**18.1 Lewis acids and bases (HL)**

**Understandings:**

● A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.

● When a Lewis base reacts with a Lewis acid a coordinate bond is formed.

● A nucleophile is a Lewis base and an electrophile is a Lewis acid.

Learning objectives

• Understand the Lewis definition of acids and bases

• Recognise Lewis acids and bases

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Lewis acid–base theory is compatible with Brønsted–Lowry theory, it does not falsify it. By changing the perspective of acid–base reactions from the proton to the lone pair of electrons, it opens up a wider field of application. The proton no longer has a central role, it is just one example of a lone pair acceptor. Lewis acids include a wide range of both organic and inorganic species that are not recognized as acids in Brønsted–Lowry theory. Yet, in many cases, as we will see in the following sections, Brønsted–Lowry theory is sufficient and could be considered a more useful theory for the description of acid–base reactions, especially those occurring in aqueous solution.

**Comparing the Lewis and Brønsted–Lowry definitions**

Realizing that the base must have a lone pair of electrons, Gilbert Lewis, whose name famously belongs to electron dot structures reasoned that the entire reaction could be viewed in terms of the electron pair rather than in terms of proton transfer.

For example the reaction between ammonia and H ions to form ammonium ions,

+

H

H

**H**+

+

 N H

**H** N H

H

H

H+ is acting as an electron pair acceptor and the nitrogen atom in ammonia is acting as an electron pair donor. From such thinking Lewis developed a new, broader definition of acids and bases.

**• A Lewis acid is a lone pair acceptor.**

**• A Lewis base is a lone pair donor.**

By either Lewis or Brønsted–Lowry definition of bases, they are **species that must have a lone pair of electrons.**

In the case of acids, however, the Lewis definition is broader than the Brønsted–Lowry theory: no longer restricted just to H+, an acid by Lewis definition is **any species capable of accepting a lone pair of electrons**. The Lewis definition will also include molecules that have an **incomplete valence shell.**

*Lewis acid–base reactions result in the formation of a covalent bond, which will always be a* ***coordinate bond*** *because both the electrons come from the base.*

**Question**

1. **Describe the reaction between BF3 and NH3 to illustrate the Lewis acid-base reactions**
2. **What other elements in the periodic table demonstrate Lewis acid- base reactions. Use Cu 2+ and water ligands to show this and identify the Lewis acid and base in this example.**

**Nucleophiles and electrophiles: alternate language to electron donor and acceptor**

At about the same time as Lewis developed his acid–base theory, alternate language was being introduced to describe the behaviour of reactants with respect to electron pairs.

A **nucleophile** (‘likes nucleus’) is an electron-rich species that donates a lone pair to form a new covalent bond in a reaction.

An **electrophile** (‘likes electrons’) is an electron-deficient species that accepts a lone pair from another reactant to form a new covalent bond.

Clearly these terms are the same as those derived by Lewis. In other words, a nucleophile is a Lewis base and an electrophile is a Lewis acid.

**Question3**

**Give some examples of nucleophiles and electrophiles completing the table below**

|  |  |
| --- | --- |
| **Nucleophiles (Electron rich)** | **Electrophiles (electron deficient)** |
| OH- | BF3 |
|  |  |
|  |  |

In conclusion, many reactions cannot be described as Brønsted–Lowry acid–base reactions, but do qualify as Lewis acid–base reactions. These are reactions where no transfer of H+ occurs.

**18.2 Calculations involving acids and bases**

**Learning objectives**

• Understand what is meant by an acid dissociation constant and a base ionisation constant

• Arrange acids and bases in order of strength based on *K*a, p*K*a, *K*b or p*K*b values

• Carry out calculations involving *K*a, *K*b, p*K*a, p*K*b, pH and pOH

• Use the relationships *K*w = *K*a × *K*b and p*K*a + p*K*b = p*K*w

**Understandings:**

* The expression for the dissociation constant of a weak acid (Ka) and a weak base (Kb).
* For a conjugate acid–base pair, Ka × Kb = Kw.

**Guidance**

* The value Kw depends on the temperature.
* Only examples involving the transfer of one proton will be assessed.
* Calculations of pH at temperatures other than 298 K can be assessed.
* The relationship between Ka and pKa is pKa = –log10Ka and between Kb and pKb is pKb = –log10Kb.

