ACIDS, BASES AND pH

1 Introduction

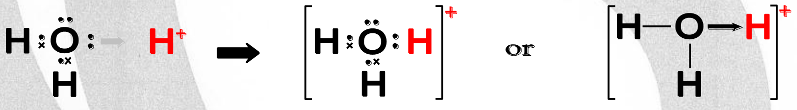
Acidity and basicity are of great importance to the environment and, indeed, pH - the measure of acidity - is one of the key factors in determining the health or, otherwise, of ecosystems. For example, the pH will determine how available nutrients and pollutants are to living organisms. As is well known, chalk and limestone areas support only a highly specialised flora due to the fact that the highly alkaline nature of the soils in these areas causes nutrients such as iron to be precipitated out of solution in the soil so making them unavailable to the plants in any appreciable amounts. Consequently, only those plants capable of scavenging very low levels of nutrient metals and then recycling them can survive. Similarly, the toxicity of heavy metals is dependent on pH. Given the critically important role of pH in the environment we need to consider the subject of acids, bases and pH in greater detail.

2 The Nature of Acids, Bases and Alkalis

The vast majority of interactions in the environment take place in aqueous solutions, therefore, although there are a number of definitions of acids and bases, the most appropriate for our purposes is that of Brϕnsted and Lowry. According to this

- an acid is a hydrogen ion (or proton) ***donor***,
- a base is a hydrogen ion ***acceptor***.

Now, a hydrogen ion (H^+) is simply a proton. This is very small and has an extremely high charge density; so high, in fact, that the hydrogen ion cannot lead an independent existence. Therefore, in an aqueous environment it binds strongly to water molecules. It seems likely that at least one water molecule makes a dative bond with the proton to form a ***hydronium ion***, H_3O^+, which is, itself, heavily hydrated with yet more water molecules. Thus:



The hydronium ion

For example, when hydrogen chloride dissolves in water the reaction which takes place can be represented by the following equation:

$$\underset{\text{acid}}{HCl(aq)} + \underset{\text{base}}{H_2O} \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad (1)$$

(The symbol (aq) denotes that the species is in aqueous solution)

Notice that in terms of the Brϕnsted-Lowry definition the hydrogen chloride is acting as an acid. It is dissociating into hydrogen ions and chloride ions, so acting as a hydrogen ion donor, while the water, by binding the hydrogen ions to form hydronium ions, is acting as a base. Thus, in such an environment if there is an acid present there must also be a base to complement that acid. In other words, for a species to act as an acid there must be a second species present which can act as a base. In the present example the water acts as a base to the hydrogen chloride's acid, so an aqueous solution of hydrogen chloride shows all the properties of an acid solution. However, if hydrogen chloride is dissolved in a non-polar solvent such as benzene the resulting solution has no acidic properties since the benzene cannot act as a base and accept hydrogen ions. Under these circumstances the hydrogen chloride cannot act as an acid and remains undissociated.

3 The Strength of Acids and Bases

(a) Acids

When discussing ionic materials in solution it is possible to distinguish between ***strong*** electrolytes and ***weak*** electrolytes. Strong electrolytes dissociate (or ionise) almost completely in solution, whereas weak electrolytes dissociate to only a small extent. Relating this to acids we can say that in an aqueous environment acids dissociate as follows:

$$HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad (2)$$

where the $\rightleftharpoons$ indicates that not only do the HA (a general term for an acid) and H_2O react to form H_3O^+ and A^- but there can be a reaction between the products to regenerate HA and water. In the case of strong acids the equilibrium lies so far to the right that *dissociation is virtually complete* and there are insignificant amounts of HA present. With weak acids, however, the equilibrium lies very much to the left hand side so that very little of the acid is dissociated and few hydronium ions are present.

