Oxidation-reduction (REDOX) Titration

Definitions

- Oxidation: It can be defined as loss of electrons or increase in oxygen content.
- Reduction: It can be defined as gain of electrons or increase of hydrogen content.
- Oxidizing agent: substance which get reduced.
- Reducing agent: substance which get oxidized.
- Both processes are combined and occur together so we combine them in one word as REDOX reaction.

Oxidation-Reduction (Redox)

Reaction of ferrous ion with ceric ion

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

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

$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$ (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.**

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 hydrides = —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.

Oxidation Numbers of Some Substances

Substance	Oxidation Numbers
$NaCl$	$Na = +1, \quad Cl = -1$
H_2	$H = 0$
NH_3	$N = -3, \quad H = +1$
H_2O_2	$H = +1, \quad O = -1$
LiH	$Li = +1, \quad H = -1$
K_2CrO_4	$K = +1, \quad Cr = +6, \quad O = -2$
SO_4^{2-}	$O = -2, \quad S = +6$
$KClO_3$	$K = +1, \quad Cl = +5, \quad O = -2$

Oxidation states of manganese and nitrogen in different species

For manganese

Species	Mn	Mn^{2+}	Mn^{3+}	MnO_2	MnO_4^{2-}	MnO_4^{-}
O.N.	0	+2	+3	+4	+6	+7

For nitrogen

Species	NH_3	N_2H_4	NH_2OH	N_2	N_2O	NO	HNO_2	HNO_3
O.N.	–3	–2	–1	0	+1	+2	+3	+5

Balancing Redox Reactions using Half-Reaction Method

- Divide the equation into an oxidation half-reaction and a reduction half-reaction
- Balance these
  - Balance the elements other than H and O
  - Balance the O by adding H_2O
  - Balance the H by adding H^+
  - Balance the charge by adding e^-
- Multiply each half-reaction by an integer such that the number of e^- lost in one equals the number gained in the other
- Combine the half-reactions and cancel

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

- Balance each half reaction:

$$MnO_4^- + 5é \longrightarrow Mn^{2+}$$

$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2é$$

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

$$2\,MnO_4^- + 5\,C_2O_4^{2-} \longrightarrow 2\,Mn^{2+} + 10\,CO_2$$

- **Balance oxygen atoms by adding water**

$$2\,MnO_4^- + 5\,C_2O_4^{2-} \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

- **Balance hydrogen atoms by adding H^+**

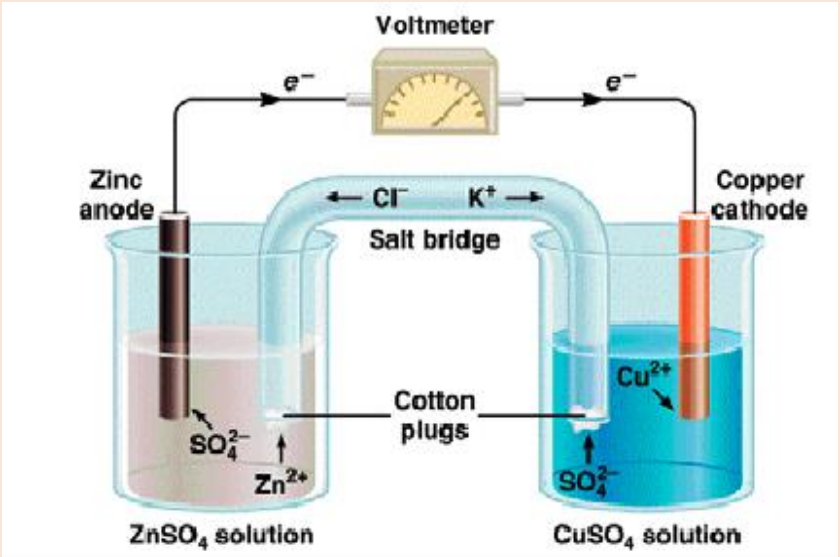
$$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

Electrochemical Cells

Electrochemical cells consist of electrodes immersed in electrolyte solution and frequently connected by a salt bridge

Solution Pressure. The tendency of the metal to dissolve in a solution of its salt.