***K*w is temperature dependent; temperature should always be stated alongside pH measurements.**

The ionic product constant of water *K*w, is given by,

 *K*w = [H+][OH–] = 1.00 × 10–14 at 298 K

As *K*w is an equilibrium constant, its value must be temperature dependent and the dissociation of water is **endothermic.**

Therefore an increase in temperature will **shift the equilibrium to the right** and increase the value of *K*w. This represents an increase in the concentrations of H+(aq) and OH–(aq), and so a decrease in pH.

In other words, the pH of pure water is 7.00 only when the temperature is 298 K.

Note that at temperatures above and below this, despite changes in the pH value, water is still a neutral substance as its H+(aq) concentration is equal to its OH–(aq) concentration.

pH and pOH scales are inter-related

pH = –log10[H+]; and was introduced in order to simplify the expression of the H+ concentration in a solution.

The same rationale can be applied to the OH– ions to simplify the expression of OH- concentration in solution.

Thus; the parallel scale, known as the **pOH scale**, is therefore used to describe the OH– content of solutions.

 **•** pOH = –log10[OH–]; and [OH–] = 10–pOH

 **•** pH = –log10[H+]; and [H+] = 10–pH

The scales are inverse, so the higher the H+ or OH– concentration, the smaller and the pH or pOH value. These values are usually positive and have no units.

From the relationship [H+]\_[OH–] = *K*w = 1.00 × 10–14 at 298 K, it follows that

 10–pH × 10–pOH = 1.00 × 10–14 at 298 K

By taking the negative logarithm to base 10 of both sides, we get

 pH + pOH = 14.00 at 298 K

The same terminology as pH and pOH can be applied to *K*w to derive **p***K***w**.

 **•** p*K*w = –log10(*K*w) and *Kw* =10- pKw

So we can rewrite the expression above in a form that will apply to all temperatures:

 pH + pOH = p*K*w

**Converting H+ and OH– into pH and pOH examples**

**Example: Lemon juice has a pH of 2.90 at 25°C. Calculate its [H+], [OH–], and pOH**.



**Strong acids and bases: pH and pOH can be deduced from their concentrations**

We assume full dissociation for strong acids and bases. Because of this we can deduce the ion concentrations and so calculate the pH or pOH directly from the initial concentration of the solution.

**Example: Worked example**

**Calculate the pH of the following at 298 K:**

**(a) 0.10 mol dm–3 NaOH(aq)**

**(b) 0.15 mol dm–3 H2SO4(aq)**

****

**Dissociation constants express the strength of weak acids and bases**

Weak acids and bases, unlike strong acids and bases, do not dissociate fully. This means we *cannot* deduce the concentrations of ions in their solutions from the initial concentrations, as the ion concentrations will depend on the extent of dissociation that has occurred. So we need some means of quantifying the extent of dissociation – and the process takes us back to equilibrium considerations.

Consider the generic weak acid HA dissociating in water:

 HA(aq) + H2O(l)  H3O+(aq) + A–(aq)

 Kc = $\frac{[H3O+][A- ]}{\left[HA \right][H2O ]}$

The concentration of water is considered to be a constant, we can combine this with *K*c to produce a modified equilibrium constant known as ***K*a**.

 Kc [H2O] = $\frac{[H3O+][A- ]}{\left[HA \right]}$

 Therefore, Ka = $\frac{[H3O+][A- ]}{\left[HA \right]}$

***K*a** is known as the **acid dissociation constant**. It will have a fixed value for a particular acid at a specified temperature.

*K*a depends on the position of the equilibrium of acid dissociation and gives a direct measure of the strength of an acid.

***The higher the value of K*a *at a particular temperature, the greater the dissociation, and so the stronger the acid*.**

Similarly, we can consider the ionization of a base using the generic weak base B.

**Questions**

1. **Derive the base constant Kb for the generic base B as above.**
2. Write the expressions for *K*a and *K*b for the following acid and base.

 **(a)** CH3COOH(aq)

 **(b)** NH3(aq)

**Calculations involving *K*a and *K*b**

The following points are to remind you of some key points and guide you in all the calculations that follow:

**•** The given concentration of an acid or base is its *initial* concentration – before dissociation occurs.

**•** The pH (or pOH) of a solution refers to the concentration of H+ ions (or OH– ions) at *equilibrium*.

**•** The concentration values substituted into the expressions for *K*a and *K*b must be the *equilibrium* values for all reactants and products.

