**3.1.12 Acids & bases**

**AS Link:**

**3.1.6 – Equilibria (Le Chatelier’s principle & Kc)**

**Brønsted-Lowry acid–base equilibria in aqueous solution**

In 1923 Johannes Brønsted and, independently, an Englishman Thomas Lowry extended the acid-base theory to give new definitions of acids and bases:

***Definitions***:

A **Brønsted-Lowry acid** is a substance which **donates a proton** in a reaction.

A **Brønsted-Lowry base** is a substance which **accepts a proton** in a reaction.

A **Brønsted-Lowry acid-base reaction** is a **transfer** of **protons** under **equilibrium** conditions.

Another definition derived by the American called Lewis states an **acid is an electron pair acceptor** and a **base is an electron pair donor**, this widens the classification.

The proton in aqueous solution

**H+ is just a proton** because hydrogen only has one electron, if it is lost then only a proton remains. Since it then has no electrons of its own it can only form a bond with a species that has a lone pair of electron. Due to its small size and high electric field it has unusual properties compared to other positive ions. It is never found in isolation; in aqueous solutions it is always **bonded to at least one water molecule to form H3O+**.

For simplicity a proton is represented as **H+ (aq)** rather than H3O+ (aq).

**Acids release hydrogen ions** when they **dissolve in water**, but hydrogen ions don’t exist on their own, they **combine with a water** molecule to form a **hydronium ion H3O+** (also called oxonium ion or hydroxonium ion).

HA (aq) + H2O (l) → H3O+ (aq) + A-(aq)

**Bases accept hydrogen ions** from water molecules when they are in solution.

B (aq) + H2O (l) → BH+ (aq) + OH-(aq)

According to Brønsted and Lowry reactions of acids and bases in aqueous solutions always involves the **transfer of protons under equilibrium conditions**:

HA (aq) + B (aq) BH+ (aq) + A-(aq)

acid base

Neutralisation

**Hydroxide ions** are Brønsted-Lowry bases as they **accept protons** and will react almost completely with **hydrogen ions or hydronium ions** to **form water**.

Simplest ionic equation:

**H3O+ (aq) + OH- (aq) 2H2O (l)**

**LEARN – neutralisation equation**

Simplified to:   
**H+ (aq) + OH- (aq) H2O (l)**

**Examples**

Brønsted-Lowry acid-base reactions:

HCl (g) + NH3 (g) → NH4Cl (s)

acid base

***Task: Identify the Brønsted-Lowry acid & base***

1. Na2CO3 + 2HCl → 2NaCl + H2O + CO2

base acid base acid

1. H2SO4 + HNO3 → H2NO3+ + HSO4-

acid base acid base

1. HCl + H2O → H3O+ + Cl-

acid base acid base

1. NH3 + H2O → NH4+ + OH-

base acid acid base

***Sheet: Brønsted-Lowry acids & bases***

**Dissociation in water**

Strong acids and strong bases

In water **strong acids** are **nearly completely dissociated** into their ions. N.B. a strong acid does not need to be 100% ionised, anything above 50% dissociation is a strong acid. At normal concentrations strong acid molecules are **fully ionised**.

|  |  |  |
| --- | --- | --- |
| **STRONG acid**  **HX (aq) →H+(aq) + X-(aq)** |  | There are only a limited number of strong acids in water:   * Hydrohalic acids   – **H**Cl, **H**Br, **H**I  (not HF it is a weak acid)   * Nitric acid – **H**NO3 * Sulphuric acid – **H**2SO4 * Phosphoric acid – **H**3PO4 |

**Monoprotic** acids dissociate to give **one** mole H+ **per mole of acid**

* **H**Cl, **H**Br, **H**I, **H**NO3

**Diprotic** acids dissociate to give **two** moles H+ **per mole of acid**

* **H**2SO4

|  |  |
| --- | --- |
| **For strong acids the equilibrium lies far to the right** – proton transfer is virtually complete:  HCl (aq) + H2O (l) H3O+ (aq) + Cl- (aq)  acid base |  |

**Alkali metal hydroxides are strong bases**, they fully dissociate when dissolved in water, forming aqueous hydroxide ions:

water

BOH (aq) B+ (aq) + OH- (aq)

Examples of **strong bases** in water (**alkalis**):

* Na**OH**

**Monobasic** or **monoacidic base** dissociates to give **one** mole **OH-** **per mole of alkali**

**Dibasic** or **diacidic base** dissociates to give **two** moles **OH-** **per mole of alkali**

* Li**OH**
* K**OH**
* Ca(**OH**)2

Weak acids and bases

The **majority** of **acids** and **bases** are **weak**, they are **partially dissociated** when dissolved in water, so at normal concentration in water they are **partially ionised**. The **concentration of acid is not equal to [H+]**.

|  |  |
| --- | --- |
| **WEAK acid**  **HA (aq) H+(aq) + A-(aq)** |  |

**Weak acid** - ethanoic acid **dissociates partially** into ethanoate ions and hydrogen ions.

CH3COOH (aq) H+ (aq) + CH3COO- (aq)

**Weak base** - ammonia **dissociates partially** into ammonium ions and hydroxide ions.

NH4OH(aq) NH4+ (aq) + OH- (aq)

Summary – strength and concentration

The **strength** of an acid or base indicates the **position of equilibrium** established when **dissolved in water**.

Equilibrium:

* right – strong
* left – weak
* Strong – complete dissociation in water
* Weak – partial dissociation in water

The **concentration** (mol dm-3) or an acid or base relates to **amount of water** present.

So it’s possible to have:

* Diluted strong acid or base
* Concentrated weak acid or base

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Strength (degree of dissociation) | |  | ***Demo: Conductivity strong & weak acid*** |
| Concentration (mol dm-3) | strong | weak |
| high | ✓ | ✓ |
| low | ✓ | ✓ |

**Ionisation of water**

**Water dissociates** into **hydronium** **ions** and **hydroxide ions**, it acts as a Brønsted-Lowry **acid** (**donating a proton**) and Brønsted-Lowry **base** (**accepting a proton**), so an **equilibrium** exists:

H2O(l) + H2O(l) H3O+(aq) + OH-(aq)

***Task: Identify the Brønsted-Lowry acid & base on both sides of the equation***

lost H+

H2O (l) + H2O (l) H3O+ (aq) + OH- (aq)

gained H+

acid base acid base

This **simplified** equilibrium is established: **H2O (l) H+ (aq) + OH- (aq)**

With the **equilibrium constant**: Kc = [H+] [OH-]

[H2O]

Water only **dissociates slightly** so the **equilibrium** **far** to the **left** (few H+ and OH-) giving a **large** **constant** **concentration of water.** By multiplying the expression [H2O]

A new constant can be derived called the **ionic product of water** with symbol, **Kw.**

Kw = Kc x [H2O(l)] = [H+] [OH-] x ~~[H~~~~2~~~~O(l)]~~

~~[H~~~~2~~~~O]~~

So Kw = [H+(aq)]eqm [OH-(aq)]eqm

**Gives the ionic product of water**

Units = (mol dm-3)2 = **mol2 dm-6**

**Kw = [H+] [OH-]**

**Kw** always has the **same** **value** for an aqueous solution at a **given temperature**. The value of **Kw changes** as the **temperature changes**. At 298K Kw = 1.00 x 10-14 mol2 dm-6.

***Fact recall: CGP98 Q1-4***

**pH scale**

In 1909 Danish biochemist Søren Sørenson worked for Carlsberg brewery. Brewing requires controlling acidity so yeast can grow but unwanted bacteria can’t and allows fermentation process. The concentrations of acid used were very small one ten-thousandth of a mole per litre so Sorenson looked for a way to avoid using numbers such as 0.0001 (1 x 10-4). By taking the log10 it gives you - 4, then he took away the negative to give a simple number 4. The pH scale was born.

The acidity of a solution depends on the **concentration of H+ (aq)** and is measured on the **pH scale**.

