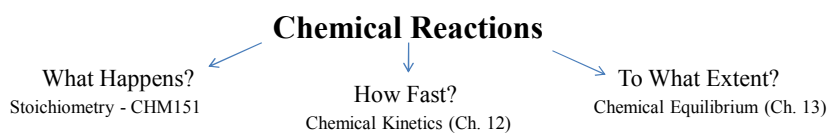


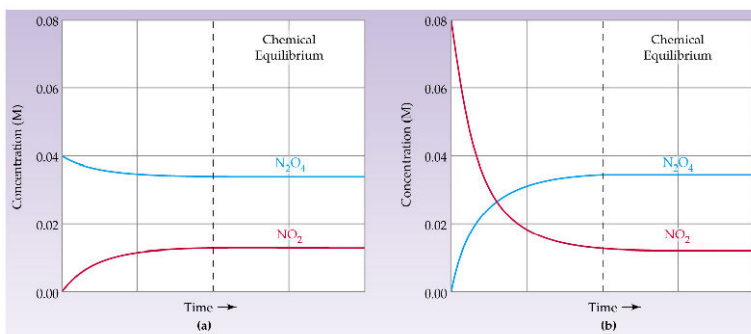
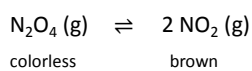
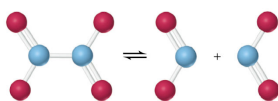
Chapter 13

Chemical Equilibrium

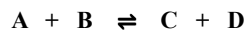


Chemistry, McMurry – Fay, 5th edition

13.1 – The Equilibrium State



Chemical reactions can move in both the forward and reverse directions.



Chemical Equilibrium: When the rate of the forward reaction *equals* the rate of the reverse reaction, the concentrations of the reactants and products remains constant .

How is equilibrium achieved?

- I. Start with reactants A and B. They are colliding to produce C and D.
 - A. What are [C] and [D]? Zero!! (Note: [] = mol/L which is concentration)
 - B. Forward reaction = $A + B \rightarrow C + D$
- II. Over time (ms to years) enough C and D are present to collide and make A and B.
 - A. Reverse Reaction = $C + D \rightarrow A + B$
 - B. How are the rates of the forward and reverse reaction effected?
The rate of the reverse reaction increases as the rate of the forward reaction decreases.
- III. Eventually equilibrium is reached: $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$
- IV. The concentrations at equilibrium are no longer changing. The reaction is still ongoing, A and B are still producing C and D, C and D are still producing A and B.
The *rates* of the forward and reverse reactions are now equal, not the concentrations!
Reached a *dynamic state* – no **net** conversion of reactants to products!

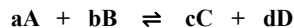
If a reaction is said to be *irreversible*, the rate of the reverse reaction is too slow to be detected.

13.2 – The Equilibrium Constant K_C

Usually one side of an equilibrium reaction is favored.

If at equilibrium 85% is products and 15% is reactants, the *products* are said to be favored.

If at equilibrium 5% is products and 95% is reactants, the *reactants* are said to be favored.



$$K = \frac{[\text{products}]^{\text{coef}}}{[\text{reactants}]^{\text{coef}}} \quad K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Write the balanced combination reaction for the formation of ammonia and the equilibrium constant expression:

Write the balanced decomposition of ammonia reaction and the equilibrium constant expression:

The equilibrium constant is just that, a constant at a specific temperature. *It is unit-less.*

Experiment Number	Initial Concentrations (M)		Equilibrium Concentrations (M)		Equilibrium Constant Expression
	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$
1	0.0400	0.0000	0.0337	0.0125	4.64×10^{-3}
2	0.0000	0.0800	0.0337	0.0125	4.64×10^{-3}
3	0.0600	0.0000	0.0522	0.0156	4.66×10^{-3}
4	0.0000	0.0600	0.0246	0.0107	4.65×10^{-3}
5	0.0200	0.0600	0.0429	0.0141	4.63×10^{-3}

What does it mean when K is a very large number (e.g. 2.30×10^9)?

