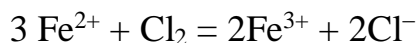## 2- Oxidation reduction (Redox) titration

Redox titrations are based on a reduction-oxidation reaction between an oxidizing agent and a reducing agent. A potentiometer or a redox indicator is usually used to determine the endpoint of the titration, as when one of the constituents is the oxidizing agent potassium dichromate. The color change of the solution from orange to green is not definite, therefore an indicator such as sodium diphenylamine is used. Analysis of wines for sulfur dioxide requires iodine as an oxidizing agent. In this case, starch is used as an indicator; a blue starch-iodine complex is formed in the presence of excess iodine, signalling the endpoint.

Some redox titrations do not require an indicator, due to the intense color of the constituents. For instance, in permanganometry a slight persisting pink color signals the endpoint of the titration because of the color of the excess oxidizing agent potassium permanganate.[31] In iodometry, at sufficiently large concentrations, the disappearance of the deep red-brown triiodide ion can itself be used as an endpoint, though at lower concentrations sensitivity is improved by adding starch indicator, which forms an intensely blue complex with triiodide.

Assay

An assay is a form of biological titration used to determine the concentration of a virus or bacterium. Serial dilutions are performed on a sample in a fixed ratio (such as 1:1, 1:2, 1:4, 1:8, etc.) until the last dilution does not give a positive test for the presence of the virus. The positive or negative value may be determined by visually inspecting the infected cells under a microscope or by an immunoenzymetric method such as enzyme-linked immunosorbent assay (ELISA). This value is known as the titer.

Oxidation-Reduction (Redox)

$$3\ Fe^{2+} + Cl_2 = 2Fe^{3+} + 2Cl^-$$

$3Fe^{2+} - 2e\ = 2Fe^{3+}$ (Loss of electrons: Oxidation)

$Cl_2 + 2e\ = 2Cl^-$ (Gain of electrons: Reduction)

In every redox reaction, both reduction and oxidation must occur. Substance that gives electrons is the reducing agent or reductant. Substance that accepts electrons is the oxidizing agent or oxidant.

Reaction of ferrous ion with chlorine gas Overall, the number of electrons lost in the oxidation half reaction must equal the number gained in the reduction half equation.

Oxidation Number (O.N)

The O.N of a monatomic ion = its electrical charge.

The O.N of atoms in free un-combined elements = zero

The O.N of an element in a compound may be calculated by assigning the O.N to the remaining elements of the compound using the aforementioned basis and the following additional rules:

The O.N. for oxygen = -2 (in peroxides = -1).

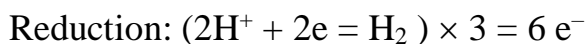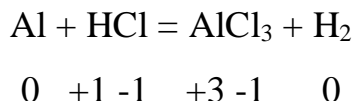The O.N. for hydrogen = +1 (in special cases = -1).

The algebraic sum of the positive and negative O.N. of the atoms represented by the formula for the substance = zero.

The algebraic sum of the positive and negative O.N. of the atoms in a polyatomic ion = the charge of the ion.
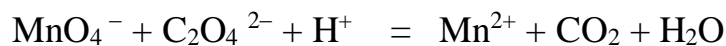
Balancing Redox Reactions using Half Reaction Method

1- Divide the equation into an oxidation half-reaction and a reduction half-reaction

2- Balance these – Balance the elements other than H and O

3- Balance the O by adding H2O – Balance the H by adding H+

4- Balance the charge by adding e-

5- Multiply each half-reaction by an integer such that the number of electron lost in one equals the number gained in the other

6- Combine the half-reactions and cancel

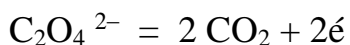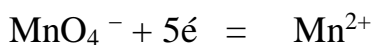7- Balancing Redox Reactions Using the Half Reaction Method

