qChemical Equilibrium

What is Equilibrium?

In Chemistry, a system is said to be at equilibrium when ………………………………………………………………..

……………………………………………..………………………………………………………………………..

For example:

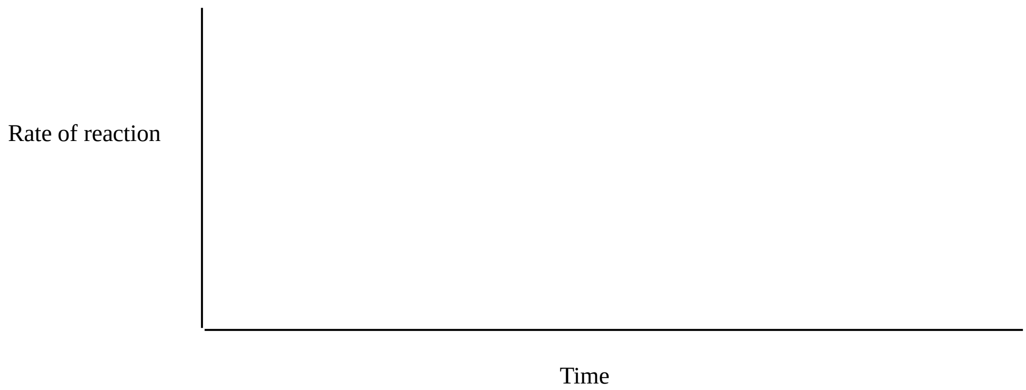
a) when a large amount of salt is added to water - the amount of solid salt present ……………………

This continues until a saturated solution is formed and the amount of solid present …………………………

When the mixture reaches this stage, the system is said to be at …………………………

This process can be explained in terms of the reaction ……………………….

When the solid is first added to the water, the rate of dissolving i.e. $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ is ………………, but as the solid's surface area decreases, the rate of dissolving will ……………………



However, a second reaction also occurs …………….. + ………………. → …………………

At the beginning, the amount of dissolved ions is very …………………. and so the rate of this reaction is very …………………., but as more NaCl dissolves, the rate of this reverse reaction ……………………..

Finally a balance stage will be reached where the rates of the ……………………. and …………………… reactions become …………………….

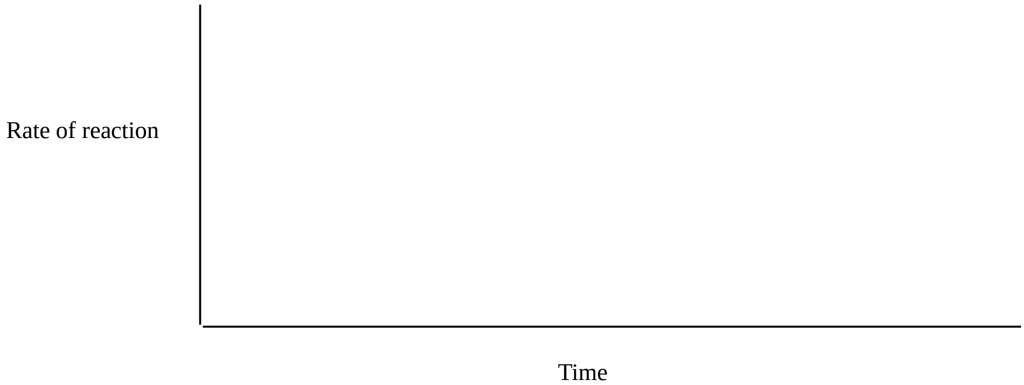
At this point the system is at ………………………………. and because the rate at which the solid ……………………… is equal to the rate at which it …………………….., the amount of solid present remains ………………………….

If you are looking at the container of the saturated mixture (i.e. examining the ………………………… properties), ………………….appears to be changing. However, at the ………………………… level, the forward and reverse reactions are still occurring. When this occurs, the system is said to be at ………………………. equilibrium.

b) when $Fe^{2+}(aq)$ is mixed with $SCN^{-}(aq)$ - the colourless solution quickly changes to a ………………. colour and this colour remains the same with time i.e. ……………………….. has been reached.

These two ions react according to the equation …………… + …………… → ………………….