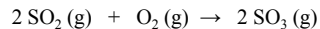
What does it mean when K is a very small number (e.g. 2.30×10^{-7})?

1. Calculate the equilibrium constant for the formation of ammonia at 500K.
The following concentrations were measured for an equilibrium mixture at 500 K:
 $[\text{N}_2] = 3.0 \times 10^{-2} \text{ M}$; $[\text{H}_2] = 3.7 \times 10^{-2} \text{ M}$; $[\text{NH}_3] = 1.6 \times 10^{-2} \text{ M}$

- A. First write a balanced equation and the equilibrium constant expression.
- B. Substitute the molar concentrations for the reactants and products to calculate K_C .
- C. What is the value of K_C ?

2. The oxidation of sulfur dioxide to give sulfur trioxide is an important step in the industrial process for synthesis of sulfuric acid. Calculate the equilibrium constant given the following equilibrium concentrations measured at 800 K:

$$[\text{SO}_2] = 3.0 \times 10^{-3} \text{ M}; [\text{O}_2] = 3.5 \times 10^{-3} \text{ M}; [\text{SO}_3] = 5.0 \times 10^{-2} \text{ M}$$



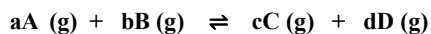
3. Lactic acid, which builds up muscle in tissue upon strenuous exercise, is partially dissociated in aqueous solution:



What is the value of K_C if the extent of dissociation in 0.100 M lactic acid is 3.65% at 25°C?

13.3 – The Equilibrium Constant K_p

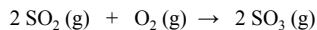
Equilibrium constant expressions for gas-phase reactions can be written using partial pressures (in atm since that is the standard-state partial pressure for gases).



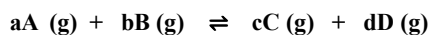
$$K = \frac{[\text{products}]^{\text{coef}}}{[\text{reactants}]^{\text{coef}}} \quad K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

1. The oxidation of sulfur dioxide to give sulfur trioxide has been implicated as an important step in the formation of acid rain. Calculate the equilibrium constant, K_p , given the following equilibrium partial pressures measured at 1000 K:

$$\text{SO}_2 = 0.564 \text{ atm}; \text{O}_2 = 0.102 \text{ atm}; \text{SO}_3 = 0.333 \text{ atm}$$



The constants K_p and K_c for a the general gas-phase reaction



are related because the pressure of each component in a mixture of ideal gases is directly proportional to its molar concentration.

$$P_A V = n_A RT \quad \text{so} \quad P_A = \frac{n_A}{V} RT = [A]RT$$

The same can be done for B, C, and D

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{(c+d)-(a+b)}$$

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

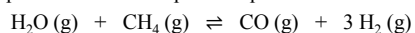
for the reaction $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$\Delta n = \Sigma \text{ moles product gas} - \Sigma \text{ moles reactant gas}$$

$$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

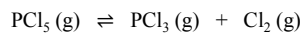
2. If $K_c = 2.0 \times 10^{33}$ at 25°C for the following reaction: $\text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{HCl}(g)$ then find K_p at the same temperature.

3. Hydrogen is produced industrially by the steam-hydrocarbon re-forming process. The reaction that takes place in the first step of this process is



If $K_c = 3.8 \times 10^{-3}$ at 1000K , what is the value of K_p at the same temperature?

4. Phosphorous pentachloride decomposes to phosphorous trichloride and chlorine gas at elevated temperatures by the following reaction:



If $K_p = 77$ at 250°C , what is the value of K_c at the same temperature?

5. The decomposition of ammonia is $2 \text{NH}_3 (\text{g}) \rightleftharpoons \text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g})$. If K_p is 1.5×10^3 at $400.^\circ\text{C}$, what is the partial pressure of ammonia at equilibrium when N_2 is 0.10 atm and H_2 is 0.15 atm ?

