REDOX TITRATIONS

- Redox titration is used to determine the oxidizing agent or reducing agent in a solution. In a redox titration, either the reducing or oxidizing agent will be used as the titrant against the other agent.
- The purpose of this titration is to determine the transfer of electrons from one substance to the other, similar to that of a redox reactions, in order to determine the reducing agent or oxidizing agent.
- The end point of such titrations can be determined by either a colour changing indicator or a potentiometer.
- There are many applications of redox titrations in chemistry, pharmaceutical preparations, environmental analysis, agriculture and many more.
- Redox titrations are important in many areas, for example, in food, pharmaceutical, and general industrial analyses. Titration of sulfite in wine using iodine is a common example. Alcohol can be determined based on its oxidation by potassium dichromate. Examples in clinical analysis are rare since most analyses involve trace determinations, but these titrations are still extremely useful for standardizing reagents.
- A **reducing agent** is the reactant that loses electrons in an oxidation-reduction reaction:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

- An **oxidizing agent** is the reactant that gains electrons in an oxidation-reduction reaction:

$$Ce^{4+} + e^{-} \rightarrow Ce^{3+}$$

- We can split any oxidation/reduction equation into two half-reactions that show which species gains electrons and which loses them.

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$

Above reaction can be shown as two half-reactions-

$$Ce^{4+} + e^{-} \rightarrow Ce^{3+} \qquad \text{(reduction of } Ce^{4+}\text{)}$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad \text{(oxidation of } Fe^{2+}\text{)}$$

- Hence, ferrous sulphate can be estimated quantitatively by its reaction with ceric sulphate.
- The rules for balancing half-reactions are the same as those for other reaction types, that is, the number of atoms of each element as well as the net charge on each side of the equation must be the same.
- Thus, for the oxidation of Fe^{2+} by MnO^{4-}, the half-reactions are

$$MnO_4^{-} + 5e^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^{-}$$

- In the first half-reaction, the net charge on the left side is (-1 -5 + 8) = +2, which is the same as the charge on the right. Note also that we have multiplied the second half reaction by 5 so that the number of electrons lost by Fe^{2+} equals the number gained by $MnO4^{-}$.
- We can then write a balanced net ionic equation for the overall reaction by adding the two half-reactions

$$MnO_4^{-} + 5Fe^{2+} + 8H^{+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

A. PERMANGANOMETRY

- **Potassium permanganate** is a widely used oxidizing agent. It acts as a self indicator for end-point detection. The solution is stable if precautions are taken in its preparation.
- When the solution is first prepared, small amounts of reducing impurities in the solution reduce a small amount of the MnO_4^{-}.
- The solution can be stabilized by removing the MnO_2. So, before standardizing, the solution is boiled to undergo oxidation rapidly of all impurities and is allowed to stand overnight.
- The MnO_2 is then removed by filtering through a sintered-glass filter. Potassium permanganate can be standardized by titrating primary standard sodium oxalate, $Na_2C_2O_4$, which, dissolved in acid, forms **oxalic acid.**

$$5H_2C_2O_4 + 2KMnO_4 + 6H_2SO_4 \rightarrow 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$
(oxalic acid) (pink) (colourless)

- **Preparation of Potassium Permanganate, 0.02 M**
  Dissolve 3.2 g of potassium permanganate in 1000 ml of water, heat on a water bath for 1 hour, allow it to stand for 2 days and filter before using.
- **Standardization of 0.02 M Potassium Permanganate Solution**
  Weigh accurately about 0.1 g of pure oxalic acid in 80 ml water using volumetric flask, add to it 5 ml of concentrated sulphuric acid along the side of the flask, mix the contents carefully. Titrate this against the potassium permanganate solution from the burette till the pink colour persists for about 20 seconds.
  Each ml of 0.02 M potassium permanganate is equivalent to 0.0067 g of $Na_2C_2O_4$

B. CERIMETRY

- Ammonium Ceric sulphate serves as a powerful oxidizing agent in an acidic medium. The salt has a bright yellow colour and so its solution. On reduction, the resulting Cerous salt obtained is colourless in appearance and, therefore, strong solutions may be considered as self-indicating.