**pH** **= -log10 [H+(aq)]**

**pH** normally quoted to **2 decimal places**

[H+] represents concentration Units: **mol dm-3**

On the pH scale:

* **Higher [H+]** the **lower** the **pH**
  + [H+] > 1.0 mol dm-3 give pH < 1 e.g. [H+] 10.0 mol dm-3 pH -1
* A difference on **one pH means a tenfold difference in [H+]**
  + e.g. pH 0 [H+] 1.0 mol dm-3 pH 2 [H+] 0.1 mol dm-3 pH 3 [H+] 0.01 mol dm-3
* **Measures alkalinity** as well – as [H+] decreases [OH-] increases
  + If solution [H+] > [OH-] – acidic with pH < 7
  + If solution [H+] = [OH-] – neutral with pH < 7 (only at 298K)
  + If solution [H+] < [OH-] – alkaline with pH > 7
* Measure using **universal** **indicators** (a mixture of indicators to give a range of colours)
* Measure using **pH meters**

***Demo: Rainbow fizz***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **[OH-]**  **mol dm-3** | **pH** | **[H+]**  **mol dm-3** | **[OH-]**  **mol dm-3** | **pH** | **[H+]**  **mol dm-3** |
| 1.0 x 10-14 | 0 | 1.0 | 1.0 x 10-6 | 8 | 1.0 x 10-8 |
| 1.0 x 10-13 | 1 | 1.0 x 10-1 | 1.0 x 10-5 | 9 | 1.0 x 10-9 |
| 1.0 x 10-12 | 2 | 1.0 x 10-2 | 1.0 x 10-4 | 10 | 1.0 x 10-10 |
| 1.0 x 10-11 | 3 | 1.0 x 10-3 | 1.0 x 10-3 | 11 | 1.0 x 10-11 |
| 1.0 x 10-10 | 4 | 1.0 x 10-4 | 1.0 x 10-2 | 12 | 1.0 x 10-12 |
| 1.0 x 10-9 | 5 | 1.0 x 10-5 | 1.0 x 10-1 | 13 | 1.0 x 10-13 |
| 1.0 x 10-8 | 6 | 1.0 x 10-6 | 1.0 | 14 | 1.0 x 10-14 |
| 1.0 x 10-7 | 7 | 1.0 x 10-7 |  |  |  |

pH of water

The equilibrium reaction for the **dissociation of water** is **endothermic**.

**H2O (l) H+ (aq) + OH- (aq) ∆H= +57.3 kJ mol**-1

**Kw = [H+] [OH-]**

In **pure water** there is always one mole H+ ion for each mole OH- ion, so **[H+] = [OH-]**.

Therefore, for pure water:

**Kw = [H+]2**

Calculating the pH of pure water

For pure water **Kw = [H+]2**. If the value of **Kw is known** then the **pH** of water can be **calculated**.

[H+] = √Kw

pH = -log10 [H+]

At 298K, Kw is 1.0 x 10-14 mol2 dm-6.

Kw = 1.0 x 10-14 = [H+]2

[H+ (aq)] = = 1.0 x 10-7 mol dm-3

**pH** = -log10 1.0 x 10-7 = **7.00**

Since **Kw is temperature dependant** and in **neutral solution** the concentration of hydrogen ions and hydroxide ions are equal, **[H+] = [OH-]**, the **pH must vary with temperature**. **Only at 298K does water have pH of 7.00**.

***Task: Calculate pH of water at these temperatures***

|  |  |  |  |
| --- | --- | --- | --- |
| **Temp/K** | **Temp/oC** | **Kw/mol2 dm-6** | **pH** |
| 273 | 0 | 0.1 x 10-14 | 7.50 |
| 293 |  | 0.7 x 10-14 | 7.08 |
| 298 | 25 | 1.0 x 10-14 | 7.00 |
| 303 |  | 1.5 x 10-14 | 6.91 |
| 333 |  | 5.6 x 10-14 | 6.63 |
| 373 | 100 | 51.3 x 10-14 | 6.14 |

This shows that when the **temperature** **increases Kw increases** and the **forward** **reaction** must be **endothermic**.

Therefore, the value of **Kw increases with temperature** as the **equilibrium** will **move** to the **right** to oppose the increase, resulting in an **increase** in **hydrogen ions** and a **decrease in pH**.

At its **boiling point water** has a **pH** ofabout **6**, it is **still neutral** because it has an **equal number of H+ and OH-**, i.e. **[H+] = [OH-]**.

***Starter: 3.1 – pH and Kw***

***Sheet: Ionic product of water***

**pH calculations for strong acids and bases**

Finding pH of a strong acid from a known concentration

**Strong acids** can be regarded as **fully ionised** in dilute aqueous solutions, so the **hydrogen ion concentration** of a **monoprotic** acid is **equal to the concentration of the acid**. If the [H+] is known then the pH can be calculated.

[monoprotic acid] = [H+] [diprotic acid] = 2 [H+]

**pH** **= -log10 [H+(aq)]**

**Example – CGP100**

Calculate the pH of a 0.10 mol dm-3 solution of HCl

Method

[H+] = [HCl] = 0.10 mol dm-3

Answer

pH = -log10 [H+] = -log10 0.10 = **1.00** **N.B. 2 d.p**

**Example – CGP100**

Calculate the pH of a 0.10 mol dm-3 solution of H2SO4

Method – diprotic acid

[H+] = 2 x [H2SO4] = 2 x 0.10 = 0.20 mol dm-3

Answer

pH = -log10 [H+] = -log10 0.20 = **0.70** **N.B. 2 d.p**

***Task:***

***Calculate pH of 1.00 mol dm-3 solution of HCl***

[H+] = [HCl] = 1.00 mol dm-3

pH = -log10 1.00 = **0.00**

***Calculate pH of 0.160 mol dm-3 solution of H2SO4***

[H+] = 2 x [H2SO4] = 0.320 mol dm-3

pH = -log10 0.320 = **0.49**

Finding concentration of a strong acid from a known pH

This is the reverse of the calculation to work out the pH, reverse or **antilogs logs**.

**[H+] = 10-pH**

**Example**

An aqueous solution of a strong monoprotic acid, HX, has a pH of 2.50. Calculate the concentration of the acid.

Method

[H+] = 10-pH

Answer

Hence [H+] = antilog (-2.50) = 10-2.5 = **3.20 x 10-3 mol dm-3** **N.B. Units**

Comment

Since monoprotic acid is strong, it’s fully dissociated [HX] = [H+] so is 3.2 x 10-3 mol dm-3

**Example – CGP99**

A solution of sulphuric acid has a pH of 1.52. What is the hydrogen ion concentration?

Method

[H+] = 10-pH

Answer

Hence [H+] = antilog (-1.52) = 10-1.52 = **3.0 x 10-2 mol dm-3**

Comment

Although a diprotic acid pH = [H+]

***Task:***

***Calculate [H+] of HCl with pH of 3.00***

pH = antilog (-3.00) = 10-3.00

[H+] = **1.0 x 10-3 mol dm-3**

***Calculate concentration of H2SO4 with pH of 5.52***

pH = antilog (-5.52) = 10-5.52

[H+] = 3.0 x 10-6 mol dm-3

[H+] = ½ [H2SO4] = 3.0 x 10-6 / 2 = **1.5 x 10-6 mol dm-3**

Dilution of a strong acid

If an acid is diluted by **adding water** the **moles** of the acid **won’t change**, but the total volume will change and so the **concentration of hydrogen ions changes**.   
The **pH will change**

**Example**

Calculate the pH of the solution formed when 50cm3 of water is added to 50cm3 of 0.10 mol dm-3 HCl.

nHCloriginal 0.1 x 50 x 10-3 = 5.00 x 10-3 mol

New total volume = 50 + 50 = 100 cm3

new [HCl] 5.00 x 10-3 / 100 x 10-3 = 0.05 mol dm-3

[H+] = 0.05

pH = -log 0.05 = **1.30**

**Example**

Calculate the volume of water which must be added to 25.0cm3 of 0.5 mol dm-3 HCl to increase its pH from 0.30 to 0.60.

Final [H+] = 10-0.6 = 0.251 mol dm-3

If n1 = n2 then c1v1 = c2v2

v2 = final volume

0.5 x 25 x 10-3 = 0.251 x v2

v2 = 0.0498 dm3 = 49.8 cm3

New total volume after adding water

Water added = 49.8 – 25 = 24.8 cm3

***Sheet: pH of strong acids***

***Application: CGP99 PQ1-3***

Finding pH of a strong base from a known concentration

**Strong bases** are nearly completely **ionised in water**, so the **concentration** of the **hydroxide ions** is the **same** as the **concentration** of the **base**. But **pH** is the **log** of the **concentration** of **hydrogen** **ions**; however, the **ionic product of water** expression can be used to **find** the **concentration** of **hydrogen** **ions** as long as the value for Kw is known. Then the **pH** can be **calculated**.

Ionic product of water

**Kw = [H+] [OH-]**

**Example – CGP101**

The value of Kw at 298K is 1.0 x 10-14 mol2 dm-6.Find the pH of a 0.100 mol dm-3 solution of NaOH at 298K.