**•** When the extent of dissociation is very small (very low value for *K*a or *K*b) it is appropriate to use the approximations:

 [acid]initial ≈ [acid]equilibrium

 [base]initial ≈[base]equilibrium

1 Calculation of *K*a and *K*b from pH and initial concentration

1. **Calculate *K*a at 298 K for a 0.01mol dm–3 solution of ethanoic acid (CH3COOH). It has a pH of 3.4 at this temperature.**

Write the equation for the dissociation of the acid. Insert the data in three rows: initial, change, and equilibrium.

From the pH we get the [H+] at equilibrium:

pH 3.4 ⇒ [H+] = 10–3.4 = 4.0 × 10–4 mol dm–3

From the stoichiometry of the reaction we know that [H+] = [CH3COO–]

CH3COOH(aq)  CH3COO–(aq) + H+(aq)

Initial (mol dm–3) 0.01

Change (mol dm–3) –4 × 10–4

Equilibrium (mol dm–3) 0.01 – (4 × 10–4)

~ 0.01

0.00

+4 × 10–4

4 × 10–4

0.00

+4 × 10–4

4 × 10–4

The approximation 0.01 ≈ 0.01 – (4 × 10–4) is valid within the precision of this data.

Write the expression for *K*a and substitute the equilibrium values.

*K*a 

[CH COO– ][H+ ] (4  10–4 )2

3

[CH3COOH]



 1.6  10

–5

0.01

1. **Calculate the *K*b for a 0.100 mol dm–3 solution of methylamine, CH3NH2 at 25°C . Its pH is 11.80 at this temperature.**

At 25 °C (298 K), pH + pOH = 14.00. Therefore pH 11.80 ⇒ pOH = 2.20

[OH–] = 10–pOH = 10–2.20 = 6.3 × 10–3

From the stoichiometry of the reaction [OH–] = [CH3NH3 ]

+

CH3NH2(aq) 0.100

–0.00630

0.0937

+

H2O(l) s

CH3NH3 (aq) 0.000

+0.00630

0.00630

+

+

initial (mol dm–3) change (mol dm–3) equilibrium (mol dm–3)

OH (aq) 0.000

–

+0.00630

0.00630

*K*b 

[CH NH + ][OH– ] (0.00630)2

3 3

[CH3NH2 ]



0.0937

 4.22  10

–4

**2 Calculation of [H+] and pH, [OH–] and pOH from *K*a and *K*b**

1. **A 0.75 mol dm–3 solution of ethanoic acid has a value for *K*a = 1.8 × 10–5 at a specified temperature. What is its pH at this temperature?**

To calculate pH we need to know [H+] at equilibrium, and therefore the amount of dissociation of the acid that has occurred: this is the ‘change’ amount in the reaction.

So let the change in concentration of CH3COOH = –*x*

Therefore change in concentration of CH3COO– and H+ = +*x*

CH3COOH(aq) 0.75

–*x*

0.75 – *x*

~ 0.75



CH3COO–(aq) + 0.00

+*x x*

initial (mol dm–3) change (mol dm–3) equilibrium (mol dm–3)

H+(aq) 0.00

+*x x*

As *K*a is very small, *x*, the amount of dissociation, is also extremely small and it is valid to approximate [CH3COOH]initial ≈ [CH3COOH]equilibrium.

*K*a 

[CH COO– ][H+ ]

3

*x*2

[CH3COOH] 0.75

  1.8  10-5

Therefore *x* =

1.8  105  0.75

= 3.7 × 10–3

[H+] = 3.7 × 10–3 ⇒ pH = 2.4

1. **A 0.20 mol dm–3 aqueous solution of ammonia has *K*b of 1.8 × 10–5 at 298 K . What is its pH?**

Let the change in concentration of NH3 = –*x*

 Therefore change in concentration of NH4+ and OH– = +*x*

NH3(aq) 0.20

–*x*

+

H2O(l) 

