Potassium Permanganate Titrations

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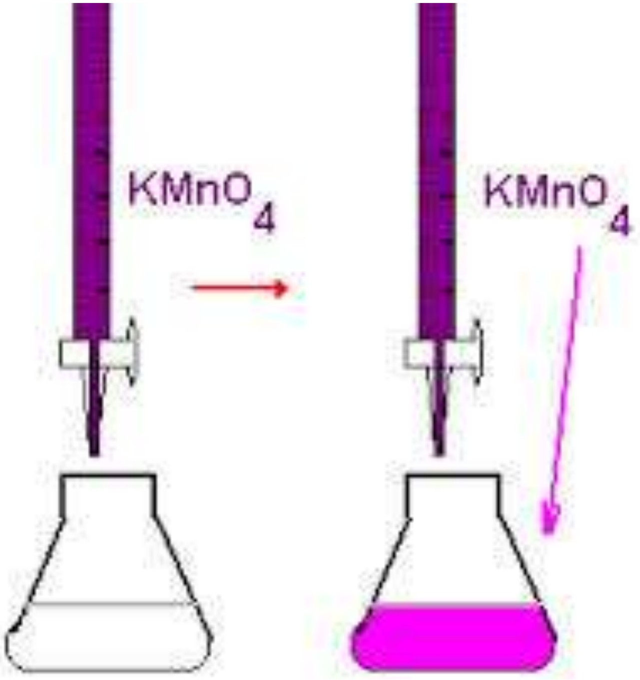
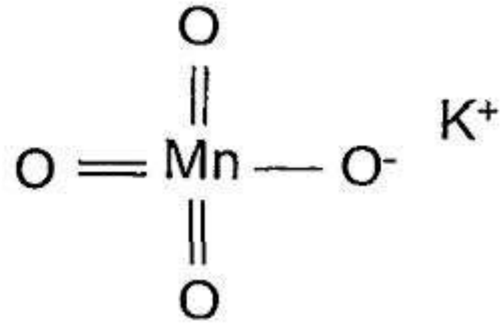


Introduction to potassium permanganate

- Potassium permanganate is an inorganic chemical compound with the formula $KMnO_4$. It is a salt consisting of K^+ and MnO− 4 ions. Formerly known as permanganate of potash or Condy's crystals, it is a strong oxidizing agent.
- **Formula**: KMnO4
- **Molar mass**: 158.034 g/mol
- **Density**: 2.70 g/cm³
- **Melting point**: 240 °C
- **IUPAC ID**: Potassium mangnate(VII)
- **Soluble in**: Water

1. Potassium permanganate (KMnO4) is used primarily to control taste and odors, remove color, control biological growth in treatment plants, and remove iron and manganese.



2. Potassium permanganate is a mild antiseptic with astringent properties. It is used in dermatology to treat weeping skin conditions. Potassium permanganate tablets are commonly used in clinical practice.

3. Potassium permanganate, KMnO4 , is a chemical **oxidizing agent** that will react with any **organic matter** in a pond including algae, bacteria, fish, particulate and dissolved organic, and organic bottom sediments. It has been used in fish ponds to treat common fish **pathogens** such as gill parasites and external **bacterial and fungal infections.**

4. Potassium permanganate is an **oxidant**, but a poor disinfectant. It's often used in well water to control odor and taste, **remove manganese**, **iron** and color from the water, and to control **biological growth.**

Why is potassium permanganate soluble in water?

- Almost all potassium-salts are soluble in water. KMnO4 is a network solid consisting of alternating K atoms and MnO4 radicals. The bonds holding K to the MnO4- are weak enough to be easily broken by the hydration of water molecules.

Self indicator ???

As we all know that the potassium permanganate (KMnO4) is the dark purple color solution ..and in titration it become colorless ..so when the titration is completed ...and the other single drop of KMnO4 solution produce pinkish color in a beaker ...which indicate that the reaction was completed just a single drop before .. we use indicator in a reaction in order to indicate ..but we don't used indicator in titration with KMnO4 because it also indicate us by changing its color ...colorless to pink

Oxidizing Agent

Potassium permanganate is used in organic chemistry in the form of an alkaline or neutral solution. Oxidation involves the gain of oxygen and an oxidizing agent is a chemical that oxidizes something else. The permanganate in potassium permanganate has the anion $MnO4-$ that is the reason for its strong oxidizing properties.

Oxidation with potassium permanganate

- $KMnO_4$ is a strong oxidant with an intense violet color. In strongly acidic solutions ($pH < 1$), it is reduced to Mn^{2+}.
- In neutral or alkaline solution, it is reduced to brown solid MnO_2.
- In strongly alkaline solution (2 M NaOH), green manganate ion (MnO_4^{2-}) is produced.

