Oxidation-Reduction Titration

Lecture five 2022-2023

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.
- Redox system refers to the system composed of the reduce and oxidized form of the species. It can be represented by (oxidized form/reduced form). For example (Fe^{3+}/Fe^{2+}), and (Cu^{2+}/Cu).

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**)

Reducing agent

$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$ (Gain of electrons: **Reduction**)

Oxidizing gent

- 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 atoms in free elements (Ag, Zn, Ca,…etc) = zero.
- The O.N of neurtal molecules (Cl_2, I_2)= zero.
- The O.N of ions of only one atom = the charge on the ion e.q (Fe^{2+}, Cr^{3+},…etc).
- The O.N of O is (-2), except in peroxides, like H_2O_2 (-1).
- The O.N of H is (+1), except when bonded to metals as a metal hydride, like LiH and NaH (-1).
- In a ployatomic ion like (SO_4^{2-}, $Cr_2O_7^{2-}$,…etc), the sum of the O.N of all atoms in the ion must equal the net charge of the ion.
- Halogens (Cl^-, Br^-, and I^-) have (-ve) O.N when present as a halide ion in their compounds, but when they combine with O_2 they have (+ve) O.N, like (ClO_3^-, ClO_4^-, and F^-).

Oxidation Numbers of Some Substances

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

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

The electrochemical Cell

- The electrochemical cell consists of two half-cells connected by a salt bridge

- <u>In any electrochemical cell:</u>

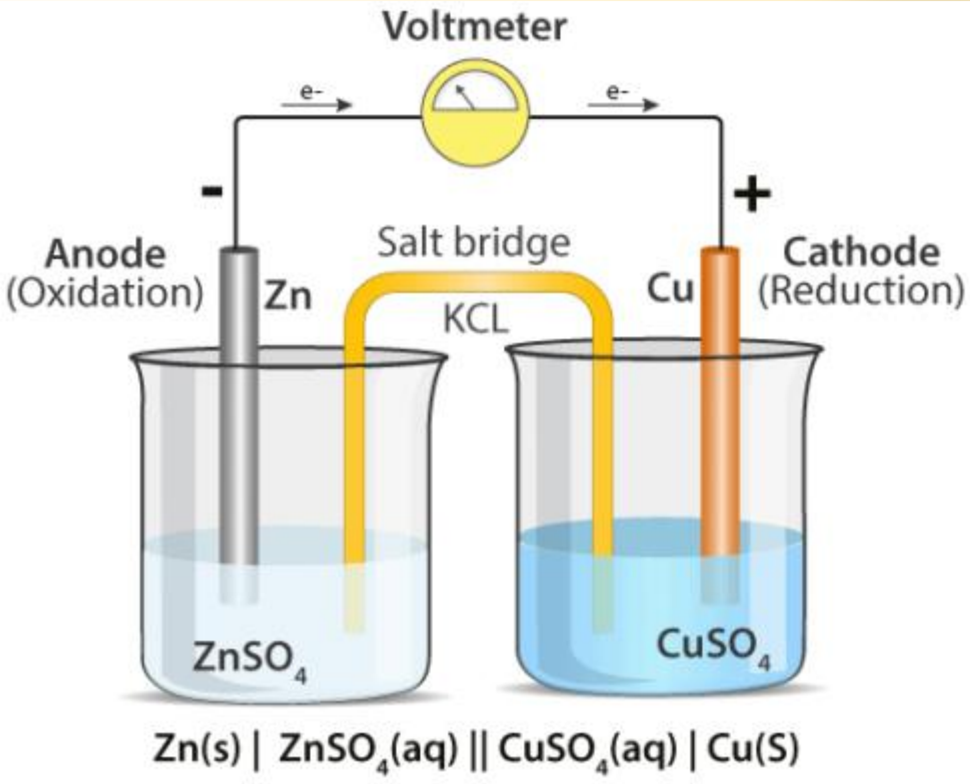
1. The Anode is the electrode where oxidation occurs.

$$Zn - 2e^{-} \longrightarrow Zn^{2+}$$

2. The Cathode is the electrode where reduction occurs.

$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

3. Salt bridge, which is made from KCl, is usually linked between the two half cells.



<u>NOTE:</u>

- Oxidation occurs at Anode (OX-AN)
- Reduction occurs at Cathode (RED-CAT)

Standard Hydrogen Electrode (SHE)