Method

Since NaOH is fully ionised in aqueous solution and will donate one mole of OH- ions per mole of base.

[NaOH] = [OH-] = 0.100 mol dm-3

Answer

Kw = [H+] [OH-] = 1.0 x 10-14 mol2 dm-6

Rearrange [H+] = Kw = 1.0 x 10-14 = 1.0 x 10-13 mol dm-3

[OH-] 0.100

So pH = -log10 (1.0 x 10-13) = **13.00**

***Task: Find the pH of 1.00 mol dm-3 NaOH***

[OH-] = 1.00 mol dm-3

Kw = [H+] [OH-] = 1.0 x 10-14 mol2 dm-6

[H+] = Kw = 1.0 x 10-14 = 1.00 x 10-14 mol dm-3

[OH-] 1.00

pH = -log10 (1.00 x 10-14) = **14.00**

***Task: Find the pH of 0.15 mol dm-3 Ca(OH)2***

[OH-] = 2 x [Ca(OH)2] = 0.30 mol dm-3

Kw = [H+] [OH-] = 1.0 x 10-14 mol2 dm-6

[H+] = Kw = 1.0 x 10-14 = 3.33 x 10-14 mol dm-3

[OH-] 0.30

pH = -log10 (3.33 x 10-14) = **13.48**

***Application: CGP101 PQ1-3***

***Fact recall: CGP101 Q1-2***

Finding concentration of a strong base from a known pH

This is the **reverse** of the calculation for **working out the pH of a strong base**. Convert the **pH into [H+]** using antilogs, then **use Kw to calculate [OH-]**.

**Example**

An aqueous solution of a strong monobasic base, MOH has a pH of 12.60. Calculate the concentration of the base.

Answer

pH = 12.60 = -log10 [H+]

Hence [H+] = antilog (-12.60) = 10-12.6 = 2.51 x 10-13 mol dm-3

Kw = [H+] [OH-] = 1.0 x 10-14 mol2 dm-6

Rearrange [OH-] = Kw = 1.0 x 10-14 = **4.0 x 10-2 mol dm-3**

[H+] 2.51 x 10-13

Comment

Monobasic base is strong it’s fully dissociated [MOH] = [OH-]

***Task: Calculate [OH-] of NaOH with pH of 10.00***

[H+] = antilog (-10.00) = 10-10 = 1.0 x 10-10 mol dm-3

Kw = [H+] [OH-] = 1.0 x 10-14 mol2 dm-6

[OH-] = Kw = 1.0 x 10-14 = **1.0 x 10-4 mol dm-3**

[H+] 1.0 x 10-10

***Calculate concentration of OH- ions and concentration of Ca(OH2) with pH of 8.00***

[H+] = antilog (-8.00) = 10-8 = 1.0 x 10-8 mol dm-3

Kw = [H+] [OH-] = 1.0 x 10-14 mol2 dm-6

[OH-] = Kw = 1.0 x 10-14 = **1.0 x 10-6 mol dm-3**

[H+] 1.0 x 10-8

N.B. [Ca(OH2)] = 2[OH-] so [Ca(OH)2] = 1.0 x 10-6 / 2 = **5.0 x 10-7 mol dm-3**

***Starter: 3.3 – pH and bases***

***Sheet: pH of strong bases***

**Acid dissociation constant for weak acids**

Since **weak acid only partially dissociate** in water, as shown by this equation:

HA (aq) H+ (aq) + A- (aq)

Therefore the **concentration of hydrogen ion** is **not** the **same** as the **concentration** of the **acid**. These assumptions can be made:

[HA(aq)] >> [H+(aq)] so [HA(aq)]start = [HA(aq)]eqm

An **equilibrium constant** can be derived.

Kc = [H+] [A-]

[HA]

For weak acid **Ka** is used instead of Kc and is called the **acid dissociation constant**.

**Ka** = [H+(aq)] [A-(aq)]

[HA (aq)]

***Task: Work out the units for the acid dissociation constant***

Ka = [H+] [A-] = (~~mol dm~~~~-3~~) (mol dm-3) = mol dm-3

[HA] (~~mol dm~~~~-3~~)

The degree of dissociation can be determined by the acid dissociation constant.

* Ka > 1 RHS strong acid
* Ka < 1 LHS weak acid

***Task: Classify acids as weak or strong***

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Acid** | **Ka/mol dm-3** | **Weak/strong** |  | Strength of an acid is **relative**, so HF is the stronger acid of the 3 weak ones. |
| HCl | 1.0 x 107 | Strong |  |
| HNO3 | 4.0 x 101 | Strong |  |
| HF | 5.6 x 10-4 | Weak |  |
| CH3COOH | 1.7 x 10-5 | Weak |  |
| HCN | 4.9 x 10-10 | Weak |  |

Weak-acid approximation

Ka= [H+(aq)] [A-(aq)]

[HA (aq)]

This expression can be **approximated** because the **extent** of **HA dissociation** is **small**. The **[HA (aq)] can be replaced by [HA]*tot*** which is the **total original concentration of HA**.

The **[H+]** can be assumed to arise **solely from the dissociation of the acid** **and not** from the ionisation of water. So **[H+] is approximately equal to [A-]**, therefore **[H+] [A-]** can be **written as [H+]2**.

This gives the **weak-acid approximation**:

|  |  |
| --- | --- |
| **Ka [H+]2**  **[HA]*tot*** | Use to find [H+]  Re-arrange H+ = [H+] = |

This can **only be used** in situations where the **acid alone is added to water**. If it is acidified or a base added, this approximation is no longer valid as the equilibrium will be disturbed.

Finding the pH for weak acids from a known Ka

With **weak acids** there is only **partial dissociation** so unable to use concentration of acid to give [H+] and so pH. The **acid dissociation expression** must be used.

**Method:**

1. Write an expression for Ka for the weak acid
2. Re-arrange the equation and substitute values to find [H+]2
3. Take the square root of number to find [H+]
4. Substitute [H+] into pH equation to find the pH.

**Example – CGP102**

Find the pH of a 0.020 mol dm-3 solution of propanoic acid (CH3CH2COOH) at 298K.

Ka for propanoic acid is 1.30 x 10-5 mol dm-3.

Method

CH3CH2COOH (aq) H+ (aq) + CH3CH2COO- (aq)

Ka= [H+(aq)] [A-(aq)] = Ka= [H+] [CH3CH2COO-]

[HA (aq)] [CH3CH2COOH]

[H+]2 *(the weak-acid approximation)* Therefore [H+] =

[HA]*tot*

Answer

Ka = 1.30 x 10-5 mol dm-3

[CH3CH2COOH]tot = 0.020 mol dm-3

So [H+] = = = 5.10 x 10-4 mol dm-3

pH = -log10 5.10 x 10-4 = **3.29**

***Task:***

***Calculate pH of 1.00 mol dm-3 ethanoic acid, Ka is 1.74 x 10-5***

Ka= [H+(aq)] [A-(aq)] = Ka= [H+ (aq)] [CH3COO-(aq)] [H+]2

[HA (aq)] [CH3COOH (aq)] [HA]*tot*

[H+] = √Ka [HA]tot = √1.74 x 10-5 x 1.00 = 4.17 x 10-3 mol dm-3

pH = -log10 4.12 x 10-3 = **2.38**

***Calculate pH of 0.10 mol dm-3 ethanoic acid, Ka is 1.74 x 10-5***

Ka= [H+(aq)] [A-(aq)] = Ka= [H+ (aq)] [CH3COO-(aq)] [H+]2

[HA (aq)] [CH3COOH (aq)] [HA]*tot*

[H+] = √Ka [HA]tot = √1.74 x 10-5 x 0.1 = 1.31 x 10-3 mol dm-3

pH = -log10 1.30 x 10-3 = **2.88**

***Starter: 3.2 – pH and acids***

Finding the concentration of weak acids from a known pH

If the **pH** is **known** then the **concentration** of a weak acid **can be calculated**.

**Method:**

1. Substitute pH into the inverse pH equations to calculate [H+]
2. Write an expression for Ka for the weak acid
3. Re-arrange the equation to give the concentration of the acid
4. Substitute the values for Ka and [H+] into the equation to find the concentration of the acid.

**Example – CGP103**

The pH of an ethanoic acid (CH3COOH) solution is 3.02 at 298K. Calculate the molar concentration. Ka for ethanoic acid is 1.75 x 10-5 mol dm-3 at 298K.