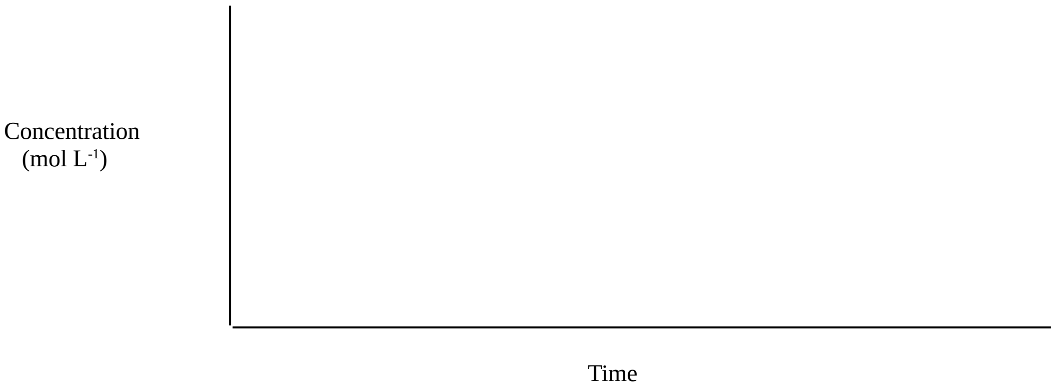
When the ions are first mixed, their concentration are rather …………………. and so the rate of this reaction is …………………….. but, as the reaction proceeds, their concentrations …………………… and so the reaction rate ……………….



However, this reaction is reversible i.e. the reaction………………. → ……………. + …………….. can occur. Initially the rate of this reaction is very …………………., but as the concentration of $FeSCN^{+}$ becomes …………………… the rate of the reverse reaction ……………………….

Finally a stage is reached where the ……………………………………………………………………… …………………………… and the amount of red …………….. remains constant with time. That is ………………………………… is reached.

A <u>concentration-time graph</u> can also de drawn to show the establishing of this equilibrium system. Assume that the initial concentration of Fe^{2+} is 0.1 mol L^{-1} and the initial concentration of SCN^{-} is 0.2 mol L^{-1}



In summary: when a <u>reaction is at equilibrium</u>:

- the amounts or concentrations of the ……………………. and the ……………………. remain …………………………………………..
- the rates of the ………………………………………………………………………………………..

The Equilibrium Law

If the reaction system $Fe^{2+}(aq) + SCN(aq) \rightleftharpoons FeSCN^{+}(aq)$ is at equilibrium at a certain temperature then the fraction

$$\frac{\qquad\qquad}{\qquad\qquad}$$

has a constant value despite how the mixture was formed.

This fraction is called the …………………………… …………. ……………………………. and its constant value is called the …………………….. …………………….. (K) of this reaction at the specific temperature.

The equilibrium law states that the value of the equilibrium law expression for a reaction will be a ……………….. ………………………… at a specific temperature.

Other examples of equilibrium law expressions are:

- for the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ K =

- for the reaction $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$ K =

- for the reaction $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$ K =

- for the reaction $CO_3^{2-}(aq) + 2H^{+}(aq) \rightleftharpoons CO_2(g) + H_2O(l)$ K =

- for the reaction $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ K =

- for the reaction $Al_2(CO_3)_3(s) + 6H^{+}(aq) \rightleftharpoons 2Al^{3+}(aq) + 3CO_2(g) + 3H_2O(l)$ K =

Note: ……………… or …………… ………………………… are not included in the equilibrium law expression.

Characteristics of the equilibrium constant:

a) it has a ………………….. ……………………..at a given temperature. If the temperature is changed, the value of the constant also ……………………..

b) it indicates the relative proportions of the …………………… and ……………………. present in the equilibrium mixture.
If K is very ………………………… then the reaction is essentially complete. But if K is very …………………. then the reaction would be almost insignificant.

c) the value of K gives no indication of the reaction…………………. i.e. how quickly the reaction reached …………………………..

<u>Predicting the effect of changes to equilibrium systems</u>

If changes such as …………………………………, ……………………………. or ………………………………are made to a system at equilibrium, the system is often put out of ……………………………..

Le Chatelier's Principle can be used to predict what needs to happen for the system to 'get back to' equilibrium again.

