Pharmaceutical Analysis Unit 4: Redox Titration

Introduction

Redox titrations are a fundamental aspect of analytical chemistry, widely used to determine the concentration of various substances. The term "redox" itself is a combination of "reduction" and "oxidation," which are two chemical processes that always occur simultaneously in any chemical reaction. You can't have one without the other!

Imagine a dance between atoms where one atom loses electrons, and another atom gains them. The atom that **loses electrons** is said to undergo **oxidation**, and it acts as a **reducing agent** because it causes another species to be reduced. Conversely, the atom that **gains electrons** is said to undergo **reduction**, and it acts as an **oxidising agent** because it causes another species to be oxidised. This transfer of electrons is the very core of a redox reaction.

For instance, consider the reaction between zinc metal and copper ions:

$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

In this reaction:

- **Zinc (Zn)** starts as a neutral atom and loses two electrons to become a positively charged zinc ion (**Zn^{2+}**). This is **oxidation**. Zinc is the **reducing agent**.
- **Copper ions (**Cu^{2+}**)**, which are positively charged, gain two electrons to become neutral copper metal (**Cu**). This is **reduction**. Copper ion is the **oxidising agent**.

Notice how electrons are not created or destroyed; they are simply transferred from one substance to another. Redox titrations precisely measure these electron transfers to determine unknown concentrations.

Oxidation Number or Oxidation State (OS)

To understand redox reactions more deeply, we need a way to keep track of electron distribution. This is where the concept of **Oxidation Number** or **Oxidation State (OS)** comes in handy. It's a hypothetical charge that an atom would have if all bonds were ionic. It can be a **positive, zero, or negative integer**.

- A **positive oxidation state** generally indicates that an atom has **lost electrons** or is sharing them unequally with a more electronegative atom. The higher the positive number, the more electrons it has effectively "lost."

- A **negative oxidation state** indicates that an atom has **gained electrons** or is sharing them unequally with a less electronegative atom. The more negative the number, the more electrons it has effectively "gained."
- An oxidation state of **zero** means the atom is in its elemental form or has not gained or lost electrons in a compound.

There are a few key rules to assign oxidation states:

1. **For a neutral molecule, the sum of the oxidation numbers of all atoms in the molecule must be zero.** If it's a polyatomic ion, the sum of the oxidation numbers must equal the charge of the ion.

    - **Example: Potassium Permanganate ($KMnO_4$)**
        - Potassium (K) is an alkali metal, always +1.
        - Oxygen (O) is usually -2 (unless in peroxides or superoxides).
        - Let Mn be 'x'.
        - So, (+1) + x + 4(-2) = 0
        - 1 + x - 8 = 0
        - x - 7 = 0
        - **x = +7**. So, Mn has an oxidation state of +7.
    - **Example: Sulfate anion (SO_4^{2-})**
        - Oxygen (O) is usually -2.
        - Let S be 'x'.
        - So, x + 4(-2) = -2 (because the ion has a -2 charge)
        - x - 8 = -2
        - **x = +6**. So, S has an oxidation state of +6.
    - **Example: Ammonium cation (NH_4^+)**
        - Hydrogen (H) is usually +1 when bonded to non-metals.
        - Let N be 'x'.
        - So, x + 4(+1) = +1 (because the ion has a +1 charge)
        - x + 4 = +1
        - **x = -3**. So, N has an oxidation state of -3.
2. **For atoms in their elemental form (like O_2, S_8, P_4, Zn, Cu), the oxidation number is always 0.** These are neutral substances made of only one type of element.

3. **In binary compounds (compounds made of only two different elements), the element with greater electronegativity is assigned a negative oxidation state equal to its charge as a**

simple monoatomic ion. The less electronegative element will have a positive oxidation state.

- **Example: Sodium Chloride (NaCl)**
  - Chlorine (Cl) is more electronegative than Sodium (Na). As an ion, Cl^- has a -1 charge. So, Cl has an OS of -1.
  - Sodium (Na) is an alkali metal, always +1. So, Na has an OS of +1.
  - Sum: (+1) + (-1) = 0, which is correct for a neutral compound.
- **Example: Magnesium Sulfide (MgS)**
  - Sulfur (S) is more electronegative than Magnesium (Mg). As an ion, S^{2-} has a -2 charge. So, S has an OS of -2.
  - Magnesium (Mg) is an alkaline earth metal, always +2. So, Mg has an OS of +2.
  - Sum: (+2) + (-2) = 0, which is correct.

