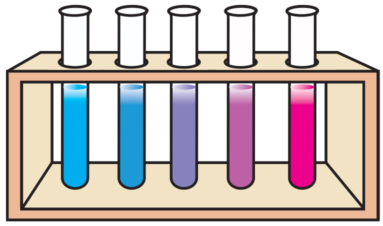
UNIT – 4

CHEMICAL EQUILIBRIUM

(IONIC EQUILIBRIUM IN SOLUTION)



CHEMICAL reactions can be classified into two categories; namely reversible and irreversible reactions. Reversible reactions take place in the same reaction vessel and can proceed in the forward and backward direction simultaneously under the same conditions of temperature and pressure. Further in the case of reversible reactions a state is reached, when the rate of the forward reaction becomes equal to the rate of the reverse reaction and it appears as though the reaction has come to a stand still. This state is referred to as the state of **dynamic equilibrium**. Consider the following simple reversible reaction at the given temperature, *T*.

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

According to the law of mass action, rate of forward reaction, r_1, will be directly proportional to the product of concentrations of A and B and the rate of backward reaction, r_2, will be directly proportional to the products of concentrations of C and D.

Thus, $r_1 = k_1[A][B]$ and $r_2 = k_2[C][D]$

where k_1 and k_2 are the rate constants for the forward and the backward reactions respectively and [A], [B], [C] and [D] are the molar concentrations of A, B, C and D respectively.

At equilibrium, r_1 will be equal to r_2

$$k_1[A][B] = k_2[C][D]$$

$$\Rightarrow \quad \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

Putting $\frac{k_1}{k_2} = K_c$ we have

$$K_c = \frac{[C][D]}{[A][B]}$$

K_c is called equilibrium constant. Its value is independent of initial concentration of reactants and is a function of temperature but remains constant at a constant temperature. At a given temperature, if the concentration of any one of the reactants or products is changed, then equilibrium is disturbed and according to Le Chatelier principle, reaction proceeds in that direction which counteracts the change in concentration , so as to maintain the equilibrium.

The state of equilibrium in any reaction is recognised by the constancy of an observable property (macroscopic property) like colour intensity of the solution. In this unit we will study about the shift in equilibrium in various reactions.

EXPERIMENT* 4.1

Aim

Study of shift in equilibrium in the reaction of ferric ions and thiocyanate ions by increasing the concentration of any one of these ions.

Theory

The equilibrium reaction between ferric chloride and potassium thiocyanate is conveniently studied through the change in the intensity of colour of the solution.

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

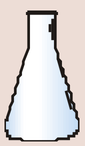
(Blood red colour)

The equilibrium constant for the above reaction may be written as:

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

Here K is constant at a constant temperature. Increasing the concentration of either Fe^{3+} ion or thiocyanate ion would result in a corresponding increase in the concentration of $[Fe(SCN)]^{2+}$ ions. In order to keep the value of K constant, there is a shift in equilibrium, in the forward direction and consequently an increase in the intensity of the blood red colour which is due to $[Fe(SCN)]^{2+}$. At equilibrium colour intensity remains constant.

Material Required



- Beakers (100 mL) : Two
- Beaker (250 mL) : One
- Boiling tubes : Six
- Burettes : Four
- Glass droppers : Two
- Test tube stand : One
- Glass rod : One

- Ferric chloride : 0.100g
- Potassium thiocyanate : 0.100g

* *The very nature of the experiment is purely qualitative. therefore, preparation of solution in terms of molarity has not been stressed.*

Ferric chloride 

Hazard Warning

- *Avoid contact with skin and eyes.*

Procedure

(i) Dissolve 0.100 g ferric chloride in 100 mL of water in a beaker and 0.100 g potassium thiocyanate in 100 mL of water in another beaker.

(ii) Mix 20 mL of ferric chloride solution with 20 mL of potassium thiocyanate solution. Blood red colour will be obtained. Fill this solution in a burette.

(iii) Take five boiling tubes of same size and mark them as a,b,c, d and e.

(iv) Add 2.5 mL of blood red solution to each of the boiling tubes from the burette.

(v) Add 17.5 mL of water to the boiling tube 'a' so that total volume of solution in the boiling tube 'a' is 20 mL. Keep it for reference.

(vi) Now take three burettes and label them as A, B, and C.

(vii) Fill burette A with ferric chloride solution, burette B with potassium thiocynate solution and burette C with water.

(viii) Add 1.0 mL, 2.0 mL, 3.0 mL and 4.0 mL of ferric chloride solution to boiling tubes b, c, d and e respectively from burette A.