Most of the mineral acids, for example hydrochloric, sulphuric and nitric acids, are strong acids and are practically 100% dissociated in aqueous solution. Many of the organic acids, however, are weak; for example, ethanoic (acetic) acid:

$$CH_3.COOH(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3.COO^-(aq) \qquad (3)$$

An important inorganic example is carbonic acid, which is formed when carbon dioxide dissolves in water. In a solution having a concentration of 2.0mol.dm^{-3}, 99.9% of the acid is undissociated:

$$\underset{0.999\text{ moles}}{H_2CO_3(aq) + H_2O} \rightleftharpoons \underset{0.001\text{ moles}}{H_3O^+(aq) + HCO_3^-(aq)} \qquad (4)$$

(b) Bases and Alkalis

When considering bases it is necessary first to distinguish between bases and alkalis. Alkalis are simply water-soluble bases which generate hydroxide, OH^-, ions on dissolving. Like acids they can be strong or weak depending on the relative amounts of hydroxide ions they generate in solution. Thus, highly soluble metal hydroxides such as sodium and potassium hydroxides are strong alkalis because they dissociate completely into the metal ions and hydroxide ions on dissolving in water:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq) \qquad (5a)$$

$$KOH(aq) \rightarrow K^+(aq) + OH^-(aq) \qquad (5b)$$

On the other hand, calcium hydroxide is considered a weak alkali because it is only slightly soluble in water and so generates few hydroxide ions in solution:

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq) \qquad (6)$$

(The symbol (s) stands for *solid* and shows that the material is undissolved)

Now, a ***strong base*** is one which is strongly attracted to hydrogen ions and binds to them very tightly. A common example is the hydroxide ion itself:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O \qquad (7)$$

A weak base, however, is one which is not strongly attracted to hydrogen ions and so does not bind them tightly. One example is ammonia which, in solution, interacts slightly with water molecules as follows:

$$\mathrm{NH_3(aq) + H_2O} \rightleftharpoons \underset{\text{ammonium ions}}{\mathrm{NH_4^+(aq)}} + \mathrm{OH^-(aq)} \qquad (8)$$

So weak is this interaction that the equilibrium lies well to the left hand side and there are actually very few ammonium ions and hydroxide ions present in the solution.

One thing to notice about this reaction is that the water is acting as an ***acid***; it is giving up a hydrogen ion to the ammonia molecule. This is in contrast to the situations involving hydrogen chloride and ethanoic acid (equations 1 and 3 above). Thus water can act either as an acid or as a base depending on its environment.

4 Conjugate Acids and Bases

In the general reaction

$$\mathrm{HA(aq) + H_2O} \rightleftharpoons \mathrm{H_3O^+(aq) + A^-(aq)} \qquad (9)$$

it will be seen that the HA is acting as an acid since it is acting a hydrogen ion donor while the water acts as a base by accepting the hydrogen ions. In the reverse reaction, however, the hydronium ion is acting as the acid while the A^- species is acting as a base, that is:

$$\mathrm{H_3O^+(aq) + A^-(aq)} \rightarrow \mathrm{HA(aq) + H_2O} \qquad (10)$$

In such situations the acid in the reverse reaction is known as the ***conjugate*** acid of water while the A^- species is the ***conjugate*** base of the acid, HA. Thus:

$$\underset{\text{acid}}{\mathrm{HA(aq)}} + \underset{\text{base}}{\mathrm{H_2O}} \rightleftharpoons \underset{\text{conjugate acid}}{\mathrm{H_3O^+(aq)}} + \underset{\text{conjugate base}}{\mathrm{A^-(aq)}} \qquad (11)$$

5 The Relationship Between Acid Concentration and Hydrogen Ion Concentration

(a) Strong Acids

Strong acids dissociate completely in aqueous solution and so release all their potentially ionisable ions. This means that for a strong monobasic acid, such as hydrochloric acid (HCl), there will be as many moles of hydrogen ions in solution as there are moles of acid. Thus:

$$\underset{\text{1 mole}}{\mathrm{HCl(aq)}} \rightarrow \underset{\text{1 mole}}{\mathrm{H^+(aq)}} + \mathrm{Cl^-(aq)} \qquad (12)$$

Example 8.1

A solution of hydrochloric acid has a concentration of 1.85×10^{-3} mol.dm^{-3}. What will be the concentration of hydrogen ions in this solution?

Hydrochloric acid is a monobasic acid and it is a strong acid, therefore it dissociates completely in water to generate as many moles of hydrogen ions as there are moles of acid. Consequently:

$$[H^+] = [HCl]$$

where [ ] stands for concentration in mol.dm^{-3}.