By following these rules, you can determine the oxidation state of almost any atom in a compound, which is crucial for identifying what is being oxidised and reduced in a redox reaction.

Balancing Simple Redox Reactions

Balancing redox reactions can seem daunting at first, but with a systematic approach, it becomes quite manageable. The goal is to ensure that both the number of atoms and the total charge are balanced on both sides of the equation. Let's illustrate this with an example involving copper and silver ions, a common reaction where copper metal reacts with silver ions to produce copper ions and silver metal.

Initial Unbalanced Equation: $Cu(s) + Ag^+(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$

Here's a step-by-step method:

Step 1: Separate the reaction into half-reactions. First, identify the elements that are changing their oxidation states. In this case, copper (Cu) and silver (Ag) are involved. Separate them into two parts, one for oxidation and one for reduction.

- **Copper half-reaction:** $Cu(s) \rightarrow Cu^{2+}(aq)$
- **Silver half-reaction:** $Ag^+(aq) \rightarrow Ag(s)$

Step 2: Balance the atoms (other than H and O, which are not present here) and then the charges for each half-reaction.

- **For the copper half-reaction:** $Cu(s) \rightarrow Cu^{2+}(aq)$
    - Atoms are already balanced (one Cu on each side).
    - To balance the charge, we need to add electrons. The left side has a charge of 0. The right side has a charge of +2. We add two electrons ($2e^-$) to the right side to balance the charge: **Cu^0 (s) → Cu^{2+} (aq) + $2e^-$**
    - Since electrons are being *lost* (they are products), this is the **oxidation half-reaction**. Cu is being oxidised to Cu^{2+}, and it acts as the reducing agent.
- **For the silver half-reaction:** $Ag^+(aq) \rightarrow Ag(s)$
    - Atoms are already balanced (one Ag on each side).
    - To balance the charge, the left side has a charge of +1, and the right side has a charge of 0. We add one electron ($1e^-$) to the left side: **Ag^+ (aq) + e^- → Ag^0 (s)**
    - Since electrons are being *gained* (they are reactants), this is the **reduction half-reaction**. Ag^+ is being reduced to Ag, and it acts as the oxidising agent.

Step 3: Make the number of electrons equal in both half-reactions. For the overall reaction, the number of electrons lost in oxidation must equal the number of electrons gained in reduction. Currently, the copper half-reaction involves 2 electrons, while the silver half-reaction involves 1 electron. To make them equal, we multiply the entire silver half-reaction by 2:

- **Oxidation half-reaction (multiply by 1):** $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
- **Reduction half-reaction (multiply by 2):** 2 [$Ag^+(aq) + e^- \rightarrow Ag(s)$] becomes **$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$**

Now, both half-reactions have 2 electrons.

Step 4: Combine the balanced half-reactions and cancel out common terms. Add the left sides of both half-reactions together and the right sides together:

$Cu(s) + 2Ag^+(aq) + 2e^- \rightarrow Cu^{2+}(aq) + 2e^- + 2Ag(s)$

The 2 electrons ($2e^-$) appear on both sides, so they cancel out.

Final Balanced Redox Equation: $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

This equation is now balanced both in terms of atoms (one Cu, two Ag on each side) and charge (total charge on left: 0 + 2(+1) = +2; total charge on right: +2 + 0 = +2). This systematic approach ensures that the fundamental principles of conservation of mass and charge are upheld in redox reactions.

Theory of Redox Titrations

Redox titrations are a powerful analytical technique used to determine the concentration of an unknown solution (the analyte) by reacting it with a solution of known concentration (the titrant) in a redox reaction. Unlike acid-base titrations which involve proton transfer, redox titrations involve **electron transfer**.

At the heart of a redox titration is a setup that often resembles an electrochemical cell. A highly selective electrolytic cell is typically used, consisting of two main components: an **indicator electrode** and a **reference electrode**.

- **Indicator Electrode:** This electrode is crucial because its potential changes significantly as the concentration of the species involved in the redox reaction changes during the titration. It's often made of a "noble metal" like **platinum (Pt)**. Platinum is chemically inert and serves as an excellent site for the transfer of electrons between the chemical species in the solution and the external circuit, without participating in the reaction itself. Its potential responds directly to the ratio of the oxidized and reduced forms of the analyte (or indicator) in the solution.

- **Reference Electrode:** This electrode maintains a **constant potential** throughout the titration, providing a stable baseline against which the indicator electrode's changing potential can be measured. Common reference electrodes used in redox titrations include the **Standard Hydrogen Electrode (SHE)** and, more practically, the **Standard Calomel Electrode (SCE)**.

