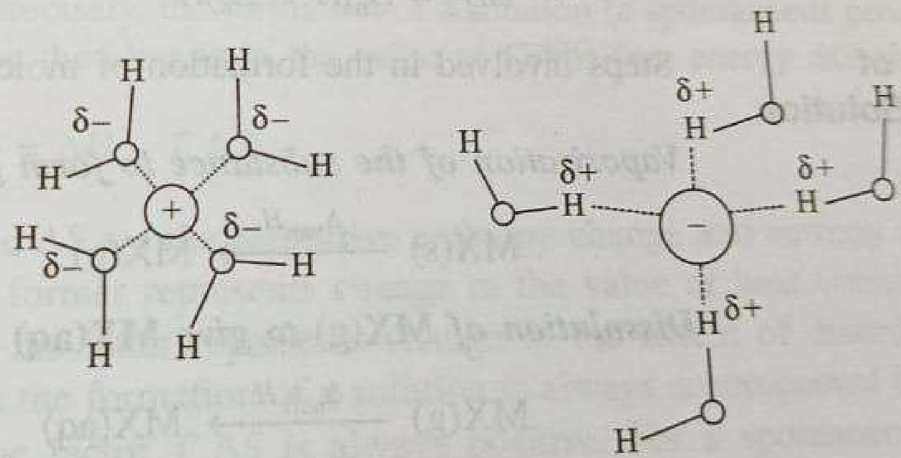
# 4 Ionic Equilibria

## 4.1 THE DISSOLUTION PROCESS

**General Principle of Solubility**

Most chemical reactions occur in solutions. The study of such solutions constitutes one of the most important branches of physical chemistry. In general, if the solubility of solutes in various solvents is analyzed, it is observed that the polar solutes are more soluble in polar solvents whereas nonpolar solutes are more soluble in nonpolar solvents. This is the general principle of solubility, i.e. *like dissolves like*. For example, sodium chloride is soluble in water whereas it is insoluble in carbon tetrachloride. The high dielectric constant and polar nature of water, makes it one of the most important solvents for ionic solutes. The higher dielectric constant weakens the forces of attraction between the oppositely charged ions of the ionic crystals and its polar character generates the ion-dipole interactions in which the positive ion is attracted by the negative end of the water dipole, whereas the negative ion is attracted by the positive end of the dipole as shown in Fig. 4.1.1. The consequence of this is that the ions are pulled out of the crystal lattice and are drifted into the liquid phase. Ions move in the solution in the hydrated forms. Certain covalent molecules with relatively high dipole moment can also dissolve in water to produce an ionic solution because of the stronger ion-dipole interactions (e.g., hydrochloric acid).




**Ion-dipole**

**Molecular**

A given substance on dissolution in a solvent (e.g., water), in general, yiel[ds] either an ionic solution or a molecular solution. In the former, the substan[ce] splits up into ions, whereas in the latter, it is present as such. The formation [of] these two types of solutions can be represented as follows:

$$MX(s) + aq \rightarrow M^+(aq) + X^-(aq) \quad (4.1$$

$$MX(s) + aq \rightarrow MX(aq) \quad (4.$$

The formation of these two solutions may be considered through the following steps.

Formation of Ionic Solutions

Steps involved in the formation of ionic solutions are given below.

*Vaporization of the substance to form gaseous molecules*

$$MX(s) \xrightarrow{\Delta_{vap}H} MX(g)$$

*Dissociation of gaseous molecules into atoms*

$$MX(g) \xrightarrow{\Delta_{diss}H} M(g) + X(g)$$

*Formation of gaseous ions from these atoms*

$$M(g) \xrightarrow{\Delta_{ioniz}H} M^+(g) + e^-$$

$$X(g) + e^- \xrightarrow{\Delta_{EA}H} X^-(g)$$

*Solvation of these gaseous ions*

$$M^+(g) + aq \xrightarrow{\Delta_{h1}H} M^+(aq)$$

$$X^-(g) + aq \xrightarrow{\Delta_{h2}H} X^-(aq)$$

The enthalpy change in the formation of an ionic solution is equal to the sum of the above changes, i.e.

$$\Delta H = \Delta_{vap}H + \Delta_{diss}H + \Delta_{ioniz}H + \Delta_{EA}H + \Delta_{h1}H + \Delta_{h2}H = \Delta H_1 + \Delta H_2$$

where $\Delta H_1 = \Delta_{vap}H + \Delta_{diss}H + \Delta_{ioniz}H + \Delta_{EA}H$

$$\Delta H_2 = \Delta_{h1}H + \Delta_{h2}H$$

Formation of Molecular Solution

Steps involved in the formation of molecular solutions are given below.