Example-1

$$Al + HCl = AlCl_3 + H_2$$
$$0 \quad +1 \ -1 \quad +3 \ -1 \quad 0$$

Oxidation: $(Al = Al^{3+} + 3e^-) \times 2 = 6 \ e^-$

Reduction: $(2H^+ + 2e = H_2) \times 3 = 6 \ e^-$

Redox: $2Al + 6H^+ = 2Al^{3+} + 3H_2$

Example-2

$$MnO_4^{\ -} + C_2O_4^{\ 2-} + H^+ \ = \ Mn^{2+} + CO_2 + H_2O$$

1- Balance each half reaction:

$MnO_4^{\ -} + 5é \ = \ Mn^{2+}$

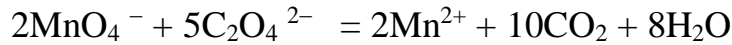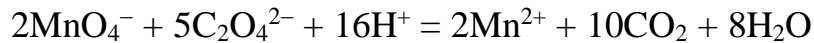$C_2O_4^{\ 2-} = 2 CO_2 + 2é$

2- Use the number of moles so as to make the electrons gained in one reaction equal those lost in the other one

$$2MnO_4^- + 5C_2O_4^{2-} = 2\ Mn^{2+} + 10CO_2$$
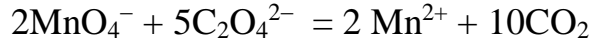
3- Balance oxygen atoms by adding water

$$2MnO_4^- + 5C_2O_4^{2-} = 2Mn^{2+} + 10CO_2 + 8H_2O$$

4- Balance hydrogen atoms by adding H+

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$

Nernest Equation for Electrode Potential

$$Et = E^o + RT/nF\ log\ [M^{n+}]$$

$$E_{25\ ^\circ C} = E^o + 0.0591/n\ log\ [M^{n+}]$$

Where

Et = electrode potential at temperature t.

E° = standard electrode potential (constant depend on the system)

R = gas constant

T = absolute Temp. (t °C + 273)

F = Faraday (96500 Coulombs) log_e = ln (natural logarithm= 2.303 log)

n= valency of the ion

$[M^{n+}]$ = molar concentration of metal ions in solution

Standard Electrode Potential (E^o)

E^o is the electromotive force (emf) produced when a half cell (consisting of the elements immersed in a molar solution of its ions) is coupled with a standard hydrogen electrode (E° = zero).

Li / Li$^+$ –3.03	Cd/Cd^{2+} –0.40	K / K$^+$ –2.92
Sn/Sn^{2+} –0.13	Mg/Mg^{2+} –2.37	H$_2$ (Pt)/H+ 0.00

Al/Al^{3+} −1.33	Cu/Cu^{2+} +0.34	Zn/Zn^{2+} −0.76
Hg/Hg^{2+} +0.79	Fe/Fe^{2+} −0.44	Ag/Ag$^+$ +0.8

Detection of End Point in Redox Titrations

1- Self Indicator (No Indicator)

$$\textbf{KMnO}_4 \textbf{ (violet)} + \textbf{Fe}^{2+} + \textbf{H}^+ \rightarrow \textbf{Mn2+ (colourless)} + \textbf{Fe}^{3+}$$

2- External Indicator

$$\textbf{Cr}_2\textbf{O}_7{}^{2-} + \textbf{3Fe}^{2+} + \textbf{14H}^+ \rightarrow \textbf{2Cr}^{3+} + \textbf{3Fe}^{3+} + \textbf{7H}_2\textbf{O}$$
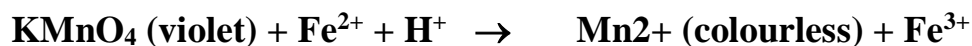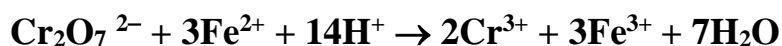
3- Internal Redox Indicator

$$\textbf{Inox} + \textbf{n e} - = \textbf{Inred}$$
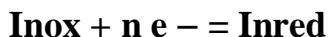
4- Irreversible Redox Indicators