    - The **Saturated Calomel Reference Electrode (SCE)** half-reaction is: $\mathbf{2Hg(l) + 2Cl^-(aq)} \rightleftharpoons \mathbf{Hg_2Cl_2(s) + 2e^-}$ Its standard electrode potential (E^0) is **0.241 V**.
    - An example of a half-reaction occurring at a platinum indicator electrode might be: $\mathbf{Fe^{3+} + e^-} \rightleftharpoons \mathbf{Fe^{2+}}$ with $E^0 = 0.767$ V or $\mathbf{Ce^{4+} + e^-} \rightleftharpoons \mathbf{Ce^{3+}}$ with $E^0 = 1.70$ V

The **net cell reaction** in such a setup can be described by combining these half-reactions. For example, if Ce^{4+} oxidises Fe^{2+}, then the net reaction would involve the Ce half-reaction and the Fe half-reaction.

Potentiometric Method

While many titrations use visual indicators, the **potentiometric method** is a physico-chemical approach particularly useful when visual indicators are not available, or when greater accuracy is required. It's also invaluable for **coloured solutions** where visual colour changes are obscured, or for very **dilute solutions** where the colour change might be too subtle.

In this method, the **potential difference** between the indicator electrode and the reference electrode is continuously measured as the titrant is added. This measured potential is related to the concentrations of the species in the solution.

Cell Representations: Electrochemical cells are often represented in a shorthand notation. For example: **Cu(s) | $CuSO_4$ (0.100 M) || $ZnCl_2$ (0.200 M) | Zn(s)** This representation reads:

- **Cu(s) | $CuSO_4$ (0.100 M)**: This is the first half-cell, which typically functions as the **anode** (where oxidation occurs). A copper electrode is immersed in a 0.100 M copper sulfate solution.
- **||**: This represents the salt bridge, which connects the two half-cells and allows ion flow to maintain electrical neutrality.
- **$ZnCl_2$ (0.200 M) | Zn(s)**: This is the second half-cell, typically the **cathode** (where reduction occurs). A zinc electrode is immersed in a 0.200 M zinc chloride solution.

The **Ecell** (cell potential) is a crucial indicator:

- If **Ecell is a positive value**, the reaction is **spontaneous** in the direction written (energy is released).
- If **Ecell is a negative value**, the reaction is **non-spontaneous** in the direction written, but it will be **spontaneous in the reverse direction**.

Measurement of Electrode Potential: The individual electrode potentials are determined by the tendency of a half-cell to gain or lose electrons.

- The **more positive half-cell potential** typically corresponds to the **oxidising agent** (where reduction occurs, the **cathode**).
- The **less positive (or more negative) half-cell potential** corresponds to the **reducing agent** (where oxidation occurs, the **anode**).

The relationship between the **concentration of species** in a half-cell and its **electrode potential** is described by the **Nernst Equation**. For a general half-reaction: $\mathbf{aA + bB + ne^- \rightleftharpoons cC + dD}$ The Nernst equation is given by:

$$\mathbf{E = E^0 - (RT / nF) \ln ([C]^c[D]^d / [A]^a[B]^b)}$$

Where:

- **E** is the observed electrode potential under non-standard conditions.
- $\mathbf{E^0}$ is the standard half-cell reduction potential.
- **R** is the universal gas constant (8.314 $J\ K^{-1}\ mol^{-1}$).
- **T** is the absolute temperature in Kelvin (usually 298.15 K for 25 °C, where T = °C + 273).
- **n** is the number of moles of electrons transferred in the cell reaction or half-reaction.

- **F** is the Faraday constant (96,485 C mol^{-1}), which is the number of coulombs per mole of electrons.
- **[C], [D], [A], [B]** are the concentrations of the species C, D, A, and B, respectively. The exponents (c, d, a, b) are their stoichiometric coefficients. (Note: solids and pure liquids are not included in the expression).

At 25 °C (298.15 K), the equation can be simplified by substituting the values for R, T, and F, and converting the natural logarithm (ln) to base-10 logarithm (log):

$E = E^0 - (0.0592 / n) \log ([C]^c[D]^d / [A]^a[B]^b)$

This equation is fundamental for calculating electrode potentials during a titration and understanding how they change with concentration.