Ionic Pressure. The tendency of the metal cations to deposit on its metal dipped into its solution.



Representation of electrochemical cells:

anode//cathode

$Cu/CuSO_4$ // $ZnSO_4$ /Zn

- **Cu/Cu^{2+} system: ionic pressure > solution pressure.**
  Cu^{2+} leaves the solution to deposit on Cu rod
- **Zn/Zn^{2+} system: solution pressure > ionic pressure.**
  Zn metal tends to dissolve forming Zn^{2+} in solution.

The potential difference between the metal rod (electrode) and the solution is known as electrode potential (E)

Nernest Equation for Electrode Potential (E)

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

E_t = 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

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

Standard Electrode Potential (E^o)

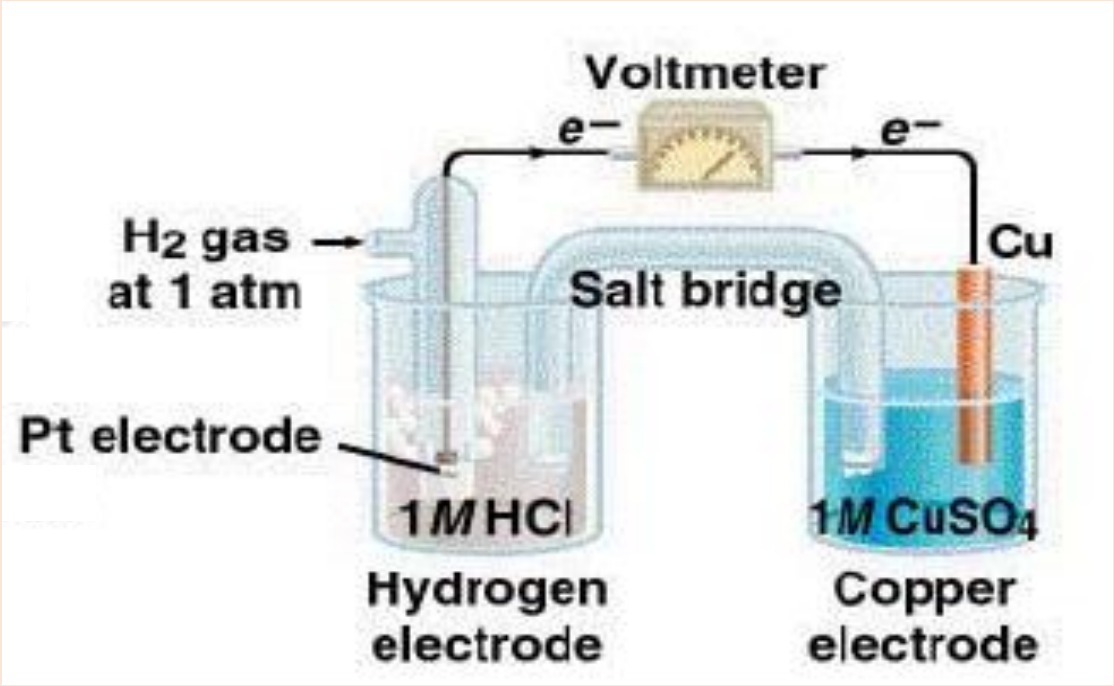
$$E_{25\,^\circ C} = E^o + \frac{0.0591}{n} \log [M^{n+}]$$

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).

System	E° (volts)	System	E° (volts)
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^+	+0.80

Measurement of the Electrode Potential

- By connecting to another electrode (galvanic cell), an electric current will then flow from the electrode having —ve potential to that having +ve potential (from Zn electrode to Cu electrode)
- The emf of the current can then be measured.
- The normal hydrogen electrode is used as a reference electrode.