Permanganate titration

Oxidation with permanganate : Reduction of permanganate

KMnO4 Powerful oxidant that the most widely used.

In strongly acidic solutions (1M H_2SO_4 or HCl, $pH \leq 1$)

$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$ $E^o = 1.51\ V$

violet color colorless manganous

$KMnO_4$ is a self-indicator.

In feebly acidic, neutral, or alkaline solutions

$MnO_4^- + 4H^+ + 3e = MnO_2(s) + 2H_2O$ $E^o = 1.695\ V$

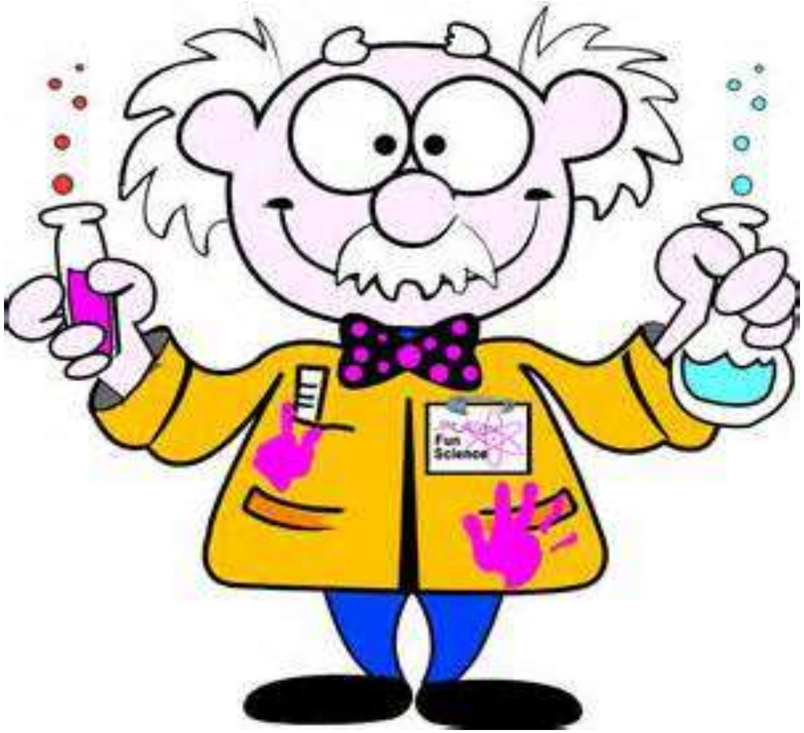
brown manganese dioxide solid

In very strongly alkaline solution (2M NaOH)

$MnO_4^- + e = MnO_4^{2-}$ $E^o = 0.558\ V$

green manganate

Primary standard ????



NO

Standardization by titration of sodium oxalate (primary standard)

Standardization of $KMnO_4$ solution

Potassium permanganate is not primary standard, because traces of MnO_2 are invariably present.

Standardization by titration of sodium oxalate (primary standard) :

$$2KMnO_4 + 5\,Na_2(COO)_2 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Na_2SO_4 + 10\,CO_2 + 8H_2O$$

$2KMnO_4 \equiv 5\,Na_2(COO)_2 \equiv$ 10 Equivalent

mw 158.03 mw 134.01

158.03 g / 5 ≡ 134.01 g / 2 ≡ 1 Eq.

31.606 g ≡ 67.005 g

1N × 1000 ml ≡ 67.005 g

x N × V ml a g

x N = (a g × 1N × 1000 ml) / (67.005 g × V ml)

Preparation of 0.1 N *potassium permanganate solution*

$KMnO_4$ is not pure. Distilled water contains traces of organic reducing substances which react slowly with permanganate to form hydrous manganese dioxide. Manganese dioxide promotes the auto decomposition of permanganate.

1) Dissolve about 3.2 g of $KMnO_4$ (mw=158.04) in 1000ml of water,

   heat the solution to boiling, and keep slightly below the boiling point for 1 hr.

   Alternatively , allow the solution to stand at room temperature for 2 or 3 days.

2) Filter the liquid through a sintered-glass filter crucible to remove solid MnO_2.
3) Transfer the filtrate to a clean stoppered bottle freed from grease with cleaning mixture.
4) Protect the solution from evaporation, dust, and reducing vapors, and keep it in the dark or in diffuse light.
5) If in time managanese dioxide settles out, refilter the solution and restandardize it.

