<u>4.0 Le Chatelier's Principle</u>

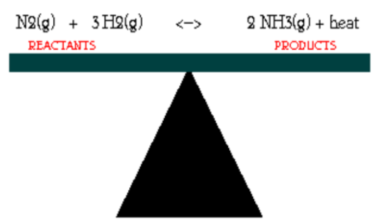
4.1 Le Chatelier's Principle

Le Châtelier's principle states that if a system at equilibrium is subjected to an external stress, <u>the equilibrium will shift to minimize the effects of that stress</u>.

External stresses in this situation are factors that will change the rate of either the forward or reverse reaction.

In other words, an action that changes the <u>temperature</u>, <u>pressure</u>, or <u>concentration</u> of reactants, or presence of a <u>catalyst</u>, in a system at equilibrium stimulates <u>a response that counteracts said change while a new equilibrium condition is established</u>.

Le Chatelier's Principle
"Restoring Balance"



If you add more to the left side (*Reactants*), the lever will tip to the left. In order to restore balance, the system responds by making more of what is on the right (*Products*) and vice versa.

4.2 Changes in Concentration

According to Le Châtelier, if we were to <u>increase</u> the concentration of A in the reaction below, the equilibrium position will move so that the concentration of A decreases again by reacting it with B to form more C and D. The equilibrium moves to the <u>right</u>.

$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the right if you increase the concentration of A.

In the opposite case, in which the concentration of A is <u>decreased</u>, the position of equilibrium will move so that the concentration of A increases again. More C and D will react to replace the A that has been removed. The position of equilibrium moves to the <u>left</u>.

$$A + 2B \rightleftharpoons C + D$$

The position of equilibrium moves to the left if you decrease the concentration of A.

4.3 Changes in Volume & Pressure

* Changing the pressure or volume will only affect the reaction if gases are present. *

Increasing the pressure (typically by reducing volume) results in the position of equilibrium moving towards the side with fewest moles of gas molecules.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the right
if you increase the pressure on the reaction.

When pressure is decreased, the equilibrium will move to favor the side with the most moles of gas.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

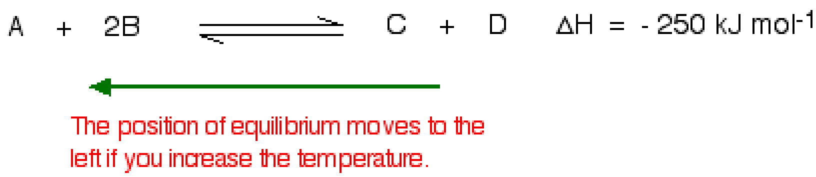
The position of equilibrium moves to the left
if you decrease the pressure on the reaction.

If both sides of the equation have the same number of moles of gas, then there will be no change in the position of equilibrium.

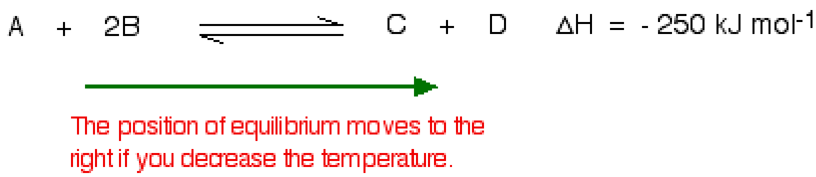
4.4 Changes in Temperature

If the temperature is increased, then the position of equilibrium will move so that the temperature is reduced again. Thus, increasing the temperature favours the endothermic reaction.

Suppose the system is in equilibrium at 300°C, and the temperature is increased 500°C. To cool down, it needs to absorb the extra heat added. In the case, the back reaction is that in which heat is absorbed. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.



<u>Decreasing</u> the temperature favours the <u>exothermic</u> reaction, thus replacing the heat that was removed.



* The main effect of temperature on equilibrium is however in changing the value of the <u>equilibrium constant</u>. *

When temperature changes cause an equilibrium to shift, one entire side of the reaction equation is favoured over the other side. Mathematically, this will alter the value of K_{eq} as follows:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

• if the forward reaction is favoured	more products are produced; fewer reactants	K_{eq} will increase
• if the reverse reaction is favoured	fewer products; more reactants	K_{eq} will decrease

4.5 Addition of a Catalyst

Adding a catalyst will <u>not</u> affect the position of an equilibrium. A catalyst speeds up both the forward and the reverse reactions, so there is no uneven change in reaction rates. Generally, a catalyst will help a reaction to reach the point of equilibrium <u>sooner</u>, but it will not affect the equilibrium otherwise.

