Chemistry 12
Tutorial 4 - LeChatelier's Principle

In Tutorial 4 you will be shown:

1. What ***LeChatelier's Principle*** is.

2. How LeChatelier's Principle can be used to *explain* or *predict* shifts in equilibrium caused by changes in:

    - temperature
    - pressure or volume
    - concentration or partial pressure of a reactant

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Do you remember getting somewhat "bogged down" in Tutorial 3, trying to always predict what will happen to an equilibrium when a change in temperature, volume, pressure etc. was made?

In Tutorial 3, you figured out which rate (forward or reverse) was affected by the change, then you predicted what should happen.

Tutorial 4 and *LeChatelier's Principle* will change all that!

It gives you a *simpler way* to look at these concepts.

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Let's look at LeChatelier's Principle first:

LeChatelier's Principle:

If a closed system at equilibrium is subjected to a change, processes will occur that tend to counteract that change.

- "*Processes*" usually mean that the equilibrium will ***shift*** to the left or right.

- "*Counteract*" means that if you do something to a system at equilibrium, the system will shift in such a way as to try to "*undo*" what you did.

- Remember, equilibrium only occurs in a ***closed system.***

Examples of *Counteracting*:

- If you ***add heat*** to a system, it will shift in a way that it tends to "***use up***" the added heat.
- If you ***remove heat*** from a system, it will shift in a way that it tends to "***produce heat***"
- If you ***increase the concentration*** of a certain substance in an equilibrium mixture, the system will shift so as to ***reduce the concentration*** of that substance.
- If you ***decrease the concentration*** of a certain substance in an equilibrium mixture, the system will shift so as to ***increase the concentration*** of that substance.
- If you ***increase the total pressure*** on an equilibrium system involving *gases*, the system will shift in a way that will ***reduce the total pressure***.
- If you ***decrease the total pressure*** on an equilibrium system involving gases, the system will shift in a way that will ***increase the total pressure***.

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Effect of Changes in Temperature

NOTE: When using LeChatelier's Principle, it is easier to have all reactions with "heat" in "*Thermochemical Form*".

eg.) The reaction: $A + B \rightleftarrows C \quad \Delta H = -56$ kJ
is ***exothermic*** (ΔH is negative), so heat is given off or written on the *right*.

Thermochemical form: $A + B \rightleftarrows C + 56\ kJ$

The reaction: $D + E \rightleftarrows F + G \quad \Delta H = 43$ kJ
is ***endothermic*** (ΔH is positive), so heat is absorbed, or written on the *left*

Thermochemical form: $D + E + 43\ kJ \rightleftarrows F + G$

Okay, let's find out how LeChatelier's Principle applies here:

Let's say we have an *endothermic* reaction:

$$\boldsymbol{A + B + heat \rightleftarrows C + D}$$

If we ***increase*** the temperature of this system, we are ***adding heat***. In order to *counteract* our change, the equilibrium will move in such a way as to ***use up heat***.

Since heat is on the *left*, the ***forward*** reaction ***uses up heat***, so it will predominate and the equilibrium will ***shift toward the right***.

Which means a ***new equilibrium*** will be established in which there is ***more C and D*** and ***less A and B*** than in the original equilibrium.

To summarize: When the ***temperature is increased***, the equilibrium will shift ***away*** from the side with the heat term.

Now, if the ***temperature was decreased***, the equilibrium would shift in such a way that would ***produce heat*** (to counteract the change).

To do this, it would shift ***toward the side with the heat term***. (in other words, produce heat)

To summarize: When the ***temperature is decreased***, the equilibrium will shift ***toward*** the side with the heat term.

Here are a couple of questions:

1. Given the reaction at equilibrium: $A_{(g)} + B_{(g)} + 32.5\ kJ \rightleftarrows C_{(g)}$

   a) If the temperature was *increased*, which way would this equilibrium shift _____

   b) If the temperature was *decreased*, which way would this equilibrium shift: _____

2. Given the reaction: $X_{(g)} + Y_{(g)} \rightleftarrows W_{(g)} + Z_{(g)} \quad \Delta H = -75\ kJ$

   a) Rewrite this as a ***thermochemical reaction***

   _____

   b) If the temperature was *increased*, which way would this equilibrium shift: ____

   c) If the temperature was *decreased*, which way would this equilibrium shift: ____

Check your answers for these on Page 1 of Tutorial 4 - Solutions.