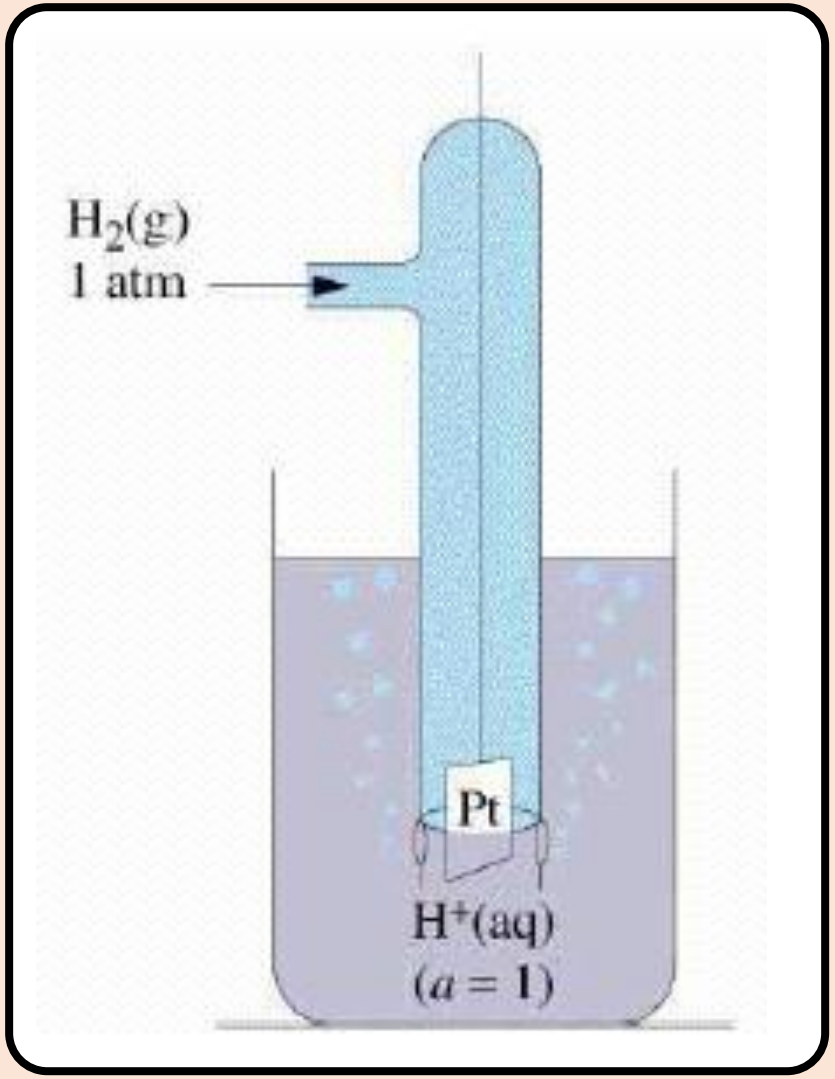
Normal Hydrogen Electrode (NHE)

- Consists of a piece of platinum foil coated with platinum black and immersed in a solution of 1 N HCl (with respect to H^+).
- H_2 gas (at 1 atm. Pressure) is passed. Platinum black layer absorbs a large amount of H_2 and can be considered as a bar of hydrogen, it also catalyses the half reaction:

$$2H^+ + 2e \rightarrow H_2$$

- **Under these conditions:**

H_2 electrode potential = zero



Factors Affecting Oxidation Potential

1. Common Ion

$$E_{25\,^{\circ}C} = E^{0} + \frac{0.0591}{n} \log [Oxid]/[Red]$$

- The potential of MnO_4^-/Mn^{2+} varies with the ratio $[MnO_4^-]/[Mn^{2+}]$.
- If ferrous is titrated with MnO_4^- in presence of Cl^- , chloride will interfere by reaction with MnO_4^- and gives higher results.

Zimmermann's Reagent ($MnSO_4$, H_3PO_4 and H_2SO_4)

- $MnSO_4$ has a common ion (Mn^{2+}) with the reductant that lowers the potential of MnO_4^-/Mn^{2+} system:
- Phosphoric acid lowers the potential of Fe^{3+}/Fe^{2+} system by complexation with Fe^{3+} as $[Fe(PO_4)_2]^{3-}$.
- Sulphuric acid is used for acidification.