*Vaporization of the substance to form gaseous molecules*

$$MX(s) \xrightarrow{\Delta_{vap}H} MX(g)$$

*Dissolution of* **MX(g)** *to give* **MX(aq)**

$$MX(g) \xrightarrow{\Delta_{solv}H} MX(aq)$$

with a total enthalpy change $\Delta H = \Delta_{vap}H + \Delta_{solv}H$, which corresponds to the enthalpy change in the formation of a molecular solution.

ation

The question whether the given substance is soluble or not and whether on dissolution it forms an ionic or a molecular solution may be answered only from the consideration of the enthalpies involved in the formation of the solution. This is illustrated by taking the typical examples of $CaCl_2$ and $HgCl_2$. The enthalpies involved in various steps of formation of the solution are listed in Table 4.1.1.

**Table 4.1.1** Enthalpies Involved in the Formation of Ionic and Molecular Solutions of $CaCl_2$ and $HgCl_2$

| | *Step* | $CaCl_2$ | $HgCl_2$ |
|---|---|---|---|
| | | $\Delta H$/kJ mol$^{-1}$ | $\Delta H$/kJ mol$^{-1}$ |
| I | *For an ionic solution* | | |
| | (a) Sublimation | 209.2 | 83.78 |
| | (b) Bond breaking | 1 004.2 | 460.2 |
| | (c) Ionization | 1 715.4 | 2 815.8 |
| | Electron affinity | 2 (– 359.8) | 2 (– 359.8) |
| | (d) Cation hydration | – 1 598.3 | – 1 845.1 |
| | Anion hydration | 2 (– 355.6) | 2 (– 355.6) |
| | Total | – 100.3 | 83.8 |
| II | *For a molecular solution* | | |
| | (a) Sublimation | 209.2 | 83.78 |
| | (b) Dissolution of gaseous molecules | – 33.5 | – 66.9 |
| | Total | 175.7 | 16.8 |

Comparison of the total enthalpy involved in the formation of the ionic solution indicates that this type of solution is more likely to be formed by $CaCl_2$ than by $HgCl_2$. Analysis of the individual enthalpies indicates that though steps (a) and (b) are more favourable to $HgCl_2$ than to $CaCl_2$, the subsequent step (c), namely, the cation formation, is highly unfavourable to Hg, with the result that $HgCl_2$ does not form an ionic solution. Similar comparison of the total enthalpy involved in the case of molecular solution indicates that the formation of such type of solution is *very* unfavourable for $CaCl_2$ and *slightly* unfavourable for $HgCl_2$.

More precisely, the formation of a solution (a spontaneous process) should be decided by the change in the value of Gibbs free energy $\Delta G$ given as

$$\Delta G = \Delta H - T\,\Delta S$$

where $\Delta H$ and $\Delta S$ are the respective enthalpy change and entropy change of the process. The former represents change in the value of heat content at constant pressure and the latter represents change in the extent of disorderlines of the system. Since the formation of a solution is always accompained by the increase in entropy, the factor $T\,\Delta S$ is always positive. For a spontaneous dissolution, $\Delta G$ should be negative. Both $\Delta H$ and $\Delta S$ favour this for an exothermic reaction, whereas, for an endothermic reaction, the entropy factor has to outweigh the enthalpy change. However, this term is usually not large, and does not contribute more than 30 kJ to the overall free energy change. Nevertheless, it becomes very important for an endothermic reaction with a very small value of $\Delta H$ as in the case of $HgCl_2$.

## 4.2 CLASSIFICATION OF SUBSTANCES

**Classification of Electrolytes**

Based on the relative values of conductivities of aqueous solutions, the dissolved substance can be classified into any one of the following categories.

(i) Strong electrolyte: high conducting
(ii) Weak electrolyte: low conducting
(iii) Nonelectrolyte: nonconducting

Table 4.2.1 records a few typical examples of strong, weak and nonelectrolytes.

