Workshop – Chem 201

SAN DIEGO MESA COLLEGE
STEM Conexiones

Section 13.7

Le Chatelier's Principle

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Quick reminder #1

Kinetics

- For calculations in Kinetics only the reactants are used to find k. For the given equation:

2A + B → C + D

$$k = \frac{Rate}{[A]^m[B]^n}$$

Or:

$$Rate = k[A]^m[B]^n$$

[A]:	**Reactant 1**
[B]:	Reactant 2
Rate:	Rate of the reaction
k:	Rate constant
m:	Order of the reactant 1
n:	Order of the reactant 2

Quick reminder #2

Equilibrium

In equilibrium calculations both reactants and products are used. For example, given the reaction:

A → B

- $\frac{K_f}{K_r} = \frac{[B]}{[A]} = K_c$
- $K_p = \frac{P_B}{P_A}$

A:	reactants
B:	products
K_f :	Forward rate or formation constant
K_r :	Reverse rate or degradation constant
K_p :	Equilibrium constant in terms of partial pressure
K_c :	Equilibrium constant in terms of concentration
Q_c :	Reaction Quotient (snapshot of reaction)

Quick reminder #3

Equilibrium

- In equilibrium reactions no solids or pure liquids are shown. Only gaseous or aqueous substances.

Reaction Quotient (Q)

- **Q** represents the **reaction quotient** – what basically is a snapshot of the reaction. Thus, if:

Q > K, too much product, therefore the reaction shifts toward reactants (or reacts in **reverse direction - left**);

Q < K, too much reactant, therefore the reaction shifts toward products (or reacts in **forward direction - right**);

Q = K, reaction is in **equilibrium**.

Le Chatelier’s Principle

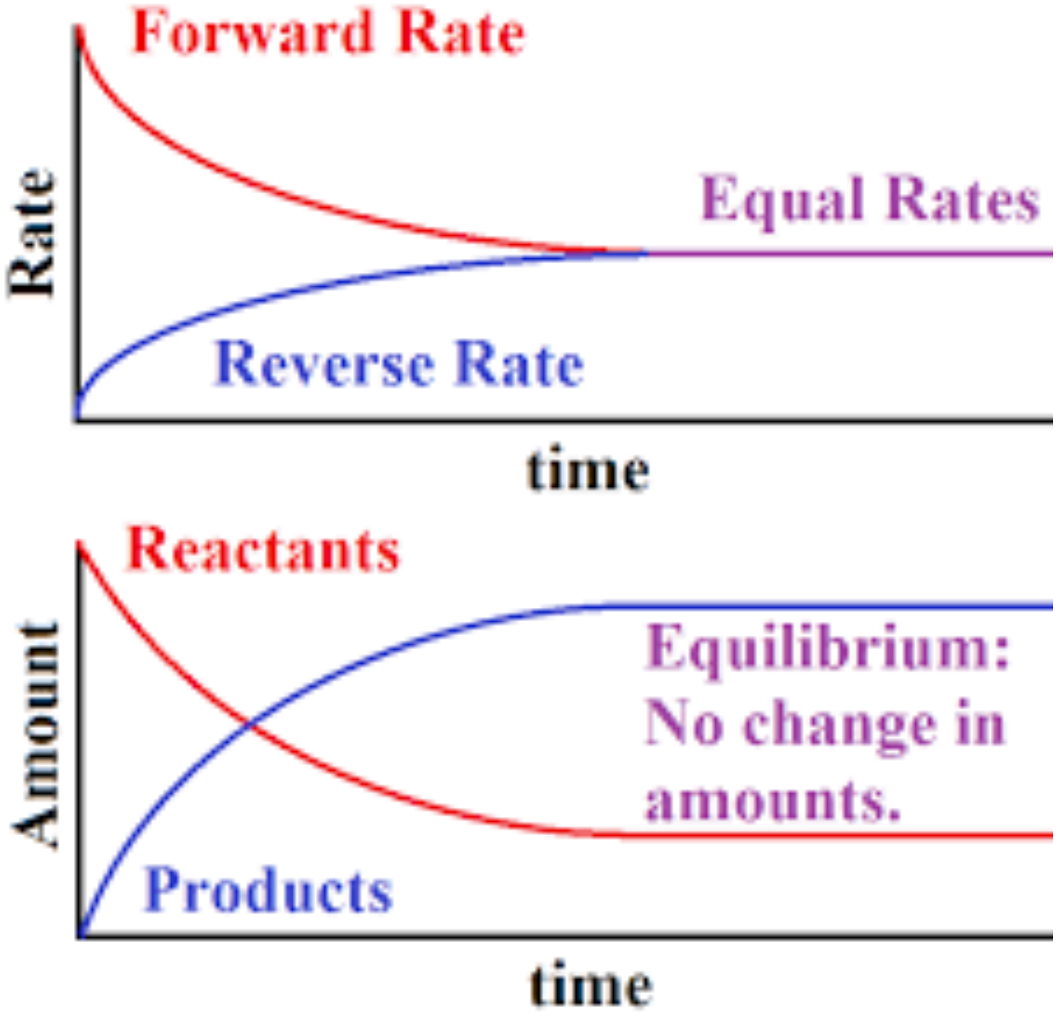
- What is it?