Some highly coloured organic compounds that undergo irreversible oxidation or reduction e.g. Methyl Orange

Properties of Oxidizing Agents

1. Potassium permanganate (KMnO4)

2. Potassium dichromate (K2 Cr2O7)

3. Iodine (I2)

4. Potassium iodate (KIO3)

5. Bromate-bromide mixture

Measuring the endpoint of a titration

Different methods to determine the endpoint include:

- Indicator: A substance that changes color in response to a chemical change. An acid–base indicator (e.g., phenolphthalein) changes color depending on the pH. Redox indicatorsare also used. A drop of indicator solution is added

to the titration at the beginning; the endpoint has been reached when the color changes.

- Potentiometer: An instrument that measures the electrode potential of the solution. These are used for redox titrations; the potential of the working electrode will suddenly change as the endpoint is reached.

An elementary pH meter that can be used to monitor titration reactions

- pH meter: A potentiometer with an electrode whose potential depends on the amount of H^+ ion present in the solution. (This is an example of an ion-selective electrode.) The pH of the solution is measured throughout the titration, more accurately than with an indicator; at the endpoint there will be a sudden change in the measured pH.

- Conductivity: A measurement of ions in a solution. Ion concentration can change significantly in a titration, which changes the conductivity. (For instance, during an acid–base titration, the H^+ and OH^- ions react to form neutral H_2O.) As total conductance depends on all ions present in the solution and not all ions contribute equally (due to mobility and ionic

strength), predicting the change in conductivity is more difficult than measuring it.

- Color change: In some reactions, the solution changes color without any added indicator. This is often seen in redox titrations when the different oxidation states of the product and reactant produce different colors.

- Precipitation: If a reaction produces a solid, a precipitate will form during the titration. A classic example is the reaction between Ag^+ and Cl^- to form the insoluble salt AgCl. Cloudy precipitates usually make it difficult to determine the endpoint precisely. To compensate, precipitation titrations often have to be done as "back" titrations (see below).

- Isothermal titration calorimeter: An instrument that measures the heat produced or consumed by the reaction to determine the endpoint. Used in biochemical titrations, such as the determination of how substrates bind to enzymes.

- Thermometric titrimetry: Differentiated from calorimetric titrimetry because the heat of the reaction (as indicated by temperature rise or fall) is not used to determine the amount of analyte in the sample solution. Instead, the endpoint is determined by the rate of temperature change.

- Spectroscopy: Used to measure the absorption of light by the solution during titration if the spectrum of the reactant, titrant or product is known. The concentration of the material can be determined by Beer's Law.

- Amperometry: Measures the current produced by the titration reaction as a result of the oxidation or reduction of the analyte. The endpoint is detected as a change in the current. This method is most useful when the excess titrant can be reduced, as in the titration of halides with Ag^+.

1- Redox reactions are those reactions which involves change in the oxidation number or transfer of electrons between reactants.

2- Oxidation is a process which involves loss of electrons.

$$Fe^{2+} - e = Fe^{3+}$$

It is a process in which an atom or an ion may lose one or more electrons.

3- Reduction is a process in which electrons are gained.

$$Cl_2 + 2e = 2Cl^-$$

It is a process in which an atom or an ion may gain one or more electrons.

