4. Chemical equilibria

Reversible Reactions

We are already familiar with reactions that are one way. They 'go to completion' and the products do not change back into the reactants.

eg $$Mg_{(s)} + 2H^{+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$

However, there are many reactions in which the products can react to reform the reactants. They are called reversible reactions.

eg heating hydrated cobalt chloride, $CoCl_2.6H_2O$

$$\underset{\text{pink}}{CoCl_2.6H_2O} \xrightarrow{\text{heat}} \underset{\text{blue}}{CoCl_2 + 6H_2O}$$

The pink hydrated form returns when water is added

$$CoCl_2 + 6H_2O \longrightarrow CoCl_2.6H_2O$$

Such a reaction can be shown using reversible arrows

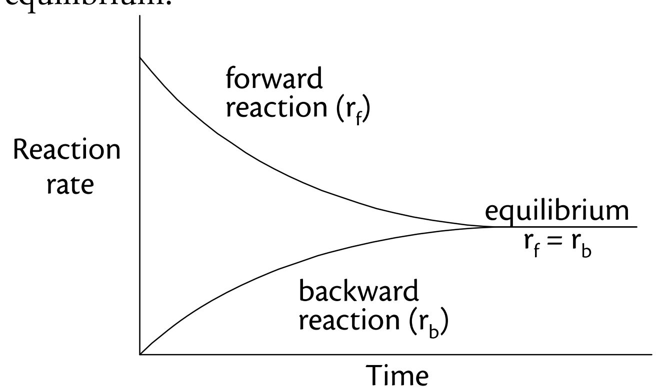
$$CoCl_2.6H_2O \rightleftharpoons CoCl_2 + 6H_2O$$

Reversible reactions give rise to a situation called equilibrium.

Consider the general reversible reaction:

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

If we start with A and B an allow them to react then, initially, the rate of the forward reaction, r_f, is high because the concentrations of A and B are high. The rate of the back reaction, r_b, is zero initially because the concentrations of C and D are zero. As the reaction proceeds the concentrations of A and B decrease while the concentrations of C and D increase. This means r_f falls and r_b increases. This continues until the two rates become equal. At this point the concentration of A, B, C and D do not change and the system is in chemical equilibrium.

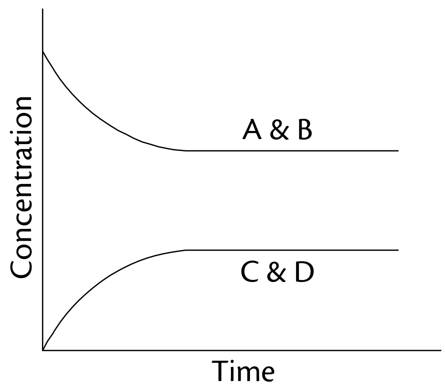


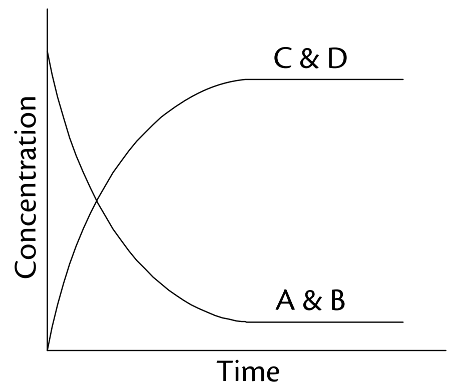
At the molecular level the forward and backward reactions are continuing but, because their rates are equal, the concentrations of the four substances remain constant. This is called dynamic equilibrium.

Note that equilibrium is reached only in a closed system. This means that no substances are added or removed.

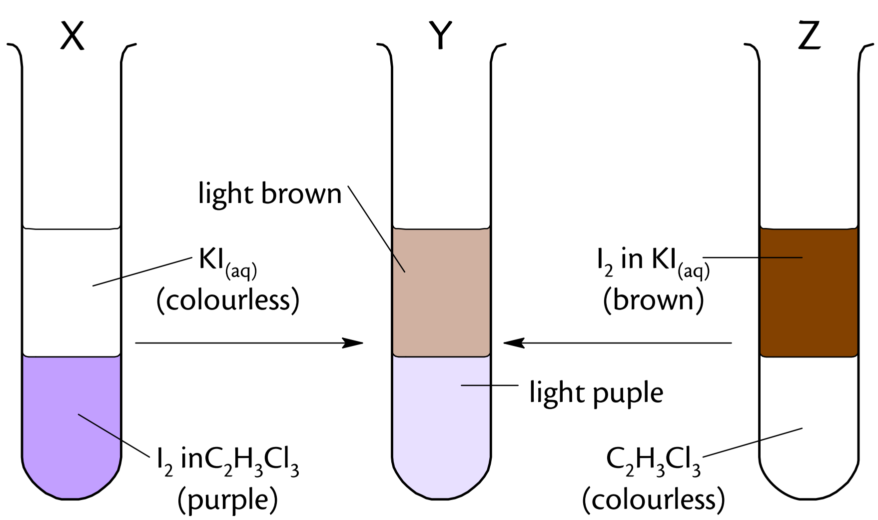
Position of Equilibrium

It is important to realise that a system in equilibrium does not imply 50% reactants and 50% products – this would be a rare occurrence. In some cases equilibrium is established when the forward reaction is nearly complete – we say that the equilibrium lies to the right. In other cases equilibrium is reached when the forward reaction is barely started. Such an equilibrium lies to the left. The two graphs below show how the concentrations of A, B, C and D might vary with time as equilibrium is being established. In the left graph the concentrations of A and B are greater than C and D at equilibrium so this equilibrium lies to the left. In the right graph the concentrations of A and B are less than C and D at equilibrium so this equilibrium lies to the right.





For a reaction, the same equilibrium position is reached whether we start from the 'reactants' or the 'products'. In the above example under the same conditions the same equilibrium position would have been reached if we had started with C and D. This can be shown using the fact that iodine is soluble in trichloroethane ($C_2H_3Cl_3$) and also in aqueous potassium iodide solution. Tubes X and Z represent the 2 starting positions. Tube Y represents the same equilibrium position attained from the 2 starting points.



Source : http://ciseche10.files.wordpress.com/2013/12/4-chemical-equilibria.pdf