Oxidation-Reduction Curves (Titration Curves)

Just like acid-base titrations have pH curves, redox titrations have **oxidation-reduction curves** (or potentiometric titration curves). These curves are generated by **measuring the potential of an indicator electrode** (e.g., a **platinum electrode**) relative to a **fixed-potential reference electrode** (like a Saturated Calomel Electrode, SCE) as the titrant is added.

The cell potential (Ecell) measured during the titration is related to the solution potential (Esolution) and the reference electrode potential (Ereference electrode) by: **Ecell = Esolution - Ereference electrode** Therefore, the **solution potential** can be determined: **Esolution = Ecell + Ereference electrode**

Let's consider an example of a **Cerimetric titration**, where iron(II) ions (Fe^{2+}) are titrated with cerium(IV) ions (Ce^{4+}). The process involves the following half-reactions: **$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$** **$Ce^{4+} + e^- \rightleftharpoons Ce^{3+}$** And the overall reaction: **$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$**

The titration curve can be divided into three main regions:

1. **Before the equivalence point:** In this region, we have an excess of Fe^{2+} that hasn't reacted yet. The potential of the solution is primarily determined by the **Fe^{2+}/Fe^{3+} couple**. We can use the Nernst equation for the iron half-reaction to calculate the electrode potential: **$E\_Fe = E^0\_Fe - (0.0592 / n\_Fe) \log ([Fe^{2+}] / [Fe^{3+}])$** Here, n_Fe = 1 (since one electron is transferred). We calculate the concentrations of Fe^{2+} and Fe^{3+} at various points and insert them into the Nernst equation. It's generally easier to use the Fe^{2+}/Fe^{3+} couple because the concentration of Ce^{4+} is very low and difficult to calculate accurately at this stage.

2. **At the equivalence point:** At this critical point, all the Fe^{2+} has been completely oxidised to Fe^{3+} by the added Ce^{4+}. Both reactants have been consumed in stoichiometric amounts. The potential

at the equivalence point (E_eqpt) is a weighted average of the standard potentials of the two half-reactions. We can combine the Nernst equations for both half-reactions and solve for E_eqpt. After combining and simplifying, the potential at the equivalence point is given by: **$E_{eqpt} = (n_{Fe} E^0_{Fe} + n_{Ce} E^0_{Ce}) / (n_{Fe} + n_{Ce})$** In our example, where $n_{Fe} = n_{Ce} = 1$, the equation simplifies to: **$E_{eqpt} = (E^0_{Fe} + E^0_{Ce}) / 2$**

3. **After the equivalence point:** Beyond the equivalence point, there is an excess of the titrant, Ce^{4+}. Now, the potential of the solution is primarily determined by the **Ce^{3+}/Ce^{4+} couple**, as the Fe^{2+} is totally consumed. It's easier to calculate the potential using the cerium half-cell: **$E_{Ce} = E^0_{Ce} - (0.0592 / n_{Ce}) \log ([Ce^{3+}] / [Ce^{4+}])$** Again, $n_{Ce} = 1$. We determine the concentrations of Ce^{3+} and Ce^{4+} from the amount of excess titrant added.

Shape of a Redox Titration Curve: A redox titration curve typically shows the **voltage (potential)** of the indicator electrode as a function of the **volume of titrant added**.

- The curve starts relatively flat, then undergoes a **sharp, steep change in potential** around the equivalence point. This steep region corresponds to the rapid change in the ratio of oxidized to reduced species.
- After the equivalence point, the curve flattens out again.
- The equivalence point is the **inflection point** of this steep segment.
- The platinum (Pt) electrode responds to the relative concentrations of both the Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} couples. The Saturated Calomel Electrode (SCE) is used as a reference electrode.

The titration curve clearly illustrates the three regions:

- Before the Equivalence Point
- At the Equivalence Point
- After the Equivalence Point

Understanding these regions and how the potential is calculated using the Nernst equation is key to mastering redox titrations.

Redox Indicators

Just as in acid-base titrations, where pH indicators signal the endpoint, **redox indicators** are used in redox titrations to visually signal the equivalence point. A good redox indicator should produce a **sudden and distinct colour change** in the electrode potential in the **vicinity of the equivalence point** of a redox titration.