Le Chatelier's principle (also known as "**Chatelier's principle**" or "The Equilibrium Law") **states** that when a system experiences a disturbance (such as concentration, temperature, or pressure changes), it will respond to restore a new equilibrium **state**.

Equilibrium

- But what does equilibrium mean?

At **equilibrium** the concentration of reactant and products remain constant but NOT necessarily equal. **Equilibrium** can only be obtained in a closed system where the **reaction** is carried out in a sealed container and none of the reactants or products are lost.



Le Chatelier’s Principle

- If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

- **So, why do I have to know the Le Chatelier’s Principle?**

Because it’s really useful and helps to predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium.

Cases

LE CHATELIER'S PRINCIPLE

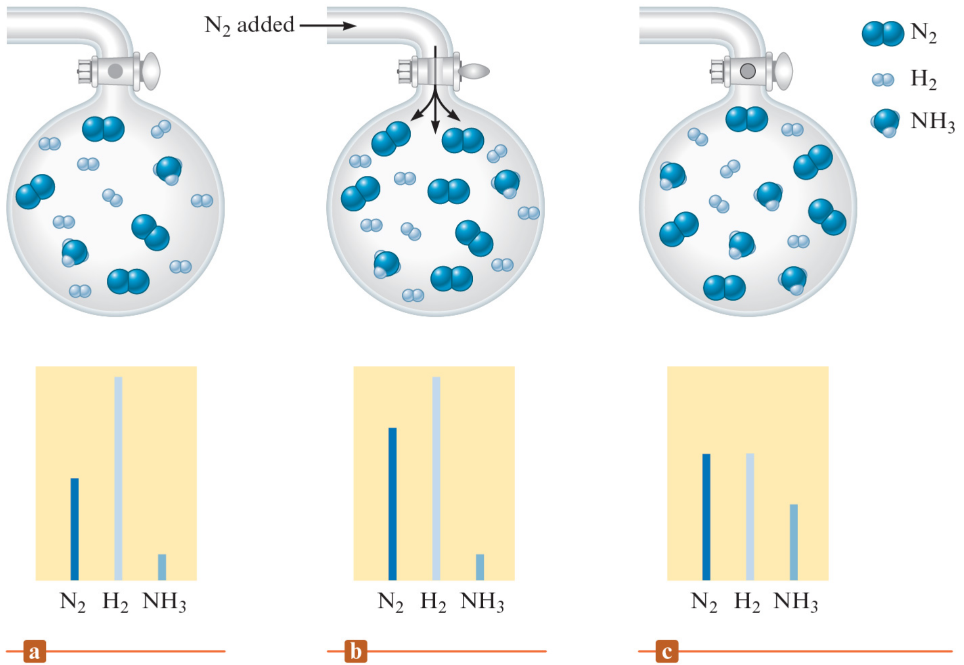
STRESS	SHIFT	WHY?
increase concentration of a substance	*away* from substance	extra concentration needs to be used up
decrease concentration of a substance	*towards* substance	need to produce more of substance to make up for what was removed
increase pressure of system	towards *fewer* moles of gas	for gas: pressure increase = volume decrease
decrease pressure of system	towards *more* moles of gas	for gas: pressure decrease = volume increase
increase temperature of system	*away* from heat/ energy *exothermic* reaction is favored	extra heat/ energy must be used up
decrease temperature of system	*towards* heat/ energy *exothermic* reaction is favored	more heat/ energy needs to be produced to make up for the loss
add a catalyst	NO SHIFT	The rates of both the forward and reverse reactions are increased by the same amount.

