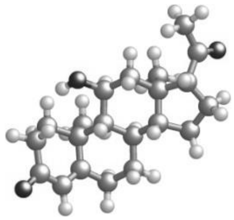

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<u>Notes on Dynamic Equilibrium</u>

What is dynamic equilibrium? Imagine that you are at Changi Airport standing at the bottom of the long escalator that will take you from the MRT station up to the departure terminal. Now imagine that you stand on the escalator. What will happen? You move in one direction – *forwards* in the direction of the departure terminal. As you approach the top of the escalator you realise, to your dismay, that you left something back at the MRT station. Without thinking, you turn and run back down the escalator. What will happen? You move in one direction – *backwards* in the direction of the MRT station. As you approach the centre of the escalator, you slow down so that the speed at which you are running back to the MRT station is equal to the speed at which the escalator is moving forwards. What will happen? To a casual observer who is standing on the stairs next to the escalator it will look like you are *stationary* – you will not be moving forwards or backwards, even though the escalator is moving and your legs are also moving. You have reached *dynamic equilibrium*!

It is a similar situation for a chemical reaction. Consider the reaction between hydrogen and iodine forming hydrogen iodide:

$$\text{hydrogen} + \text{iodine} \rightleftharpoons \text{hydrogen iodide}$$

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

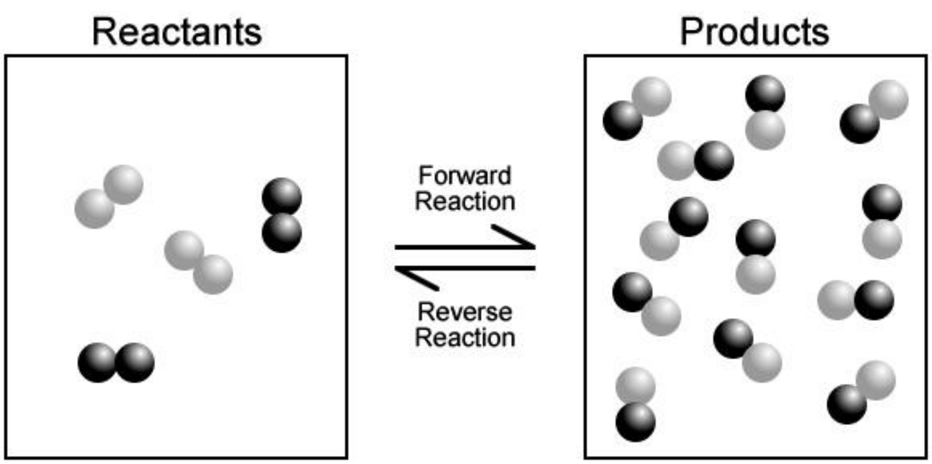
- **Note**: For reversible reactions, it is important to use the $\rightleftharpoons$ symbol instead of the $\rightarrow$ symbol to show that the reaction can move both from left-to-right and also from right-to-left.

Initially, when the hydrogen and iodine are combined together, the reaction can only move in one direction – from left-to-right. This is known as the *forward* reaction.

However, once the hydrogen iodide starts to form, it can decompose to form hydrogen and iodine once again. This reaction, moving from right-to-left, is known as the *reverse* reaction. When the rate of the forward reaction and the rate of the reverse reaction are *equal*, then the concentrations of hydrogen, iodine and hydrogen iodide will remain *constant*. On a large scale (*i.e.* to the chemist who is studying the reaction) it will look as though the reaction has stopped. However, at a molecular level, chemical reactions are still taking place. At this point the chemical reaction is said to have reached its *equilibrium* position. **Note**: equilibrium is only achieved in a *closed system* – from which nothing can escape – and only applies to *reversible reactions*.

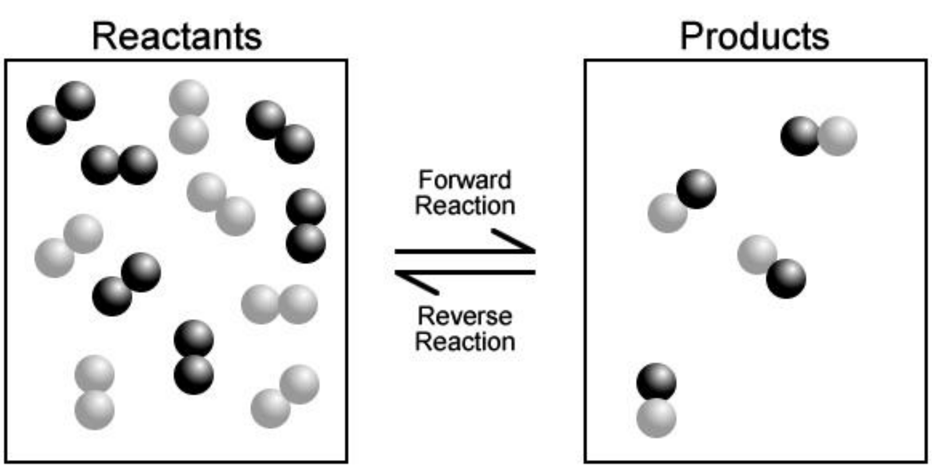
Each chemical reaction has its own equilibrium position. For some reactions, the equilibrium position lies towards the *right*, *i.e.* equilibrium is reached when a high concentration of reaction product is formed (Figure 1).

