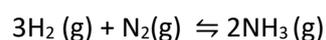


## Lesson 1 Dynamic Equilibrium

In this unit we will only consider homogeneous equilibria where the state of all products and reactants is the same.

Not all chemical reactions are irreversible, as we learnt in our early years of chemistry, some that occur in a closed system are reversible and are written with a double arrow ( $\rightleftharpoons$ ). A closed system is one where reactants and products are not exchanged with the environment and generally occur in sealed reaction vessels. Take the formation of ammonia for example.



What the double arrows indicate is that the reaction can proceed in both the forward and backward direction. This is a reversible reaction in that the products can react to form reactants just as much as reactants react to form products.

A reaction reaches equilibrium when the rate of the forward reaction equals the rate of the reverse reaction. At this point, if nothing disturbs the equilibrium, no net product is being formed and the concentrations of each product and reactant remain constant at a given temperature. This is known as a **dynamic equilibrium**. That is, products are formed at the same rate as they are broken down.

When a reaction reaches a state of dynamic equilibrium the expression below gives a value which is constant at a given temperature. This is known as the equilibrium constant ( $K_c$ ). More of this in Lesson 2

Take equation  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ . The expression for the  $K_c$  is given below.

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

So for the reaction  $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  the expression for  $K_c$  is

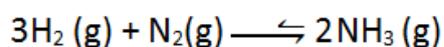
$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]}$$

When a reaction, at equilibrium, is disturbed, as long as the temperature does not change, it will respond to partially undo the change and maintain the value of  $K_c$ . This is known as Le Chatelier's principle.

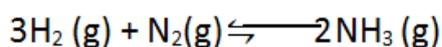
Examples follow

The system  $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  has reached equilibrium where upon:

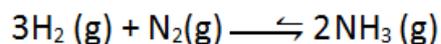
- extra  $\text{H}_2$  is added to the reaction chamber. This will result in a net forward reaction to partially remove the  $\text{H}_2$  added.



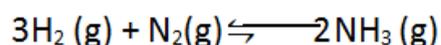
-  $\text{N}_2$  gas is removed. This will result in a net reverse reaction to undo the addition of  $\text{N}_2$



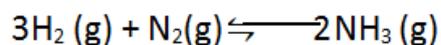
- NH<sub>3</sub> gas is removed. This will result in a net forward reaction to partially undo the change and increase NH<sub>3</sub>



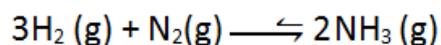
- NH<sub>3</sub> gas is added. This will result in a net reverse reaction to partially undo the change and decrease NH<sub>3</sub>



- The volume of the container is doubled and **pressure is decreased**. The reaction will move in the direction of most particles, in this case it will move in a net reverse reaction, to partially restore pressure.



- The volume of the container is halved and **pressure is increased**. The reaction will move in the direction of least particles, in this case it will move in a net forward reaction, to the number of particles and partially restore pressure.

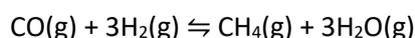


- Pressure of the reaction vessel is increased by the addition of an **inert gas**, such as helium. As the gas is not part of the reaction the reaction does not respond. Status quo prevails.

- A **catalyst** is used to increase the speed of the reaction reaching equilibrium. Since the reaction is already at equilibrium no change occurs as a catalyst acts to increase the forward and backward rates of reaction equally. Hence, status quo prevails.

**\*\* If the reaction has the same number of particles on both sides, such as  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$  then the reaction does not respond to changes in volume.**

Predict the response of the reaction, below, which is at equilibrium, to the following stresses .



- CO (g) is added
- Pressure is increased by the addition of N<sub>2</sub> gas
- Steam is removed
- Pressure is decreased when volume is doubled
- Addition of a catalyst.
- CH<sub>4</sub> gas is added.

When considering a temperature change then the value of K<sub>c</sub> will change and the reaction will move in the direction to partially either remove or increase the heat energy added or removed.

In order to see clearly how the reaction will respond it is helpful to write exothermic reactions with energy as a product  $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{Energy}$  and endothermic reactions as energy as a reactant  $\text{Energy} + \text{CH}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 2\text{H}_2(\text{g})$