NH4 (aq) 0.00

+*x x*

+

+

OH (aq) 0.00

+*x* x

–

initial (mol dm–3) change (mol dm–3)

equilibrium (mol dm–3) 0.20 – *x*

≈ 0.20

As *K*b is very small, *x* the amount of dissociation is also extremely small, and so it is valid to approximate [NH3]initial ≈ [NH3]equilibrium

*K* b 

[NH + ][OH– ]

4

  1.8 

*x*2

–5

[NH3 ] 0.20

Therefore *x* = 1.8  10–5  0.20 = 1.9 × 10–3

[OH–] = 1.9 × 10–3

pOH = –log10 (1.9 × 10–3) = 2.72

Therefore at 298 K, pH = 14.00 – 2.72 = 11.28

**p*K*a and p*K*b**

Like pH and POH due to very small values it is convenient to use p*K*a and pKb as follows:

**•** p*K*a = –log10*K*a;and *K*a = 10– p*K*a

**•** pKb = –log10*K*b; and*K*b = 10 – p*K*b

Some examples of *K*a and p*K*a, *K*b and p*K*b values are given below, all at 298 K.

Table 1Weak acids

|  |  |  |  |
| --- | --- | --- | --- |
| **Acid**methanoic | **Formula**HCOOH | ***K*a**1.8 × 10–4 | **pKa**3.75 |
| ethanoic | CH3COOH | 1.8 × 10–5 | 4.76 |
| propanoic | C2H5COOH | 1.4 × 10–5 | 4.87 |
| Table 2 Weak Bases  |  |  |  |
| **Table 2 Weak bases**  |  **Formula**  |  **Kb p** |  **pKb** |
| ammonia | NH3 | 1.8 × 10–5 | 4.75 |  |
| methylamine | CH3NH2 | 4.6 × 10–4 | 3.34 |  |
| ethylamine | C2H5NH2 | 4.5 × 10–4 | 3.35 |  |

**The following points follow from the table.**

1. p*K*a and p*K*b numbers are usually positive and have no units.
2. The relationship between *K*a and p*K*a and between *K*b and p*K*b is inverse.
3. A change of one unit in p*K*a or p*K*b represents a 10 fold change in the value of *K*a or *K*b.
4. pKa and pKb must be quoted at a speci­fied temperature.
5. The lower the value of p*K*a, the stronger the acid.
6. The lower the value of p*K*b, the stronger the base.

**Relationship between *K*a and *K*b, p*K*a and p*K*b for a conjugate pair**





**18.3 pH curves**

**Learning objectives**

• Sketch titration curves (pH curves) for titrations involving any combination of strong and weak acids and bases

• Explain the important features of titration curves

• Understand how to work out p*K*a or p*K*b values from a titration curve

• Explain how an acid–base indicator works

• Understand what is meant by the pH range of an indicator

 • Select a suitable indicator for a titration

**Understandings:**

● The characteristics of the pH curves produced by the different combinations of strong and weak acid and bases.

● An acid–base indicator is a weak acid or a weak base where the components of the conjugate acid–base pair have different colours.

**Acid–base titrations**

Even when equivalent numbers of moles of acid and alkali have been added the pH is not necessarily 7.

This is why different indicators, which change colour at different pH values, are required for different titrations – for instance, phenolphthalein changes colour around pH 9 and is usually used for weak acid–strong base titrations.

The pH can be monitored during a titration by using a pH meter or a pH probe attached to a data logger

**Strong acid–strong base**

The titration curve (pH curve) for adding 0.100 mol dm−3 sodium hydroxide solution to 25.0 cm3 of 0.100 mol dm−3 hydrochloric acid is shown in Figure **8.17**.

The reaction that occurs is:

HCl(aq) + NaOH(aq) → NaCl(aq) + H2O(l)

The initial pH is 1.0 because the initial solution is 0.100 mol dm−3 hydrochloric acid.

The concentration of H+ ions is 0.100 mol dm−3 and the pH = −log100.10, i.e. 1.00.

 

 *A strong acid–strong base titration curve*

**Question**

1. **Describe the pH curve for strong acid-strong base titration above. What is the equivalence point?**
2. **If, instead of adding 0.100 mol dm−3 NaOH to 25 cm3 of 0.100 mol dm−3 HCl, we add 0.200 mol dm−3 NaOH what would be the titration curve? Describe the curve.**
3. **Draw the curve for adding 0.100 mol dm−3 HCl to 25 cm3 of 0.100 mol dm−3 NaOH**

 **Weak acid–strong base**

Let us consider adding 0.100 mol dm−3 NaOH to 25 cm3 of 0.100 mol dm−3 CH3COOH (ethanoic acid) (*K*a = 1.74 × 10−5). The titration curve is shown.