13.4 – Heterogeneous Equilibria

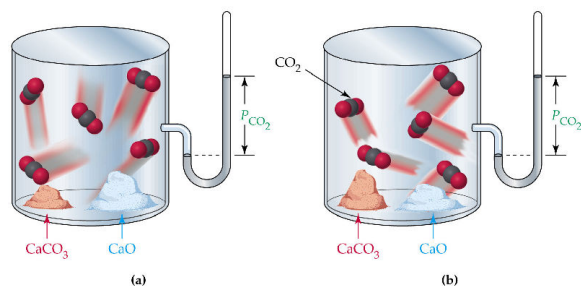
Solids and liquids are NOT included in the equilibrium expression.

Why? - Not dissolved!!

We only include the concentrations of gases and the concentrations of solutes in solution.

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

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

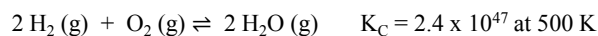


1. Write K_C and K_p expressions for $2 \text{Cu}_2\text{S}(\text{s}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{Cu}_2\text{O}(\text{s}) + 2 \text{SO}_2(\text{g})$
2. Write K_C and K_p expressions for $\text{CaCO}_3(\text{s}) + 2 \text{HCl}(\text{aq}) \rightleftharpoons \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$
3. $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ Calculate K_C , K_p and find the pressure of ammonia given $[\text{H}_2] = 0.104 \text{ M}$, $[\text{N}_2] = 0.554 \text{ M}$, $[\text{NH}_3] = 0.418 \text{ M}$, 27.0°C , hydrogen gas pressure is 1.24 atm and nitrogen gas pressure is 2.17 atm.

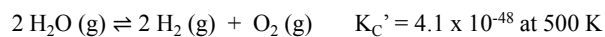
13.5 – Using the Equilibrium Constant

Knowing the value of the equilibrium constant allows us to determine the extent of reaction.

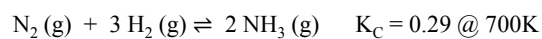
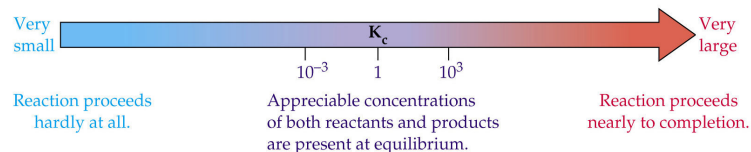
What if K is large?



What if K is small?



If K is between 10^{-3} and 10^3 then both reactants and products are present in the equilibrium mixture in appreciable amounts.



If the equilibrium concentrations of N_2 and $\text{H}_2 = 1.0 \text{ M}$ each, then what is the equilibrium concentration of NH_3 ?

The Reaction Quotient, Q

The reaction quotient, Q , is defined similarly to K except the values are not necessarily equilibrium values.

When $Q = K$, the system is at equilibrium

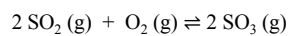
Look at the reaction $\text{A} \rightleftharpoons \text{B}$ with $K = 500 @ 25^\circ\text{C}$

$$Q = \frac{[\text{B}]}{[\text{A}]}$$

What happens when Q is 10?

What happens when Q is 1000?

Which way will the reaction proceed to reach equilibrium if $K_c = 5.55 \times 10^{-2}$, and $[\text{SO}_2] = 1.58 \times 10^{-5} \text{ M}$, $[\text{O}_2] = 4.2 \times 10^{-4} \text{ M}$, and $[\text{SO}_3] = 9.9 \times 10^{-5} \text{ M}$ for:



Problem 13.9: The equilibrium constant K_c for the reaction $2 \text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons 2 \text{NO}_2 (\text{g})$ is 6.9×10^5 at 500 K. A 5.0 L vessel at this temperature was filled with 0.060 mol of NO, 1.0 mol O_2 , and 0.80 mol NO_2 . Is the reaction at equilibrium? If not, which direction does the net reaction proceed?