This is possible because the indicator itself is **redox active**. It can undergo its own reversible oxidation or reduction process, and crucially, its oxidized and reduced forms must have a **noticeable difference in their colours**. For a redox indicator, the potential (E) at which its colour changes is related to the ratio of its oxidized and reduced forms by a specific Nernst equation:

$E = E^0\_red - (RT / zF) \ln (a\_ox / a\_red)$

Where:

- **E** is the potential at which the indicator shows its colour.
- **E^0_red** is the standard reduction potential of the indicator.
- **R** is the universal gas constant.
- **T** is the absolute temperature.
- **z** is the number of electrons transferred in the indicator's half-reaction.
- **F** is the Faraday constant.
- **a_ox** is the activity (or concentration) of the oxidized form of the indicator.
- **a_red** is the activity (or concentration) of the reduced form of the indicator.

The indicator's colour change occurs over a specific potential range, typically centered around its E^0_red. For an indicator to be effective, its potential range for colour change must overlap with the steep rise in the titration curve around the equivalence point.

There are several types of redox indicators:

1. **Self-Indicator:** In some titrations, the titrant itself is so strongly coloured that it can serve as its own indicator. After the equivalence point, even a single drop of excess titrant will impart a definite colour to the solution, signalling the end-point.

    - **Example: Potassium permanganate ($KMnO_4$)** is a deep purple solution. When used as a titrant, it gets reduced to colourless Mn^{2+}. Once all the analyte is consumed, the first excess drop of $KMnO_4$ colours the solution a persistent pink, marking the end-point.
    - Other examples include Ceric sulphate (pale yellow) and Iodine (brown).
    - **Disadvantage:** A slight over-titration is often necessary to obtain a visible colour, which can introduce a small error.
2. **External Indicator:** These indicators are based on observing the reaction of a small portion of the titrated solution, removed periodically, with a suitable reagent *outside* the main titration flask. The end-point is marked by the failure of this external test to elicit a reaction, indicating that the analyte has been completely consumed.

- **Example:** In the titration of ferrous iron with $K_2Cr_2O_7$ (potassium dichromate), drops of the solution are removed to a spotting tile during the titration. If ferrous ions (Fe^{2+}) are still present, they will react with a drop of potassium ferricyanide to give a deep Prussian Blue colour. At the end-point, when all ferrous ions are oxidised to ferric ions (Fe^{3+}), there will be no ferrous ions left, and thus no blue colour will be produced with potassium ferricyanide, indicating the end of the titration.
- **Disadvantage:** This method is tedious, time-consuming, and involves taking samples out, which slightly reduces the volume of the analyte, introducing a small error. It is largely replaced by internal indicators or potentiometric methods.

3. **Internal or Redox Indicator:** These are substances added directly to the solution in the titration flask. They undergo a reversible colour change within the solution as they are themselves oxidised or reduced. Most internal redox indicators are organic dyes, and often their reduced forms are colourless or have a very different colour compared to their oxidised forms.

Here are some common internal redox indicators and their colour changes:

SN	Indicator	Oxidized State	Reduced State
1	Nitroferroin	Pale-Blue	Red
2	Ferroin	Pale-Blue	Red
3	n-phenyl anthranilic acid	Purple-Red	Colourless
4	Diphenylamine	Violet	Colourless
5	Diphenylamine Sulphonic acid	Red-violet	Colourless
6	**Starch-Iodine**	**Blue**	**Colourless**

7	Methylene Blue	Blue	Colourless

Starch is a particularly important indicator, not strictly a redox indicator but an indicator for iodine. It forms an intense **blue-black complex** with iodine (I_2). This complex is very sensitive, allowing for the detection of even tiny amounts of iodine. When iodine is absent or is reduced to iodide (I^-), the blue colour disappears. This makes starch invaluable in iodimetric and iodometric titrations.

The choice of indicator depends on the redox potential of the titration reaction. The indicator's colour change potential range must bracket the equivalence point potential to ensure an accurate and sharp end-point detection.

Iodimetry and Iodometry

Iodine titrations are a very important class of redox titrations, specifically involving the element iodine. They are broadly categorised into two types: **Iodimetry** and **Iodometry**. Both rely on the redox couple of iodine (I_2) and iodide ions (I^-).

Iodine is an oxidising agent, meaning it can accept electrons and get reduced to iodide ions: $\mathbf{I_2 + 2e^- \rightarrow 2I^-}$

Conversely, iodide ions can be oxidised to iodine: $\mathbf{2I^- - 2e^- \rightarrow I_2}$

Let's look at each type:

Iodimetry

Iodimetry involves the **direct titration of a reducing agent with a standard solution of iodine (I_2)**. In this method, iodine acts as the titrant. Since iodine is only a **weak oxidising agent**, it can only be used to titrate relatively strong reducing agents.