> **If a system at equilibrium is subjected to a change in conditions, the system will adjust to re-establish equilibrium in such a way as to partially counteract (oppose) the imposed change.**

<u>1. Addition a reactant or product</u>

a) Consider the equilibrium system $Fe^{2+}(aq) + SCN(aq) \rightleftharpoons FeSCN^{+}(aq)$.

If **more Fe^{2+}(aq) is added** (without significantly changing the volume) to the equilibrium mixture (system)

i) is the system put out of equilibrium?

ii) how do you know?

iii) using Le Chatelier's principle, predict what will happen to the added Fe^{2+} as the system re-establishes equilibrium?

iv) i.e. what direction will the system move to get back to equilibrium?

v) what will happen to the amount of $FeSCN^{+}$ and SCN^{-} during the re-establishment of equilibrium?

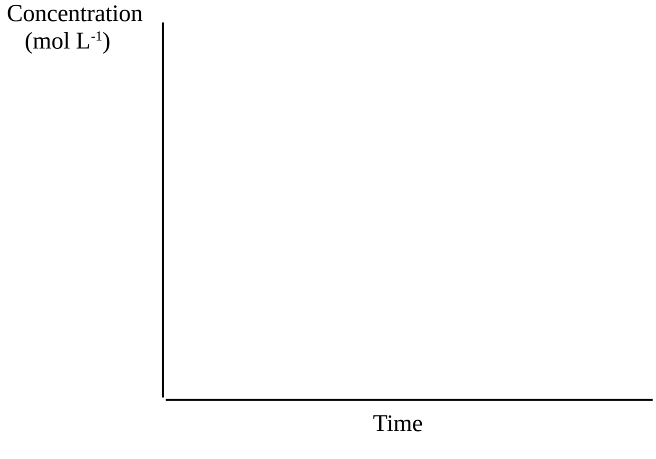
vi) for the new equilibrium mixture, will the following have increased, decreased or remain unchanged compared to that in the original equilibrium mixture

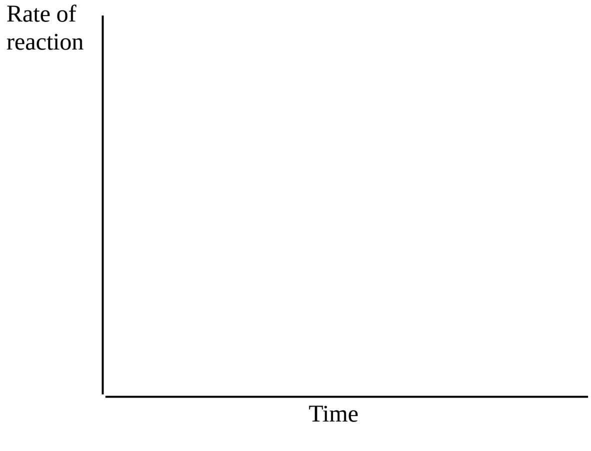
the mass of $FeSCN^{+}$?

the mass of SCN^{-}?

the mass of Fe^{2+}?

the equilibrium constant?





b) Consider the equilibrium system $Fe^{2+}(aq) + SCN(aq) \rightleftharpoons FeSCN^{+}(aq)$.

If **more $FeSCN^{+}$(aq) is added** (without significantly changing the volume) to the equilibrium mixture (system)

i) is the system put out of equilibrium?

ii) i.e. what direction will the system move to get back to equilibrium?

iii) for the new equilibrium mixture, will the following have increased, decreased or remain unchanged compared to that in the original equilibrium mixture

the mass of Fe^{2+}? the mass of SCN^{-}?

the mass of $FeSCN^{+}$? the equilibrium constant?

c) Consider the equilibrium system $Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^{+}(aq)$

If a few drops of concentrated **HCl are added** to the equilibrium mixture (system)

i) is the system put out of equilibrium?

ii) i.e. what direction will the system move to get back to equilibrium?

iii) for the new equilibrium mixture, will the following have increased, decreased or remain unchanged compared to that in the original equilibrium mixture

the conc of $Cr_2O_7^{2-}$? the conc of $2CrO_4^{2-}$?

the conc of H^{+}? the equilibrium constant?

iv) how will the colour of the mixture change?

d) The following equilibrium is set up in a sealed rigid container:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

What effect will increasing the partial pressure of Cl_2 have on the concentration of H_2 and HCl?

e) The following equilibrium is set up in a beaker $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$

What effect will the following changes have on the concentration of Cl^{-} in the mixture?

i) adding more solid AgCl

ii) adding a few drops of concentrated silver nitrate solution

iii) adding a few drops of concentrated HCl

2. Removing a reactant or product

a) Consider the equilibrium system $Fe^{2+}(aq) + SCN(aq) \rightleftharpoons FeSCN^{+}(aq)$.