Calculating Equilibrium Concentrations

Creating ICE Tables

Given initial concentrations of 0.100 M for A and B, the equilibrium concentrations can be calculated.

	2A	+	B	\rightleftharpoons	2C
Initial	0.100 M		0.100 M		0 M
Change					
Equilibrium					

quadratic formula: $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

1. $\text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{Cl}(\text{g})$ $K_C = 7.9 \times 10^{-6}$.
Find all equilibrium concentrations if you start with 0.0214 M chlorine gas.
2. $2 \text{ICl}(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + \text{Cl}_2(\text{g})$ $K_C = 0.11$.
What is the equilibrium concentration of ICl if 0.25 mol of I_2 and 0.25 mol of Cl_2 are initially mixed in a 2.0 L flask?
3. The equilibrium constant K_p for the reaction $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$ is 2.44 at 1000 K. What are the equilibrium partial pressures of H_2O , CO , and H_2 if the initial partial pressures are $P_{\text{H}_2\text{O}} = 1.20 \text{ atm}$, $P_{\text{CO}} = 1.00 \text{ atm}$, and $P_{\text{H}_2} = 1.40 \text{ atm}$?

13.6 – Factors That Alter the Composition of an Equilibrium Mixture

- The concentrations of reactants or products can be changed.
- The pressure and volume can be changed.
- The temperature can be changed.

Le Chatelier's Principle:

When a chemical system in a state of chemical equilibrium is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance.

Activity

Recall: At equilibrium $Q = K$

When $Q \neq K$ the system has been stressed, or disturbed.

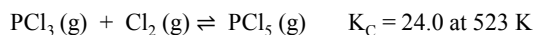
Le Chatelier's principle allows us to predict the direction of the shift to reattain equilibrium.

13.7 –Altering an Equilibrium Mixture: Changes in Concentration

Le Chatelier's principle is helpful in predicting changes in the composition of an equilibrium mixture, but it doesn't explain the why.

When a system is stressed by a change in concentration, the system reacts in the direction that reduces that stress.

- If the concentration increases, the system reacts to consume some of it.
- If the concentration decreases, the system reacts to produce some of it.



Suppose the equilibrium was established with the following concentrations:

$$[\text{PCl}_5] = 0.600 \text{ M}, [\text{Cl}_2] = 0.125 \text{ M}, [\text{PCl}_3] = 0.200 \text{ M}$$

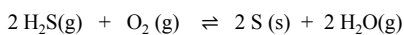
Now we add enough Cl_2 to increase its concentration by 0.075 M.

Predict the shift in equilibrium.

If experiments show the new equilibrium concentration of PCl_5 is 0.637 M, what are the new equilibrium concentrations of PCl_3 and Cl_2 ?

	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$	$K_c = 24.0 \text{ at } 523 \text{ K}$
Original Equil.	0.200 M		0.125 M		0.600 M	
Disturbance						
Initial (New)						
Change						
Equil. (New)						(0.637 M experimentally)

To improve air quality and obtain a useful product, sulfur is often removed from coal and natural gas by treating the fuel contaminant hydrogen sulfide with O_2 :



What happens to:

- $[H_2O]$ if O_2 is added?
- $[H_2S]$ if O_2 is added?
- $[O_2]$ if H_2S is removed?
- $[H_2S]$ if sulfur is added?

13.8 –Altering an Equilibrium Mixture: Changes in Pressure and Volume

Recall: Gases take up the shape and volume of their container with more space between the molecules versus liquids and solids..

Pressure changes can occur in three ways:

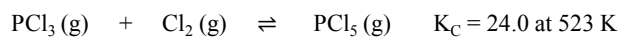
- Changing the concentration of a gaseous component
- Changing the volume of the reaction vessel
- Adding an inert gas (one that does not take part in the reaction)

$$PV = nRT \quad \text{and} \quad M = \frac{n}{V}$$

As $P \downarrow$, $V \uparrow$ since they are inversely related.

$M = n/V$ so $\uparrow V$ will ultimately $\downarrow M$ (concentration)

Let's revisit this reaction:



Changes in Volume:

Increase volume – more space available so more gases can be produced.