Therefore:

$$[H^+] = [HCl] = 1.85 \times 10^{-3}\ \text{mol.dm}^{-3}$$

1.85×10^{-3} mol.dm^{-3} **Answer**

(b) Weak Acids

When any weak, monobasic acid, HA, is dissolved in water the following equilibrium is established:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad (13)$$

Therefore the concentrations of HA, H^+ and A^- will remain constant, as will the ratio of $[H^+]$ and $[A^-]$ to [HA]. So we can write:

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad (14)$$

where K_a is the ***dissociation constant*** of the acid.

Now, the position of equilibrium is well over to the left hand side and so very little acid is actually dissociated. As a result:

$$[HA]_{equilibrium} = [HA]_{original} = C \qquad (15)$$

Also, providing the solution is not too dilute we can ignore any hydrogen ions produced by the auto-ionisation of water, consequently:

$$[H^+] = [A^-] \qquad (16)$$

Therefore:

$$K_a = \frac{[H^+]^2}{C} \qquad (17)$$

Hence:

$$[H^+] = \sqrt{K_a C} \qquad (18)$$

Example 8.2

Calculate the concentration of hydrogen ions in a solution containing 2.5 × 10^{-3} $mol.dm^{-3}$ ethanoic acid, given that the K_a of ethanoic acid = 1.8 × 10^{-5}.

$$\left[H^{+}\right] = \sqrt{K_a C}$$

Therefore:

$$\begin{aligned}\left[H^{+}\right] &= \sqrt{\left(1.8\times10^{-5}\right)\left(2.5\times10^{-3}\right)}\\ &= \sqrt{4.5\times10^{-6}}\\ &= 2.12\times10^{-3}\,mol.dm^{-3}\end{aligned}$$

2.12 × 10^{-3} $mol.dm^{-3}$ **Answer**

6 Hydroxide Concentration and Base Strength

We have seen that on dissolving in water bases generate hydroxide ions and so form alkaline solutions. The greater the number of hydroxide ions produced per mole of base then the stronger is that base and the more alkaline is the solution.

(a) Strong Bases

Bases such as sodium hydroxide and potassium hydroxide are very strongly alkaline because they dissociate completely in aqueous solution

$$NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq) \qquad (19)$$

The sodium hydroxide is 100% ionised; thus ***the concentration of hydroxide ions is the same as the concentration of the base***. Such bases are obviously ***strong*** bases.

Example 8.3

A solution of sodium hydroxide has a concentration of 2.24 × 10^{-4} $mol.dm^{-3}$. What is the concentration of hydroxide ions in this solution?

Inspection of equation (15) shows that for every mole of sodium hydroxide in solution there are the same number of hydroxide ions present. Therefore, a solution containing 2.24 × 10^{-4} $mol.dm^{-3}$.sodium hydroxide contains 2.24 × 10^{-4} $mol.dm^{-3}$.hydroxide ions. Thus:

$[OH^{-}]$ = 2.24 × 10^{-4} $mol.dm^{-3}$. **Answer**

(b) Weak Bases

These generate only a few hydroxide ions in solution; for example ammonia:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq) \qquad (20)$$

where the equilibrium lies well to the left hand side and there are very few ammonium and hydroxide ions present in solution.

By analogy with weak acids it is possible to show that for any weak base, B, the hydroxide concentration is given by:

$$\left[OH^-\right] = \sqrt{K_b[B]} \qquad (21)$$

or

$$\left[OH^-\right] = \sqrt{K_b C} \qquad (22)$$

where C = [B] = the concentration of base in mol.dm^{-3} and K_b = the dissociation constant of the base.