Method

[H+] = 10-pH = 10-3.02 = 9.5 x 10-4 mol dm3

Ka= [H+] [CH3COO-] = [H+]2

[CH3COOH] [CH3COOH]

Re-arrange to give concentration of weak acid

[CH3COOH] = [H+]2

Ka

Answer

Ka = 1.75 x 10-5 mol dm-3

[H+] = 9.5 x 10-4 mol dm-3

[CH3COOH] = (9.5 x 10-4)2 = **0.052 mol dm-3**

1.75 x 10-5

***Task: Calculate concentration of methanoic acid (HCOOH) with pH 3.77,***

***Ka is 1.78 x 10-4 mol dm-3***

Ka= [H+] [HCOO-] = [H+]2

[HCOOH] [HCOOH]

Re-arrange to give concentration of weak acid

[HCOOH] = [H+]2

Ka

[H+] = 10-pH = 10-3.77 = 1.70 x 10-4 mol dm3

[COOH] = (1.7 x 10-4)2 = **1.62 x 10-4 mol dm-3**

1.78 x 10-4

Finding the Ka for weak acids

If the **concentration** and **pH** are **known** for a weak acid then the **Ka** for that acid **can** **be** **found** by substituting them into the weak-acid approximation.

**Example – CGP103**

A solution of 0.162 mol dm-3 HCN has a pH of 5.05 at 298K. What is the value of Ka?

Equation HCN (aq) H+(aq) + CN- (aq)

Method

Use pH to find [H+]

[H+] = 10-pH = 10-5.05 = 8.91 x 10-6 mol dm-3

Ka = [H+] [CN-] = [H+]2

[HCN] [HCN]

Answer

[H+] = 8.91 x 10-6

[HCN] = 0.162

Ka = (8.91 x 10-6)2 = **4.90 x 10-10** **mol dm-3**

0.162

***Task:*** A 0.28 mol dm-3 solution of a weak acid (HA) has a pH of 4.11 at 298K. Calculate the Ka value.

[H+] = 10-pH = 10-4.11 = 7.76 x 10-5 mol dm-3

Ka = [H+] [A-] = [H+]2

[HA] [HA]

Ka = (7.76 x 10-5)2 = **2.15 x 10-8** **mol dm-3**

0.28

Definition of pKa

The value of **Ka varies** from one acid to another which can make the **numbers difficult** to **work with** so **pKa is often** used. **pH** is used for **strong acids and bases**, with **weak acids** and bases **pKa** is used and it’s calculated in the same way as pH.

N.B. 2 d.p.

**Ka = 10-pKa**

**pKa = -log10 Ka**

**Example – CGP104**

An acid with Ka value of 1.50 x 10-7 mol dm-3. Calculate pKa.

pKa = -log10 Ka = -log10 1.50 x 10-7 = **6.82**

**Example – CGP104**

An acid with pKa value of 4.32. Calculate Ka.

Ka = 10-pKa = 10-4.32 = **4.79 x 10-5 mol dm-3**

***Task: Add pKa and find out how it relates to the strength of an acid***

|  |  |  |  |
| --- | --- | --- | --- |
| **Acid** | **Ka/mol dm-3** | **Weak/strong** | **pKa**  **Trend:**  **Smaller Ka**  **Bigger pKa**  **Weaker the acid** |
| HCl | 1.0 x 107 | Strong | -7.00 |
| HNO3 | 4.0 x 101 | Strong | -1.60 |
| HF | 5.6 x 10-4 | Weak | 3.25 |
| CH3COOH | 1.7 x 10-5 | Weak | 4.77 |
| HCN | 4.9 x 10-10 | Weak | 9.31 |

In relative terms – the stronger the acid the equilibrium will:

* > RHS

Ka= [H+] [A-] so if **[H+] & [A-] increase** then **Ka increases**

[HA]

* > [H+] [A-] & < [HA]
* >Ka & < pKa

***Prac: Finding Ka for a weak acid***

Calculating pH from pKa

**Example – CGP104**

Calculate the pH of a 0.050 mol dm-3 solution of methanoic acid with a pKa 3.75 at 289K.

Method

HCOOH(aq) H+ (aq) + HCOO- (aq)

Ka= [H+] [HCOO-] ≈ [H+]2 *(the weak-acid approximation)*

[HCOOH] [HCOOH]tot

Therefore [H+] = √Ka [HCOOH]tot

Answer

Not given Ka so use pKa and convert to Ka

Ka = 10-3.75 = 1.78 x 10-4 mol dm-3

[HCOOH]tot = 0.050 mol dm-3

[H+] = √1.78 x 10-4 x 0.050 = √8.9 x 10-6 = 2.98 x 10-3 mol dm-3

pH = -log10 (2.98 x 10-3) = **2.53**

***Task: Calculate the pH of a 0.025 mol dm-3 solution of nitric(III)acid (nitrous acid), pKa = 3.37***

HNO2 (aq) H+ (aq) + NO2- (aq)

Ka= [H+] [NO2-] ≈ [H+]2

[HNO2] [HNO2]

Therefore [H+] = √Ka [HNO2]

Hence Ka = 10-3.37 = 4.26 x 10-4 mol dm-3

[HNO2]tot = 0.025 mol dm-3

[H+] = √4.26 x 10-4 x 0.025 = 3.27 x 10-3

pH = -log10 (3.27 x 10-3) = **2.49**

***Task: Calculate pH of 0.50 mol dm-3 solution of ammonium chloride, work out if NH4Cl is an acid or base? pKa = 9.25. When ammonium chloride dissolves in water they form aqueous ammonium ions which dissociate according to this equation.***

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

Ka= [H+] [NH3] [H+]2

[NH4+] [NH4+]*tot*

Therefore [H+] = √Ka [NH4 +]tot

Ka = 10-9.25 = 5.62 x 10-10 mol dm-3

[NH4+]tot = 0.5 mol dm-3

[H+] = √5.62 x 10-10 x 0.50 = 1.68 x 10-5

pH = -log10 (1.68 x 10-5) = **4.78**

Comment

The **aqueous ammonium ions**, formed when ammonium chloride dissolves in water, is a **weak acid**. The pH of the resulting solution is on the **acid** side of neutral.

***Application: CGP105 PQ1-9***

***Fact recall: CGP105 Q1-4***

***Sheet: Weak acids***

**pH curves, titrations and indicators**

**AS Link:**

**3.1.2 – Amount of substance**

A **titration** is used to find the **concentration** of a solution by gradually adding it to a second solution which reacts to it. One of the **solutions** needs to be of a **known concentration** and the **equation of the reaction** must also be known.

pH curves

|  |  |
| --- | --- |
| In **acid-base titrations** the **concentration** of the **acid** or **alkali** can be **determined**. The use of a **pH meter** or data logger allows the **neutralisation reaction** during a titration to be **followed** **by measuring the pH**; therefore an indicator is not needed. |  |

The data **pH** can be **plotted** **against** the **volume** of acid or base added giving a **pH curve**. They have a characteristic **S-shape** but vary slightly depending on whether it is a strong or weak acid or strong or weak base involved in the titration.

|  |  |
| --- | --- |
| **Alkali added to acid** | **Acid added to alkali** |
|  |  |

The **shape** of each curve is **typical for the type of acid-base titration**.

|  |  |
| --- | --- |
|  |  |
| strong acid – strong base | strong acid – weak base |
|  |  |
| weak acid – strong base | weak acid – weak base |

***Required practical 9***: Investigate how pH changes when a weak acid reacts with a strong base

Equivalence point from a pH curve

All the graphs except the weak acid-weak base curve have a vertical section; the **mid-point** of the vertical section is called the **equivalence point**. At this point **tiny amounts** of either **acid** or **base** result in a **large change in pH** because **neutralisation** takes place at this point.

|  |  |
| --- | --- |
|  | |
|  |  |
|  |  |

At this point there are **stoichiometrically equal amounts of acid and base** i.e.

**[H+] = [OH-]**. The equivalence point will be a **pH value**; it’s **not always exactly 7** depending on the combination of acid and base titrated.

***Definition***:

**Equivalence-point** is the point on a titration curve at which stoichiometrically equivalent amounts of acid and base have been added **N.B. pH value**

The **equivalence point** **corresponds** to the **end-point** (this will be a **volume**), which is the term used to describe the point at which the **colour changes with an indicator**.

The change in pH during the titration can be used to determine the **equivalence point**, (also known as the **stoichiometric point**).

Indicators

The purpose of an **acid-base indicator** is to **change** **colour** at exactly the **end point** of a titration, a specific pH range.