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Effect of Changes in Concentration or Partial Pressure

Consider the equilibrium equation:

$$H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$$

If we ***add some H_2*** to a flask containing this mixture at equilibrium, ***[H_2] will immediately increase.***

In order to ***counteract*** this change, the equilibrium will ***shift to the right*** in order to "use up" some of the extra H_2. (In other words to decrease the [H_2]).

Consider the equilibrium equation: $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$

Let's say now that we somehow ***take away some I_2***. [I_2] will immediately ***decrease***.

In order to ***counteract*** this change, the equilibrium will ***shift to the left*** in order to ***increase [I_2] again*** .

If we were to ***add some HI***, the [HI] would immediately _____crease.

In order to ***counteract*** this change, the equilibrium would shift to the _____.

To answer the last question, adding HI will ***increase*** [HI] . In order to *counteract* this change the equilibrium will ***shift to the left***. In shifting to the left, [H_2] and [I_2] will go up and [HI] will go down.

We can summarize the effects of changing concentrations by saying:

> If the ***concentration*** of a substance in an equilibrium system is ***increased*** by us, the equilibrium will ***shift toward the other side*** of the equation, in order to counteract the change.

or

> If the ***concentration*** of a substance in an equilibrium system is ***decreased*** by us, the equilibrium will ***shift toward the side of the equation with that substance***, in order to counteract the change.

Let's have you do some examples:

3. Given the equilibrium equation:

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

a) If the [PCl_5] is *increased*, the equilibrium will shift to the ..... _____

b) If the [PCl_5] is *decreased*, the equilibrium will shift to the ..... _____

c) If the [PCl_3] is *increased*, the equilibrium will shift to the ..... _____

d) If the [PCl_3] is *decreased*, the equilibrium will shift to the ..... _____

e) If the [Cl_2] is *increased*, the equilibrium will shift to the ..... _____

f) If the [Cl_2] is *decreased*, the equilibrium will shift to the ..... _____

Check page **1** of Tutorial 4 - Solutions for the answers to these.

Changing the ***Partial Pressure*** of a gas in an equilibrium system has the *same effect* as changing the ***concentration*** of that gas.

For example:

Given the equilibrium equation: $H_{2(g)} + Br_{2(g)} \rightleftarrows 2HBr_{(g)}$

If the ***partial pressure*** of H_2 is *increased*, the equilibrium will shift to the ***right.***

If the ***partial pressure*** of H_2 is *decreased*, the equilibrium will shift to the ***left.***

If the ***partial pressure*** of HBr is *increased*, the equilibrium will shift to the ***left.***

If the ***partial pressure*** of HBr is *decreased*, the equilibrium will shift to the ***right.***

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Effect of Changes in Total Pressure or Volume for Gaseous Systems

Recall from the last tutorial that:

> The ***more moles*** of gas in a certain volume, the ***higher the pressure.***

Also, recall LeChatelier's Principle:

> ***LeChatelier's Principle:***
> ***If a closed system at equilibrium is subjected to a change, processes will occur that tend to counteract that change.***

Thus:

> If the ***total pressure*** of a system at equilibrium is ***increased***, the equilibrium will shift ***toward the side with less moles of gas*** (as shown by coefficients) in order to *reduce* the total pressure.

For example:

Given the equilibrium equation: $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

1 + 3 = 4 moles of gas on this side.

2moles of gas on this side.

If the ***total pressure*** on this system is ***increased***, the equilibrium would ***shift to the right*** (the side with fewer moles of gas). This *counteracts* the imposed change by *reducing* the pressure.

To review:

A ***shift to the right*** in this case would mean that once the new equilibrium is established, the [NH_3] would be *higher* than before, the [N_2] and the [H_2] would be *lower* than before.

If the ***total pressure*** on this system is ***decreased***, the equilibrium would ***shift to the left*** (the side with more moles of gas). This *counteracts* the imposed change by *increasing* the pressure.

To see what happens when we change the total volume of the container we must remember that:

> ***Increasing the volume*** of a closed system with gases will ***decrease the pressure.***
> (the molecules have more room so they exert less pressure on the sides of the container)

So, given changes in volume of the container, just remember that the changes in pressure are just the opposite. For example:

Given the equilibrium equation: $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

1 + 3 = 4 moles of gas on this side.

2moles of gas on this side.

If the *total volume* of the container is ***increased***, this means that the *total pressure is decreased*.