**Table 4.2.1** A Few Typical Examples of Strong, Weak and Nonelectrolytes

| *Compounds* | *Crystal type* | *Solutions* |
|---|---|---|
| Halides, hydroxides and acetates of Gp. 1 and Gp. 2 elements | Ionic | Strong electrolytes |
| Nitrate, chlorate and sulphates of $M^+$ and $M^{2+}$ cations | Ionic | Strong electrolytes |
| $PbBr_2$, $PbCl_2$, $PbAc_2$, $HgCl_2$, $CuCl_2$ | Ionic to molecular | Weak electrolytes |
| HCl, HBr, HI | Molecular | Strong electrolytes |
| $H_2SO_4$, $HClO_4$, $HNO_3$, | Molecular (H bonding) | Strong electrolytes |
| RCOOH, $H_2CO_3$ | Molecular | Weak electrolytes |
| ROH, HCN, other organic compounds | Molecular | Nonelectrolytes |

**Limitation of Classification**

The classification of compounds in terms of strong and weak electrolytes is based on their behaviour in a particular solvent, namely, water. However, such classification suffers from a great disadvantage in the sense that a particular electrolyte, though weak in water, might behave as a strong one when dissolved in some other solvent or vice versa. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water. However, when acetic acid and sodium chloride are dissolved in ammonia, their conductivity values are comparable, indicating a strong electrolytic behaviour for acetic acid (Table 4.2.2).

**Table 4.2.2** Molar Conductivity Values

| *Solute* | *Solvent* | |
|---|---|---|
| | *Water* $\Lambda/S\ cm^2\ mol^{-1}$ | *Ammonia* $\Lambda/S\ cm^2\ mol^{-1}$ |
| Sodium chloride | 106.7(s) | 284.0(s) |
| Acetic acid | 4.7(w) | 216.0(s) |

Thus, the above classification depends upon the solvent used.

**True and Potential Electrolytes**

Another classification which is largely based on the characteristics of the solute and not on that of the solvent, is to label them as the *true electrolyte* and the *potential electrolyte*. The essential characteristics of true electrolyte is that even in the pure liquid state it is an ionic conductor. In dissolution process, all that a polar solvent does is that it uses ion-dipole forces to disengage ions from their lattice sites, solvates them and disperses them into the solution. Examples are NaCl, KCl, etc. The potential electrolyte, however, does not conduct electricity in the pure liquid state, though it provides a conducting solution on dissolution in an ionic solvent. Examples are hydrochloric acid, acetic acid, etc.

## 4.3 THE ARRHENIUS THEORY OF DISSOCIATION

The increase in molar conductivity with decreasing concentration observed in dilute solutions of all electrolytes led Arrhenius to postulate that a chemical equilibrium exists between the molecule of undissociated electrolyte and the ions that result from dissociation

$$AB \rightleftharpoons A^+ + B \qquad (4.3.1)$$

On dilution, more of AB dissociates to give $A^+$ and $B^-$, which accounts for the increase in molar conductivity. In dilute solutions, it is known today that the above equilibrium is valid only for weak electrolytes. Strong electrolytes are already present in the form of ions in the solid state. Evidence for the existence of equilibrium in weak electrolytes can be seen from the study of colligative properties (properties which depend only on the number of species and not on their nature). Such properties are osmotic pressure, relative lowering of vapour pressure, elevation of boiling point and depression of freezing point.

For example, if we have 0.01 mol kg$^{-1}$ solutions of $CH_3OH$ and NaCl, the depression of freezing point in the latter is double that of the former. It is because of the fact that solution of NaCl would be 0.01 mol kg$^{-1}$ with respect to $Na^+$ and 0.01 mol kg$^{-1}$ with respect to $Cl^-$ and that the total concentration of the species in solution is 0.02 mol kg$^{-1}$. Thus:

Depression of freezing point in 0.01 mol kg$^{-1}$ $CH_3OH$ = 0.018 6 °C

Depression of freezing point in 0.01 mol kg$^{-1}$ NaCl = 0.037 2 °C

Similarly,

Depression of freezing point in 0.01 mol kg$^{-1}$ $Al_2(SO_4)_3$ = 0.093 0 °C

**Dissociation of a Weak Electrolyte**

The depression of freezing point in case of a weak electrolyte AB (0.01 mol kg$^{-1}$) is in between the values of 0.018 6 °C and 0.037 2 °C. Thus, the total concentration of species in the solution is greater than 0.01 mol kg$^{-1}$ but less than 0.02 mol kg$^{-1}$.

