[O] = 1.0 M$. $[NO]^2 = 4.6 \times 10^{-31} * 1.0 * 1.0$ $[NO] = 6.8 \times 10^{-16} M$

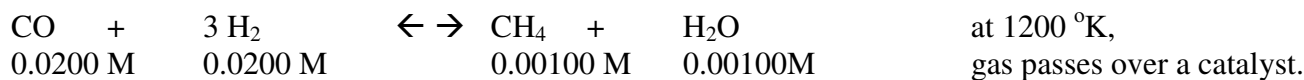
So the concentration of the product is very small compared to that of the reactants.



Does the equilibrium mixture contain mostly reactants or products?

If $[\text{NO}] = [\text{O}_2] = 2.0 \times 10^6 \text{ M}$, what is the concentration of NO_2 ?

2. Predicting the direction of the reaction



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. This is an example reaction where the gases are directed to pass over a catalyst and then removed from the area. This is NOT a reaction at equilibrium.

$$Q_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{[0.00100] * [0.00100]}{[0.0200] * [0.0200]^3} = 6.25$$

In Experiment 1 and 2 above, for the equilibrium reaction, $K_c = 3.92$. So to go from this **gas phase over a catalyst to an equilibrium state**, the equilibrium constant must go from 6.25 down to 3.92. The reaction would then favor going to the left.

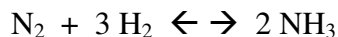
For the general reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ where $Q_c = [\text{C}]^c [\text{D}]^d / [\text{A}]^a [\text{B}]^b$

If $Q_c > K_c$ the reaction will go to the left

If $Q_c < K_c$ the reaction will go to the right

If $Q_c = K_c$ the reaction is already at equilibrium

Example 14.5 A 50.0 L reactor contains 1.00 mole N_2 , 3.00 mole H_2 , 0.500 mole NH_3 . $K_c = 0.500$ at 400°C



When the mixture goes to equilibrium, will more ammonia form or disappear?

$$\text{N}_2 = 1.00 \text{ mole} / 50.0 \text{ L} = 0.0200 \text{ M} \qquad \text{H}_2 = 3.00 \text{ mole} / 50.0 \text{ L} = 0.0600 \text{ M}$$

$$\text{NH}_3 = 0.500 \text{ mole} / 50.0 \text{ L} = 0.0100 \text{ M}$$

$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.0100 \text{ M})^2}{(0.0200 \text{ M})(0.0600 \text{ M})^3} = 23.1$$

$Q_c = 23.1$ and $K_c = 0.500$, so Q_c is greater, so the reaction will go to the left and ammonia will disappear.

Concept Check 14.3 $\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ At equilibrium the volume is compressed so the concentrations of all substances initially double. What will happen when equilibrium is attained?

Plug in the values of x for the Equilibrium Concentrations

$$x = 2.33 \quad \text{H}_2 = 1.00 - x = -1.33 \quad \text{Which is impossible}$$

$$x = 0.93 \quad \text{H}_2 = 1.00 - x = 0.07 \text{ mol} \quad \text{Which is the answer}$$

$$\text{I}_2 = 2.00 - x = 1.07 \text{ mol}$$

$$2\text{HI} = 2x = 1.86 \text{ mole}$$

Exercise 14.11 $\text{PCl}_5 \leftrightarrow \text{PCl}_3 + \text{Cl}_2$

Initial $\text{PCl}_5 = 1.00 \text{ mol/L}$. $K_c = 0.0211$ at 160°C . What is the equilibrium composition of the mixture

Changing the Reaction Conditions: La Chatelier's Principle

La Chatelier's Principle is when a system in chemical equilibrium is disturbed by a change of temperature, pressure or concentration, the system shifts in equilibrium composition in a way that tends to counteract this change of a variable.

Three ways to alter the equilibrium composition of a gaseous reaction:

1. Change the concentration by removing products or adding reactants to the reactor

| | | | | | | | | |
|-------------|-------------|---|----------------|-------------------|---------------|---|----------------------|--|
| | CO | + | 3H_2 | \leftrightarrow | CH_4 | + | H_2O | |
| Start | 1.000 mol | | 3.000 mol | | | | | in a 10.00 L reactor at 1200°K |
| Equilibrium | 0.613 mol | | 1.839 mol | | 0.387 mol | | 0.387 mol | |

So we remove the water:

| | | | | | | | | |
|-----------------------------|-----------|--|-----------|--|-----------|--|-----------|--|
| Remove H_2O | 0.613 mol | | 1.839 mol | | 0.387 mol | | 0.0 mol | |
| New Equilibrium | 0.491 mol | | 1.473 mol | | 0.509 mol | | 0.122 mol | |

Step 1 : Determine K_c from the Equilibrium

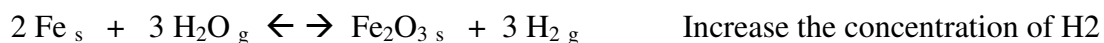
Step 2: Determine the New Equilibrium Values **HOMEWORK ASSIGNMENT 4 NEXT CLASS**

Adding a cheap reactant to force the reaction to products. $\text{N}_2 + 3 \text{H}_2 \leftrightarrow \text{NH}_3$

If the reaction is at equilibrium and you add more nitrogen, it will force the reaction to the right.