****

*A titration curve for adding 0.100 mol dm−3 NaOH to 25 cm3 of 0.100 mol dm−3 CH3COOH.*

1. **Describe the pH curve for strong acid-strong base titration above. Discuss the equivalence point and the change of pH at equivalence point?**

In Figure below the weak acid–strong base titration curve is compared with a strong acid–strong base titration curve.

****

Note that the strength of the acid does not affect the volume of base required to reach the equivalence point for a titration.

The volume of base required to reach the equivalence point depends only on the original volume of acid used, the concentration of the acid and the concentration of the base.

**Important differences**

For a weak acid-strong base titration:

• The initial pH is higher. The weak acid is only partially dissociated.

• The initial part of the curve, up to a volume of about 24 cm3 NaOH added, is steeper. Because the weak acid is only partially dissociated, the concentration of H+ ions in the solution is lower, and adding a certain volume of NaOH has a greater relative effect on the pH than for a strong acid, in which the concentration of H+ ions is higher.

• The steep part of the curve is more in the alkaline region.

• The pH at the equivalence point is higher than 7.

 **Determination of p*K***a **from a titration curve**

In the above example of the titration of 0.100 mol dm−3 ethanoic acid with 0.100 mol dm−3 NaOH, 25.0 cm3 of NaOH is required to reach the equivalence point. Here we will consider the point in the titration when half this amount of NaOH has been added, i.e. 12.5 cm3.

When 12.5 cm3 of NaOH has been added, half of the CH3COOH has been converted to CH3COONa, and therefore the concentrations of CH3COOH and CH3COONa are equal.

****

The p*K*a value of the acid is equal to the pH at the half-equivalence point.

So at the half-equivalence point we can read the value of p*K*a from the graph shown

Note: [CH3COONa(aq)] is equal to [CH3COO−(aq)], as the ionic salt is fully dissociated in solution.

**Strong acid–weak base titrations**

Let us consider adding 0.100 mol dm−3 NH3(aq) to 25 cm3 0.100 mol dm−3 HCl(aq)). The pH at the equivalence point for a strong acid– weak base titration is at a pH lower than 7. At the equivalence point the NH3 has reacted with HCl to form NH4Cl:

NH3(aq) + HCl(aq) → NH4Cl(aq)

****

The ammonium ion is, however, the conjugate acid of a weak base and as such will dissociate to a certain extent in aqueous solution according to the equation:

NH4+(aq) NH3(aq) + H+(aq)

So the concentration of H+ ions in the solution is increased, and the pH is lower than 7.

**Titration curve for adding a weak base to a strong aci**d.



At the half–equivalence point of this titration, 12.5 cm3 of HCl has been added. The equilibrium that exists in this solution is:

 NH3(aq) + H2O(l) NH4+(aq) + OH−(aq)

The expression for *K*b is:

 *K*b= $\frac{\left[[NH4+(aq) \right][OH-(aq)]}{[NH3 aq ]}$

 

When 12.5 cm3 of HCl has been added, half of the NH3 will have been converted into NH4+, and so the concentration of NH3 will be equal to the concentration of NH4+.

Therefore, at the half equivalence point: *K*b = [OH−].

Taking −log10 of both side we get: p*K*b = pOH.

At 25 °C, pH + pOH = 14, so, at the half equivalence point, 14 − pH = p*K*b. So we can thus work out the p*K*b for ammonia from the graph.

The pH at the half–equivalence point is 9.25, so the p*K*b of ammonia is given by:

14 − 9.25 = p*K*b

 p*K*b for ammonia is 4.75.

**Weak acid–weak base**

An example of titration of a weak acid and a weak base is the addition of 0.100 mol dm−3 NH3(aq) to 25.0 cm3 of 0.100 mol dm−3 CH3COOH.

There is no very steep (almost vertical) part in this titration curve.

The pH at the equivalence point may be lower than 7 or higher than 7, depending on the relative strength of the acid and the base.

