To study the shift of equilibrium between ferric ions and thiocyanate ions by increasing the concentration of either of them.

Theory

When a system in equilibrium is suddenly disturbed, it will respond in some way until equilibrium is re-established. Consider the equilibrium between ferric ions and thiocyanate ions:

$$\underset{\text{pale yellow}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{deep red}}{[Fe(SCN)^{2+}(aq)} \quad ...(7.2)$$

The equilibrium constant for the above reaction can be written as

$$K = \frac{[Fe(SCN)]^{2+}}{[Fe^{3+}][SCN^{-}]} \quad ...(7.3)$$

where $[Fe(SCN)]^{2+}$, $[Fe^{3+}]$ and $[SCN^{-}]$ are the equilibrium concentrations of the respective species while K is the equilibrium constant. For a particular reaction the value of K is constant at a particular temperature. When concentration of any species involved in the equilibrium is disturbed, the concentration quotient,

$$\frac{[Fe(SCN)]^{2+}}{[Fe^{3+}][SCN^{-}]}$$

remains no longer equal to K. In order to re-establish the equilibrium, the ions interact in such a way so that the concentration quotient again becomes equal to the equilibrium constant K.

(a) **Effect of increasing concentration of ferric ions.** When ferric chloride solution is added to the red solution containing ferric ions, thiocyanate ions and ferric-thiocyanate complex, concentration of ferric ions increases and therefore, the concentration of thiocyanate ions should decrease or that of $[Fe(SCN)]^{2+}$ should increase so as to keep concentration quotient equal to equilibrium constant at a given temperature. Therefore, increase in concentration of ferric ions results in more of thiocyanate ions combining with ferric ions to give more of $[Fe(SCN)]^{2+}$ complex and therefore, the colour intensity of red-solution increases. Thus, increase in concentration of Fe^{3+} ions shifts the above equilibrium in the forward direction.

(b) **Effect of increasing concentration of thiocyanate ions.** Since thiocyanate ion is in the denominator in the equilibrium law equation, the addition of more and more of thiocyanate results in more of ferric ions reacting with thiocyanate ions to give more of $[Fe(SCN)]^{2+}$ complex. Hence, the colour intensity of red-solution increases. Thus, increase in the concentration of SCN^- ions shifts the above equilibrium in the forward direction.

(c) **Effect of increasing the concentration of potassium ions.** When potassium chloride is added to the red solution, concentration of K^+ ions increases. It affects the equilibrium between potassium and thiocyanate ions.

$$KCNS \rightleftharpoons K^+ + SCN^- \qquad ...(7.4)$$

$$KCl \longrightarrow K^+ + Cl^- \qquad ...(7.5)$$

Increase in concentration of K^+ ions shifts the equilibrium (7.4) in the backward direction. This results in decrease in concentration of SCN^- ions which in turn shifts the equilibrium (7.2) in the backward direction. In other words, some of the $[Fe(SCN)]^{2+}$ complex dissociates to give Fe^{3+} ions and SCN^- ions. Due to decrease in concentration of $[Fe(SCN)]^{2+}$ the intensity of red colour decreases. Thus increase in concentration of K^+ ions shifts the above equilibrium in the backward direction.

Requirements

(a) **Apparatus.** Test tubes, test tube stand, droppers, glass rod, beakers, weight box, measuring flask and measuring cylinders.

(b) **Chemicals.** Ferric chloride (0.1 M), potassium thiocyanate (0.1 M) and potassium chloride (0.1 M).

Procedure

1. Take a 250 ml beaker thoroughly washed and clean.
2. Put 10 ml of 0.1 M $FeCl_3$ solution in it by using a measuring cylinder.
3. Add 10 ml of 0.1 M KSCN solution with the help of measuring cylinder.
4. A deep red colour is obtained due to complex formation $[Fe(SCN)]^{2+}$ (aq).
5. Dilute the above deep red solution by adding 50 ml of distilled water.
6. Take four test tubes and label them as A, B, C and D. Add 10 ml of the deep red solution to each of the four test-tubes.
7. Arrange the test tubes in a test tube stand [Fig. 7.1].
8. Add 5 ml of distilled water to test tube A; 5 ml of 0.1M $FeCl_3$ solution to test tube B ; 5 ml of 0.1 M KSCN solution to test tube C and 5 ml of 0.1 M KC1 solution to test tube D.
9. Shake all the tubes well.
10. Now compare the intensity of the colours in test tubes, B, C and D with the red colour in test tube A taken as reference tube.
11. The intensity of the red colour corresponds to concentration of complex $[Fe(SCN)]^{2+}$ and if the concentration of this ion increases, the colour intensity will also increase.

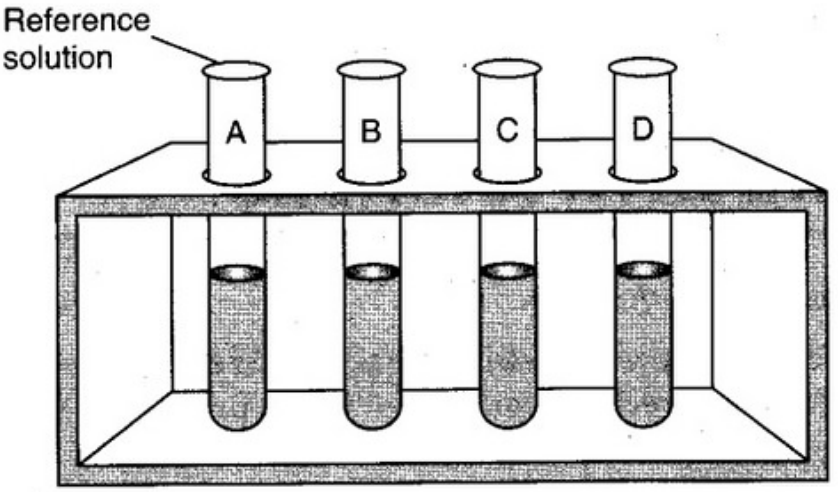

Fig. 7.1. Placing of test tubes.

Observations

Test tube	Substance added at equilibrium	Change in colour	Effect on the concentration of $[Fe(SCN)]^{2+}$	Shift of equilibrium
A	5 ml of water	Reference colour	—	—
B	5 ml of 0.1 M $FeCl_3$ solution	Colour deepens	Increases	Towards right
C	5 ml of 0.1 M KSCN solution	Colour deepens	Increases	Towards right
D	5 ml of 0.1 M KC1	Colour	Decreases	Towards left

solution	becomes lighter

Conclusion

Increase in concentration of either of the reactants (Fe^{3+} ions or SCN^{-} ions) shifts the equilibrium ‘ in the forward direction (towards right), on the other hand decrease in concentration of any of the reactants shifts the equilibrium in the backward direction (towards left).

Precautions

1. Use tubes of almost identical diameter.
2. Dilute solutions of thiocyanate should be used.
3. The intensity of colour of a solution should be compared by keeping it and reference side by side and then observing from top.