Figure 1.



For other reactions, the equilibrium position lies towards the *left*, *i.e.* equilibrium is reached when only a small concentration of reaction product is formed (Figure 2).

Figure 2.



The *equilibrium constant* (symbol K_c) for a reaction tells us whether the reaction's equilibrium position lies to the left or to the right.

$$K_c \quad = \quad \frac{\text{Concentration of Products}}{\text{Concentration of Reactants}}$$

In Chemistry, square brackets are used to represent concentration. The above equation can therefore be re-written:

$$K_c \quad = \quad \frac{[\text{ Products }]}{[\text{ Reactants }]}$$

For the chemical reaction:

$$\text{ethanoic acid + ethanol} \rightleftharpoons \text{ethyl ethanoate + water}$$

$$CH_3COOH \;+\; CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 \;+\; H_2O$$

The expression for the equilibrium constant would be written:

$$K_c \quad = \quad \frac{[\, CH_3COOCH_2CH_3 \,] \times [\, H_2O \,]}{[\, CH_3COOH \,] \times [\, CH_3CH_2OH \,]}$$

If the equilibrium constant for the reaction is *large*, then this would indicate that the concentration of the reaction products is *large* while the concentration of the reactants is *small* (a large number divided by a small number will give a large number as the result). The equilibrium position for this reaction therefore lies to the right-hand-side (Figure 1).

However, if the equilibrium constant for the reaction is *small*, then this would indicate that the concentration of the reaction products is *small* while the concentration of the reactants is *large* (a small number divided by a large number will give a small number as the result). The equilibrium position for this reaction therefore lies to the left-hand-side (Figure 2).

Is it possible to alter the equilibrium position of a reaction? For example, if a reaction's equilibrium position lies towards the left-hand-side, is it possible to move it towards the right-hand-side to increase the amount of reaction product that is formed?

Consider the scenario on the escalator at Changi Airport again. In addition to the casual observer who is standing on the stairs, you have now attracted the attention of a security guard who is standing at the top of the escalator. The security guard shouts out for you to stop running down the escalator. If you obey these instructions and stand still on the escalator, then you will move *forwards* in the direction of the departure terminal (and the security guard) and will probably have some explaining to do. If you disobey these instructions and continue to run down the escalator, then you will move *backwards* in the direction of the MRT station where you can search for the item that you left there. What will happen? You will probably do the exact opposite to what the security guard asked you to do. The security guard wanted you to move *forwards*, towards them. You chose to run *backwards*, away from them.

In a similar way, it is possible to alter the equilibrium position of a chemical reaction (shift it more to the left or more to the right) by altering variables such as temperature, concentration and pressure. How these changes will affect the equilibrium position of the chemical system can be predicted by *Le Chatelier's theory*.

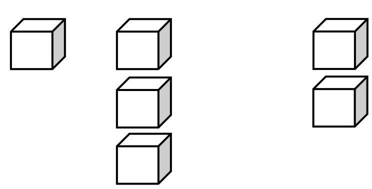
> *Le Chatelier's theory* states that *whatever chemical or physical change is imposed upon a chemical system, the equilibrium position of the chemical system shifts to oppose or minimise the change*.

Consider the example below:

nitrogen + hydrogen $\rightleftharpoons$ ammonia

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

4 volumes (moles) of gas.



2 volumes (moles) of gas.

In the forward direction (left-to-right) the reaction is *exothermic* (gives off energy therefore causing a rise in temperature). The boxes below each of the chemicals represents a volume (mole) of gas.

• If the *temperature* of this system was *increased*, the equilibrium position would shift to *reduce* the temperature by moving in the *endothermic* (energy absorbing) direction, which is from right-to-left.
• If the *pressure* of this system was *increased*, the equilibrium position would shift to *reduce* the pressure by moving towards the side of the equation which has the smaller volume (moles) of gas, which is from left-to-right.
• Note: the addition of a *catalyst* only *increases the rate* of a chemical reaction, it does *not* affect the equilibrium position.

Questions

The balanced chemical equation for the decomposition of phosphorus(V) chloride, PCl_5, is given below:

phosphorus(V) chloride $\rightleftharpoons$ phosphorus(III) chloride + chlorine

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

The equilibrium constant, K_c = 0.19 mol dm^{-3} at 250°C. At equilibrium the mixture contains 0.200 mol dm^{-3} PCl_5 and 0.010 mol dm^{-3} PCl_3.

1. Write an expression for the equilibrium constant, K_c.

2. Calculate the equilibrium concentration of Cl_2 and state the units.

3. How will *reducing* the pressure affect the equilibrium position of this reaction?

- Click on the QR code below for the answers to this assignment.

http://www.chemist.sg/ammonia_equilibrium/equilibrium_notes_ans.pdf