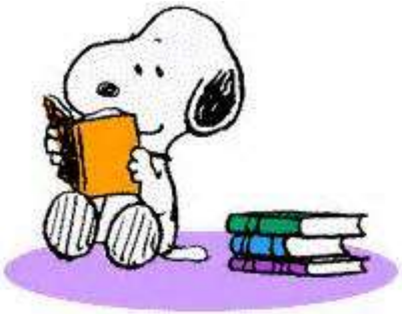
What is a titration ?

The act of adding standard solution in small quantities to the test solution till the reaction is complete is termed titration.

What is redox titration ?

A TITRATION WHICH DEALS WITH A REACTION INVOLVING OXIDATION AND REDUCTION OF CERTAIN CHEMICAL SPECIES.

What is a standard solution?



A standard solution is one whose concentration is precisely known.

What is a test solution?

A test solution is one whose concentration is to be estimated.

What is oxidation?

Old definition:

Combination of substance with oxygen

$$C\,(s) + O_2(g) \longrightarrow CO_2(g)$$

Current definition:

Loss of Electrons is Oxidation (LEO)

$$Na \longrightarrow Na^+$$

Positive charge represents electron deficiency

ONE POSITIVE CHARGE MEANS DEFICIENT BY ONE ELECTRON

What is reduction?

Old definition:

Removal of oxygen from a compound

$$WO_3\,(s) + 3H_2(g) \longrightarrow W(s) + 3H_2O(g)$$

Current definition:

Gain of Electrons is Reduction (GER)

$$Cl + e^- \longrightarrow Cl^-$$

Negative charge represents electron richness

ONE NEGATIVE CHARGE MEANS RICH BY ONE ELECTRON

OXIDATION-REDUCTION

Oxidation and reduction go hand in hand. In a reaction, if there is an atom undergoing oxidation, there is probably another atom undergoing reduction.

When there is an atom that donates electrons, there is always an atom that accepts electrons.

Electron transfer happens from one atom to another.

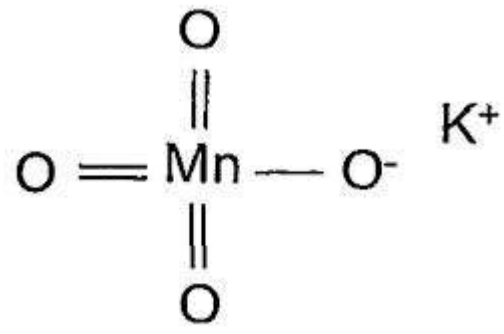
Rules for assigning Oxidation State

The sum of the oxidation numbers of all of the atoms in a molecule or ion must be equal in sign and value to the charge on the molecule or ion.

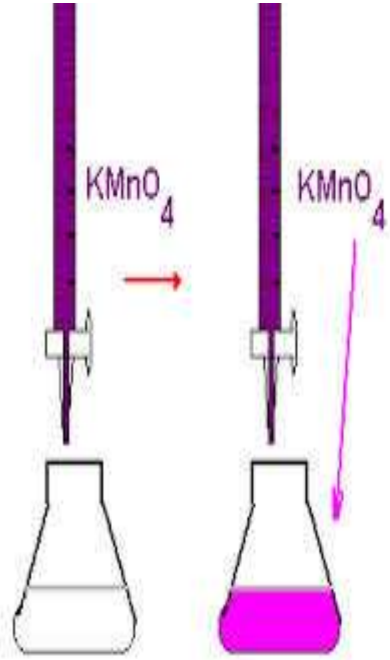
Potassium Permanganate

$KMnO_4$

OS of K + OS of Mn + 4(OS of O) = 0



Potassium permanganate titration

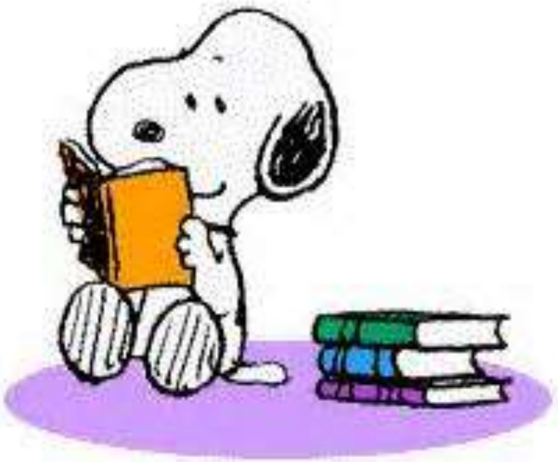


Permanganate titration

- **Permanganometry** is one of the techniques used in quantitative analysis in Chemistry.
- It is a redox titration and involves the use of permanganates and is used to measure the amount of analyte present in unknown chemical samples.
- It involves two steps, namely the titration of the analyte with potassium permanganate solution and then the standardization of potassium permanganate solution with standard sodium oxalate solution.