2. Effect of pH

$$E_{MnO_4^-/Mn^{2+}} = E^0 + \frac{0.0591}{5} \log \frac{[MnO_4^-][H^+]}{[Mn^{2+}]}$$

The oxidation potential of an oxidizing agent containing oxygen increases by increasing acidity and vice versa.

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

$$E_{MnO_4^-/Mn^{2+}} = E^0 + \frac{0.0591}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

Potassium dichromate: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$$E_{Cr_2O_7^{2-}/Cr^{3+}} = E^0 + \frac{0.0591}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]}$$

3. Effect of Complexing Agents

Iodine: $I_2 + 2e^- \rightarrow 2I^-$

$$E_{I_2/I^-} = E^o + \frac{0.0591}{2} \log \frac{[I_2]}{[I^-]^2}$$

- E ($I_2/2I^-$) system increases by the addition of $HgCl_2$ since it complexes with iodide ions.

$$Hg^{2+} + 4I^- \rightarrow [HgI_4]^{2-}$$ (low dissociation complex)

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

$$E_{Fe^{3+}/Fe^{2+}} = E^o + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

- E (Fe^{3+}/Fe^{2+}) is reduced by the addition of F^- or PO_4^{3-} due to the formation of the stable complexes $[FeF_6]^{3-}$ and $[Fe(PO_4)_2]^{3-}$ respectively. Thus, ferric ions, in presence of F^- or PO_4^{3-} cannot oxidize iodide although $E^o(Fe^{3+}/Fe^{2+}) = 0.77$ while $E^o(I_2/2I^-) = 0.54$.

4. Effect of Precipitating Agents

Ferricyanide: $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$

$$E_{Ferri/Ferro} = E^o + \frac{0.0591}{1} \log \frac{[[Fe(CN)_6]^{3-}]}{[[Fe(CN)_6]^{4-}]}$$

Addition of Zn^{2+} salts which precipitates ferrocyanide:

$$[Fe(CN)_6]^{4-} + Zn^{2+} \rightarrow Zn_2\,[Fe(CN)_6]\downarrow$$

The oxidation potential of ferri/ferrocyanide system to oxidize iodide to iodine, although the oxidation potential of $I_2/2I^-$ system is higher.

4. Effect of Precipitating Agents

Copper: $2\ Cu^{2+} + 4\ I^- \rightarrow 2Cu_2I_2\ (ppt) + I_2$

$$E_{Cu^{2+}/Cu^{+}} = E^{o} + \frac{0.0591}{1} \log \frac{[Cu^{2+}]}{[Cu^{+}]}$$

In this reaction Cu^{2+} oxidized I^- although:

$$E^{o}_{Cu^{2+}/Cu^{+}} = 0.16 \text{ and } E^{o}I_2/2\ I^- = 0.54.$$

Due to slight solubility of Cu_2I_2, the concentration of Cu^+ is strongly decreased and the ratio Cu^{2+}/Cu^+ is increased with a consequent increase of the potential of Cu^{2+}/Cu^+ redox couple to about + 0.86 V, thus becoming able to oxidize iodide into iodine.

Properties of Oxidizing Agents

- Potassium permanganate ($KMnO_4$)
- Potassium dichromate ($K_2Cr_2O_7$)
- Iodine (I_2) Potassium iodate (KIO_3)
- Bromate-bromide mixture

1. Potassium permanganate ($KMnO_4$)

Very strong oxidizing agent, not a primary standard, self indicator.

In acid medium: $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

It can oxidize: oxalate, Fe^{2+}, Ferrocyanide, As^{3+}, H_2O_2, and NO_2^-.

In alkaline medium: $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$

In neutral medium: $4MnO_4^- + 2H_2O \rightleftharpoons MnO_2 + 4OH^- + 3O_2$

Unstable

2. Potassium dichromate ($K_2Cr_2O_7$)

It is a primary standard (highly pure and stable).

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

Used for determination of Fe^{2+} (Cl^- does not interfere); ferroin indicator.

3. Iodine (I_2)

Solubility of iodine in water is very small.