If **a few drops of concentrated NaOH solution is added** (without significantly changing the volume) to the equilibrium mixture (system)

i) is the system put out of equilibrium?

ii) how do you know?

iii) using Le Chatelier's principle, predict what will happen to the concentration of Fe^{2+} as the system re-establishes equilibrium?

iv) i.e. what direction will the system move to get back to equilibrium?

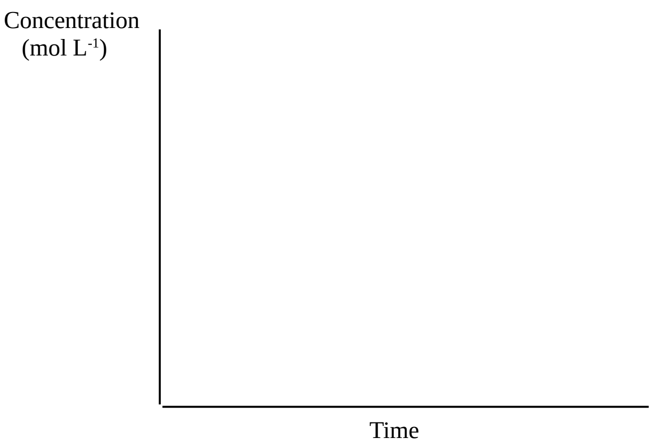
v) what will happen to the amount of $FeSCN^{+}$ and SCN^{-} during the re-establishment of equilibrium?

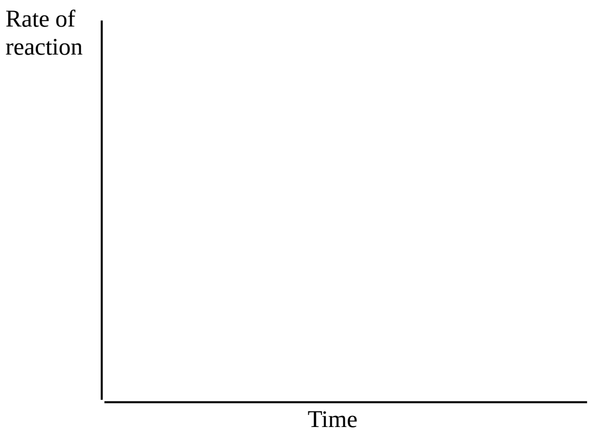
vi) for the new equilibrium mixture, will the following have increased, decreased or remain unchanged compared to that in the original equilibrium mixture

the mass of $FeSCN^{+}$? the mass of SCN^{-}?

the mass of Fe^{2+}? the equilibrium constant?

vii) What colour change will occur because of the addition of the NaOH solution?





b) Consider the equilibrium system $Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^{+}(aq)$

If a few drops of concentrated **NaOH are added** to the equilibrium mixture (system)

i) is the system put out of equilibrium?

ii) i.e. what direction will the system move to get back to equilibrium?

iii) for the new equilibrium mixture, will the following have increased, decreased or remain unchanged compared to that in the original equilibrium mixture

the conc of $Cr_2O_7^{2-}$?   the conc of $2CrO_4^{2-}$?

the conc of H^+?   the equilibrium constant?

iv) how will the colour of the mixture change?

c) For the equilibrium mixture $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ what would be the effect of the following changes on the concentrations of the three substances (assume temperature and volume remain constant)?

i) addition of some $N_2(g)$ (sometimes expressed as "increase in the partial pressure of N_2")

ii) removal of some $H_2(g)$

iii) addition some $NH_3(g)$

iv) addition of a small amount of water

3. Changing the temperature

a) Revision:

i) Consider the following system: $2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H = -57\ kJ$

1) is the forward reaction exothermic or endothermic?

