HSC Chemistry – Module 5: Equilibrium & Acid Reactions – Factors that Affect Equilibrium Study Notes

Inquiry question: What factors affect equilibrium and how?

Students:

- investigate the effects of temperature, concentration, volume and/or pressure on a system at equilibrium and explain how Le Chatelier's principle can be used to predict such effects, for example:
  - heating cobalt(II) chloride hydrate
  - interaction between nitrogen dioxide and dinitrogen tetroxide
  - iron(III) thiocyanate and varying concentration of ions
- explain the overall observations about equilibrium in terms of the collision theory
- examine how activation energy and heat of reaction affect the position of equilibrium

Le Chatelier's Principle

Le Chatelier's Principle states that a closed system will stay at equilibrium, unless there is a **disturbance**. When there is a disturbance, the equilibrium will **shift** its position to minimise the effects of the disturbance.

An equilibrium as learnt in the previous chapter is a reversible reaction. In an equilibrium both reactants and products are present in the system, but at different amounts corresponding to the type of chemical reaction. You must remember that in an equilibrium **rate of forward reaction = rate of reverse reaction**.

The equilibrium can shift forward (right) or reverse (left) to minimise this disturbance.

Note: Le Chatelier's Principle will only take effect in closed systems, not open systems.

There are many factors that can affect the position of the equilibrium, and these include:

1. Concentration
2. Pressure and/or volume
3. Temperature

Concentration

In a system, you can either add or remove concentrations of a substance(s). This can either be the reactants or products.

$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$

In this equilibrium, you can either add or remove concentrations of $CO_{2(aq)}$ and $H_2CO_{3(aq)}$. It is important to note that **only** changing the concentrations of **aqueous solutions** and **gas** will affect the position of the equilibrium. Changing the amount of liquids and solids will not affect the position of the equilibrium as they do not have concentrations (water does not have a concentration. In an equilibrium graph, a change in concentration is denoted by a sudden drop/increase of the particular species.

According to Le Chatelier's Principle, if a concentration of a substance is added, then it will shift to the side to reduce the extra amount. For example, if $CO_{2(aq)}$ is added to the system this will increase its concentration. To remove the extra $CO_{2(aq)}$, the equilibrium will shift to the right-hand side, as it will remove $CO_{2(aq)}$. However, if $CO_{2(aq)}$ was taken out of the system, effectively removing the concentration, then the equilibrium will shift to the left-hand side as it will produce more $CO_{2(aq)}$ to minimise the loss.

In essence, if you add concentration of a substance, the equilibrium will shift to the opposite side where this species is not present. However, if you remove concentration of a substance, the equilibrium will shift to that same side where the species is present.

Pressure

In a system, you can change the pressure by either increasing or decreasing the volume. Pressure is inversely proportional to volume, meaning that if you half the volume then you double the pressure and vice versa.

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

You can either increase or decrease the pressure, by decreasing or increasing the volume of the system respectively. It is important to note that changing the pressure will only affect **gaseous states**. Change in pressure is denoted on an equilibrium graph by a sudden drop/increase in concentration of all gaseous species.

According to Le Chatelier's Principle, if there is a change in pressure, the equilibrium will shift to minimise the change. If the pressure was increased, then the equilibrium will move to the side with **less** moles of gas to remove the pressure. As there are 2 moles of gas on the right-hand side, and 4 moles of gas on the left-hand side, then the equilibrium will shift to the right. If the pressure was decreased, then the equilibrium will move to the side with **more** moles of gas to increase the pressure. Therefore, it will shift to the left-hand side as there are 4 moles of gas. If both sides have the same moles of gases, then the equilibrium will not shift whether the pressure is increased or decreased.