Its aqueous solution has appreciable vapour pressure: Prepared in I^-

$$I_2 + I^- \rightleftharpoons I_3^- \text{ (triiodide ion)}$$

Iodine solution is standardized against a standard $Na_2S_2O_3$

Iodimetry: Direct titration of reducing substances with iodine

- The reducing substances (Eº < + 0.54 V) are directly titrated with iodine.

$$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$$

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

(Self indicator or starch as indicator)

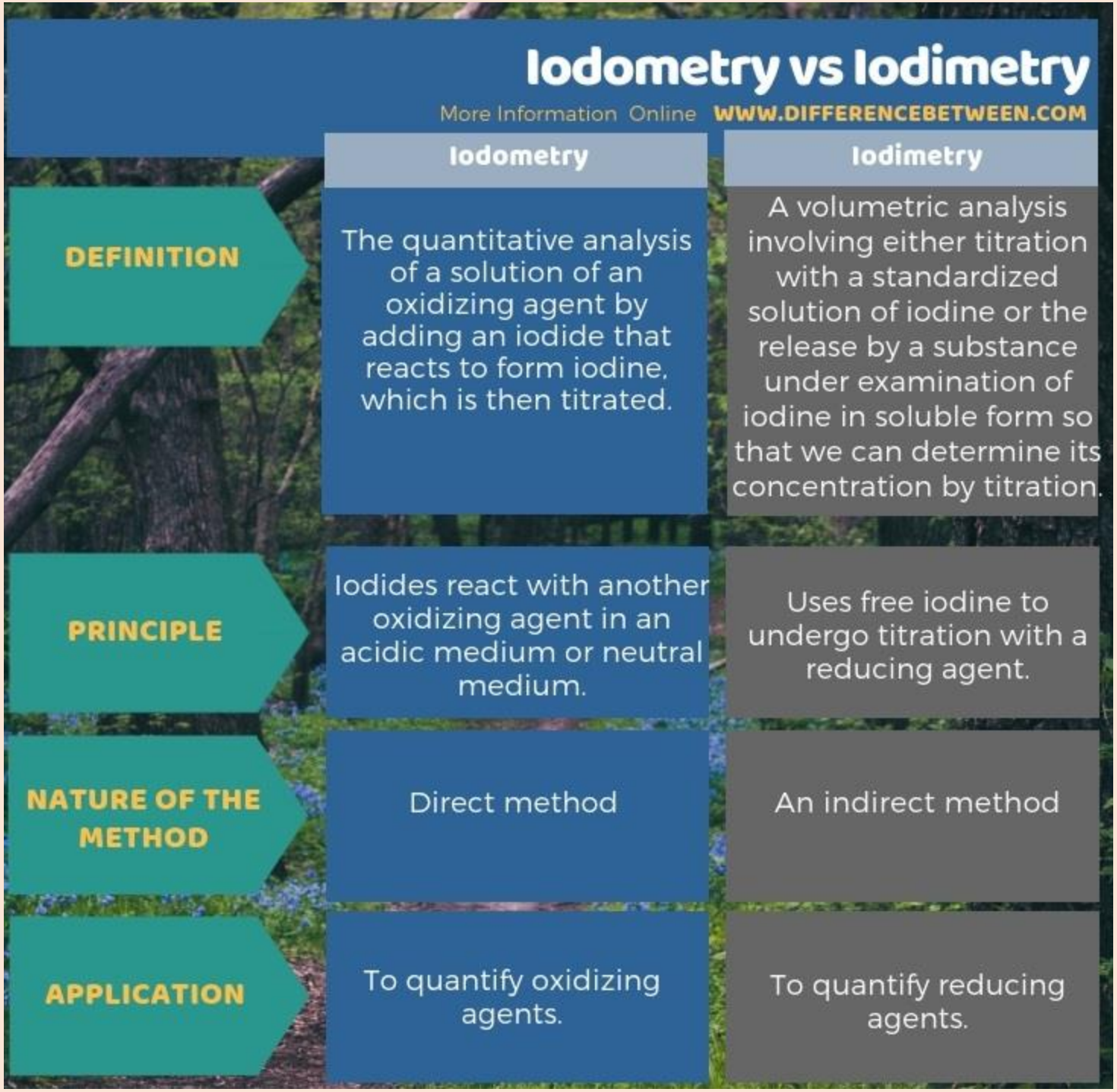
Iodometry: Back titration of oxidizing substances