(ix) Now add 16.5 mL, 15.5 mL, 14.5 mL, and 13.5 mL of water to boiling tubes b, c, d and e respectively from burette C so that total volume of solution in each boiling tube is 20 mL.

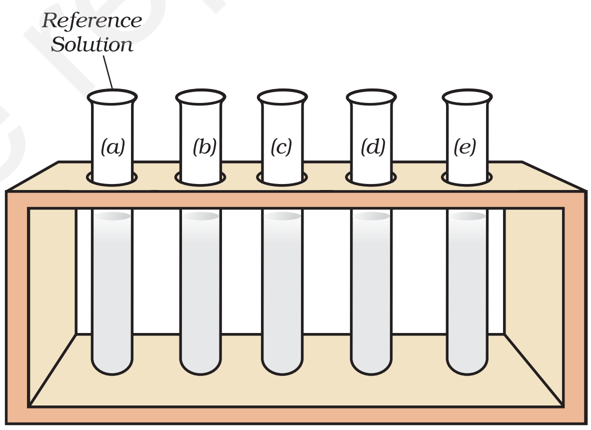


Fig. 4.1 **:** *Set up of experiment for observing equilibrium, each boiling tube contains 20 mL solution*

Note :
- *Colour intensity of the solution will decrease very much on dilution. It will not be deep blood red colour.*
- *Total volume in each test tube is 20 mL.*
- *Each test tube has 2.5 mL equilibrium mixture.*
- *Amount of $FeCl_3$ is increasing from test tubes 'b' to 'e'.*

(x) Compare the colour intensity of the solution in each boiling tube with the colour intensity of reference solution in boiling tube 'a'.

(xi) Take another set of four clean boiling tubes. Add 2.5 mL of blood red solution to each of the boiling tubes from the burette. Repeat the experiment by adding 1.0 mL, 2.0 mL, 3.0 mL and 4.0 mL of potassium thiocynate solution from burette B to the boiling tubes b′, c′, d′, and e′ respectively followed by addition of 16.5 mL, 15.5 mL, 14.5 mL and 13.5 mL of water respectively to these test tubes. Again compare the colour intensity of the solution of these test tubes with reference equilibrium solution in boiling tube 'a'.

(xii) Record your results in tabular form as in Tables 4.1 and 4.2.

(xiii) You may repeat the observations with different amounts of potassium thiocyanate and ferric chloride solution and compare with the reference solution.

Table 4.1 : Equilibrium shift on increasing the concentration of ferric ions

Boiling Tube	Volume of ferric chloride solution taken in the system in mL	Change in colour intensity as matched with reference solution in boiling tube "a"	Direction of shift in equilibrium
a	Reference solution for matching colour containing 2.5 mL blood red solution + 17.5 mL water (20 mL equilibrium mixture)		Equilibrium position
b	1.0		
c	2.0		
d	3.0		
e	4.0		

Table 4.2 : Equilibrium shift on increasing the concentration of thiocyanate ions

Boiling Tube	Volume of thiocyanate solution taken in the system in mL	Change in colour intensity as matched with reference solution in boiling tube "a"	Direction of shift in equilibrium
a	Reference solution for matching colour containing 2.5 mL blood red solution + 17.5 mL water (20 mL equilibrium mixture)		Equilibrium position
b′	1.0		
c′	2.0		
d′	3.0		
e′	4.0		

Precautions

(a) Use very dilute solutions of ferric chloride and potassium thiocyanate.

(b) Compare the colour of the solutions by keeping the boiling tube and the reference test tube side by side.

(c) To judge the change in colour of the solution in an effective manner, note the colour change in diffused sunlight.

(d) Use boiling tubes of the same size.

Discussion Questions

(i) Explain why representing the ionic reaction between ferric and thiocyanate ions as given in the text viz.

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

is more appropriate in the following form ?

$$[Fe(H_2O)_6]^{3+} + SCN^{-}(aq) \rightleftharpoons [Fe(H_2O)_5(SCN)]^{2+} + H_2O.$$

(ii) Does the constancy in colour intensity indicate the dynamic nature of equilibrium? Explain your answer with appropriate reasons.

(iii) What is equilibrium constant and how does it differ from the rate constant?

(iv) It is always advisable to carry out the present experiment with dilute solutions. Why?

(v) What will be the effect of adding solid potassium chloride to the system at equilibrium? Verify your answer experimentally.

(vi) Why boiling tubes of same size are used in the experiment?

EXPERIMENT 4.2

Aim

Study of the shift in equilibrium in the reaction between $[Co(H_2O)_6]^{2+}$ and Cl^{-} ions, by changing the concentration of any one of these ions.