 

  ***A weak acid–weak base titration curve.***

 **18.4 Indicators**

Acid–base titrations are carried out to establish the equivalent amounts of acid and base that react with each other, and hence the concentration of the acid or the alkali.

These indicators are themselves weak acids or weak bases in which the undissociated and dissociated forms have different colours.

If we consider an indicator HIn that is a weak acid, it exists in equilibrium in solution as follows:

 HIn(aq)  H+(aq) + In–(aq)

 colour A colour B

By applying Le Chatelier’s principle, we can predict how this equilibrium will respond to a change in the pH of the medium.

**•** Increasing [H+]: the equilibrium will shift to the left in favour of HIn.

**•** Decreasing [H+]: the equilibrium will shift to the right in favour of In–.

At low pH colour A will dominate and at higher pH colour B will dominate.

**pH range of an indicator; Indicators change colour when the pH is equal to their pKa**

The change in colour of methyl orange, known as its **change point** or **end-point**, happens in the range pH 3.1–4.4. What determines the pH at which this occurs for an indicator?

We can answer this by considering the equilibrium expression for the above reaction.

The acid dissociation constant is defined as follows:

 *Ka* =$\frac{\left[H+\right][In-]}{[HIn]}$

At the point where the equilibrium is balanced between the acid and its conjugate base, that is where [In–] = [HIn], the indicator is exactly in the middle of its colour change. As these values cancel in the equation

 *Ka* = [H+]

the expression becomes simplified as *K*a = [H+] or p*K*a = pH.

At this point, the addition of a very small volume of acid or base will shift the equilibrium as described above, and so cause the indicator to change colour – this is its end-point.

**The pH range of an indicator is the pH values between which the indicator has intermediate colours because comparable amounts of the un-ionised and ionised forms are present.**

***The pH ranges of various indicators are given in Table 22 on the data booklet.***

**Where possible, an indicator should be chosen so that the equivalence point of the titration occurs within the pH range of the indicator.**

In order to have a clear/sharp end point for a titration, the range of the indicator must occur completely within the very steep part of the titration curve.

For an indicator that is a weak base, the pH range will be (14 − p*K*b) ± 1 and so an indicator will be suitable for a titration if 14 − p*K*b is close to the pH at the equivalence point of the titration.

**Questions**

**Discuss how suitable bromothymol blue is for a titration curve below.**

 

 ***The colour changes of bromothymol blue during a strong acid–strong base titration.***

**Questions**

1. **What happens in the above titration if, we do the same titration with an indicator that changes colour from red to yellow and has a pH range of 1.2–2.8**

 The curve below shows weak acid- strong base titration and various indicators range

 

 ***The ranges of various indicators superimposed on a weak acid–strong base titration curve.***

1. **Identify the most suitable indicators for this titration and suitability of bromothymol blue.**
2. **Comment on how suitable is an indicator in the weak acid- weak base titration?**

**18.5 Salt hydrolysis**

**Learning objectives**

• Work out whether a solution of a salt will have a pH of lower than, equal to or higher than 7

• Understand that the pH of a solution of a salt depends on the charge (and size) of the cation

A salt will be formed when an acid reacts with a base:

 acid + base → salt + water

When a solid salt is dissolved in water, the resulting solution may be acidic, basic or neutral, depending on the particular salt dissolving.

**Salt of a weak acid and a strong base (pH > 7)**

Consider the salt sodium ethanoate (CH3COO−Na+), formed when NaOH reacts with ethanoic acid (CH3COOH):

 CH3COOH(aq) + NaOH(aq) → CH3COONa(aq) + H2O(l)

If some solid sodium ethanoate is dissolved in water, the pH of the solution will be greater than 7.

When the salt dissolves in water, the two ions separate from each other – the solution contains CH3COO−(aq) and Na+(aq) ions.

The CH3COO− ion is the conjugate base of ethanoic acid (a weak acid) and so, acting as a base, will react with water molecules to accept a proton according to the equilibrium:

 CH3COO−(aq) + H2O(l) CH3COOH(aq) + OH−(aq)

The concentration of OH− ions in the solution has been increased and the solution is alkaline. This process is called **salt hydrolysis** – the salt has reacted with water.

The other ion from CH3COONa present in this solution, the Na+ ion, comes from a strong base (NaOH), which is fully ionised. There is therefore no tendency for Na+ to react with the OH− ions produced.