Overall shift towards more moles of gases.

Decrease volume – less space available so gases are consumed.

Overall shift towards less moles of gases.

Changes in Pressure:

Increase pressure – since P is inversely related to V, as P ↑, V ↓ it's more crowded.

Overall shift towards less moles of gases.

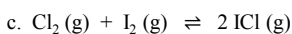
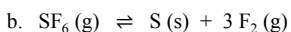
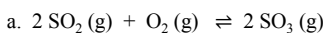
Decrease pressure – it is less crowded, volume ↑, so more gases can be produced.

Overall shift towards more moles of gases.

Addition of an Inert Gas:

As long as the gas is not involved with the overall reaction, *no effect*.

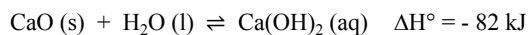
How would you change the volume of each of the following reactions to *increase* the yield of the products?

**13.9 –Altering an Equilibrium Mixture: Changes in Temperature**

Consider heat as a component of the equilibrium system:

A rise in T adds heat to the system and a drop in T removes heat from the system.

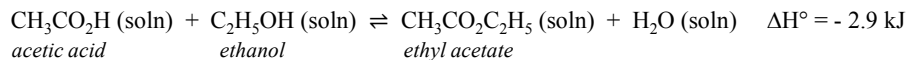
The system will shift to reduce the effect of the change.



A temperature rise will increase K_C for a system with a positive $\Delta H^\circ_{\text{rxn}}$.
 $\Delta H^\circ > 0$ is endothermic (*heat-absorbing*)

A temperature rise will decrease K_C for a system with a negative $\Delta H^\circ_{\text{rxn}}$.
 $\Delta H^\circ < 0$ is exothermic (*heat-releasing*)

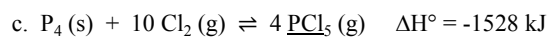
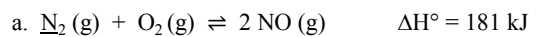
Problem 13.20 Ethyl acetate, a solvent used as fingernail-polish remover, is made by reaction of acetic acid with ethanol:



Does the amount of ethyl acetate in an equilibrium mixture increase or decrease when the temperature is increased?

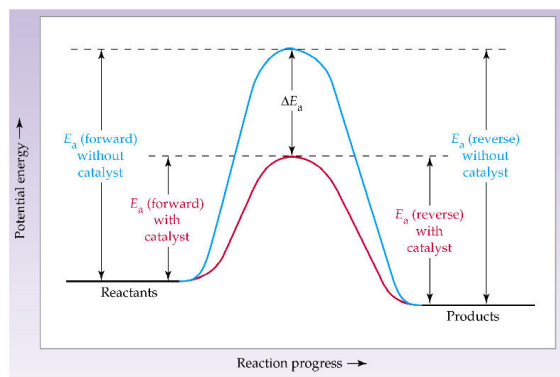
How does K_C change when the temperature is decreased?

How does an increase in temperature affect the equilibrium concentration of the underlined substance and K_C for the following reactions?



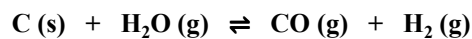
13.10 – The Effect of a Catalyst on Equilibrium

A catalyst lowers the activation energy for a reaction.
 The forward and reverse reactions increase by the same factor.
 Once the forward reaction rate = the reverse reaction rate, equilibrium is achieved.



So a catalyst increase the rate at which equilibrium is achieved,
 but has no effect on the composition of the equilibrium mixture.
Therefore no effect on K!

Consider the exothermic reaction of solid carbon plus water vapor:



Using Le Chatelier's Principle, predict the shift in chemical equilibrium.

1. Adding more C (s)
2. Adding more CO (g)
3. Removing water vapor
4. Removing hydrogen gas
5. Increasing T
6. Decreasing T
7. Decreasing P
8. Increasing V
9. Adding a catalyst
10. Adding neon gas