Chemistry 12 : Lesson 4 – Equilibrium
Le Chatalier's Principle.

Le Chatelier's Principle:

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

In other words WHAT EVER YOU DO, THE SYSTEM WILL UNDO

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 ↑ 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 increase total pressure on an equilibrium system involving *gases*, the system will shift in a way that will reduce total pressure

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Effect of Changes in Temperature

We have an *endothermic* reaction:

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

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 increased, the equilibrium will shift toward the side with the heat term.

Here are a couple of questions:

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

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

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

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***

   $X_{(g)} + Y_{(g)} \rightleftarrows W_{(g)} + Z_{(g)} + 75\ kJ$

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

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

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

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 left in order to ***increase $[I_2]$ again***.

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

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

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 ..... right
b) If the $[PCl_5]$ is *decreased*, the equilibrium will shift to the ..... left
c) If the $[PCl_3]$ is *increased*, the equilibrium will shift to the ..... left
d) If the $[PCl_3]$ is *decreased*, the equilibrium will shift to the ..... right
e) If the $[Cl_2]$ is *increased*, the equilibrium will shift to the ..... left
f) If the $[Cl_2]$ is *decreased*, the equilibrium will shift to the ..... right

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

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

The more moles of gas in certain volume, the higher the pressure

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.

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.

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

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.

4. Given the equilibrium equation: $N_2O_{4(g)} \rightleftarrows 2O_{2(g)} + N_{2(g)}$

   1 3

   a) If the total pressure of this system is increased, the equilibrium will shift left
   b) If the total pressure of this system is decreased, the equilibrium will shift right
   c) If the total volume of this system is increased, the equilibrium will shift right
   d) If the total volume of this system is decreased, the equilibrium will shift left.

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 "*shift 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!!***

than before

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.

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

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

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

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

   d) Decreasing the temperature will cause the equilibrium to shift left.

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

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

   b) Increasing the temperature will cause the equilibrium to shift ~~right~~ left

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

   d) Decreasing the temperature will cause the equilibrium to shift right.