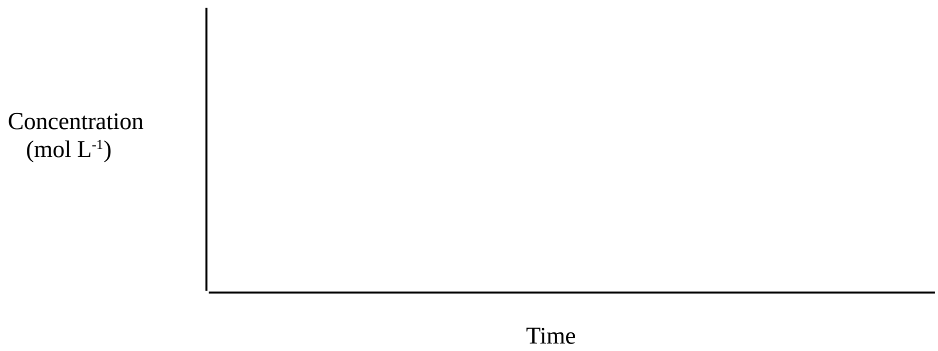
2) when the forward reaction occurs, will heat energy be produced or absorbed by the system?

3) rewrite the equation showing the ‘heat’ as part of the equation

b) A change in ………………………………….. will always put a system out of equilibrium

c) When the equilibrium system $2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H = -57\ kJ$ is cooled, the following can be predicted using Le Chatelier’s principle:

If the temperature is decreased, that is, heat is ……………….. removed, the system will adjust by trying to ………………….. ………………… heat. To do this it would have to move in the …………………….. direction. This would result in a ……………………….. in the amount (mass and concentration) of NO_2 present and a ……………………. in the amount (mass and concentration) of N_2O_4 present.



If the equilibrium system is heated, the equilibrium position moves towards the ………….. (in an attempt to …………………. the added heat). This would result in an increase in the concentration of …………………………… and a decrease in the concentration of …………………………

In summary:

- if an equilibrium system is heated, the equilibrium position will move in the ……………………………….direction
- if an equilibrium system is cooled, the equilibrium position will move in the ……………………………….direction

d) Other examples

Predict the effect of the given temperature change on the substances present in the following equilibrium systems.

i) $CaCO_3(s) + 179\ kJ \rightleftharpoons CaO(s) + CO_2(g)$ - temperature is increased i.e. the reaction mixture is heated

ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\ kJ$ - temperature is decreased

iii) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = +52$ kJ - temperature is decreased

e) <u>Another example</u>:

When hydrogen reacts with nitrogen, the following equilibrium system is obtained:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ}$$

Predict the effect of the following changes on the concentration of the NH_3 :

i) the partial pressure of N_2 is increased

ii) some H_2 is removed

iii) a few drops of concentrated HCl is added

iv) the temperature is increased

v) some argon gas is added at constant volume

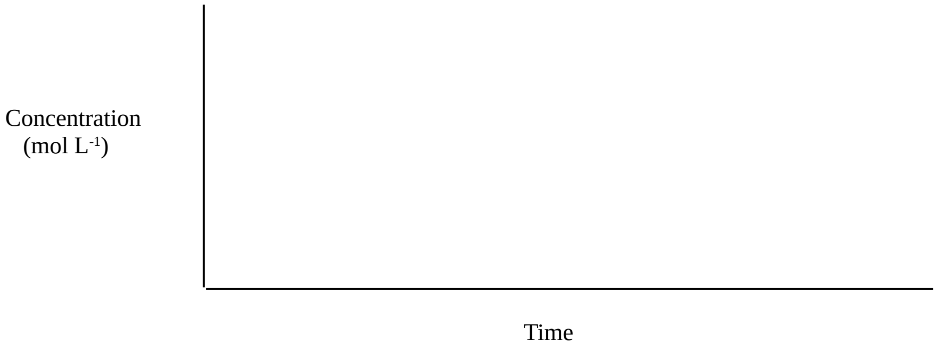
4. <u>Changing the volume</u> of the equilibrium system