**Salt of a strong acid and a weak base (pH < 7)**

Consider ammonium chloride (NH4Cl). This is the salt of a strong acid (HCl) and a weak base (NH3):

 NH3(aq) + HCl(aq) → NH4Cl(aq)

When this is dissolved in water, an acidic solution is formed.

The NH4+ is the conjugate acid of the weak base NH3 and will therefore dissociate according to the equation:

 NH4+(aq)  NH3(aq) + H+(aq)

H+ is generated, and so the solution of NH4Cl is acidic. The pH of a 0.500 mol dm−3 solution of NH4Cl is 4.78.

Cl− is the conjugate base of the strong acid, HCl. It is therefore an extremely weak base (the stronger the acid, the weaker the conjugate base).

**Salt of a strong acid and a strong base (pH = 7)**

Consider sodium chloride, NaCl. This is made from the strong acid HCl and the strong base NaOH. These are both fully dissociated in aqueous solution, so a solution of NaCl is neutral (pH 7 at 25 °C).

**Salt of a weak acid and a weak base (pH = ?)**

Consider ammonium ethanoate CH3COO−NH4+. This is the salt of the weak acid (CH3COOH) and the weak base (NH3(aq)). It is not possible to predict whether the solution is acidic or alkaline without looking at the p*K*a values.

When ammonium ethanoate is dissolved in water, CH3COO− acts as a base and NH4+ acts as an acid:

CH3COO−(aq) + H2O(l)  CH3COOH(aq) + OH−(aq) p*K*b = 9.24

 NH4+ (aq)  NH3(aq) + H+(aq) p*K*a = 9.25

Because the p*K*b value is slightly lower (lower value = stronger) than the p*K*a value, the solution will be slightly alkaline. However, the values are very close together, so the pH of a solution of ammonium ethanoate will be very close to 7.0.

**Question**

1. **Predict with a reason the pH for a solution of ethylammonium ethanoate (C2H5NH3+CH3COO−) given the following information:**

CH3COO−(aq) + H2O(l)  CH3COOH(aq) + OH−(aq) p*K*b = 9.24

 C2H5NH3+(aq) C2H5NH2(aq) + H+(aq) p*K*a = 10.73

**Acidity due to positive ions in solution**

Let us consider a solution of iron(III) chloride. A 0.100 mol dm−3 solution of iron(III) will have a pH of less than 2

Positive ions in solution are hydrated to form aqueous ions, e.g. Fe3+(aq). The formula of Fe3+(aq) is [Fe(H2O)6]3+. This ion dissociates in solution according to the equation:

[Fe(H2O)6]3+(aq) [Fe(H2O)5(OH)]2+(aq) + H+(aq)

Hence the solution is acidic due to the H+ ions produced.

The reason that this occurs with 3+ ions is because of the high charge density (or charge to radius ratio) of the ion, which causes the water molecule to be sufficiently **polarised** for H+ to dissociate. The Fe3+ ion pulls electrons away from the H2O molecules, which increases the δ+ charge on the hydrogen so that it is more readily lost as H+

The larger an ion is and the lower its charge, then the smaller the charge density of the ion and the lower its tendency to polarise water molecules. So the Fe2+ ion will cause less polarisation of water molecules and, although a solution of Fe2+(aq) will still be acidic, it will have a higher pH than a solution of Fe3+(aq) of the same concentration.

H

H

H

H

H+

H+

H

O–

H

H

H

O

O

Fe3+

 O

O

O

H H

The polarisation of one of the water ligands in [Fe(H2O)6]3+.

**18.6 Buffer solutions**

**Learning objectives**

• Understand what is meant by a buffer solution and how both acidic and basic buffers can be made

• Describe how a buffer solution works when small amounts of acid/base are added

The blue line on the graph in Figure belowshows the result of adding 10 cm3 of 0.100 mol dm−3 hydrochloric acid in stages to 100 cm3 of water.

The orange line shows the effect of adding the hydrochloric acid to 100 cm3 of a buffer solution formed by mixing 50 cm3 of 1.00 mol dm−3 ethanoic acid and 50 cm3 of 1.00 mol dm−3 sodium ethanoate. The pH of the water changes from 7.00 to 2.04 when 10 cm3 of hydrochloric acid are added – the pH of the buffer solution changes from 4.76 to 4.74. When 10 cm3 of 0.100 mol dm−3 sodium hydroxide are added to 100 cm3 of the ethanoic acid/sodium ethanoate buffer solution, the pH changes from 4.76 to 4.78.