**Dissociation in Terms of Extent of Reaction**

In general, if $\xi$ (known as extent of reaction) is the amount of AB that has dissociated, then the amounts of various species in solution are

$$\underset{0.01\,\text{mol} - \xi}{AB} \rightleftharpoons \underset{\xi}{A^+} + \underset{\xi}{B^-} \qquad (4.3.2)$$

Total amount of species in the solution is (0.01 mol + $\xi$) and, therefore, the depression of freezing point will be equal to (0.01 + $\xi$/mol) (1.86 °C).

**Dissociation in Terms of Degree of Dissociation**

The extent of dissociation of a substance can also be expressed in terms of *degree of dissociation*, which is, by definition, equal to the fraction of the total substance that is present in the form of ions. If $\alpha$ is the degree of dissociation, it means that the amount $\alpha$ mole out of 1 mol of the solute is present in the form of ions and thus the remaining amount of the undissociated species is $(1 - \alpha)$ (1 mol). If $c$ is the concentration of the solute AB, then the concentrations of various species in solution are as follows:

$$\underset{c(1-\alpha)}{\mathrm{AB}} \rightleftharpoons \underset{c\alpha}{\mathrm{A^+}} + \underset{c\alpha}{\mathrm{B^-}} \tag{4.3.3}$$

Similarly, for the electrolyte $A_2B$ (assuming single-step dissociation):

$$\underset{c(1-\alpha)}{\mathrm{A_2B}} \rightleftharpoons \underset{c(2\alpha)}{\mathrm{2A^+}} + \underset{c\alpha}{\mathrm{B^{2-}}} \tag{4.3.4}$$

In general,
$$\underset{c(1-\alpha)}{\mathrm{A}_x\mathrm{B}_y} \rightleftharpoons \underset{c(x\alpha)}{x\mathrm{A}^{y+}} + \underset{c(y\alpha)}{y\mathrm{B}^{x-}} \tag{4.3.5}$$

**Expression of Equilibrium Constant**

A chemical equilibrium is a dynamic equilibrium and can be characterized by an equilibrium constant,* which by definition is

$$K_{eq} = \frac{\text{Product of concentrations of species appearing on the right side of equilibrium, each raised to the corresponding stoichiometric number}}{\text{Product of conentrations of species appearing on the left side of equilibrium, each raised to the corresponding stoichiometric number}} \tag{4.3.6}$$ [†]

In the above examples, $K_{eq}$s are

$$K_{eq}(\mathrm{AB}) = \frac{[\mathrm{A^+}][\mathrm{B^-}]}{[\mathrm{AB}]} \tag{4.3.7}$$

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*Concentrations are to be expressed in mol dm$^{-3}$. By convention the ions are written on the right side of the dissociation reaction.

[†]In general, a chemical reaction is written as

$$0 = \Sigma_B\, \nu_B\, B$$

where $\nu_B$, the stoichiometric number, is positive for products and negative for reactants. The expression of equilibrium constant is written as

$$K_{eq} = \Pi_B\, [B]^{\nu_B}$$

Taking the example of dissociation of $A_2B$, we have

Equilibrium reaction: $0 \rightleftharpoons 2A^+ + B^- - A_2B$ i.e. $A_2B \rightleftharpoons 2A^+ + B^-$

Equilibrium constant: $K_{eq} = [A^+]^2[B^-][A_2B]^{-1}$ i.e. $K_{eq} = \frac{[A^+]^2[B^-]}{[A_2B]}$

Through out the treatment of ionic equilibria, we write equilibrium reaction and its equilibrium constant the way these are written at the end of the above two expressions

$$K_{eq}(A_2B) = \frac{[A^+]^2[B^{2-}]}{[A_2B]} \qquad (4.3.8)$$

In general, $$K_{eq}(A_xB_y) = \frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]} \qquad (4.3.9)$$

The value of the equilibrium constant is a characteristic of a given weak electrolyte and depends only on the temperature. It is independent of the individual concentrations of AB, $A^+$ and $B^-$. If a strong electrolyte containing either $A^+$ or $B^-$ is added to the solution of a weak electrolyte AB, even then the above expression for the equilibrium constant holds good. The effect of a strong electrolyte is to suppress the extent of dissociation of the weak electrolyte, i.e. the degree of dissociation of the weak electrolyte is decreased.