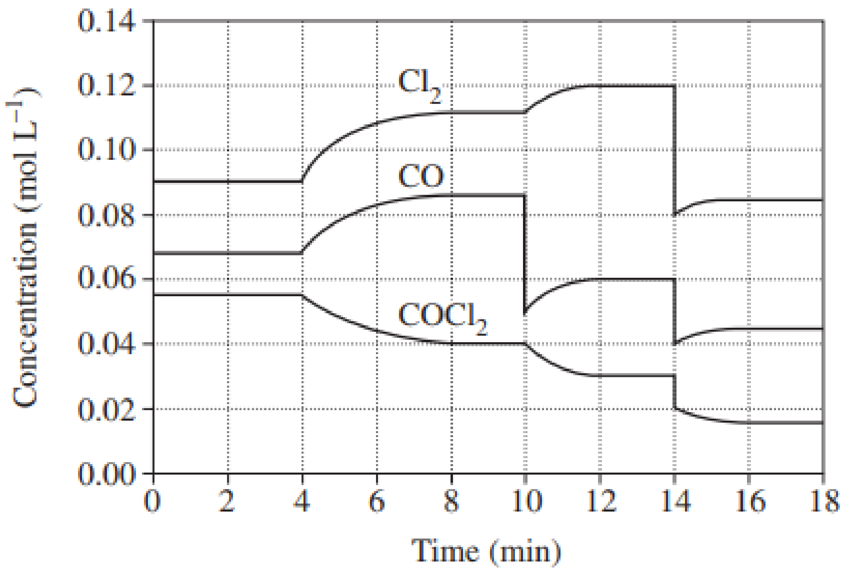
Temperature

In a system, you can change the temperature by either increasing or decreasing it.

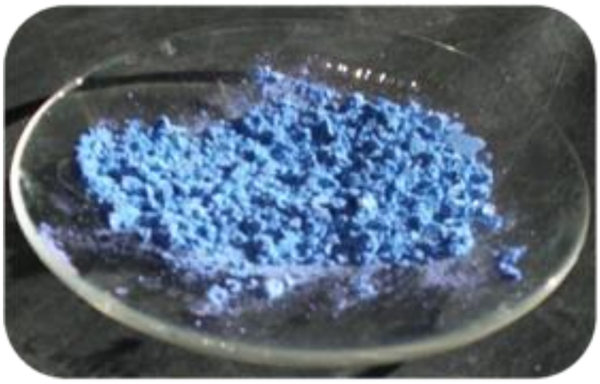
$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \quad \Delta H>0$$

Again, only **gaseous** and **aqueous states** will be affected in the equilibrium. Change in temperature is denoted on an equilibrium graph by gradual increase/decrease in concentration of all aqueous and gaseous species.

According to Le Chatelier's Principle, if there is a change in temperature, the equilibrium will shift to minimise the change. If the temperature was increased, then the equilibrium will move to the endothermic side. As this is an exothermic reaction, the left-hand side is endothermic and so the equilibrium will shift to the left-hand side. If the temperature was decreased, then the equilibrium will move to the exothermic side, which is the right-hand side.



Heating cobalt(II) chloride hydrate



Anhydrous Cobalt(II) Chloride

Cobalt(II) Chloride Hexahydrate

$CoCl_2.6H_2O_{(s)} \rightleftharpoons CoCl_{2(s)}$

As stated in the earlier chapter, hydrous cobalt(II) chloride is pink in colour, whilst anhydrous cobalt(II) chloride is blue in colour. Heat and presence of water will affect the position of the equilibrium.

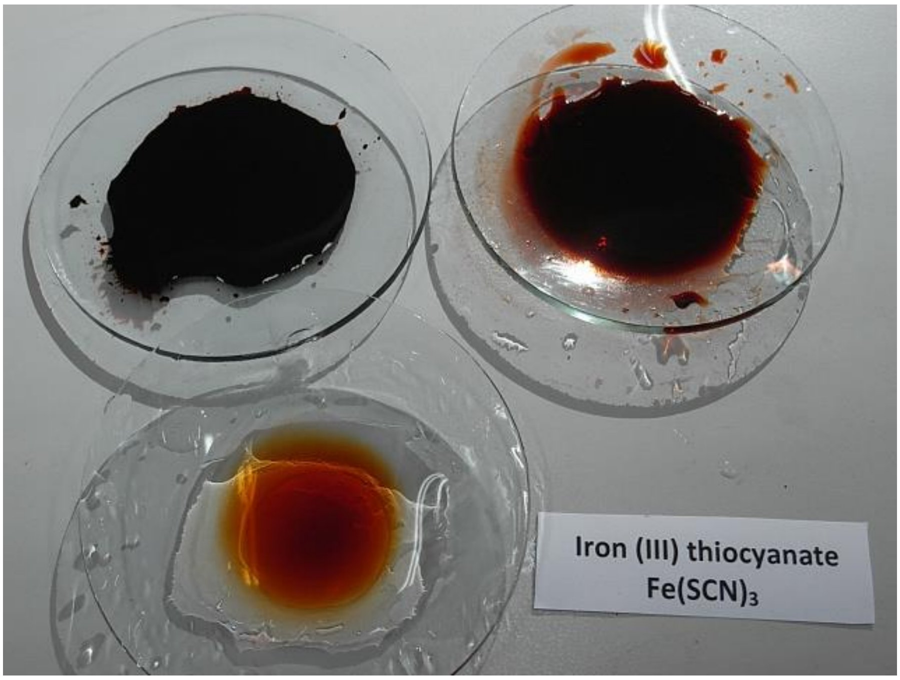
Nitrogen dioxide and dinitrogen tetroxide

$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ $\Delta H>0$

$NO_{2(g)}$ is brown in colour and $N_2O_{4(g)}$ is colourless. These two are in an equilibrium, and is easily affected by concentration, pressure and temperature.