Example 8.4

What is the concentration of hydroxide ions in a solution containing 0.075 mol.dm^{-3}.hydroxylamine (NH_2OH), given that the dissociation constant of hydroxylamine is 6.6×10^{-9} mol.dm^{-3}?

$$\left[OH^-\right] = \sqrt{K_b C}$$

$$= \sqrt{6.6 \times 10^{-9} \times 0.075}$$

$$= \sqrt{4.95 \times 10^{-10}}$$

$$\therefore \quad \left[OH^-\right] = 2.22 \times 10^{-5} mol.dm^{-3}$$

2.22×10^{-5} mol.dm^{-3}. **Answer**

7 The Ionic Product of Water, K_w

Pure water is an extremely weak electrolyte since it ***auto-ionises*** very slightly:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad (23)$$

As this is an equilibrium situation we can write an expression for K_c, the equilibrium constant:

$$K_c = \frac{\left[H^+\right]\left[OH^-\right]}{\left[H_2O\right]} \qquad (24)$$

But, since the degree of dissociation is so slight

$$[H_2O]_{\text{equilibrium}} = [H_2O]_{\text{original}} \qquad (25)$$

In other words, the concentration of the undissociated water remains virtually constant. Hence we can write:

$$K_c[H_2O] = [H^+][OH^-] \qquad (26)$$

Replacing the $K_c[H_2O]$ by a single constant term K_w, this becomes:

$$K_w = [H^+][OH^-] \qquad (27)$$

where K_w is known as the ***ionic product*** of water.

At normal room temperatures $K_w \approx 1.0 \times 10^{-14}$ mol^2.dm^{-6}, and because it is a constant it follows that if, in an aqueous solution, the concentration of hydrogen ions is increased then the concentration of hydroxide ions must be reduced accordingly, and *vice versa*. This is illustrated in the following table:

solution	**$[H^+]$ (mol.dm^{-3})**	**$[OH^-]$ (mol.dm^{-3})**	**$[H^+][OH^-]$ (K_w)**
1.0 mol.dm^{-3} HCl	1.0	1×10^{-14}	1×10^{-14}
pure water	1×10^{-7}	1×10^{-7}	1×10^{-14}
1.0 mol.dm^{-3}.NaOH	1×10^{-14}	1.0	1×10^{-14}

8 The Hydrogen Ion Concentration and pH; The Hydroxide Concentration and pOH

Because the hydrogen ion concentration can vary so widely in the environment, and because the majority of the concentrations encountered are less than 1.0 mol.dm^{-3}, Sϕrensen suggested that it would be more convenient to express hydrogen ion concentrations in terms of the common logarithm of their reciprocals, for which he coined the term “pH.” Thus:

$$pH = -\log_{10}\left[H^+\right] \qquad (28)$$

The hydroxide concentration can be dealt with in exactly the same way. Therefore, we can write:

$$pOH = -\log_{10}\left[OH^-\right] \qquad (29)$$

Given that the ionic product of water, K_w, is 1×10^{-14} then from equation 23 above it can be shown that:

$$\text{pH} + \text{pOH} = 14 \qquad (30)$$

Therefore,

$$\text{pH} = 14 - \text{pOH} \qquad (31)$$

and

$$\text{pOH} = 14 - \text{pH} \qquad (32)$$

It now becomes possible to determine the pH values of the solutions in the table on page 6. In the hydrochloric acid the $[H^+] = 1.0$ mol.dm^{-3}. Since $-\log_{10}1.0 = 0$ this solution will have a pH = 0. In pure water the $[H^+] = 1.0 \times 10^{-7}$ mol.dm^{-3}. Therefore, pH = $-\log_{10}1.0 \times 10^{-7} = 7$. Finally, in the sodium hydroxide solution the $[H^+] = 1.0 \times 10^{-14}$ mol.dm^{-3} and so the pH = $-\log_{10} 1.0 \times 10^{-14} = 14$. Thus, the complete table is:

solution	**$[H^+]$ (mol.dm^{-3})**	**$[OH^-]$ (mol.dm^{-3})**	**$[H^+][OH^-]$ (K_w)**	**pH**
1.0 mol.dm^{-3} HCl	1.0	1×10^{-14}	1×10^{-14}	0
pure water	1×10^{-7}	1×10^{-7}	1×10^{-14}	7
1.0 mol.dm^{-3}.NaOH	1×10^{-14}	1.0	1×10^{-14}	14