- In general practice, 0.05 N solutions are used for estimations. As this concentration is very dilute for observation of the respective end-point, hence use of an appropriate indicator becomes necessary. The oxidation reaction involved may be expressed as follows

$$Ce^{4+} + e^{-} \rightleftharpoons Ce^{3+}$$

(yellow) (colourless)

- Titrations are usually performed in sulfuric acid or perchloric acid. Cerium (IV) can be used for most titrations in which permanganate is used, and it possesses a number of advantages.
- It is a very strong oxidizing agent and its potential can be varied by choice of the acid used. An added advantage of cerium is that a salt of cerium(IV) can be obtained as a primary standard, and the solution does not have to be standardized.
- The main disadvantage of Cerium (IV) is its increased cost over potassium permanganate.
- Ferroin sulphate is a suitable indicator for many Cerium (IV) titrations.
- Cerium (IV) solutions can be standardized against primary standard Arsenic trioxide (As_2O_3), Sodium oxalate ($Na_2C_2O_4$). The reaction with arsenic(III) is slow, and it must be catalyzed by adding either osmium tetroxide *(*OsO_4*)* or iodine monochloride (ICl). Ferroin is used as the indicator.
- **Preparation of 0.1M Ammonium Ceric sulphate**
  Dissolve 65 g of Ammonium Ceric sulphate, with gentle heat, in a mixture of 30 ml of sulphuric acid and 500 ml of water. Cool it and filter and dilute to 1000 ml with water.
- **Standardization of 0.1M Ammonium Ceric sulphate Solution**
  Weigh accurately about 0.2 g of arsenic trioxide, transfer to a 500 ml conical flask. Wash down the inner walls of the flask with 25 ml of 8.0 % w/v solution of sodium hydroxide, add 100 ml of water and mix. Add 30 ml of dilute sulphuric acid, 0.15 ml osmic acid solution, 0.1 ml of ferrion sulphate solution and slowly titrate with the ceric ammonium sulphate solution until the pink colour is changed to a very pale blue.

$$As_2O_3 + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2O$$

$$2Ce(SO_4)_2 + Na_3AsO_3 + H_2O \rightarrow Ce_2(SO_4)_3 + Na_3AsO_4 + H_2SO_4$$

Each ml of 0.1 m ceric ammonium sulphate is equivalent to 0.004946 g of As_2O_3

C. DICHROMETRY

- Potassium dichromate, $K_2Cr_2O_7$, is a slightly weaker oxidizing agent than potassium permanganate. The great advantage of this reagent is its availability as a primary standard, and thus, generally the solution need not be standardized.
- Potassium dichromate exhibits much greater stability in aqueous solution in comparison to potassium permanganate. Potassium dichromate possesses an inherent orange colour that is not intense enough to serve its own end-point signal, specifically

in the presence of the green Cr3+ ion, which is supposed to be present at the end-point.

- Hence, redox indicators are usually employed to locate the exact end-point *e.g.*, barium diphenylamine sulphonate.
- **Preparation of Potassium dichromate, 0.1M**
  Weigh accurately 0.49 g of potassium dichromate previously dried at 20°C for 4 hours and dissolve in sufficient distilled water to produce 100 ml in a volumetric flask.
- **Standardization of 0.1 M Potassium dichromate solution**
  To 20ml of above solution, add 1g of potassium iodide and 7ml of 2M HCl. Add 250ml water and titrate with 0.1M sodium thiosulphate using starch indicator added towards the end point. The end point is obtained when colour changes from blue to green.
  Each ml of 0.1 M sodium thiosulphate is equivalent to 0.0049g $K_2Cr_2O_7$.

TITRATIONS INVOLVING IODINE: IODIMETRY AND IODOMETRY

D. IODIMETRY

- Iodine is a moderately strong oxidizing agent and can be used to titrate reducing agents. Titrations with I_2 are called **iodimetric methods**.

Reduction

$$I_2 + 2e^- \rightleftharpoons 2I^-$$

(Blue colour) (Colourless)

OR

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_2O_6$$

- These titrations are usually performed in neutral or mildly alkaline (pH 8) to weakly acidic solutions. If the pH is too alkaline. I_2 will convert to hypoiodate and iodide.
- **Preparation of 0.1M Iodine Solution**
  Dissolve 2.0 g of iodine and 3 g of potassium iodide in water to produce 100 ml.
- **Standardization of 0.1M Iodine Solution**
  Weigh accurately 0.5 g arsenic trioxide into a beaker, add to it 2 ml of sodium hydroxide solution, and heat to dissolve. Cool and transfer the contents quantitatively to a 100 ml volumetric flask and make up the volume upto the mark with distilled water. Pipette 20 ml into an iodine-flask. Now, titrate with 0.1 N iodine solution and add Starch solution till the end-point is achieved by the appearance blue colour.

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4H^+ + 4I^-$$

Each ml of 0.1 M Iodine solution is equivalent to 0.00496g of Arsenic trioxide.

E. IODOMETRY

- Iodide ion is a weak reducing agent and will reduce strong oxidizing agents.