**Properties of indicators**:

* **sharp colour change** at end point (only 1 drop acid or base needed to give change)
* **end point** must be **same** as **equivalence point**, colour change occurs over equivalence point
* **distinct colour change.**

There are many different indicators, methyl orange and phenolphthalein are often used, each changes colour over a different pH range:

|  |  |  |  |
| --- | --- | --- | --- |
| **Indicator** | **Colour at low pH**  **Acid (HIn)** | **Transition pH range** | **Colour at high pH**  **Base (In-)** |
| **Methyl orange** | red | **3.1-4.4** | yellow |
| **Phenolphthalein** | colourless | **8.2-10.0** | pink |

**Acid-base indicators** are used to **find** the **concentration** of a solution of acid or alkali; they show the **end-point** of a titration with a **colour change**, this allows the **volume** of acid or alkali added to be measured.

Acid-base **indicators** are **water-soluble**, **weak organic acids** that have **different coloured acid** (HIn) and **base** (In-) forms.

The indicator **equilibrium**:

|  |  |
| --- | --- |
| HIn H+ + In-  colour 1 colour 2  lower pH higher pH  acid base  proton donor proton acceptor | * **Low pH** (excess H+) – more HIn due to H+ from acid pushing equilibrium to **left**   + **Colour of HIn** * **High pH** (excess OH-) – more In- due to OH- reacting with H+ and equilibrium being pushed to **right**   + **Colour of In-** |

The **equivalence point** is when there are equal amounts **[H+] and [OH-]**. The correct indicator must be chosen if the equivalence point and end point are to be the same. At the **equivalence-point** of the **pH changes very rapidly** through several pH units, so the **indicator equilibrium swings** from almost **all HIn** **to** virtually **all In-** (or vice-versa) and a **colour change** is seen as its equilibrium is moved due to the changing concentration of H+ ions.

Choice of indicators

***Demo: Indicators***

The **colour change** of most indicators takes place over a **pH range of 2 units**, centred around the **pKa** for the indicator, so that a colour change is seen.

Not all indicator are suitable for all titrations, **universal is not suitable for any titration because of its gradual colour change**.

An indicator is **appropriate if the rapid change of pH at the equivalence point overlaps the range of activity of the indicator**, so the **pH range of the indicator’s colour change must be within the range of the pH change at the end-point**.

|  |  |  |  |
| --- | --- | --- | --- |
| Phenolphthalein | colourless | 8.2-10.0 | pink |
| Methyl orange | red | 3.1-4.4 | yellow |

**Methyl orange**

|  |  |
| --- | --- |
| BC_Methyl Orange |  |

**Phenolphthalein**

|  |  |
| --- | --- |
| BC_Phth deep pink |  |

pH curve graphs compare suitability of these indicators for different titrations by looking to see if the **indicator changes at the pH equivalence**.

**Example**

Find a suitable indicator

|  |  |
| --- | --- |
| Strong acid-strong base | Strong acid-weak base |
|  |  |
| Phenolphthalein  Methyl orange | Methyl orange |
| Weak acid-strong base | Weak acid-weak base |
|  |  |
| Phenolphthalein | None suitable  vertical position of curve < 2 pH units |

***Task: Find a suitable indicator***

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| A strong acid is added to a weak base; select an indicator form the table below.   |  |  | | --- | --- | | **Indicator** | **pH range** | | Bromothymol blue | 3.0 – 4.6 | | Litmus | 5.0 – 8.0 | | Cresol purple | 7.6 – 9.2 | |  |
| Answer  Graph shows vertical part is in range pH 2-6.  So only suitable indicator that will change colour within that range is **bromothymol blue**. |

***Starter: 3.4 – Acid-base titrations***

***Sheet: pH curves & indicators***

***Application: CGP109 PQ1-2***

***Fact recall: CGP109 Q1-3***

Working out concentrations from titrations

The **equivalence point as shown by the pH curves** can be used to give the **neutralisation** **volume** and so **work** **out** the **concentration** of the **unknown** acid or base.

**Method:**

1. Balanced equation
2. Number of moles of known substance n = cv
3. Equivalence moles from the balanced equation
4. Number of moles of unknown substance
5. Concentration of unknown substance c = n/v

**Monoprotic acids**

**Example – CGP111**

25.0 cm3 of a 0.500 mol dm-3 solution of HCl was titrated against 35.0 cm3 of NaOH. Calculate the concentration of the NaOH.

HCl + NaOH → NaCl + H2O

nHCl = 0.5 x 25.0 x 10-3 = 0.0125 mol

From equation 1 mole HCl neutralises 1 mole NaOH

nNaOH = 0.0125 mol

cNaOH = 0.0125 / 35.0 x 10-3 = **0.357 mol dm-3**

**Diprotic acids**

|  |  |
| --- | --- |
| A **diprotic acid** can release **two** **hydrogen ions** so when it is neutralised with a monobasic base such as sodium hydroxide the reaction occurs in two stages. This means that there are **two equivalence points** as shown on the pH curve. | Image result for diprotic acid titration curve |

**Example**

Ethanedioic acid (HOOC-COOH) is neutralised like this.

1st equivalence point: HOOC-COOH + OH- → HOOC-COO- + H2O

2nd equivalence point: HOOC-COO- + OH- → -OOC-COO- + H2O

Combined: HOOC-COOH + 2OH- → -OOC-COO- + 2H2O

The calculations are the same as for monoprotic acids, only the molar ratio changes.

**Example – CGP112**

25.0 cm3 of ethanedioic acid was completely neutralised by 20.0cm3 of 0.100 mol dm-3 of KOH solution. Calculate the concentration of the acid.

H2C2O4 + 2KOH → K2C2O4+ 2H2O

nKOH = 0.1 x 20.0 x 10-3 = 0.002 mol

From equation 2 mole KOH neutralises 1 mole C2H2O4

nH2C2O4 = 0.002 / 2 = 0.001 mol

cH2C2O4 = 0.001 / 25.0 x 10-3 = **0.040 mol dm-3**

***Task: Calculate the concentration of ethanedioic acid***

25 cm3 of a solution of ethanedioic acid (H2C2O4) is neutralised by 28.6 cm3 0.28

mol dm-3 solution of NaOH.

H2C2O4 (aq) + 2NaOH (aq) → Na2C2O4 (aq) + 2H2O (l)

nNaOH = 0.28 x 28.6 x 10-3 = 8.01 x 10-3 mol

ratio 2 NaOH : 1 H2C2O4

nH2C2O4 = 8.01 x 10-3 / 2 = 4.04 x 10-3 mol

cH2C2O4 = 4.04 x 10-3 / 25 x 10-3 = **0.16 mol dm3**

***Task: Calculate the concentration of this dibasic base***

28.4 cm3 of a 0.22 mol dm-3 solution of Ba(OH)2 are required to neutralise 25.0 cm3 of a solution of HCl. Calculate the concentration of the HCl solution.

2HCl (aq) + Ba(OH)2 (aq) → BaCl2 (aq) + 2H2O (l)

nBa(OH)2: 0.22 x 28.4 x 10-3 = 6.25 x 10-3

ratio 2 HCl : 1 Ba(OH)2

nHCl = 2 x 6.25 x 10-3 = 1.25 x 10-2 in 25cm3

cHCl = 1.25 x 10-2 / 25 x 10-3 = **0.5 mol dm3**

***Sheet: Concentrations from strong acid-strong base titrations***

The pH of a weak acid at half-neutralisation point

|  |  |
| --- | --- |
| On a titration curve there is always a very **gently sloping**, almost horizontal, part of the curve **before the steep line** on which the **equivalence point** lies. As acid or base is added there is **very little change in pH**, almost up to the volume of the equivalence point.  The point **half-way between** the **zero** and the **equivalence** **point** is the **half-neutralisation point**. |  |

This shows that an **acid or base** can be **added almost up to this point** with **little change** in the **pH** which is relevant to the theory of **buffers** made between a **weak acid** and a **strong base**. It also **allows** the **pKa** of the **weak acid** to be **determined**.

HA + OH- → A- + H2O

At the **half-neutralisation** point half the **HA has been converted into A-** and half remains, so **[HA] = [A-]** for a weak acid HA.

For equilibrium: **HA H+ + A-**

The expression for Ka can be used to find [H+] and so pH:

Ka = [H+] [A-]

[HA]

[H+] = Ka [HA] If [HA] = [A-] at ½ equivalence then [H+] = Ka [~~HA~~]

[A-] [~~A~~~~-~~]

For a **weak acid** **only**

So [H+] = Ka and **pH = pKa**

So if the **pH is measured** in a titration at **half-neutralisation** point then **pKa** is able to be determined. It also allows the **value** for **Ka** to be worked out.