4- The equivalent weight of an oxidizing agent (oxidant) or reducing agent (reductant) is equal to its molecular weight divided by the number of electrons lost or gained by this substance during the reaction:

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

$$The\ eq.wt. = \frac{MnO_4^-}{5} = \frac{KMnO_4}{5}$$

$$Cr_2O_7^{--} + 6e + 14H^+ = 2Cr^{3+} + 7H_2O$$

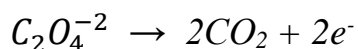$$The\ eq.wt. = \frac{Cr_2O_7^{--}}{6} = \frac{K_2Cr_7O_7}{6}$$

5- Indicators in oxidation - reduction reaction:

Potassium permanganate may act as a self-indicator as it has a distinct purple color and becomes colorless on reduction. In the case of potassium dichromate an indicator must be used for the determination of the end point which may be an internal or an external indicator. The types of indicators used may be as follows: Self-indicator - Internal indicator - External Indicator

Oxalic acid is oxidized by potassium permanganate , in acid solution to carbon dioxide and water.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$
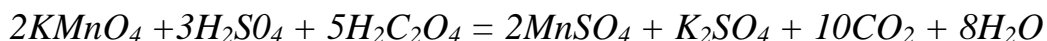
The reaction is complete at a temperature of about 60-90°C

$$C_2O_4^{-2} \rightarrow 2CO_2 + 2e^-$$

Oxidation with potassium permanganate:

KMnO$_4$ is a strong oxidizing agent in acid medium

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

HCl, could not be used instead of H$_2$SO$_4$ as it is readily oxidized to chlorine in presence of permanganate.

$$2KMnO_4 + 16HCI = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

Nitric acid is stronger than KMnO$_4$

In strong alkaline medium, heptavalent manganese is reduced as follows:

$$2KMnO_4 = K_2O + 2MnO_2 + 3O$$
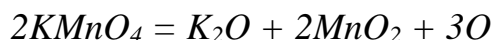
And the eq.wt. in alkaline sol.=1/3 the molecular weight. The formed manganese dioxide which is black in color may mask the end point in alkaline medium. KMnO$_4$, however is not a primary standard as it is difficult to obtain in a purified state due to the fact that it is always contaminated with manganese dioxide.

$$4MnO_4^- + 2H_2O \rightarrow 4MnO_2 + 3O_2 + 4OH^-$$
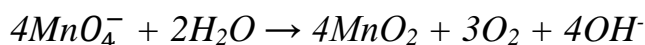
(I) Standardization of sodium thiosulphate solution with potassium iodate:

Theory

Potassium iodide reacts in acid medium with potassium iodate with the liberation of Iodine:

$$KIO_3 + 3H_2SO_4 + 5KI \rightarrow 3K_2SO_4 + 3I_2 \uparrow + 3H_2O$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$
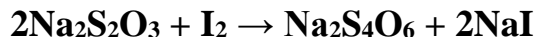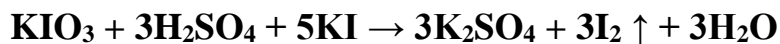
(II) Determination of copper in copper sulphate ($CuSO_4.5H_2O$)

Theory

Copper sulphate reacts with potassium iodide according to the following equation:

$$2CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2 \uparrow + 2K_2SO_4$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

i.e. $\quad 2CuSO_4 \equiv I_2 \equiv 2Na_2S_2O_3$
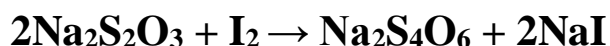
Titration of Hydrogen Peroxide

EXPERIMENTAL GOALS:

The purpose of this lab is to learn how to use a titration to standardize a solution and to determine the concentration of an unknown solution.

INTRODUCTION:

A chemist or biochemist will often find it necessary to determine the concentration of something in a solution or sample. One method that can accomplish this is the method of **titration**. In a titration, a solution of known concentration is allowed to react with a solution of unknown concentration until all of the "known" is consumed in the reaction. By carefully measuring the volume of each solution, one can easily calculate the concentration of the unknown solution.

Titration is performed on the basis of stoichiometry. For example, consider two substances that react on a 2:1 stoichiometric basis. If it is known that one mole of a reactant reacts on a 2:1 basis with another reactant of known concentration, then we can use the stoichiometric relationship between the two reactants to figure out the concentration of the reactant of unknown concentration. The important consideration here is that the titration must be stopped at the point where the substances have reacted in stoichiometrically equivalent amounts. This point is referred to as the **equivalence point**. Underestimating or overestimating the volume of either the reactant of known or unknown concentration during the titration can lead to an inaccurate experiment.