The equilibrium will then shift to the side with ***more moles*** (to the ***left*** in this case), in order to counteract the change and try to increase the pressure again.

If the *total volume* of the container is ***decreased***, this means that the *total pressure is increased*.

The equilibrium will then shift to the side with ***less moles*** (to the ***right*** in this case), in order to counteract the change and try to decrease the pressure again.

Try the following:

4. Given the equilibrium equation:

$$N_2O_{4(g)} \rightleftarrows 2O_{2(g)} + N_{2(g)}$$

a) If the total pressure of this system is increased, the equilibrium will shift _____

b) If the total pressure of this system is decreased, the equilibrium will shift _____

c) If the total volume of this system is increased, the equilibrium will shift _____

d) If the total volume of this system is decreased, the equilibrium will shift _____

5. Given the equilibrium equation:

$$NO_{(g)} + CO_{2(g)} \rightleftarrows CO_{(g)} + NO_{2(g)}$$

a) If the total pressure of this system is increased, the equilibrium will _____

b) If the total pressure of this system is decreased, the equilibrium will _____

c) If the total volume of this system is increased, the equilibrium will _____

d) If the total volume of this system is decreased, the equilibrium will _____

Check your answers on page **2** of Tutorial 4 - Solutions.

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Shifting Equilibrium and Rate of Reaction

Just a little note here about the difference between ***rate of reaction*** and the ***equilibrium shifting right or left***!

First of all, a "s*hift to the left* "means that once the new equilibrium is reached, there will be ***more reactants and less products***. It does ***not*** say anything about the ***rate of the reaction!!***

For example, consider the reaction:

$$A + B \rightleftarrows C + heat$$

If the *temperature* of this system was ***increased***, the equilibrium would shift to the ***left***.

This does ***not*** mean that the rate will be slower! It simply means that a new equilibrium will be reached which has ***more A and B and less C***.
In fact, as we might recall from Unit 1, *increasing the temperature always increases the rate* of a reaction. (more molecules have the minimum energy necessary for an effective collision.)
Increasing the temperature just causes equilibrium to be reached faster.
Try these:

6. Given the equilibrium equation: $X + Y + heat \rightleftarrows Z$

a) Increasing the temperature will _____ the rate of reaction.

b) Increasing the temperature will cause the equilibrium to shift _____

c) Decreasing the temperature will _____ the rate of reaction.

d) Decreasing the temperature will cause the equilibrium to shift _____

7. Given the equilibrium equation: $D + E \rightleftharpoons F + heat$

a) Increasing the temperature will _____ the rate of reaction.

b) Increasing the temperature will cause the equilibrium to shift _____

c) Decreasing the temperature will _____ the rate of reaction.

d) Decreasing the temperature will cause the equilibrium to shift _____

Check your answers on pages **2** and **3** of Tutorial 4 - Solutions

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Self-Test on Tutorial 4

1. Given the following equilibrium equation:

$$N_2H_{4(g)}? + 6H_2O_{2(g)} \rightleftharpoons 2NO_{2(g)} + 8H_2O_{(g)} + heat$$

Which way will the equilibrium shift when each of the following changes are made?

a) The $[NO_2]$ is increased ..... _____

b) The $[H_2O_2]$ is increased ..... _____

c) The partial pressure of N_2H_4 is increased ..... _____

d) The temperature is increased ..... _____

e) The partial pressure of H_2O_2 is decreased ..... _____

f) The partial pressure of H_2O is increased ..... _____

g) The temperature is decreased ..... _____

h) The total volume of the container is decreased ..... _____

i) The total pressure of the system is decreased ..... _____

j) The $[N_2H_4]$ is decreased ..... _____

2. Given the equilibrium equation: $N_2O_{(g)} + NO_{2(g)} + heat \rightleftharpoons 3NO_{(g)}$

What effect will each of the following changes have on the equilibrium ***partial pressure*** of NO? (The first question is done as an example.)

a) the $[N_2O]$ is increased .....**The partial pressure of NO increases because the equilibrium shifts to the right.**

b) the total pressure of the system is decreased ..... _____

c) the temperature is decreased..... _____

d) the partial pressure of NO_2 is decreased..... _____

e) more NO_2 is added ..... _____

f) a catalyst is added ..... _____

g) the temperature is increased ..... _____

h) the total volume of the container is increased ..... _____

Check the answers for the Self-Test on page 3 of Tutorial - 4 Solutions.