- **Process:** A known volume of the reducing agent (analyte) is placed in a conical flask (often called an iodine flask). A standard solution of iodine is added from a burette.
- **Indicator: Starch solution** (or sodium starch glycolate, which is more stable than starch) is added to the flask. Starch forms an intense **blue-black complex with free iodine**.
- **Endpoint:** As iodine is added, it reacts with the reducing agent and is converted to colourless iodide ions. Once all the reducing agent has reacted, the first excess drop of iodine titrant will react with the starch indicator, turning the solution a distinct **blue-black colour**. This persistent blue-black colour signals the end-point of the titration.

- **Key Idea:** The disappearance of the reducing agent is detected by the appearance of free iodine, which then complexes with starch.

Examples of Reducing Agents titrated by Iodimetry:

- **Stannous chloride ($SnCl_2$): $Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$**
- **Sodium thiosulphate ($Na_2S_2O_3$):** This is a very common reaction, especially when standardising iodine solutions or as the titrant in iodometry. **$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$** (Thiosulphate is oxidised to tetrathionate)

Iodometry

Iodometry is an **indirect titration method**. Instead of directly titrating with iodine, it involves the **titration of iodine that has been liberated** by a chemical reaction. This method is used to determine the concentration of **strong oxidising agents**.

- **Process:** A known amount of the strong oxidising agent (analyte) is made to react with a **large excess of potassium iodide (KI)** solution, usually in the presence of acid. The strong oxidising agent will oxidise the iodide ions (I^-) from the KI, liberating an amount of **free iodine (I_2)** that is stoichiometrically equivalent to the amount of the original oxidising agent. **Oxidising agent + $2I^-$ → Reduced form of Oxidising agent + I_2**
- **Titration:** The **liberated iodine (I_2)** is then immediately titrated with a **standard solution of sodium thiosulphate ($Na_2S_2O_3$)**. **$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$** (or simply $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$)
- **Indicator: Starch solution** is added towards the end of the titration, when the solution's colour has faded from a deep brown (due to I_2) to a pale yellow. Adding starch too early can cause it to complex too strongly with a large amount of iodine, leading to an inaccurate endpoint.
- **Endpoint:** As the thiosulphate reacts with the liberated iodine, the blue-black starch-iodine complex gradually disappears. The end-point is reached when the solution becomes **colourless**, indicating that all the liberated iodine has been reduced back to iodide.
- **Key Idea:** The amount of thiosulphate used is equivalent to the amount of iodine liberated, which in turn is equivalent to the amount of the original strong oxidising agent.

Example: Determination of Copper(II) ions (Cu^{2+}) Copper(II) ions are a strong oxidising agent.

1. **Liberation of Iodine:** When excess KI is added to a solution containing Cu^{2+} ions, the Cu^{2+} oxidises the I^- ions, producing free iodine and reducing Cu^{2+} to Cu(I) (which often precipitates as CuI): **$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$** (Alternatively, written as $2Cu^{2+} + 2I^- \rightarrow 2Cu^+ + I_2$ followed by $2Cu^+ + 2I^- \rightarrow 2CuI$, thus $2Cu^{2+} + 4I^- \rightarrow 2Cu_2I_2 + I_2$). The amount of liberated iodine (I_2)

is directly equivalent to the amount of Cu^{2+} initially present.

2. **Titration of Liberated Iodine:** The liberated iodine is then titrated with a standard sodium thiosulphate solution: $\mathbf{I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI}$

By knowing the volume and concentration of the thiosulphate used, the amount of iodine liberated can be calculated, and from that, the original concentration of Cu^{2+} can be determined.

Important Considerations for Iodine Titrations:

- **Starch Indicator:** Starch is excellent, but it should be added just before the end-point in iodometry (when the iodine colour is pale yellow) to avoid premature complex formation and improve accuracy. Starch also degrades over time and should be freshly prepared.
- **Volatility of Iodine:** Iodine is volatile, so solutions should be kept cool and stoppered to prevent loss.
- **Stability of Thiosulphate:** Sodium thiosulphate solutions are not perfectly stable and can decompose due to bacterial action or CO_2 absorption from air. They are usually standardised against a primary standard like potassium dichromate or potassium iodate.
- **Acidic Conditions:** Many iodometric reactions require acidic conditions to proceed effectively.

Iodimetry and Iodometry are crucial in pharmaceutical analysis, environmental monitoring, and food chemistry for determining oxidising and reducing substances.