- As more $N_2O_{4(g)}$ is added, this increases its concentration. Consequently, the equilibrium will favour the reverse reaction and produce more $NO_{2(g)}$. This increases the brown colour. If $N_2O_{4(g)}$ is removed from the system, this decreases its concentration. Consequently, the equilibrium will favour the forward reaction and produce more $N_2O_{4(g)}$. This will decrease the brown colour as $NO_{2(g)}$ is being removed from the equilibrium.
- As more $NO_{2(g)}$ is added, there will be an initial increase in the brown colour. As the equilibrium shifts to the right, there will be a decrease in the brown colour. However, the final brown colour will be slightly darker than the original colour. As $NO_{2(g)}$ is removed, there will be an initial decrease in the brown colour. As the equilibrium shifts to the left, there will be a decrease in the brown colour. However, the final brown colour will be slightly lighter than the original colour.
- If the pressure is increased, the equilibrium will shift to the right-hand side as there are less moles of gas on that side. This will decrease the brown colour. If pressure is decreased, the equilibrium will shift to the left-hand side as there are moles of gas. This will increase the brown colour.
- If the temperature is increased, the equilibrium will shift to the endothermic side. As this reaction is exothermic, the left-hand side is endothermic causing there to be an increase in brown colour. If the temperature is decreased, the equilibrium will shift to the exothermic side, which is the right-hand side causing there to be less of a brown colour.

Iron(III) thiocyanate and differing concentration of ions.



$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$

Fe^{3+} is yellow in colour, SCN^- is colourless and $FeSCN^{2+}$ is blood-red.

- If the concentration of SCN^- is increased, then the equilibrium will shift to the right-hand side. This will increase the blood-red colour.
- If the concentration of SCN^- is decreased, then the equilibrium will shift to the left-hand side. This will decrease the blood-red colour and increase the yellow colour.
- If the concentration of Fe^{3+} is increased, then initially there would be a sudden increase in the yellow colour. However, the equilibrium will shift to the right and it will increase the blood-red colour.
- If the concentration of Fe^{2+} is decreased, then initially there would be a sudden decrease in the yellow colour. However, the equilibrium will shift to the left and it will decrease the blood-red colour.
- If the concentration of $FeSCN^{2+}$ is increased, then there would be an initial increase in the blood-red colour. Afterwards, the equilibrium will shift to the left and decrease that colour, however, it will still be slightly stronger than the original colour.
- If the concentration of $FeSCN^{2+}$ is decreased, then there would be an initial decrease in the blood-red colour. Afterwards, the equilibrium will shift to the right and increase that colour, however, it will still be slightly lighter than the original colour.

Collision Theory and Equilibrium

Recall that collision theory and rate of reaction had a strong relationship. There is also a strong relationship between collision theory and equilibrium.

Concentration

If the concentration of the reactants is increased, there would be a higher chance of collisions and hence higher numbers of successful collisions. If there are more successful collisions, then more products are made and hence the equilibrium is pushed to towards the forward reaction. If products are increased, then it will shift towards the reverse reaction. The opposite is true if you decrease concentration.

Pressure

If the pressure of the system is increased, then there is less volume for the reactants and products to interact. As a result, because there are more moles of gas on one side, then that side will have more successful collisions and will push the equilibrium to the opposite side. Hence, increasing pressure will shift the equilibrium to the side with less moles of gas. The opposite is true if you decrease the pressure.

Temperature

If the temperature of the system is increased, then there will be an increase in the number of species undergoing the endothermic reaction that will have their collision energy equal to or greater than the activation energy. This number will be greater than the amount undergoing the exothermic reaction. As there is more in the endothermic reaction that is reaching the activation energy, then there will be more successful collisions shifting the equilibrium to the endothermic side. The opposite will be the case if the temperature was decreased.

Activation Energy and Equilibrium

Recall that activation energy is the energy required to break the chemical bonds of the reactants and reform as products.

Lowering the activation energy will mean that the equilibrium is **reached faster**, but it **does not affect** the position of the equilibrium. Effectively, it only increases the rate of reaction.

Using a catalyst will only affect the activation energy, not the position of the equilibrium.