***Definition***:

At **half-neutralisation**, the **pH** of a solution of a weak acid has the **same value as pKa**

In practical terms a titration is carried out to determine equivalence point and then the titration is repeated with half the volume at the equivalence point.

Working out pH values – strong acid-strong base titrations

**Two stages** are involved in calculating the **pH at any point** **during a titration**:

* find the **number of moles** of the component that is in excess
  + if base is added to acid – acid will be in excess before equivalence point and the base after equivalence
  + if acid is added to base – base will be in excess before equivalence point and the acid after equivalence
* find the **total volume** of solution

Once both are known the **concentration of the excess component** can be calculated and from this the **pH at this point of the titration can be found**.

**Method:**

1. moles H+/OH- at start
2. moles H+/OH- added

N.B. If OH- in excess use

Kw = [H+] [OH-] to find [H+]

1. moles H+/OH- in excess (to determine if it’s the acid or base)
2. total volume (acid + base)
3. concentration H+/OH- in excess
4. concentration H+
5. pH

**Example (base added, acid in excess)**

|  |  |
| --- | --- |
| Calculate the **pH** in the titration of 10.0 cm3 of a 0.15 mol dm-3 solution of HCl at the point when 10.0 cm3 of a 0.10 mol dm-3 solution of NaOH has been added. |  |

Method

Calculate the number of **moles of acid originally present**, the number of **moles of base added**, the number of **moles of acid in excess**, and the **total volume** of the solution.

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

Answer

Moles H+ originally: = 0.15 x 10 x 10-3 = 0.0015 mol

Moles OH- added: = 0.01 x 10 x 10-3 = 0.0010 mol

Moles H+ in excess = moles H+ originally added – moles H+ reacted with OH-

(i.e. moles OH- added - in this example ratio is 1:1)

Moles H+ in excess = 0.0015 – 0.0010 = 0.0005 mol

Total volume = 10.0 + 10.0 = 20.0 cm3

Hence [H+] =n/v = 0.0005 / 20x10-3 = 0.025 mol dm-3

pH = -log10 [H+] = **1.60**

Comment

The acid is in excess, so the titration has not yet reached equivalence. The concentration of the excess acid gives [H+] and so the pH.

**Example (acid added, base in excess)**

|  |  |
| --- | --- |
| Calculate the **pH** in the titration of 16.0 cm3 of a 0.16 mol dm-3 solution of NaOH at the point when 12.0 cm3 of a 0.10 mol dm-3 solution of H2SO4 has been added. |  |

Method

2NaOH (aq) + H2SO4 (aq) → Na2SO4 (aq) + 2H2O (l)

H2SO4 is a diprotic acid so acid-base stoichiometry is 1:2

Ionises: H2SO4 (aq) → 2H+ (aq) + SO42- (l)

1 mole → 2 moles (i.e. for every 1 mole acid added 2 moles H+ added)

Answer

Moles OH- originally: = 0.16 x 16 x 10-3 = 0.00256 mol

Moles H2SO4 added: = 0.10 x 12 x 10-3 = 0.00120 mol

Moles H+ added: = **2** x 0.10 x 12 x 10-3 = 0.00240 mol

Moles OH- in excess = moles OH- originally added – moles OH- added

Moles OH- in excess = 0.00256 – 0.00240 = 0.00016 mol

Total volume = 16.0 + 12.0 = 28.0 cm3

[OH-] =n/v = 0.00016 / 28.0 x 10-3 = 0.00571 mol dm-3

Use ionic product of water equation to calculate [H+] Kw = [H+] [OH-] = 1.0 x 10-14

[H+] = Kw

[OH-]xs

[H+] = 1.0 x 10-14 / 0.00571 = 1.75 x 10-12 mol dm-3

pH = -log10 [H+] = **11.76**

Comment

The base is in excess, so the concentration of the excess base is used to calculate the [H+] and so the pH of the mixture at this point in the titration.

***Sheet: pH values of strong acid-strong base titrations***

***Application: CGP112/3 PQ1-6***

***Fact recall: CGP113 Q1-4***

Working out pH values – weak acid-strong base titrations

The technique used depends on how far the titration has progressed.

**Before equivalence** – relative proportions of weak acid and its anion have to be determined and then used to calculate Ka, from this [H+] can be calculated and so pH.

**Example (base added, weak acid in excess)**

|  |  |
| --- | --- |
| Calculate the **pH** in the titration of 10.0 cm3 of a 0.10 mol dm-3 solution of NaOH has been added to 10.0 cm3 of a 0.25 mol dm-3 solution of ethanoic acid (Ka = 1.76 x 10-5 mol dm-3). |  |

Method

Reaction equation: CH3COOH + OH- → CH3COO- + H2O

Because acid is in excess and it’s weak it’s not fully disassociated, the extent of dissociation is not known so need to find the concentration of the alkali that reacts with the ethanoic acid to form ethanoate ions.

Write equation for acid dissociation, then equilibrium constant equation.

CH3COOH (aq) CH3COO- (aq) + H+ (aq)

Answer

Moles CH3COOH originally = 0.25 x 10 x 10-3 = 0.0025 mol

Moles OH- added = 0.10x 10 x 10-3 = 0.0010 mol

Moles CH3COOH remaining = excess – reacted = 0.0025 – 0.0010 = 0.0015 mol

Moles CH3COO- formed = moles OH- added (molar ratio is 1:1) = 0.0010 mol

c = n/v

So [CH3COOH] = 0.0015/v

and [CH3COO-] = 0.0010/v

Since ethanoic acid and ethanoate ions both exist together in same overall volume, concentration ratio = mole ratio and volumes cancel.

Ka = [H+] [CH3COO-]

[CH3COOH]

So [H+] = Ka x [CH3COOH]eqm

[CH3COO-]eqm

So [H+] = Ka x mole ratio = 1.76 x 10-5 x 0.0015 / 0.0010 = 2.64 x 10-5 mol dm3

pH = -log10 [H+] = **4.58**

Comment

pH is in the acidic region. Only the ratio of the concentration of the weak acid and its anion that matters here, so there is no need to consider the total volume as

***mole ratio concentration ratio***.

**After equivalence** – excess of strong base has to be found, plus the total volume, then the concentration can be calculated and hence the pH as in the above calculations

**Example (strong base added, base in excess)**

Calculate the **pH** in the titration of 16.0 cm3 of a 0.16 mol dm-3 solution of NaOH has been added to 12.0 cm3 of a 0.20 mol dm-3 solution of ethanoic acid

Method

Because alkali is in excess and it’s reacting with a weak acid it will fully react with the acid just as it would with a strong acid, so follow the calculation for a strong acid- strong base.

Reaction equation: CH3COOH + OH- → CH3COO- + H2O

Answer

Moles OH- added (nOH-): = 0.16 x 16 x 10-3 = 0.00256 mol

Moles H+ originally (nH+): = 0.20 x 12 x 10-3 = 0.00240 mol

Moles OH- in excess = moles OH- originally added – moles OH- reacted with added H+

Moles OH- in excess = 0.00256 – 0.00240 = 0.00016 mol

Total volume = 16.0 + 12.0 = 28.0 cm3

[OH-] = n/v = 0.00016 / 28.0 x 10-3 = 0.00571 mol dm-3

Kw = [H+] [OH-] = 1.0 x 10-14 so [H+] = Kw

[OH-]xs

Hence [H+] = 1.0 x 10-14 / 0.00571 = 1.75 x 10-12 mol dm-3

pH = -log10 [H+] = **11.76**

***Sheet: pH values of weak acid-strong base titrations***

**Buffer action**

Buffers are solutions that **resist changes of acidity or alkalinity**, so when **small** amounts of **acid or alkali** are **added** or it is **diluted** their **pH remains almost constant**.

They work by keeping the **concentration of hydrogen ions and hydroxide ions almost unchanged**. They are based on an **equilibrium** reaction which will **move** in the direction **to remove** either additional **hydrogen** ions or **hydroxide** ions.

Buffers **don’t ensure no change in pH**, the addition of acids or alkalis will still **change** the **pH slightly**. It’s also possible to **‘saturate’ a buffer solution** by **adding too much acid or alkali.**

***Definitions***:

A **buffer solution** is one that is able to resist change in pH when **small amounts of acid or base are added**. It is also able to **maintain its pH in the face of dilution with water**.