- The oxidizing substance (Eº > + 0.54 V)is treated with excess iodide salt:

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O$$

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

- **The liberated Iodine is titrated with standard sodium thiosulphate (starch as indicator)**


Iodometry vs Iodimetry
More Information Online WWW.DIFFERENCEBETWEEN.COM
Iodometry
Iodimetry
DEFINITION
The quantitative analysis of a solution of an oxidizing agent by adding an iodide that reacts to form iodine, which is then titrated.
A volumetric analysis involving either titration with a standardized solution of iodine or the release by a substance under examination of iodine in soluble form so that we can determine its concentration by titration.
PRINCIPLE
Iodides react with another oxidizing agent in an acidic medium or neutral medium.
Uses free iodine to undergo titration with a reducing agent.
NATURE OF THE METHOD
Direct method
An indirect method
APPLICATION
To quantify oxidizing agents.
To quantify reducing agents.

4. Potassium iodate (KIO_3)

It is strong oxidizing agent, highly pure, its solution is prepared by direct weighing.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad \text{(in 0.1 N HCl)} \quad \text{Eq.W} = MW/5$$

$$IO_3^- + 2I_2 + 6H^+ \rightarrow 5I^+ + 3H_2O \quad \text{(in 4-6 N HCl)} \quad \text{Eq.W} = MW/4$$

$$IO_3^- + 2I^- + 6H^+ \rightarrow 3I^+ + 3H_2O \qquad \text{Eq.W} = MW/4$$

Andrew's Reaction

Determination of iodide with potassium iodate in 4-6 N HCl

(chloroform as indicator)

Starch can not be used.

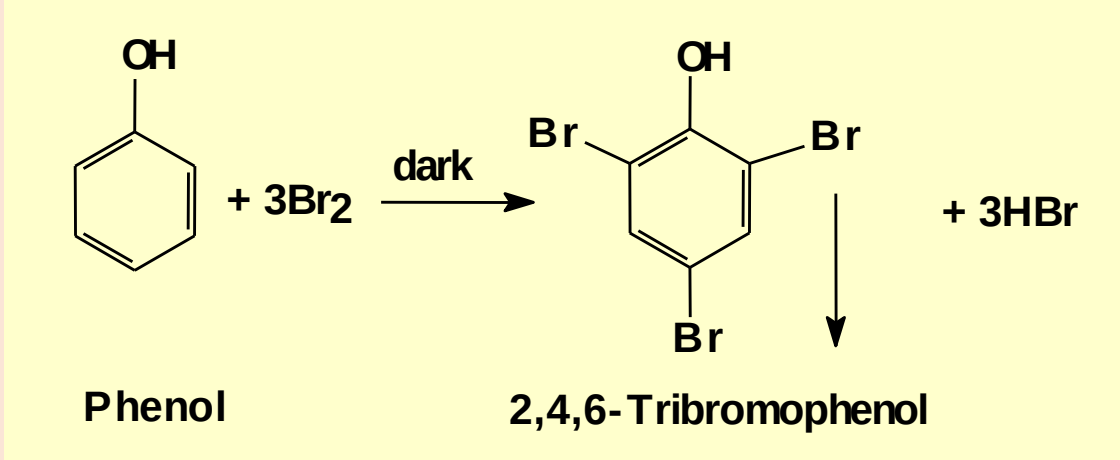
Potassium iodate prepared in molar

5. Bromate-bromide mixture

Upon acidification of bromate/bromide mixture, bromine is produced:

$$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$$

Used for the determination of phenol and primary aromatic amines:



The excess Br_2 is determined:

$$Br_2 + 2I^- \rightarrow I_2 + 2\ Br^- \quad \& \quad I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ I^-$$

Chloroform is added (dissolve TBP & indicator). Starch can be used

Detection of End Point in Redox Titrations

1. Self Indicator (No Indicator)

When the titrant solution is coloured ($KMnO_4$):

$$\mathbf{KMnO_4\ (violet) + Fe^{2+} + H^{+} \rightarrow Mn^{2+}\ (colourless) + Fe^{3+}.}$$

The disappearance of the violet colour of $KMnO_4$ is due to its reduction to the colourless Mn^{2+}.