Theory

In the reaction between $[Co(H_2O)_6]^{2+}$ and Cl^{-} ions, the following displacement reaction takes place.

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}} + 4Cl^{-} \rightleftharpoons \underset{\text{Blue}}{[CoCl_4]^{2-}} + 6H_2O$$

This reaction is known as ligand displacement reaction and the equilibrium constant, K, for this is written as follows:

$$K = \frac{[[CoCl_4]^{2-}]}{[[Co(H_2O)_6]^{2+}][Cl^-]^4}$$

Since the reaction occurs in the aqueous medium, it is believed that concentration of H_2O is almost constant and is included in the value of K itself and is not shown separately in the expression for equilibrium constant.

Now if at equilibrium the concentration of either $[Co(H_2O)_6]^{2+}$ ion or Cl^- ions is increased, then this would result in an increase in $[CoCl_4]^{2-}$ ion concentration thus, maintaining the value of K as constant. In other words we can say that equilibrium will shift in the forward direction and will result in a corresponding change in colour.

Hydrochloric acid

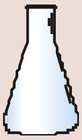
Acetone

Alcohol

Hazard Warning

- *Acetone and alcohol are inflamable, do not let the bottles open when not in use.*
- *Keep the bottles away from flames.*
- *Wash your hands after use.*
- *Wear safety spectacles.*

Material Required



- Conical flask (100 mL) : One
- Beakers (100 mL) : Three
- Burettes : Three
- Test tubes : Six
- Test tube stand : One
- Glass rod : One

- Acetone/alcohol : 60 mL
- Concentrated hydrochloric acid : 30 mL
- Cobalt chloride : 0.6000 g

Procedure

(i) Take 60 mL of acetone in a 100 mL conical flask and dissolve 0.6000 g $CoCl_2$ in it to get a blue solution.

(ii) Take 5 test tubes of same size and mark them as A, B, C, D and E. Add 3.0 mL of cobalt chloride solution in each of the test tubes from 'A' to 'E' respectively. Now add 1.0 mL, 0.8 mL, 0.6 mL, 0.4 mL and 0.2 mL of acetone respectively in these test tubes. Add 0.2 mL, 0.4 mL, 0.6 mL and 0.8 mL of water to test tubes B, C, D and E respectively, so that the total volume of solution in each of the test tubes is 4.0 mL.

(iii) Note the gradual change in colour of the mixture from blue to pink with an increase in the amount of water.

(iv) Take 10 mL cobalt chloride solution in acetone prepared above and add 5 mL distilled water to it. A solution of pink colour will be obtained.

(v) Take 1.5 mL of pink solution from step (iv) in five different test tubes labeled as A′ B′, C′, D′ and E′. Add 2.0 mL, 1.5 mL, 1.0 mL and 0.5 mL of water to the test tubes labelled

Note :
- *In the first set of experiments concentration of chlorocomplex is constant and concentration of water is changing.*
- *In the second set concentration of aqua complex is constant and concentration of chloride ions is increasing.*

from A′ to D′ and 0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL concentrated HCl respectively in the test tubes A′ to E′ so that total volume of solution in the test tubes is 4 mL.

(vi) Note the gradual change in colour of pink solution to light blue with increasing amounts of hydrochloric acid. Record your observations in tabular form (Tables 4.3 and 4.4).

Table 4.3 : Shift in equilibrium on adding water

Sl. No.	Test tube	Volume of acetone added in mL	Volume of $CoCl_2$ solution added in mL	Volume of water added in mL	Colour of mixture
1.	A	1.0	3.0	0.0	
2.	B	0.8	3.0	0.2	
3.	C	0.6	3.0	0.4	
4.	D	0.4	3.0	0.6	
5.	E	0.2	3.0	0.8	

Table 4.4 : Shift in equilibrium on adding Cl^- ions

Sl. No.	Test tube	Volume of conc. HCl added in mL	Volume of aquo complex solution added in mL	Volume of water added in mL	Colour of mixture
1.	A′	0.5	1.5	2.0	
2.	B′	1.0	1.5	1.5	
3.	C′	1.5	1.5	1.0	
4.	D′	2.0	1.5	0.5	
5.	E′	2.5	1.5	0.0	

Precautions

(a) Take all the precautions of experiment 4.1.

(b) Use distilled water for the experiment.

(c) Use burette or graduated pipette for adding water or solutions.

Discussion Questions

(i) What will be the effect of increasing the temperature of the reaction mixture at equilibrium?

(ii) Can an aqueous solution of sodium chloride replace concentrated HCl? Verify your answer experimentally.

(iii) Why should the total volume of the solution in each test tube be kept same?