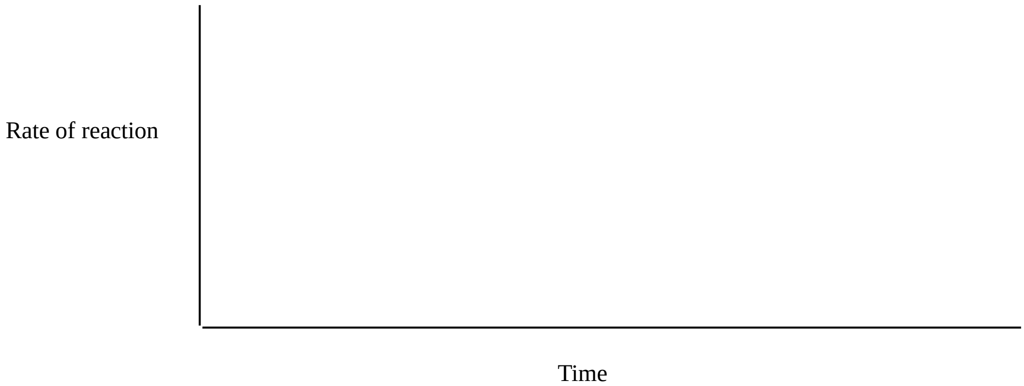
When the volume of the equilibrium mixture $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

- is decreased, the following colour change occurs: ……………………… then ………………………………

This colour change can be explained as follows:

When the volume of the system is decreased, an ……………………. in the pressure will occur. The system tries to oppose this change by ……………………. the pressure. The only way this can be done is by ………………………. the number of particles present. This could be achieved by the ………………… reaction occurring quicker than the ………………….. reaction. This would result in an ………………… in the mass of N_2O_4 and a ……………… in the mass of NO_2. However, the change is never completely opposed, and so the concentrations of both N_2O_4 and NO_2 remain ………………. than before the change i.e. the mixture will be …………… than before the change.





NOTE: - a change in volume of an equilibrium system in a liquid e.g. $Fe^{2+}(aq) + SCN(aq) \rightleftharpoons FeSCN^{+}(aq)$ can not be explained in terms of pressure using Le Chatelier's principle. If you attempt to use "change in volumes" with Le Chatelier's principle - you will get the wrong answer. Probably the quickest way to work out your answer is to remember

- if the volume of the system is increased, the system moves towards the side of the reaction with the ……………….. number of particles (shown in the equation)
- if the volume of the system is increased, the system moves towards the side of the reaction with the ……………….. number of particles (shown in the equation)

<u>**BUT**</u> if the equilibrium reaction being investigated contains the same number of particles (not including ……………. and pure ………………..) on both sides of the equation, such as $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ then a change in volume will not put the system out of ………………………….. . The concentrations of the substances will be altered, but the mass of the substances present will not be ……………………..

Examples:

For each of the following equilibrium systems, state the effect of the volume change on the mass and concentration of the substances present:

i) $Fe^{2+}(aq) + SCN(aq) \rightleftharpoons FeSCN^{+}(aq)$ - volume is increased

ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ - volume is decreased

iii) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ - volume is increased

5. Addition of a catalyst

Adding a catalyst to a system at equilibrium does not put the system out of ………………………… i.e. there will be no ……………………. in the amounts of products and reactants present. However, the rates of both the forward and reverse reactions will have been ………………………… equally.

The only way a catalyst may help is that it will allow the system to reach equilibrium …………………

6. Addition of an inert gas, such as …………………………. at constant volume

- this will have ……………………………… on an equilibrium system.

7. Addition of an inert gas at constant pressure

- to keep the pressure constant, the volume of the system must increase - this will drive the equilibrium system towards the side of the equation with the ……………………… number of particles

Examples:

When copper hydroxide very slightly dissolves in water, the following equilibrium is set up:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^{-}(aq) \qquad \Delta H = -12 \text{ kJ}$$

Comment on the solubility of copper hydroxide in water when the following changes are made:

i) the temperature is decreased

ii) some water is added

iii) some solid $Cu(OH)_2$ is added

iv) a few drops of a concentrated solution of $CuSO_4$ is added

v) a few drops of concentrated HCl is added

Compare the solubility of $Cu(OH)_2$ in water with its solubility in a solution of sodium hydroxide and in a solution of HCl.