When all the reducing sample (Fe^{2+}) has been oxidized (equivalence point), the first drop excess of MnO_4^- colours the solution a distinct pink.

2. External Indicator

In Titration of Fe^{2+} by $Cr_2O_7^{2-}$

$$Cr_2O_7^{2-} + 3Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Fe^{3+} + 7H_2O$$

The reaction proceeds until all Fe^{2+} is converted into Fe^{3+}

Fe^{2+} + Ferricyanide (indicator) → Ferrous ferricyanide (blue)].

$Fe^{2+} + [Fe(CN)_6]^{3-} \rightarrow Fe_3[Fe(CN)_6]^{2-}$.

- The end point is reached when the drop fails to give a blue colouration with the indicator (on plate)
- Less accurate method and may lead to loss or contamination of sample.

3. Internal Redox Indicator

Redox indicators are compounds which have different colours in the oxidized and reduced forms.

$$In_{ox} + n\ e^- = In_{red}$$

They change colour when the oxidation potential of the titrated solution reaches a definite value:

$$E = E° + 0.0591/n \log [In_{OX}]/[In_{red}]$$

When $[In_{ox}] = [In_{red}]$, $E = E°$

Indicator colours may be detected when: $[In_{ox}]/[In_{red}] = 1/10$ or $10/1$

hence, Indicator range: $E = E°_{In} \pm 0.0591/n$

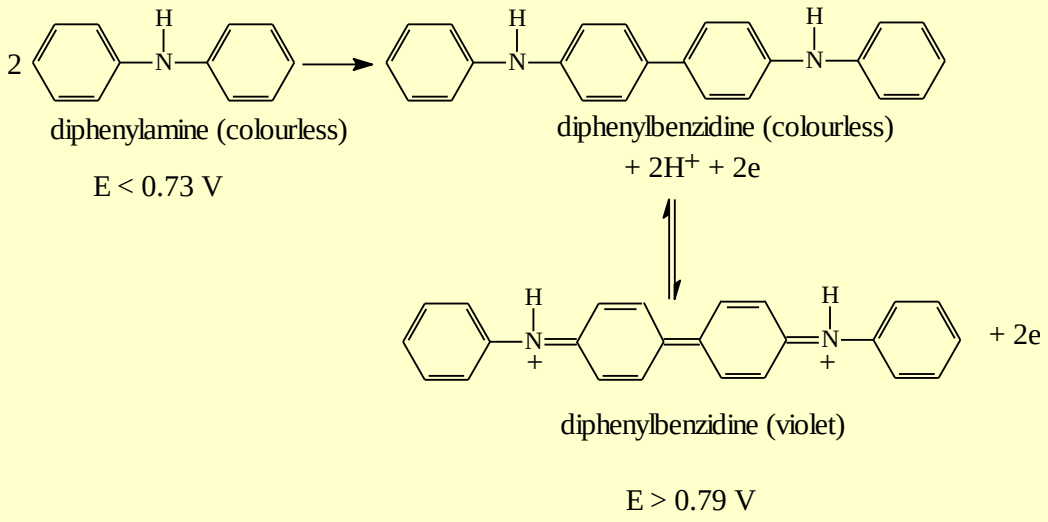
Diphenylamine

E° = 0.76, n = 2.

Range = 0.73 – 0.79 V.

E < 0.73 V, colourless (red.).

E > 0.79 V, bluish violet (ox.).