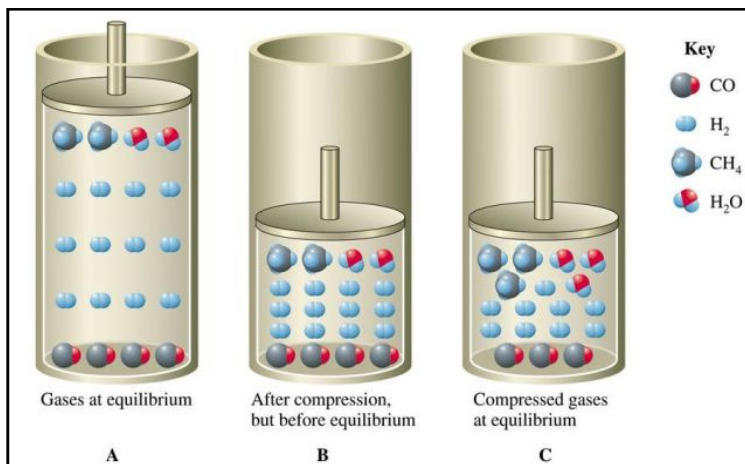
Example 14.9 Predict the direction of the reaction if hydrogen is removed from a mixture at equilibrium:
 $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$

Exercise 14.12 Predict the direction of the reaction

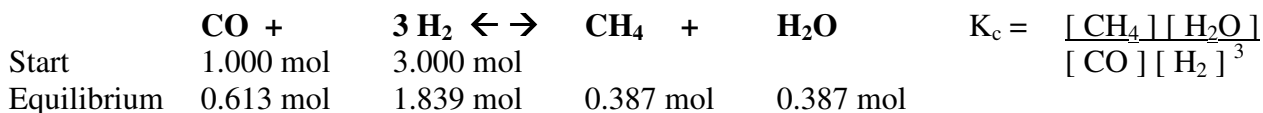


2. Change the partial pressure of the gaseous reactions and products by changing the volume

If the products in a gaseous reaction contain fewer moles of a gas than the reactants [it requires less space] then reducing the volume of the reactor would favor the products. If the number of moles of reactants = moles of products, there is no effect.



In a 10.0 L Reactor, $K_c = 3.92$, at 1200 °K



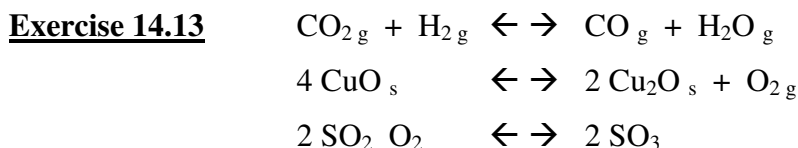
If you half the volume of the gases, so the concentration has doubled, K_c and Temp are the same.

See example 14.8 to resolve for these new concentrations. The above concentration of CO started at 1.000 mol / 10.0 L. Halving the volume, the starting concentration of CO is now 1.000 mol / 5.0 L. You need to re-calculate the equilibrium concentrations to get:

0.495 mol 1.485 mol 0.505 mol 0.505 mol

Note the amount of methane concentration has increased from 0.387 mol to 0.505 mol

Example 14.10 If the pressure is increased, what happens to the amount of products formed:



3. Change the temperature.

Reactions rates usually increase with an increase in temperature, so equilibrium is reached sooner.

But, equilibrium constants vary with temperature: **Methanation:**



| | | | | |
|----------------------|------------------------|------------------------|------------------------|-------------|
| Temp °K | <u>298</u> | <u>800</u> | <u>1000</u> | <u>1200</u> |
| K_c | 4.9 x 10 ²⁷ | 1.38 x 10 ⁵ | 2.54 x 10 ² | 3.92 |

If you increase the temperature, you favor the reaction to the right, so the K_c will be smaller at higher temperatures.

Example 14.11 For the reaction $\text{CO}_2\text{g} + \text{C}_{\text{graphite}} \rightleftharpoons 2 \text{COg}$ $\Delta H^\circ = 172.5 \text{ kJ}$.

Does high or low temperature favor the formation of CO?

Rewrite the equation to: $\text{Heat} + \text{CO}_2 + \text{C} \rightleftharpoons 2 \text{CO}$

So when the temp is raised, for forward reaction if favored.

Example 14.14 For the reaction: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ reaction is endothermic

Does high or low temp favor the production of CO?

Synthesis of Ammonia $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ $\Delta H^\circ = -91.8 \text{ kJ}$

1. Reaction is exothermic, so formation of ammonia is favored by lower temp
2. Formation of ammonia decreases the volume, so higher pressure favors formation of ammonia
3. Removal of ammonia by condensation will also favor the forward reaction.

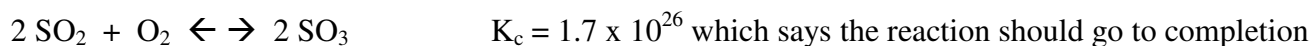
Exercise 14.15 $2 \text{CO}_2 \rightleftharpoons 2 \text{CO} + \text{O}_2$ $\Delta H^\circ = 566 \text{ kJ}$

What are the effects of temp and pressure to form carbon monoxide?

Effects of a Catalyst

A **catalyst** is a substance that increases the rate of a reaction but is not consumed in the reaction.

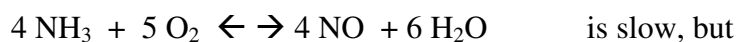
A catalyst does not have an effect on the equilibrium constant of a reaction mixture



But without a catalyst, the reaction proceeds very slowly. With a cat, the rate of the reaction is very fast. This is used in the **Contact Process** for making sulfuric acid.

Nitric Acid can be made using this as a starting reaction: $\text{N}_2 + \text{O}_2 \rightleftharpoons 2 \text{NO}$ with $K_c = 4.6 \times 10^{-31}$
What effect would adding a catalyst have to this reaction?

Ostwald Process to make Nitric Acid:



But, Ostwald found out the 1st reaction is catalyzed by Platinum.

How does this effect the making Nitric Acid?