Examples:

1. For the reaction below, predict the direction the equilibrium will shift given the following changes. Temperature and volume are held constant.

$$2\ NO_{2\ (g)} + 7\ H_{2\ (g)} \leftrightarrow 2\ NH_{3\ (g)} + 4\ H_2O_{(g)}$$

a. addition of ammonia

b. removal of nitrogen dioxide

c. removal of water vapour

d. addition of hydrogen

2. The pressure on each of the following systems is increased by decreasing the volume of the container. Explain whether each system would shift in the forward direction, the reverse direction, or stay the same.

a. $2\ SO_{2\ (g)} + O_{2\ (g)} \rightleftarrows 2\ SO_{3\ (g)}$

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

c. $CaCO_{3\ (s)} \rightleftarrows CaO_{(s)} + CO_{2\ (g)}$

d. $AgCl_{(s)} \rightleftarrows Ag^{1+}{}_{(aq)} + Cl^{1-}{}_{(aq)}$

3. In each of the following equilibria, would you increase or decrease the temperature to force the reaction in the forward direction?

a. $H_{2\ (g)} + CO_{2\ (g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}$ $\Delta H° = +41.0$ kJ

b. $2\ SO_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2\ SO_{3\ (g)}$ $\Delta H° = -198$ kJ

4. For each of the equilibria in Question 3 will the value for K_{eq} increase or decrease if the temperature is raised?

4.0 Le Chatelier's Principle

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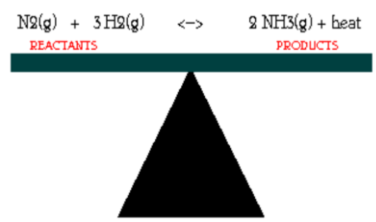
Le Châtelier's principle states that if a system at equilibrium is subjected to an external stress, ____.

External stresses in this situation are factors that will change the rate of either the forward or reverse reaction.

In other words, an action that changes the____________, ____________, or ____________ of reactants, or presence of a ____________ in a ____________________________ ____________________________ ____________________________.

Le Chatelier's Principle
"Restoring Balance"



If you add more to the left side (*Reactants*), the lever will tip to the left. In order to restore balance, the system responds by making more of what is on the right (*Products*) and vice versa.

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According to Le Châtelier, if we were to ____________ the concentration of A in the reaction below, the equilibrium position will move so that the concentration of A decreases again by reacting it with B to form more C and D. The equilibrium moves to the ____________.

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The position of equilibrium moves to the right if you increase the concentration of A.

In the opposite case, in which the concentration of A is ____________, the position of equilibrium will move so that the concentration of A increases again. More C and D will react to replace the A that has been removed. The position of equilibrium moves to the ____________.

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The position of equilibrium moves to the left if you decrease the concentration of A.

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* Changing the pressure or volume will only affect the reaction if gases are present. *

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$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the right
if you increase the pressure on the reaction.

When pressure is ______________, the equilibrium will move to favor the side with the ______________ moles of gas.

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The position of equilibrium moves to the left
if you decrease the pressure on the reaction.

If both sides of the equation have the ______________ number of moles of gas, then there will be ______________in the position of equilibrium.

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If the temperature is increased, then the position of equilibrium will move so that the temperature is reduced again. Thus, ______________ the temperature favours the ______________ reaction.

Suppose the system is in equilibrium at 300°C, and the temperature is increased 500°C. To cool down, it needs to absorb the extra heat added. In the case, the back reaction is that in which heat is absorbed. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250\ kJ\ mol^{-1}$$

←

The position of equilibrium moves to the left if you increase the temperature.

______________ the temperature favours the ______________ reaction, thus replacing the heat that was removed.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250\ kJ\ mol^{-1}$$

→

The position of equilibrium moves to the right if you decrease the temperature.

* The main effect of temperature on equilibrium is however in changing the value of the ______________ ______________. *

When temperature changes cause an equilibrium to shift, one entire side of the reaction equation is favoured over the other side. Mathematically, this will alter the value of K_{eq} as follows:

$$K_{eq} = \frac{[products]}{[reactants]}$$

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Examples

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c. removal of water vapour ____________________

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2. The pressure on each of the following systems is increased by decreasing the volume of the container. Explain whether each system would shift in the forward direction, the reverse direction, or stay the same.

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

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b. $2\ SO_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2\ SO_{3\ (g)}$ $\Delta H° = -198$ kJ

4. For each of the equilibria in Question 2 will the value for K_{eq} increase or decrease if the temperature is raised?