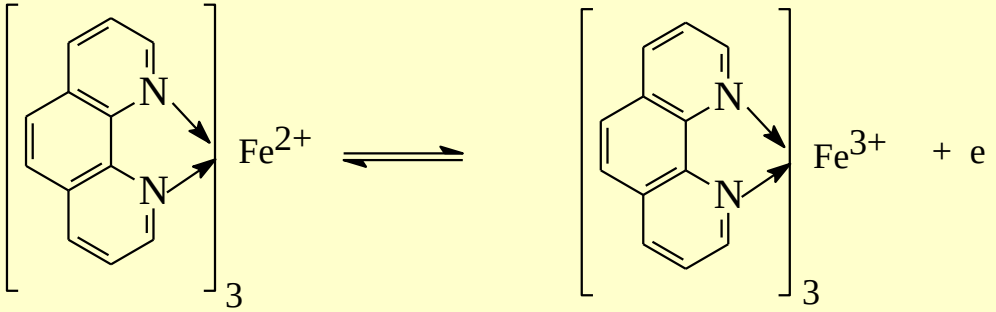
Ferroin indicator (1,10-phenanthroline-ferrous chelate).

E° = 1.147, n = 1.

Range = 1.088 – 1.206 V.

E < 1.088 V, red (red.).

E > 1.206 V, pale blue (ox.).



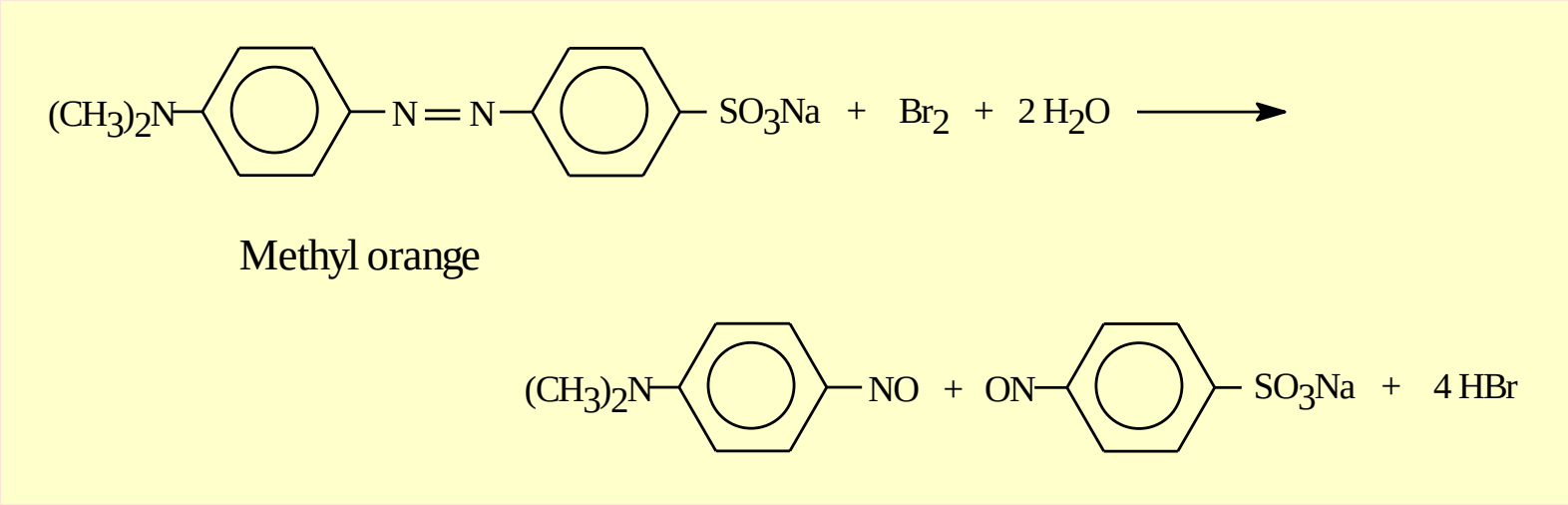
Redox indicators

Indicator	Color		E°
	Oxidized	Reduced	
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29

4. Irreversible Redox Indicators

Some highly coloured organic compounds that undergo irreversible oxidation or reduction

Methyl Orange



- In acid solutions, methyl orange is red.
- Addition of strong oxidants (Br_2) would destroy the indicator and thus it changes irreversibly to pale yellow colour