Changes in pressure

When the pressure of a system increases, there are more particles in a particular space. The equilibrium will shift in a direction that reduces the number of gas particles so that the pressure is also reduced.

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

Increasing pressure will make reaction shift to the left, so less particles are present



Note: adding an inert gas won't affect the concentration of any substance just the total pressure of the system

Changes in concentration

- Consider the synthesis of ammonia
  - Suppose there is an equilibrium position described by the following concentrations:
    - $[N_2] = 0.399\ M$
    - $[H_2] = 1.197\ M$
    - $[NH_3] = 0.202\ M$
  - Assume that 1.000 mol/L of N_2 is injected into the system
    - Predicting the result involves calculating the value of Q

Changes in concentration

- The concentrations before the system adjusts are

$$[N_2]_0 = 0.399\ M + \underbrace{1.000\ M}_{\text{Added } N_2} = 1.399\ M$$

$$[H_2]_0 = 1.197\ M$$

$$[NH_3]_0 = 0.202\ M$$

  - These are labelled as initial concentrations as the system is no longer at equilibrium

Changes in concentration

- Determine the value of *Q*

$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}$$

  - The value of *K* must be calculated from the first set of equilibrium concentrations

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}$$

Changes in concentration

- $Q < K$ because the concentration of N_2 was increased
  - The system will shift to the right to come to the new equilibrium position

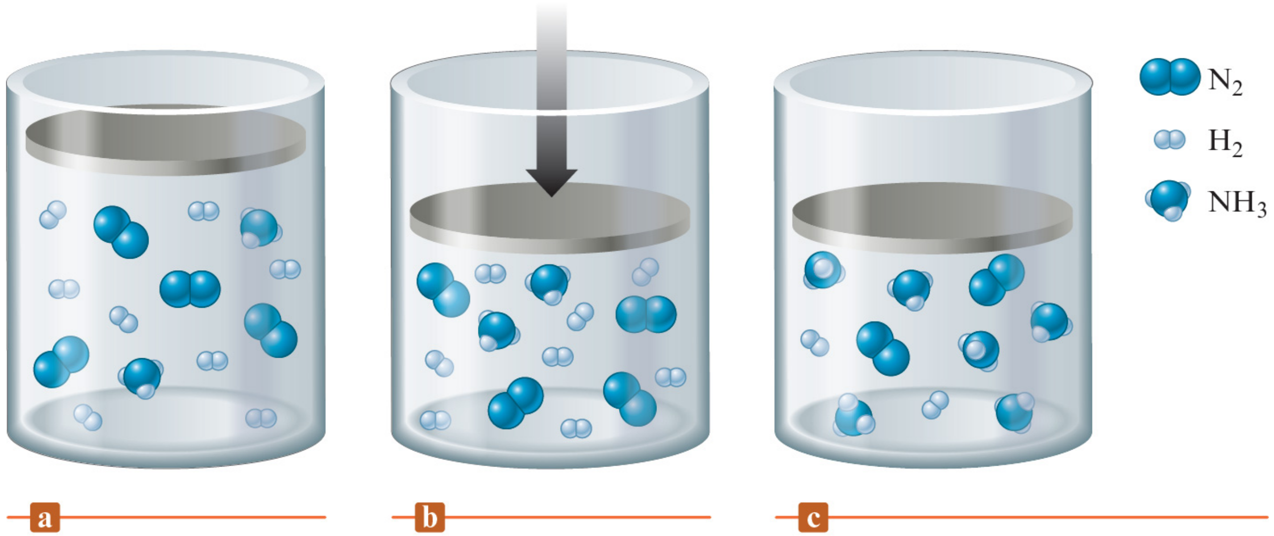
Equilibrium Position I		Equilibrium Position II
$[N_2] = 0.399\ M$	1.000 mol/L	$[N_2] = 1.348\ M$
$[H_2] = 1.197\ M$	$\Longrightarrow$	$[H_2] = 1.044\ M$
$[NH_3] = 0.202\ M$	of N_2 added	$[NH_3] = 0.304\ M$