## 4.4 EFFECT OF DILUTION ON DEGREE OF DISSOCIATION

**Ostwald Dilution Law**

We write the equilibrium for a weak electrolyte AB as

$$AB + H_2O \rightleftharpoons A^+(aq) + B^-(aq) \qquad (4.4.1)$$

If $\alpha$ is the degree of dissociation at a given concentration $c$ of AB, then the concentrations of various species in solution are

$$[AB] = c(1-\alpha); \qquad [A^+(aq)] = c\alpha; \qquad [B^-(aq)] = c\alpha$$

Substituting these in the expression of equilibrium constant, we have

$$K_{eq} = \frac{[A^+][B^-]}{[AB][H_2O]} = \frac{[A^+][B^-]}{[AB](1\,000\text{ g dm}^{-3}/18\text{ g mol}^{-1})}$$

$$= \frac{c\alpha^2}{(1-\alpha)(55.56\text{ M})} \qquad (4.4.2)$$

The water concentration will practically remain the same (i.e. 55.56 M) since only very small quantity of this will combine with $A^+$ and $B^-$. Combining this concentration with $K_{eq}$ gives another constant $K_{diss}$ which is called the *dissociation constant* or *the ionization constant*. Thus

$$K_{diss} = K_{eq} \times (55.56\text{ M}) = \frac{c\alpha^2}{(1-\alpha)} \qquad (4.4.3)$$

Since $\alpha$ is usually a very small quantity, it is, therefore, negligible in comparison to unity, i.e. $(1-\alpha) \approx 1$. Thus

$$K_{diss} = \frac{c\alpha^2}{1} \qquad (4.4.4)$$

or $$\alpha = \sqrt{\frac{K_{diss}}{c}} = \sqrt{K_{diss}V_m}$$

where $V_m$ is the volume containing 1 mol of the solute. Its unit is taken as $dm^3$ $mol^{-1}$.

It follows from Eq. (4.4.4) that as $c$ decreases (dilution), $\alpha$ increases. In the limit when $c \rightarrow 0$, $\alpha$ will approach 1, i.e. at *infinite dilution, the whole of the weak electrolyte gets ionized*. This is the *Ostwald dilution law*.

The expression

$$\alpha = \sqrt{K_{\text{diss}} V_{\text{m}}}$$

can be used to determine the $K_{\text{diss}}$, if the value of $\alpha$ is known at a given concentration. The value of $\alpha$ can be determined by using any other physicochemical technique such as molar conductivity, colligative properties, etc. A plot of $\alpha^2$ versus $V_{\text{m}}$ will be a straight line; the slope of the resulting plot gives the value of $K_{\text{diss}}$.

*Example 4.4.1* At 25 °C, acid dissociation constant of HCN is $4.9 \times 10^{-10}$ M. Calculate the degree of dissociation of HCN, if its concentrations are (i) 0.1 M and (ii) 0.01 M.

*Solution* If $\alpha$ is the degree of dissociation of HCN, then the concentrations of various species in solution are

$$\underset{c(1-\alpha)}{HCN} + H_2O \rightleftharpoons \underset{c\alpha}{H_3O^+} + \underset{c\alpha}{CN^-}$$

Substituting these in the dissociation expression, we have

$$K_{\text{diss}} = \frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(c\,\alpha)(c\,\alpha)}{c(1-\alpha)} = \frac{c\,\alpha^2}{1-\alpha} \simeq c\,\alpha^2$$

Thus (i) $\alpha = \sqrt{\frac{K_{\text{diss}}}{c}} = \sqrt{\frac{(4.9 \times 10^{-10}\ \text{M})}{0.1\ \text{M}}} = 7 \times 10^{-5}$

(ii) $\alpha = \sqrt{\frac{(4.9 \times 10^{-10}\ \text{M})}{0.01\ \text{M}}} = 2.21 \times 10^{-4}$

