Le Châtelier's Principle

1. What is Le Châtelier's Principle?

   Le Châtelier's Principle states that if a change in conditions (i.e. pressure, temperature, concentration) is imposed on a system at equilibrium, and that change pushes the system out of equilibrium, the reaction will shift to the direction – either left (making more reactant) or right (making more products) – that reduces the effects of that change.

2. How can you cause changes in the following? How does a change in them affect equilibrium?

   a. Concentration

   Concentration can be changed by adding or subtracting moles of reactants/products.

   If a gaseous/aqueous reactant or product is added to a system at equilibrium, the system will shift away from the added component. If a gaseous/aqueous reactant or product is removed from the system at equilibrium, the system will shift toward the removed component.

   Note that I did specify gaseous/aqueous states. Once again we ignore solid and liquids substances as they do not contribute to the position of the equilibrium system. This means that if the moles of a solid/liquid are added or subtracted there will be no shift in the system – equilibrium has not been perturbed.

   b. Pressure

   Pressure can be change by:

   1. Adding or subtracting moles of gaseous reactants/products at constant volume.

The system will behave in the same way as above.

2. Increasing/decreasing the volume of the container.

When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is accomplished by shifting in the direction that results in fewer moles of gas.

When the volume of the container holding a gaseous system is increased, the system responds by increasing its own volume. This is accomplished by shifting in the direction that results in a great number of moles of gas.

3. Adding an inert (non-reactive) gas at constant volume.

There will be no shift in this system; this is because the system is never pushed out of equilibrium.

c. Temperature

The temperature is changed by increasing or decreasing the heat put into the system.

To understand how a reaction will be affected by this type of change – you must know whether the reaction is exothermic or endothermic.

<u>Exothermic</u>: This means that heat is released by the reaction (you can picture heat as being a product).
<u>Endothermic</u>: This means that heat is absorbed by the reaction (you can picture heat as being a product).

Once you have established exothermicity or endothermicity you will treat the problem in the same way as changes in concentration.

Adding heat results in a shift away from heat.
Removal of heat results in a shift towards heat.

i.e.

$$aA + bB \rightleftharpoons cC + dD + heat$$

Because heat is located on the product side we know this is an exothermic reaction. If we were to add heat to the system, the reaction would shift to the left – away from the heat source in the reaction.

An important point to mention is that this is the only change that also results in a change of K. This will become important in a later example.

3. Why does a change in pressure caused by volume change result in a shift but not a pressure change cause by an inert gas addition?

K_p is based on partial pressures. If you change the partial pressures of the gases in the reaction you shift out of equilibrium.

When you add an inert gas into the reaction vessel, the total pressure is increased but the partial pressures of the gases involved in the reaction never changes. This means that the reaction never comes out of equilibrium so a shift is unnecessary.

When the volume of the container is changed, the partial pressures of the gases involved in the reaction are changed. This means the reaction has moved away from the equilibrium. So by decreasing/increasing it's own volume the partial pressures are brought back to a point where the values, when plugged into the equilibrium constant expression, yields K_p.

4. Consider:

$$2\ NBr_{3\,(s)} \rightleftharpoons N_{2\,(g)} + 3Br_{2\,(g)}$$

How would the reaction shift if….

a. The concentration of N_2 is decreased?

The reaction would shift to the right (toward the N_2) in order to bring the reaction back to its equilibrium position.

b. The concentration of Br_2 is increased?

The reaction would shift to the left (away from the Br_2) in order to bring the reaction back to its equilibrium position.

c. The amount of NBr_3 is doubled?

No shift. NBr_3 is a solid; solids do not affect the equilibrium position, thus no shift is required.

d. The pressure is decreased by changing the volume?

The volume would have to be increased in order to lower the pressure. This means that the reaction would have to shift right towards more moles of gas. This would result in an increase in pressure which would allow for a return to the equilibrium position.

e. The pressure is increased by adding $He_{(g)}$?

No shift. $He_{(g)}$ is not part of the reaction and therefore would not cause the system to shift out of equilibrium.

5. Consider:

$$aA + bB \rightleftharpoons cC + dD$$

Determine if the above reaction is endothermic or exothermic based on the following information:

TEMPERATURE	K
150K	0.0053
500K	12
2000K	65

My first step is to look at the trend for K, the equilibrium constant, as I look down the row.

TEMPERATURE	K
150K	0.0053
500K	12
2000K	65

If you notice, the value of K increases. What does an increasing value of K mean? Remember that the larger K is, the more it favors products. So, the increase in K indicates that this reaction is favoring the products more and more - So I'm going to draw an arrow facing the products.

$$aA + bB \rightleftharpoons cC + dD$$

Now I'm going to examine how the temperature changed as the value for K increased.

TEMPERATURE	K
150K	0.0053
500K	12
2000K	65

The temperature increases as K increases. So let's think of this in a non-chemistry mindset. If the day was getting hotter and hotter outside, would you walk toward a heat source or away from a heat source? Hopefully you agree and said – AWAY!

Now looking at this again

$$aA + bB \overset{\longrightarrow}{\rightleftharpoons} cC + dD$$

Picture the arrow as the direction you are going. You have decided you are walking AWAY from the heat source so heat should be behind you.

$$HEAT + aA + bB \overset{\longrightarrow}{\rightleftharpoons} cC + dD$$

Thus, this is an **endothermic reaction**.