The pH of the buffer solution remains virtually constant when an acid or a base is added.

**A buffer is a solution that resists changes in pH when small amounts of acid or alkali are added.**

pH

8

7

6

5

4

3

2

1

0

Buffer solution

Water

0 2 4 6 8 10

Volume of hydrochloric acid added/ cm3

The **‘small amount’** in this definition is important. If, for instance, 33.3 cm3 of 2.00 mol dm−3 hydrochloric acid is added to 100 cm3 of the ethanoic acid/sodium ethanoate buffer solution we have just considered, the pH will change by about 4.5 units! A buffer solution always contains an acid and a base.

Buffers are important in many industrial processes and biological systems (for example, the blood – the pH of blood is about 7.4, and if it changes by about 0.5 in either direction you would die!). They are also used in products such as contact lens solutions, cosmetics and shampoos.

 **Acid buffer solutions**

An acid buffer solution consists of a weak acid (e.g. ethanoic acid) and a salt of that weak acid (e.g. sodium ethanoate). The equilibrium in this solution is:

CH3COOH(aq)  CH3COO−(aq) + H+(aq)

If some hydrochloric acid is added to this solution, the added H+ reacts with the CH3COO− in the solution:

CH3COO−(aq) + H+(aq) → CH3COOH(aq)

If some sodium hydroxide is added to the solution, the added OH− reacts with the CH3COOH in the solution:

 CH3COOH(aq) + OH−(aq) → CH3COO−(aq) + H2O(l)

**Question**

1. **Using the expression for for *K*a explain why the pH of the ethanoic acid- sodium ethanoate buffer changes so little.**

 **Basic buffer solutions**

A basic buffer solution consists of a weak base (e.g. ammonia) and a salt of that weak base (e.g. ammonium chloride). The equilibrium in this solution is:

NH3(aq) + H2O(l) NH4+(aq) + OH−(aq)

If some hydrochloric acid is added to this solution, the added H+ reacts with the NH3 in the solution:

NH3(aq) + H+(aq) → NH4+(aq)

If some sodium hydroxide is added to the solution, the added OH− reacts with the NH4+ in the solution:

NH4+(aq) + OH−(aq) → NH3(aq) + H2O(l)

As above, if the concentrations of NH3 and NH4+ in the solution are both high, any small change in their concentrations has very little effect on the [NH4+(aq)] : [NH3(aq)] ratio in the *K*b expression.

 *K*b = $\frac{\left[NH4+\left(aq\right)\right][OH-\left(aq\right)]}{[NH3\left(aq\right)]}$

**Making buffer solutions by partial neutralisation of a weak acid/base**

A buffer solution can be made by partial neutralisation of a weak acid with a strong base – for example by adding sodium hydroxide to ethanoic acid. The reaction that occurs is:

 CH3COOH(aq) + NaOH(aq) → CH3COONa(aq) + H2O

When 10 cm3 of 0.100 mol dm−3 NaOH is added to 25 cm3 of 0.100 mol dm−3 CH3COOH, some of the ethanoic acid will be converted to sodium ethanoate, but there will still be some ethanoic acid left.

As long as the number of moles of sodium hydroxide added is fewer than the number of moles of ethanoic acid present in the original solution, the solution will contain both ethanoic acid and sodium ethanoate and act as a buffer.

The graph in Figure belowshows the titration curve of a weak acid (ethanoic acid) with a strong base (NaOH). The shaded region in the figurerepresents the pH range over which this solution acts as buffer.

 

A buffer solution can be also be made by partial neutralisation of a weak base with a strong acid – for example when hydrochloric acid is added to ammonia solution. The reaction that occurs is:

NH3(aq) + HCl(aq) → NH4Cl(aq)

As long as the number of moles of hydrochloric acid added is lower than the number of moles of ammonia in the solution, the solution will contain some NH3 and some NH4Cl and will act as a buffer. The titration curve for adding 0.100 mol dm−3 HCl to 25 cm3 of 0.100 mol dm−3 ammonia solution is shown in figure below.

 