## 4.5 DISSOCIATION OF PURE WATER

**Equilibrium Constant of Water** Pure water is itself a very weak electrolyte and ionizes according to the equation

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \tag{4.5.1}$$

The equilibrium constant of the reaction is

$$K_{\text{eq}} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \tag{4.5.2}$$

**Ionization Constant of Water** The ionization of water may be written as

$$H_2O \rightleftharpoons H^+ + OH^- \tag{4.5.3}$$

for which the ionization constant is given by

$$K_i = \frac{[H^+][OH^-]}{[H_2O]} \tag{4.5.4}$$

It is obvious that $K_i = K_{eq}\,[H_2O]$. (4.5.5)

**Ionic Product of Water**

Since water is found to be poorly ionized (degree of dissociation is $1.8 \times 10^{-9}$ at 25 °C), concentration of water remains practically the same $\{(1\,000\ g\ dm^{-3})/(18\ g\ mol^{-1}) = 55.56\ M\}$. Its concentration can be combined with the ionization constant $K_i$ to give a new constant, known as the *ionic product* of water, $K_w$. From Eq. (4.5.4), we get

$$K_w = K_i\,[H_2O] = [H^+]\,[OH^-] \tag{4.5.6}$$

The concentration of $OH^-$ in pure water will be the same as that of $H^+$; therefore

$$K_w = [H^+]^2 \tag{4.5.7}$$

The value of $[H^+]$ in water at 25 °C is found to be $1.0 \times 10^{-7}$ M. The value of ionic product at 25 °C is thus equal to

$$K_w = (1.0 \times 10^{-7}\ M)\,(1.0 \times 10^{-7}\ M)$$
$$= 1.0 \times 10^{-14}\ M^2 \tag{4.5.8}$$

Because of equal concentrations of hydrogen and hydroxyl ions in pure water, the latter is neutral in its behaviour.

**Nature of Solution**

Acidity or alkalinity of a solution depends upon the concentration of hydrogen ions relative to that of hydroxyl ions. In any aqueous solution, both hydrogen and hydroxyl ions coexist in accordance with Eq. (4.5.3). The product of hydrogen and hydroxyl ion concentrations is given by Eq. (4.5.6), the value of which depends only on the temperature and not on the individual ionic concentrations. *If the concentration of hydrogen ions exceeds that of the hydroxyl ions, the solution is said to be acidic; whereas, if concentration of hydroxyl ions exceeds that of the hydrogen ions, the solution is said to be alkaline.* Taking into account Eq. (4.5.6), it amounts to

| | | | |
|---|---|---|---|
| For neutral solution | $[H^+] = [OH^-] = \sqrt{K_w}$ | | |
| For acidic solution | $[H^+] > [OH^-]$ | or | $[H^+] > \sqrt{K_w}$ |
| For alkaline solution | $[H^+] < [OH^-]$ | or | $[H^+] < \sqrt{K_w}$ |

At 25 °C, these reduce to

| | |
|---|---|
| Neutral solution | $[H^+] = 10^{-7}$ M |
| Acidic solution | $[H^+] > 10^{-7}$ M |
| Alkaline solution | $[H^+] < 10^{-7}$ M |

## 4.6 THE pH-SCALE

**Definitions of pH and pOH**

Since hydrogen-ion concentrations commonly met within solutions vary considerably over the range $10^{-14}$ to 1 M, Sorenson introduced a logarithmic scale for the sake of convenience, and gave it a symbol pH. It is expressed as

$$pH = -\log_{10}\{[H^+]/M\} = \log\left\{\frac{1}{[H^+]/M}\right\} \quad (4.6.1)$$

Thus, it is equal to the logarithm of the reciprocal of $[H^+]/M$. For neutral water at 25 °C, pH is given by

$$pH = -\log(1.0 \times 10^{-7}) = -(-7) = 7 \quad (4.6.2)$$

The pH corresponding to the acidic and alkaline solutions at 25 °C will be less than and greater than seven, respectively.