From this it can be seen that on a pH scale of 0 - 14, pH 7.0 is neutral, since $[H^+] = [OH^-]$. Values <7 are acidic while values >7 are alkaline. Thus the pH scale of acidity takes the following form:

pH	**0, 1, 2, ...**	**.. 5,6,**	**7**	**8, 9, ..**	**.. 12, 13, 14**
	very acidic	**weakly acidic**	**neutral**	**weakly alkaline**	**strongly alkaline**

In summary:

(a) For weak acids $\left[H^+\right] = \sqrt{K_a C}$

(b) For weak bases $\left[H^+\right] = \sqrt{K_b C}$

(c) $$pH = \log_{10} \frac{1}{\left[H^+\right]}$$

$$= -\log_{10} [H^+]$$

(d) $$pOH = -\log_{10} [OH^-]$$

(e) $$pH + pOH = 14$$

Worked Examples of Calculations Involving pH

1. Calculate the pH of a solution of hydrochloric acid, HCl, which has a concentration of 2.5×10^{-1} mol.dm^{-3}.

   [H+] = [HCl]

   = 2.5×10^{-1} mol.dm^{-3}

   Therefore,

   pH = $-\log_{10} 2.5 \times 10^{-1}$

   = 0.60

   Thus, the solution has a pH = 0.60 **Answer**

2. Calculate the pH of a solution of ethanoic acid having a concentration of 7.3×10^{-2} mol.dm^{-3}, given that the K_a of ethanoic acid is 1.8×10^{-5} mol.dm^{-3}..

$$\left[H^{+}\right] = \sqrt{K_a c}$$

$$= \sqrt{1.8 \times 10^{-5} \times 7.3 \times 10^{-2}}$$

$$= \sqrt{1.31 \times 10^{=6}}$$

$$= 1.15 \times 10^{-3}\, mol.dm^{-3}$$

Now

   pH = $-\log_{10}$[H+]

   = $-\log_{10} 1.15 \times 10^{-3}$

   = 2.94

   Thus the ethanoic acid solution has a pH = 2.94 **Answer**

3. Calculate the pH of a solution of sodium hydroxide having a concentration of 1.0×10^{-3} mol.dm^{-3}.

   Sodium hydroxide is a strong alkali and dissociates completely when dissolved in water. Therefore:

   [OH$^-$] = [NaOH]

   = 1.0×10^{-3} mol.dm^{-3}

   Now:

   pOH = $-\log_{10}$[OH$^-$]

   = $-\log_{10} 1.0 \times 10^{-3}$

   = 3.0

   Since

   pH = 14 - pOH

   ∴ pH = 14 - 3.0

   = 11.0

   Thus the solution of sodium hydroxide has a pH = 11.0 **Answer**

4. Calculate the pH of a solution of ammonia having a concentration of 8.63 × 10^{-2} mol.dm^{-3}, given that the K_b of ammonia is 1.8 × 10^{-5} mol.dm^{-3}.

$$\left[OH^-\right] = \sqrt{K_b c}$$

Therefore,

$$\left[OH^-\right] = \sqrt{1.8 \times 10^{-5} \times 8.63 \times 10^{-2}}$$

$$= \sqrt{1.5534 \times 10^{-6}}$$

$$= 1.25 \times 10^{-3} mol.dm^{-3}$$

Since pOH = $-\log_{10}$ [OH^-]

$$\begin{aligned} pOH &= -\log_{10} 1.25 \times 10^{-3} \\ &= 2.90 \\ pH &= 14 - pOH \\ \therefore\ pH &= 14 - 2.90 \\ &= 11.10 \end{aligned}$$

Thus the ammonia solution has a pH = 11.10 **Answer**

Exercise 1

Calculate the pH of the following solutions:

(a) 0.1mol.dm^{-3} hydrochloric acid. (pH = 1.0)

(b) 0.1 mol.dm^{-3} ethanoic acid (K_a = 1.8 × 10^{-5} mol.dm^{-3}). (pH = 2.87)

(c) 0.05 mol.dm^{-3} sodium hydroxide. (pOH = 1.3; pH = 12.7)

(d) 0.05 mol.dm^{-3} ammonia (K_b = 1.8 × 10^{-5} mol.dm^{-3}) (pOH = 3.02; pH = 10.98)