An **acidic buffer** is one which maintains a solution at a **pH below 7** and, typically, consists of a weak acid and one of its salts.

A **basic buffer** is one which maintains a solution at a **pH above 7** and, typically, consists of a weak base and one of its salts.

**Two method of making a buffer:**

* weak acid or base plus salt of the acid or base
* partial neutralisation of weak acid with strong base

Uses of buffers

* Buffers are used to calibrate pH meters.
* Biological systems e.g. growth of bacteria in hospital tests.
* Blood – maintained at exactly 7.4, a change of 0.5 units would be fatal, many mechanism are in operation, the most important one is:

CO2 (aq) + H2O (l) H+ (aq) + HCO3- (aq)

* Detergents and shampoos contain buffers to prevent damage to fabric or skin or hair if they were too acidic or basic.
* Oceans and seas are buffered slightly alkaline, pH 7.5 -8.4.

***Sheet: HSW – Biological buffers***

***Fact recall: CGP116 Q1-6***

Acidic buffers – maintain pH < 7

These are made from **weak acids** and one of its **soluble** **salts** (sodium or potassium), they work because the **dissociation** of the **acid** is in **equilibrium**, so with a weak acid:

HA (aq) H+ (aq) + A- (aq)

This shows **[H+] is equal to [A-]** and as it is a weak acid both are **very small** because most of **HA is undissociated**. To ensure there is a **high concentration of A-** a soluble **salt** (**fully ionises**)of the acid is mixed with the acid which.

NaA(aq) → Na+(aq) + A-(aq)

This is important in the functioning of the buffer when an acid is added to **prevent the supply of A- running out**.

|  |  |
| --- | --- |
| Resisting a base | Resisting an acid |
| The **added OH- ions** will **react** with **H+** to **produce** **water**. This **removes H+ ions** and **affects** the **weak acid equilibria**, this **opposes** the **change** by **moving** to the **right**, and the weak acid dissociates to **increase** the **H+**. The **hydrogen ion concentration is restored** and the **hydroxide** **ions** have been **removed** so the**pH** **remains** almost the **same**.  **OH-** (aq) + H+ (aq) → H2O (l) | The **added H+ reacts** with the **A-** to **produce** **HA**.  **H+** (aq) + A- (aq) → HA (aq)  This **reduces the hydrogen ion** concentration, so the **concentration** is **restored** as the **H+** have been **removed** and the**pH** **remains** almost the **same**.  The **fully ionised salt** of the acid (Na+A-) **ensures a plentiful supply of A- ions** so **more** of the **H+ can be used up**. If there was only a weak acid present the supply of A- would soon runs out because the concentration is low and it would no longer act as a buffer. |
| addition of OH- | addition of H+ |
| HA (aq) H+ (aq) + A- (aq) | HA (aq) H+ (aq) + A- (aq) |

**Example – CGP114**

A mixture of ethanoic acid & sodium ethanoate (CH3COO-Na+)

The ethanoic acid is only slightly dissociated:

CH3COOH (aq) CH3COO- (aq) + H+ (aq)

The salt is fully dissociated:

CH3COO-Na+ (aq) → CH3COO- (aq) + Na+ (aq)

***Task – Explain what would happen if a little acid is added***

Added H+ will react with ethanoate ions to produce ethanoic acid will move equilibrium to left and cause the hydrogen ion concentration to return to its previous concentration and pH remains the same.

***Task – Explain what would happen if a little base is added***

The OH- will react with the ethanoic acid producing ethanoate ions and water, the weak acid equilibrium opposes this change in hydrogen ion concentration by moving to the right to increase the hydrogen ion concentration and pH remains the same.

Basic buffers – maintain pH > 7

They are made from **weak bases** and a **soluble salt of the base**, usually a chloride.

The **weak base** is **slightly dissociated** according to this **equilibrium**:

B (aq) + H2O (l) BH+ (aq) + OH- (aq)

The **salt** is **fully dissociated**:

BCl (aq) → B+ (aq) + Cl- (aq)

It is added to prevent the B+ from running out.

|  |  |
| --- | --- |
| Resisting a base | Resisting an acid |
| The addition of a **small amount of base** causes the **hydroxide ion concentration** to **increase**. The extra **OH-** ions will **react** with the **base cations** (BH+) to **form** the **base** and **water**. To **oppose** this change the **equilibrium** will **shift** to the **left**, **removing** the extra **hydroxide** **ions** and the **pH** **remains** almost the **same**. | The addition of **small amounts of acid** causes the **hydrogen ion concentration** to **increase**. The **H+** ions will **react** with **OH-** ions from the dissociated base to **form water**. To **oppose** this the **equilibrium** to **move** to the **right** to replace the **hydroxide ions** that have been used up. Since the **hydrogen** **ions** have been **removed** the **pH** **remains** almost the **same**. |
| addition of OH- | addition of H+ |
| B (aq) + H2O (l) BH+ (aq) + OH- (aq) | B (aq) + H2O (l) BH+ (aq) + OH- (aq) |

*CGP116*

**Example – CGP115**

A solution of ammonia and ammonium chloride.

The ammonia will react with water to give this equilibrium:

NH3 (aq) + H2O (l) NH4+ (aq) + OH- (aq)

The salt is fully dissociated:

NH4Cl (aq) → NH4+ (aq) + Cl- (aq)

Diluting buffer solutions

Adding **small amounts of water** to a buffer will **not affect the pH** because the number of **moles of each component will be the same** hence the **ratio of the concentration** will **remain the same** and so the **pH is unchanged**. Although **water is slightly dissociated** the extra **hydrogen ions** and **hydroxide ions** will **push** the **buffer** **equilibrium** **equally in both directions**, leaving it unchanged.

Buffers can be represented by this chemical equation: HA (aq) H+ (aq) + A- (aq)

So Ka = [H+] [A-]

[HA]

Since Ka is a constant and if water is added the ratio of [HA] to [A-] isn’t changed the [H+] will remain the same.

And [H+] = Ka [HA]

[A-]

***Prac: Making a buffer solution***

Calculating the pH of a buffer

This is for a buffer solution may be made by mixing solutions of the **weak acid and its salt**.

**Method:**

1. Write out the expression for **Ka** of the weak acid
2. **Re-arrange** to give an expression for **[H+]**
3. **Substitute** the value for Ka and the concentration of the acid [HA] and salt [A-]
4. **Solve** the equation to give the [H+]
5. Substitute [H+] into **pH equation** to **calculate the pH**.

**Example – CGP117**

A buffer solution contains 0.400 mol dm-3 methanoic acid, HCOOH, and 0.600 mol dm-3 sodium methanoate, HCOO-Na+. For methanoic acid Ka = 1.6 x 10-4 mol dm-3. What is the pH of the buffer?

HCOOH (aq) HCOO- (aq) + H+ (aq) Ka = [H+] [HCOO-]

[HCOOH]

from salt

from acid

[H+] = Ka [HCOOH]

[HCOO-]

Substitute initial concentration of acid and salt.

[H+] = 1.6 x 10-4 x 0.400 = 1.07 x 10-4 mol dm-3

0.600

pH = -log[H+] = -log(1.07 x 10-4) = **3.97**

***Task: A buffer consists of 0.100 mol dm-3 solution of ethanoic acid and 0.100 mol dm-3 sodium ethanoate. (Ethanoic acid Ka = 1.74 x 10-5 mol dm-3). Calculate the pH.***

CH3COOH (aq) CH3COO- (aq) + H+ (aq) Ka = [H+] [CH3COO-]

[CH3COOH]

[H+] = Ka [CH3COOH]

[CH3COO-]

Volumes not given so use:

[CH3COOH] = 0.100 mol dm-3

[CH3COO-] = 0.100 mol dm-3

[H+] = 1.74 x 10-5 x 0.100 = 1.74 x 10-5

0.100

pH = **4.76**

***Calculate the pKa***

pKa = -logKa = **4.76**

Comment

When equal concentrations of acid and salt are used the pH is equal to the pH of the acid used and the half neutralisation point.