- It is not used, however, as a titrant mainly because of the lack of a convenient visual indicator system, as well as other factors such as speed of the reaction.
- When an excess of iodide is added to a solution of an oxidizing agent, I_2 is produced in an amount equivalent to the oxidizing agent present.
- This I_2 can, therefore, be titrated with a reducing agent, and the result will be the same as if the oxidizing agent were titrated directly. The titrating agent used is sodium thiosulfate.

$$Cr_2O_7^{2-} + 6I^- \text{ (excess)} + 14H^+ \rightarrow 2Cr_3+ + 3I_2 + 7H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

- The end point for iodometric titrations is detected with starch. The disappearance of the blue starch − I_2 colour indicates the end of the titration. The starch is not added at the beginning of the titration when the iodine concentration is high. Instead, it is added just before the end point when the dilute iodine colour becomes pale yellow.

Iodimetry	Iodometry
In iodimetry, the titrant is I_2 and the analyte is a reducing agent.	In iodometry, the analyte is an oxidizing agent that reacts with I^- to form I^2.
The end point is detected by the appearance of the blue starch–iodine colour.	The liberated I_2 is titrated with thiosulfate, using disappearance of the starch–iodine colour for the end point.
In iodimetry, we directly titrate with iodine solution (filled in burette).	In iodometry, we titrate liberated iodine.
It is a direct method.	It is an indirect method.
Iodimetry can be used to determine oxidizing agents.	Iodometry can be used to determine reducing agents.

F. BROMATOMETRY (Titrations with Potassium Bromate)

- Potassium bromate can also be employed as an oxidizing agent in the assay of a number of pharmaceutical substances.

$$BrO_3^- + I^- \rightarrow IO_3^- + Br^-$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

- **Preparation of 0.1M Potassium Bromate**
  Weigh accurately 0.2784 g of potassium bromate into a beaker and dissolve it in sufficient distilled water. Transfer the solution quantitatively into a 100 ml volumetric flask and make up the volume to the mark.
- **Standardization of 0.1M Potassium Bromate**
  Transfer an accurately measured volume of about 30.0 ml of 0.1 N potassium bromate solution into a 250 ml iodine flask. Add to it 3.0 g potassium iodide, followed by 3.0

ml of hydrochloric acid. Titrate liberated iodine with 0.1 N sodium thiosulphate, using 3.0 ml of freshly prepared starch solution as an indicator at the end-point.
Each ml of 0.1 N sodium thiosulphate is equivalent to 0.002784 g of KBrO3.

END POINT DETECTION/REDOX INDICATORS

Self-Indicators

- If the titrant is highly coloured, this colour may be used to detect the end point. For example, a 0.02 *M* solution of potassium permanganate is deep purple. A dilute solution of potassium permanganate is pink.
- The product of its reduction, Mn^{2+}, is extremely faint pink, nearly colourless. During a titration with potassium permanganate, the purple colour of the MnO^{4-} is removed as soon as it is added because it is reduced to Mn^{2+}. As soon as the titration is complete, a fraction of a drop of excess MnO^{4-} solution imparts a definite pink colour to the solution, indicating that the reaction is complete.

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$
(oxalic acid) (pink) (colourless)

- Obviously, the end point does not occur at the equivalence point, but at a fraction of a drop beyond. The titration error is small and can be corrected for by running a blank titration, or it is accounted for in standardization.

Starch Indicator

- This indicator is used for titrations involving iodine. Starch forms a complex with that is a dark-blue colour. The colour reaction is sensitive to very small amounts of iodine. In titrations of reducing agents with iodine, the solution remains colourless up to the equivalence point. A fraction of a drop of excess titrant turns the solution a definite blue.
- **Why Starch solution added near to the equivalence point?**
  Starch decomposes irreversibly in solutions containing large concentrations of iodine. Therefore, in titrating solutions of iodine with thiosulfate ion, as in the indirect determination of oxidants, addition of the indicator is delayed until the colour of the solution changes from red-brown to yellow; at this point, the titration is nearly complete. The indicator can be introduced at the outset when thiosulfate solutions are being titrated directly with iodine.
- The second reason is that most iodometric titrations are performed in strongly acid medium and the starch has a tendency to hydrolyze in acid solution.

Redox Indicators

- The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms are different in colour.
- When we add a **redox indicator**, the indicator produces a colour that depends on the potential of solution. As the potential changes with the addition of titrant, the indicator changes oxidation state and changes colour, signalling the end point.

Redox Indicators

Indicator	Color	
	Reduced Form	Oxidized Form
Nitroferroin	Red	Pale blue
Ferroin	Red	Pale blue
Diphenylaminesulfonic acid	Colorless	Purple
Diphenylamine	Colorless	Violet
Methylene blue	Blue	Colorless
Indigo tetrasulfonate	Colorless	Blue