Bromatomety

Bromatomety is a type of redox titration where **Potassium bromate ($KBrO_3$)** is used as the titrant. Potassium bromate is a **strong oxidising agent**, especially in acidic solutions.

- **Mechanism:** In acidic medium, bromate ions (BrO_3^-) react with bromide ions (Br^-) to produce **elemental bromine (Br_2)**: $\mathbf{BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O}$ The oxidising capacity of the bromate system is determined by the Br_2/Br^- couple, with a standard electrode potential (E^0) of **+1.08 V**. This bromine then acts as the primary oxidising species that reacts with the analyte.
- **Titrant Preparation:** Potassium bromate is an excellent primary standard. It can be recrystallised to obtain a high purity salt, and its standard solutions can be prepared by direct weighing and dissolving. These solutions are **very stable** and do not need frequent restandardisation.
- **Acidic Conditions: Hydrochloric acid (HCl)** is typically used to maintain the necessary acidic pH for the reaction to proceed efficiently.
- **Indicator: Methyl orange** is a commonly used indicator in bromatomety. It shows an **irreversible colour change from red to colourless** at the end-point. The red colour of methyl orange is

destroyed by the first excess of bromine produced after the analyte has been consumed. This disappearance of the indicator's colour signals the end of the titration. Other indicators like indigo carmine can also be used.

- **Applications:** Bromatomety is used to determine the concentration of various reducing substances, including:
    - **Azophenum**
    - **Antimony (Sb)**
    - **Arsenic (As)**
    - **Iodide (I^-)**
    - Some organic compounds that react with bromine (e.g., phenols, anilines, which undergo bromination).

In bromatomety, the appearance of a persistent pale yellow colour (due to excess Br_2) or the bleaching of an added indicator marks the end-point. It's a precise and reliable method due to the stability and strong oxidising power of potassium bromate.

Dichrometry

Dichrometry is another important redox titration method that uses **Potassium dichromate ($K_2Cr_2O_7$)** as the titrant. Similar to bromate, potassium dichromate is a **strong oxidising agent** and is particularly effective in **highly acidic solutions**.

- **Mechanism:** In acidic medium, the orange dichromate ion ($Cr_2O_7^{2-}$) is reduced to the green chromium(III) ion (Cr^{3+}): $\mathbf{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O}$ The standard electrode potential (E^0) for this half-reaction is **+1.36 V**, indicating its strong oxidising power.
- **Advantages over $KMnO_4$:** Potassium dichromate offers several significant advantages over potassium permanganate ($KMnO_4$), another common strong oxidising agent:
    - **Stability:** Potassium dichromate can be obtained in a very pure form, and its standard solutions can be prepared by direct weighing, making it an excellent **primary standard**. Its solutions are highly stable over time.
    - **Precision:** Solutions prepared from pure potassium dichromate are very precise.
    - **Insensitivity to Chloride Ions:** Unlike permanganate, which can be reduced by chloride ions (Cl^-) in acidic solution, dichromate is generally **not sensitive to chloride ions**. This is a major advantage, as many samples contain chloride, and using permanganate in such cases would lead to erroneous results.
- **Indicator: Diphenylamine** (or its derivatives like diphenylamine sulphonic acid) is a common indicator used in dichrometry. In its reduced form, diphenylamine is colourless. When it gets oxidised by the excess dichromate at the end-point, it changes to a **dark blue or violet colour**, signaling the completion of the titration.

- **Applications:** Dichrometry is primarily used for the determination of **Iron (II) salts**, as iron(II) is readily oxidised to iron(III) by dichromate. **$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$** It can also be used to determine other reducing agents such as sulfites, nitrites, and some organic compounds.

Due to its stability, primary standard quality, and insensitivity to chloride, potassium dichromate is a highly reliable and widely used titrant in analytical chemistry, especially for iron determinations.

Titration with Potassium Iodate

Titrations involving **Potassium Iodate (KIO_3)** are a versatile redox method, often used to determine the concentration of substances like **Vitamin C (ascorbic acid)**. This method is a form of iodometry, where iodine is first generated and then reacts with the analyte.

- **Principle:** The method determines Vitamin C concentration in a solution by a redox titration in the presence of **potassium iodide (KI)** and an acidic medium. Ascorbic acid is an essential antioxidant and acts as a reducing agent.

- **Mechanism of Reaction:** The titration proceeds in a series of sequential reactions:

    - **Generation of Iodine:** When iodate ions (IO_3^-) from the potassium iodate titrant are added to an acidic solution containing iodide ions (I^-) from potassium iodide, a redox reaction occurs that generates **elemental iodine (I_2)**: **$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$** In this reaction, the iodate is reduced, and the iodide is oxidised to form iodine.