The equivalence point of a titration can be detected by various means. In today's lab, we are going to use the reaction between potassium permanganate and hydrogen peroxide in order to learn more about titrations as well as stoichiometry. This particular reaction is actually an oxidation/reduction reaction rather than an acid/base reaction. The sulfuric acid solution (H_2SO_4) is being used to provide an acidic environment for the oxidation-reduction reaction to take place in. Finally, it is important to remember that balancing of some oxidation/reduction reactions is more complicated than other reactions because you have to balance mass (# of atoms of each element) as well as charge (related to the number of electrons lost/gained).

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$$

In this particular reaction, we use the faint pink color of the permanganate ion as an indicator rather than using an additional dye to determine the end point. In essence, the permanganate in the $KMnO_4$ solution acts as its own
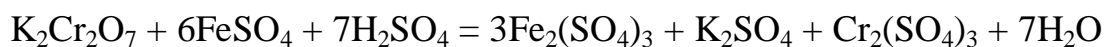
indicator. The Mn^{2+} ion is actually colorless, but when MnO_4^- is in excess, the solution will turn from colorless to pink, indicating that the equivalence point has been reached.

When performing a titration, it is necessary to first determine the concentration of the known solution as accurately as possible. This process is referred to as *standardization*. For example, in this experiment, the titrant is an aqueous solution of potassium permanganate, $KMnO_4$; however, solid $KMnO_4$ contains traces of other impurities, such as MnO_2, so a solution of known concentration cannot be made by simply measuring out a certain number of grams of $KMnO_4$ and dissolving it in the appropriate amount of water. To determine the concentration of the $KMnO_4$, it is titrated against something that can be measured accurately, such as solid oxalic acid, $H_2C_2O_4$, whose mass can be measured very precisely. By using the stoichiometry of the standardization reaction, the concentration of the titrant solution can be determined.

$$2MnO_4^- \ + \ 5H_2C_2O_4 \ + \ 6H^+ \ \rightarrow \ 2Mn^{2+} \ + \ 10CO_2(g) \ + \ 8H_2O$$
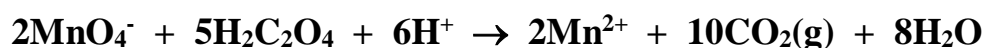
The level of accuracy afforded by graduated cylinders is not sufficient for a titration, so more accurate instruments must be used. Burets or pipettes typically are used in titrations. It is important to utilize the significant figures that a buret allows one to use. Burets are very accurate pieces of equipment. In order to determine the volume dispensed from a buret, the initial and final volumes are recorded and subtracted. (See the Introduction for the "Stoichiometry III: Titration of Vinegar" section for a more thorough discussion of the use of burets in titrations.)

Determination of strength (g/L) of ferrous ammonium sulphate (FeSO$_4$.(NH$_4$)$_2$SO$_4$.6H$_2$O) by titrating it against standard (1.0 g/L) potassium dichromate (K$_2$Cr$_2$O$_7$) solution

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$6\ FeSO_4 + 3H_2SO_4 + 3O \rightarrow 3Fe_2(SO_4)_3 + 3H_2O$$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

$$(Cr_2O_7)^{2-} + 6Fe^{2+} + 14H^+ \quad = \quad 6Fe^{3+} + 2Cr^{3+}$$

N-phenyl anthranilic acid is used as an indicator. Indicator is not oxidized as long as Fe^{2+} ions are there in the solution. The slight excess amount of dichromate will oxidize the indicator when all of the Fe^{2+} ions have been converted to Fe^{3+} ions resulting in colour change of the solution from greenish (due to Cr^{3+}) to purple.