- Depending on how the titration is performed, the permanganate ion can be reduced to Mn^x, where x is +2, +3, +4 and +6.

- Using permanganometry we can estimate the quantitative presence of Fe^{+2}, Mn^{+2}, Fe^{+2} and Mn^{+2} when they are both present in a mixture, $C_2O_4^{2-}$, NO_2^-, H_2O_2 etc.



•In the most cases **permanganometry** is performed in a very **acidic solution** in which the following reaction occurs:

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

The standard potential of this electrochemical reaction is:

$$E^o=+1.52\ V$$

which shows that $KMnO_4$ (in an acidic medium) is a very strong oxidizing agent. With this method we can oxidize:

Fe^{+2} ($E^o_{Fe^{+3}/Fe^{+2}}=+0.77\ V$)

Sn^{+2} ($E^o_{Sn^{+4}/Sn^{+2}}=+0.2\ V$)

and even

Cl^- ($E^o_{Cl2/Cl^-}=+1.36\ V$) etc.

- In **weak acidic medium** MnO_4^- can not accept 5 electrons to form Mn^{+2}, this time it accepts only 3 electrons and forms MnO_2(s) by the following electrochemical reaction:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

$$E^o = +1.69 \text{ V.}$$

For the reaction: $MnO_4^- + 8\ H^+ + 5\ e^- = Mn^{2+} + 4\ H_2O$

$$E^o = +1.51 \text{ V}$$

And if the solution has a concentration $C_{(NaOH)} > 1$ mol dm^{-3} the following reaction occurs:

$$MnO_4^- + e^- \rightarrow MnO_4^{2-}\ E^o = +0.56 \text{ V.}$$

Standardization of potassium permanganate solution

Background

- The standardization of the $KMnO_4$ solution is carried out by titration against a standard solution of oxalic acid.
- Oxalic acid is a good primary standard because the compound is available in solid form, as H2 C 2 0 4 .2H 20, which can be prepared to a very high degree of purity and is not hygroscopic nor efflorescent.

The reaction is

The permanganate ion is strong oxidizing reagent.

The half-reaction is:

$MnO^{4-} + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$ $E^0 = 1.51$ V

- **Potassium permanganate** is not primary standard substance because it contains reduced products like **manganese oxide** MnO_2 where the concentration of **KMnO** $_{\mathbf{4}}$ changed after preparation because it dissociated via **reducing agents** such as **ammonia and organic substances in water** ;therefore, potassium permanganate must be standardized before use it and keep it at least 7-10 days after preparation at **dark place and dark bottle**

- **Sodium oxalate** is commonly used as a primary standard for determining the concentration of many strong oxidizers used in oxidation/reduction analyses.
- **Sodium oxalate**, $Na_2C_2O_4$, is a strong electrolyte that dissociates completely in water according to the following equation:

$$\mathbf{Na_2C_2O_4 \rightarrow 2\,Na^{+}\,(aq) + C_2O_4^{2-}\,(aq)}$$

Apparatus

- burette
- 250-mL Erlenmeyer flasks
- 10-mL pipette
- 250-mL volumetric flask

Chemicals

- Potassium Permanganate
- Sodium Oxalate (AR grade) (0.1 N)
- Sulfuric acid (6 N)

Procedure

1. Transfer 10.0 ml of sodium oxalate (0.1 N) to 250 ml conical flask.
2. Add 5.0mL of 6.0 N sulfuric acid.
3. shake the solution well and warm it (75-80 ^{o}C)
4. Titrate the hot solution against potassium Permanganate solution.
5. Continue with titration drop by drop till the color is changed from colorless to pink (permanganate dye)
6. Repeat the titration for three times and record the mean.

Calculations

No.	Start point	End point	Volume of $KmnO_4$	The average volume
1			V_1	$\frac{V_1+V_2+V_3}{3}$
2			V_2	
3			V_3	

From reaction equation:

2 moles of $KMnO_4$ ≡ 5 moles of oxalic acid

1000mL of 2M $KMnO_4$≡ 1000mL of 5M Oxalic acid

V_{mL} of ? M $KMnO_4$ 10mL of 0.1M Oxalic acid

$$\text{Molarity of } KMnO_4 = \frac{10 \times 0.1}{V_{mL} \text{ of } KMnO_4}$$

$$\text{Normality of } KMnO_4 = 5 \times \text{Molarity}$$

$$\text{Conc(g/L)of permenganate} = N \times \text{eq.wt.}$$