Changes in volume

$V \propto n$

(volume is direct proportional to the number of moles)

If volume decreases, number of moles decreases as well. Thus, in a smaller container (smaller volume) the number of molecules will be smaller, so more product will be formed.



(1)$N_{2(g)}$ + 3$H_{2(g)}$ → 2$NH_{3(g)}$

Reactants: 4 moles (1 mole N, 3 moles H)

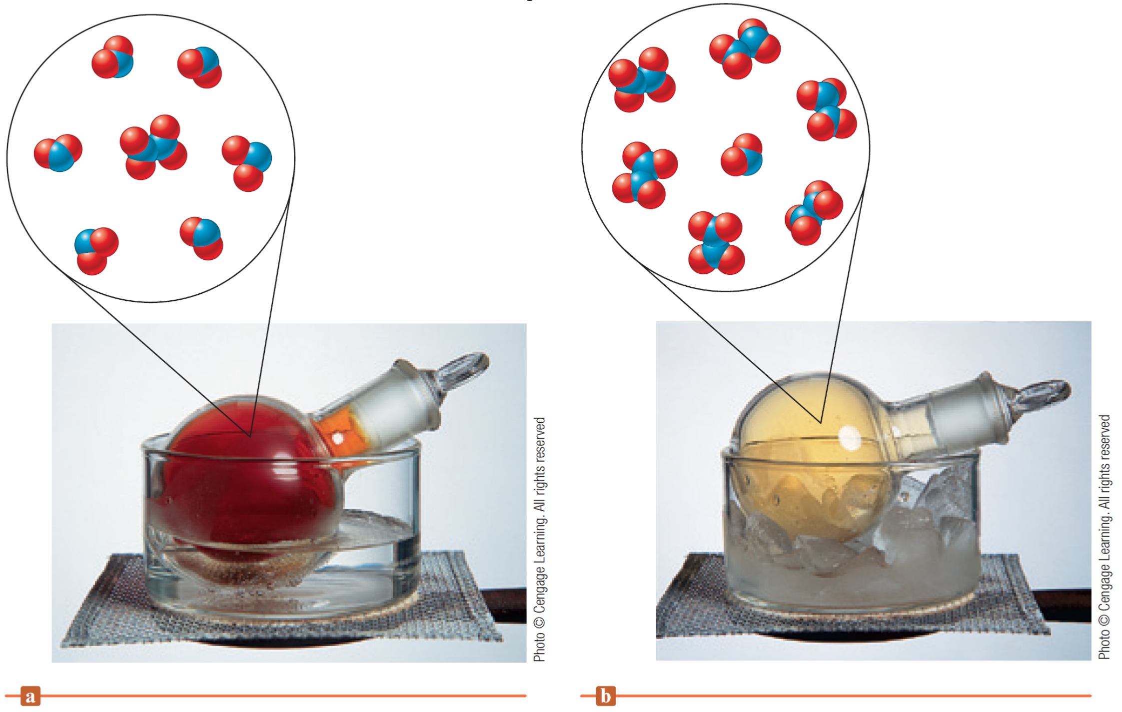
Products: 2 moles of NH_3

Changes in temperature

If energy is added to a system at equilibrium (by heating the system). Le Chatelier's principle predicts that system will shift toward the direction that consumes energy. If the temperature of a reaction mixture is increased, the equilibrium will shift to decrease the temperature.