    - **Reaction with Ascorbic Acid:** The iodine (I_2) that is formed immediately reacts with the **ascorbic acid (Vitamin C)** present in the sample. Ascorbic acid is oxidised to **dehydroascorbic acid**, while the iodine is reduced back to **colourless iodide ions (I^-)**: **Ascorbic acid + $I_2 \rightarrow 2I^-$ + Dehydroascorbic acid** As long as there is ascorbic acid present in the solution, any iodine generated will be instantaneously consumed and converted back to iodide, so no free iodine will accumulate.

    - **Endpoint Detection:** Once **all the ascorbic acid has been oxidised**, there is no longer anything to react with the generated iodine. Therefore, any further iodine produced from the reaction of iodate and iodide (Step 1) will remain in solution as free I_2. This excess iodine will then react with a **starch indicator** (added near the end of the titration), forming a characteristic **blue-black starch-iodine complex**. The appearance of this blue-black colour signals the **endpoint** of the titration.

- **Reliability:** This method is often considered **more reliable** than directly titrating with an iodine solution. This is because **potassium iodate solutions are significantly more stable than iodine solutions**. Iodine solutions are volatile and can decompose, leading to changes in concentration over time. Potassium iodate, being a stable salt, allows for the preparation of stable standard solutions.

- **Applications:** This titration method is widely used for the determination of Vitamin C in various samples, including:

    - **Vitamin C tablets**
    - **Fresh or packaged fruit juices**
    - **Solid fruits and vegetables**

In summary, the titration with potassium iodate is an effective and robust method for quantifying reducing substances, particularly ascorbic acid, by indirectly generating iodine as the active titrating species.

Some Common Oxidants and Reductants

To summarise, here are some common substances that act as oxidising and reducing agents in various redox reactions and titrations:

Oxidising Agents (They get reduced)

- **Potassium Permanganate ($KMnO_4$)**: A very strong oxidising agent, often used as a self-indicator due to its intense purple colour.
- **Potassium Dichromate ($K_2Cr_2O_7$)**: A strong oxidising agent, stable and a primary standard, often used for iron(II) determinations.
- **Potassium Iodate (KIO_3)**: Used as a source of iodine for titrations, particularly for Vitamin C.
- **Potassium Bromate ($KBrO_3$)**: A strong oxidising agent, used in bromatomety, often generating bromine in situ.
- **Ceric Sulphate ($Ce(SO_4)_2$)**: A strong oxidising agent, typically used in acidic conditions, can also act as a self-indicator (pale yellow colour).
- **Iodine (I_2)**: A relatively weak oxidising agent, used directly in iodimetry or liberated in iodometry.
- **Lead Dioxide (PbO_2)**
- **Potassium Periodate (KIO_4)**

Reducing Agents (They get oxidised)

- **Ferrous Sulphate ($FeSO_4$)**: A common reducing agent, often titrated with permanganate or dichromate.

- **Sodium Thiosulphate ($Na_2S_2O_3$)**: A crucial reducing agent, particularly for titrating liberated iodine in iodometry.
- **Stannous Chloride ($SnCl_2$)**: A strong reducing agent.
- **Oxalic Acid ($H_2C_2O_4$)**: A common reducing agent, can be used to standardise permanganate solutions.
- **Titanous Sulphate ($Ti_2(SO_4)_3$)**
- **Sodium Arsenite (Na_3AsO_3)**

Primary Standards for Redox Titrations

A **primary standard** is a highly pure, stable chemical that can be weighed accurately and used to prepare a solution of precisely known concentration directly. This known concentration is then used to standardise other solutions. Many of the titrants mentioned above can be prepared as primary standards or can be used to standardise other solutions.

- **Potassium Iodate (KIO_3)**
- **Potassium Bromate ($KBrO_3$)**
- **Potassium Dichromate ($K_2Cr_2O_7$)**
- **Potassium Bi-iodate ($KH(IO_3)_2$)**
- **Iodine (I_2)** (can be purified for direct use but its volatility and reactivity make it less ideal than others)
- **Arsenious Oxide (As_2O_3)**
- **Sodium Oxalate ($Na_2C_2O_4$)**

These substances are valuable because their high purity and stability allow for the direct preparation of standard solutions, which is fundamental for accurate quantitative analysis in redox titrations.