***Task: Calculate the pH of a buffer made by mixing 14.0 cm3 of a 2.0 mol dm-3 solution of ethanoic acid (Ka = 1.74 x 10-5 mol dm-3) with 15.0 cm3 of a solution of 1.50 mol dm-3 sodium ethanoate.***

CH3COOH (aq) H+ (aq) + CH3COO- (aq)

Ka = [H+] [CH3COO-]

[CH3COOH]

[H+] = Ka [CH3COOH]

[CH3COO-]

Use n = cv

Moles (CH3COOH) = 2.0 x 14.0 x 10-3 = 0.0280 mol

Moles (CH3COO-) = 1.5 x 15.0 x 10-3 = 0.0225 mol

[H+] = Ka 0.0280/v N.B. v cancels

0.0225/v

= 1.74 x 10-5 x 2.0

= 2.17 x 10-5 mol dm-3

pH = -log [H+] = **4.66**

***Starter: 3.3 – Buffer solutions***

***Sheet: Buffer solutions – Extension Q1***

Partial neutralisation buffers

|  |  |
| --- | --- |
| See section on pH of weak acid at  half-equivalence point. | https://www.learner.org/courses/chemistry/images/text_img/titration_curve.jpg |

Buffers can also be made **by partial neutralisation of the weak acid with a strong base** (e.g. by adding about half the stoichiometric amount of sodium hydroxide to a solution of ethanoic acid). In either case **an equimolar mix of components or a half neutralised weak acid** will have:

[H+] = Ka and hence pH = pKa

The find the equimolar mix of HA and H+ (half-equivalence):

* Titrate with phenolphthalein to note equivalence volume
* Repeat with ½ equivalence and no indicator
* Solution has [HA] = [A-]

**Method:**

1. Write out balanced equation for neutralisation: acid + base → salt + water
2. Calculate number of mole of acid and base at start
3. Use molar ratios to work out moles of acid and salt left at end of reaction
4. Calculate concentration of acid and salt in buffer solution by dividing by the volume of solution (total volume of acid and base)
5. Calculate pH

**Example – CGP118**

A buffer is formed by mixing 15cm3 of 0.1 mol dm-3 NaOH and 30cm3 of 0.6 mol dm-3 propanoic acid (CH3CH2COOH). Calculate the pH of the buffer solution.

Ka = 1.35 x 10-5 mol dm-3.

CH3CH2COOH + NaOH → CH3CH2COONa + H2O

*excess limiting same number of moles as NaOH added*

As reactions proceed the **moles** of **acid decrease** and **moles** of **salt increase** by the **number** of **moles** of **base added**.

**Partial neutralisation** so some acid has reacted with the base

initial nCH3CH2COOH = 0.6 x 30 x 10-3 = 0.018 mol

nNaOH = 0.1 x 15 x 10-3 = 0.0015 mol limiting

acid and base react in 1:1 molar ratio so 0.0015 moles base will react with 0.0015 moles acid giving 0.0015 mol salt

acid is in excess nCH3CH2COOH 0.018 – 0.0015 = 0.0165 mol acid remains

Don’t need to calculate concentration as it’s the same total volume Can use moles

Ka = [H+] [CH3CH2COO-]

[CH3CH2COOH]

[H+] = Ka [CH3CH2COOH] = 1.35 x 10-5 x 0.0165/v = 1.485 x 10-4 mol dm-3

[CH3CH2COO-] 0.0015/v

pH = -log10 (1.485 x 10-4) = **3.83**

***Task: Calculate the pH of the buffer formed when 500 cm3 of 0.400 mol dm-3 NaOH is added to 500 cm3 1.00 mol dm-3 HA. Ka = 6.25 x 10-5 mol dm-3***

HA + NaOH → NaA + H2O

nHA = 1.00 x 500 x 10-3 = 0.500 mol

nOH- = 0.400 x 500 x 10-3 = 0.200 mol

HA in excess so at the end there was 0.500 – 0.200 = 0.300 mol HA left

nA- = 0.200 mol (i.e. same as OH- moles)

Ka = [H+] [A-]

[HA]

[H+] = Ka [HA]

[A-]

[H+] = 6.25 x 10-5 x 0.300 = 9.375 x 10-5

0.200

pH = **4.03**

***Sheet: Buffer solutions – Extension Q2&3***

Calculating changes in pH when acids or bases are added to a buffer solution

**Example – addition of acid**

A buffer with a pH 4.66 is made by mixing 14.0 cm3 of a 2.0 mol dm-3 solution of ethanoic acid with 15.0 cm3 of a solution of 1.50 mol dm-3 sodium ethanoate. Calculate the change in pH after the addition of 10.0 cm3 of 0.1 mol dm-3 hydrochloric acid.

Ka = 1.74 x 10-5 mol dm-3

Method

The addition of acid shifts the equilibrium to the left, as it reacts with the ethanoate ions (acid increases by same amount as anions decrease):

CH3COOH (aq) H+ (aq) + CH3COO- (aq)

Need to decrease the number of moles of CH3COO- by the number of moles of HCl added and increase the number of moles of CH3COOH by the same amount.

Answer

Use c = n/v so n = cv

Moles (H+ in HCl) = 0.10 x 10.0 x 10-3 = 0.0010 mol

Initial moles (CH3COO-) = 1.5 x 15.0 x 10-3 = 0.0225 mol

So new moles (CH3COO-) = 0.0225 – 0.0010 = 0.0215 mol

Initial moles (CH3COOH) = 2.0 x 14.0 x 10-3 = 0.0280 mol

So new moles (CH3COOH) = 0.0280 + 0.0010 = 0.0290 mol

Ka = [H+] [CH3COO-]

[CH3COOH]

[H+] = Ka [CH3COOH] = 1.74 x 10-5 x 0.0290/v = 2.347 x 10-5 mol dm-3 N.B. v cancels

[CH3COO-] 0.0215/v

pH = -log [H+] = 4.63 Previously it was 4.66

So the change in pH is reduced by **0.03** units

Comment

Adding a substantial volume of a 0.10 mol dm-3 solution of HCl has only a slight effect on the pH, as is predicted by a buffer solution.

***Task: 1.00 dm3 of a buffer solution consisting of 0.10 mol dm-3 ethanoic acid and 0.10 mol dm-3 of sodium ethanoate. Ka 1.74 x 10-5 and pH 4.77. 10.0 cm3 of 1.00 mol dm-3 HCl is added, virtually all the H+ will react with the ethanoate ions A- to form ethanoic acid. Calculate the new pH and work out the difference.***

Method

CH3COOH (aq) CH3COO- (aq) + H+ (aq) Addition of HCl shifts equilibrium to left

as the H+ ions react with the ethanoate ions

Answer

Moles H+ in HCl = 1 x 10.0 x 10-3 = 0.01 mol

Initial moles (CH3COO-) = 0.1 x 1 = 0.10 mol

So new moles (CH3COO-) = 0.1 – 0.01 = 0.09 mol

Initial moles (CH3COOH) = 0.1 x 1 = 0.10 mol

So new moles (CH3COOH) = 0.1 + 0.01 = 0.11 mol

[H+] = Ka [CH3COOH]

[CH3COO-]

[H+] = 1.74 x 10-5 x 0.11/v = 2.13 x 10-5 mol dm-3

0.09/v

pH = 4.67 Previously it was 4.77 (from earlier task)

So the change in pH is reduced by **0.10** units

**Example – addition of base**

A buffer with a pH 3.78 was prepared by adding 0.013 mol of a salt NaA to 250 cm3 of a 0.500 mol dm-3 solution of a weak acid HA and thoroughly mixing. Calculate the pH of the buffer after the addition of 3.00 x 10-3 mol NaOH.

Ka = 1.74 x 10-5 mol dm-3

Method

The addition of base shifts the equilibrium to the right, as it reacts with the H+ (acid decreases by same amount as anions increase):

HA (aq) H+ (aq) + A- (aq)

Need to decrease the number of moles of NaOH by the number of moles of HA in the buffer and increase the number of moles of A- by the same amount.

Answer

Moles OH- in NaOH = 3.00 x 10-3 mol

Initial moles (HA) = 0.5 x 250 x 10-3 = 0.125 mol

So new moles (HA) = 0.125 – 3.00 x 10-3 = 0.122 mol

Initial moles (A-) = 0.0130 mol

So new moles (A-) = 0.0130 + 3.00 x 10-3 = 0.016 mol

Ka = [H+] [A-]

[HA]

[H+] = Ka [HA] = 1.74 x 10-5 x 0.122/v N.B. v cancels

[A-] 0.016/v

= 1.33 x 10-4 mol dm-3

pH = -log [H+] = 3.89

***Sheet: Buffer solutions***

***Sheet: Stretch & challenge - Buffer solutions***

***Starter: 3.6 – More complex buffer solutions***

***Sheet: Exam questions***

***Application: CGP119 PQ1-4***

***Exam questions: Oxford p78-79 Q1-4***