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ (− 92 kJ / exothermic)

When reaction occurs heat is released. Thus, increasing temperature more product will be formed



Applications of Le Chatelier's principle in our daily life

- **Ocean acidification**

$CO_{2(g)} + H_2O_{(l)} \rightleftarrows H_2CO_{3(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + HCO_3^-{}_{(aq)} \rightleftarrows H^+_{(aq)} + H_3O^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

$H^+_{(aq)}$: free H cation & $H_3O^+_{(aq)} \rightarrow$ acidic behavior

$Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CaCO_{3(s)}$

$Mg^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow MgCO_{3(s)}$

} Solid rocks

Applications of Le Chatelier's principle in our daily life

- Changes of pH in our body

$$CO_{2(g)} + H_2O_{(l)} \rightleftarrows H_2CO_{3(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + HCO_3^{-}{}_{(aq)}$$

Regular pH of human blood: 7.4

Increase of $CO_{2(g)}$ → reaction shifts forward (right)

Increase in $H_3O^+_{(aq),}$ which has acidic behavior making our blood more acidic

In the lungs: breathe out $CO_{2(g)}$, so system can shift to left again.

Practice time!

1. For a certain reaction at 25.0°C, the value of K is 1.2×10^{-3}; at 50.0°C, the value of K is 3.4×10^{-1}

This means that the reaction is:

a. Exothermic

b. Endothermic

c. More information is needed to answer the question

2. When the following reaction is at equilibrium and the volume of the container is decreased,

$$COCl_{2(g)} \rightarrow CO_{(g)} + Cl_{2(g)}$$

a. Forward reaction rate increases
b. Reverse reaction rate increases
c. Forward reaction rate decreases
d. Equilibrium remains unchanged

3. Suppose we have the following reaction at equilibrium

$$PCl_{5(s)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$$

Which of the following statements is false?

a. Adding PCl_3 to the container shifts the equilibrium to form more PCl_5
b. Decreasing the volume of the container shifts the equilibrium to form more PCl_5
c. Removing PCl_5 from the container shifts the equilibrium to form more PCl_3

4. The following reaction is allowed to reach equilibrium.

$$CaO_{(s)} + CO2_{(g)} \rightleftharpoons CaCO_{3(s)}$$

What happens to the reaction when some $CaCO_{3(s)}$ is removed?

a) Favors forward reaction
b) Favors reverse reaction
c) The reaction is still at equilibrium
d) The pressure increases

5. For the reaction below, which change would cause the equilibrium to shift to the right?

$$CH_4(g) + 2H_2S(g) \leftrightarrow CS_2(g) + 4H_2(g)$$

a) Decrease the concentration of dihydrogen sulfide.

b) Increase the pressure on the system.

c) Increase the temperature of the system.

d) Increase the concentration of carbon disulfide.

e) Decrease the concentration of methane.

6. In a reaction, 2.00 M $CO_{(g)}$ is mixed with 1.00 M $H_2O_{(g)}$. If Kc is 1.56, what are the equilibrium concentrations of all species?

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$$

7. Considering the previous reaction, what happens with the system if:

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \text{ (+2.85 kJ endo)}$$

a) The concentration of $CO_{(g)}$ is decreased to 0.500 M
b) The temperature of the system is decreased
c) If volume of container is decreased

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- Chemistry by Steven S. Zumdahl (Copyright Cengage Learning, 2018)
- Openstax (https://cnx.org/contents/49PF5FCK@2.1:RD3H3zkr@1/Le-Chateliers-principle)
- Khan Academy – (https://www.khanacademy.org/science/chemistry/chemical-equilibrium/factors-that-affect-chemical-equilibrium/e/using-le-chatelier-s-principle-exercise)
- http://mmsphyschem.com/lechatP.pdf