In a similar manner, we can define a pOH scale as the negative logarithm of numerical value of the hydroxyl-ion concentration. However, the acidity or alkalinity of a solution is often expressed in terms of pH of a solution. Both pH and pOH are related to each other through the expression

$$pH + pOH = pK_w^o \quad (4.6.3)^\dagger$$

where $pK_w^o$, like pH and pOH, is equal to $-\log\{K_w/M^2\}$. Its value at 25 °C is equal to 14.

*Example 4.6.1* The values of ionic product of water at various temperatures are given below.

| $\theta_c/°C$ | 0 | 10 | 25 | 40 | 50 |
|---|---|---|---|---|---|
| $K_w \times 10^{14}/M^2$ | 0.114 | 0.292 | 1.008 | 2.919 | 5.474 |

What are the pH values of the pure water at these temperatures?

*Solution* Since $[H^+] = \sqrt{K_w}$, therefore

$$pH = -\log\{[H^+]/M\} = -\frac{1}{2}\log\{K_w/M^2\}$$

Thus, the calculated values of pH at the given temperatures are as follows.

| *Temperature* | pH |
|---|---|
| 0 °C | $-\frac{1}{2}\log(0.114 \times 10^{-14}) = 7.472$ |
| 10 °C | $-\frac{1}{2}\log(0.292 \times 10^{-14}) = 7.267$ |
| 25 °C | $-\frac{1}{2}\log(1.008 \times 10^{-14}) = 7.002$ |
| 40 °C | $-\frac{1}{2}\log(2.919 \times 10^{-14}) = 6.767$ |
| 50 °C | $-\frac{1}{2}\log(5.474 \times 10^{-14}) = 6.631$ |

† Throughout, the equilibrium constant, $K$, carries the unit of $(mol\ dm^{-3})^{\Sigma\nu}$. The expression $K/(mol\ dm^{-3})^{\Sigma\nu}$ is written as $K^o$ and is spelled as standard equilibrium constant. It is a unitless quantity.

*Example 4.6.2*

At 25 °C, the degree of ionization of water was found to be $1.8 \times 10^{-9}$. Calculate the ionization constant and the ionic product of water at this temperature.

*Solution*

If $\alpha$ is the degree of dissociation of water, then we have

$$H_2O \rightleftharpoons H^+ + OH$$

$$[H^+] = [OH^-] = c\alpha$$

If mass of 1 $dm^3$ water is taken as 1000 g, than

$$c = \frac{n}{V} = \frac{m/M}{V} = \frac{(1000\ g)/(18\ g\ mol^{-1})}{1\ dm^3} = 55.56\ M$$

Thus $$K_i = \frac{[H^+][OH^-]}{[H_2O]} = \frac{(c\alpha)^2}{c(1-\alpha)} = c\alpha^2 \quad \text{(assuming } \alpha << 1)$$

$$= (55.56\ M)(1.8 \times 10^{-9})^2 = 1.8 \times 10^{-16}\ M$$

and $$K_w = [H^+][OH^-] = (c\alpha)^2 = \{(55.56\ M)(1.8 \times 10^{-9})\}^2$$

$$= 1.0 \times 10^{-14}\ M^2$$

*Example 4.6.3*

What is the pH at 25 °C, if a solution which is twice as alkaline (i.e. which contains twice as many hydroxide ions) as pure water?

*Solution*

For a solution to have twice alkalinity, we have

$$[OH^-] = 2.0 \times 10^{-7}\ M$$

Thus $$pOH = -\log\{[OH^-]/M\} = -\log(2.0 \times 10^{-7}) = 7 - 0.30 = 6.70$$

and hence pH = 14 − pOH = 7.30

*Example 4.6.4*

The ionic product of water at 100 °C is 55 times than that at 25 °C. (i) Calculate the value of pH of water at 100 °C. (ii) A given solution at 100 °C has a pH value 5.0. Indicate whether the solution is acidic or alkaline or neutral.

*Solution*

(i) Given that

$$K_w(100\ °C) = 55 \times K_w(25\ °C) = 55 \times (1.0 \times 10^{-14}\ M^2)$$

Thus $$pH(100\ °C) = -\frac{1}{2}\log\{K_w/M^2\} = -\frac{1}{2}\log(55 \times 10^{-14}) = 6.13$$

(ii) Since for a given solution, pH equal to 5.0 is less than the corresponding pH of pure water at 100 °C, the solution is acidic.