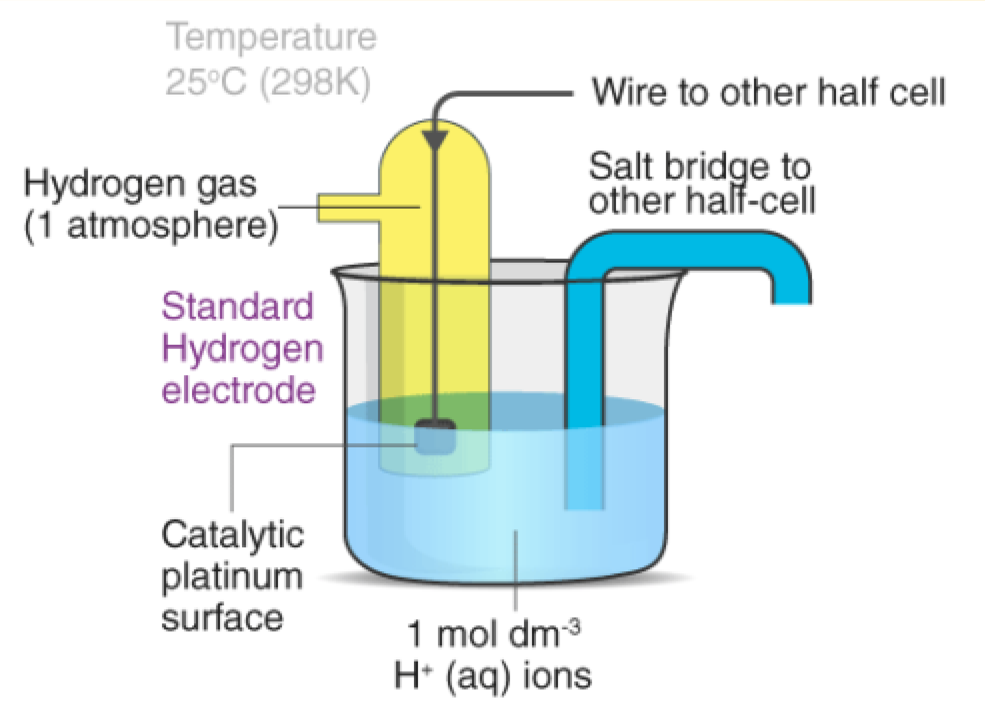
A. Consists of a piece of platinum foil coated with platinum black and immersed in a solution of 1 N HCl (with respect to H^+).

B. 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



Standard electrode potential

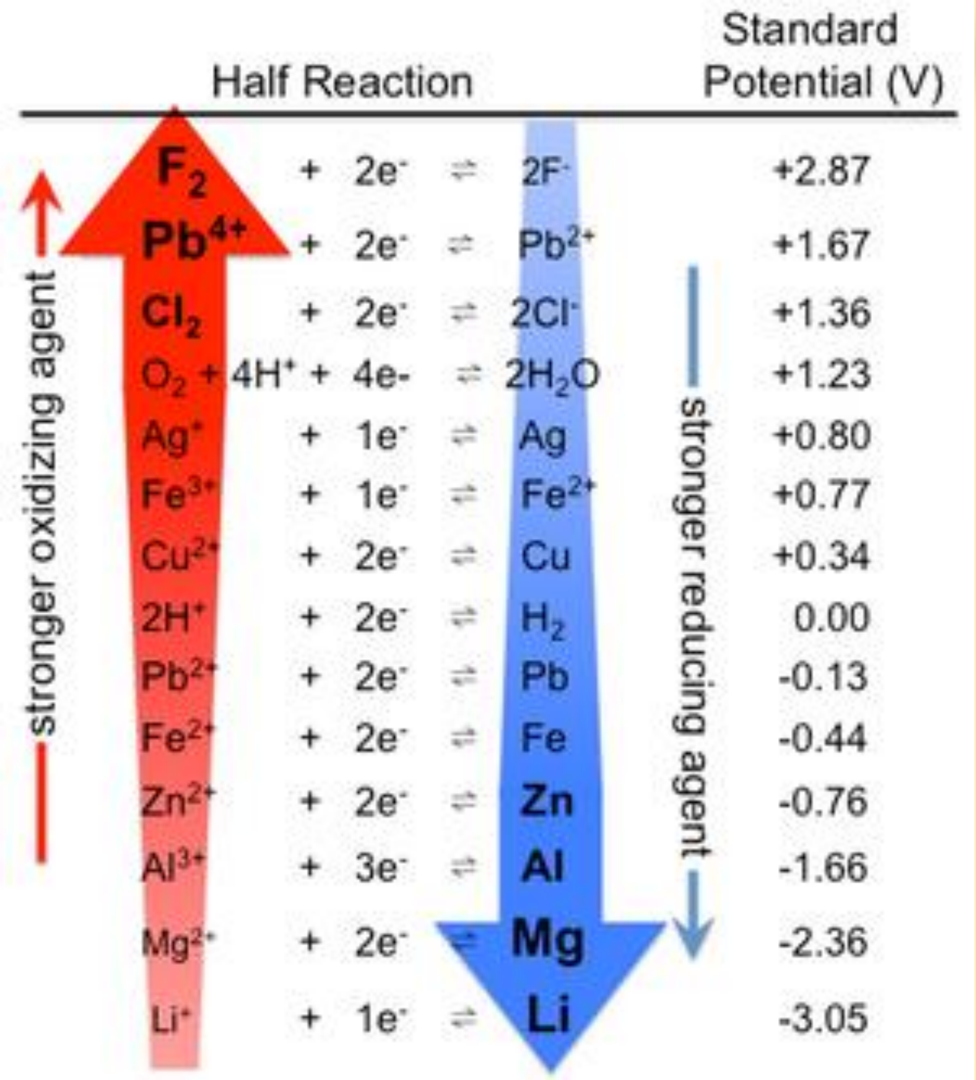
1. It is measured at standard conditions (1 M solution at a temperature of 25 °C or 298 K).

2. It is denoted by the letter E°.

3. E° is a physical constant for each redox system NOT affected by pH, complexing agents, precipitating agents, common ion effect,…etc.

4. It represents the potential of a half cell relative to a standard reference.

5. (E°= +ve) means the system has higher redox potential than (H^+/H^2) system and vice versa.



Nernest Equation for Electrode Potential (E)

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

E_t = electrode potential at temperature t.

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

R = gas constant

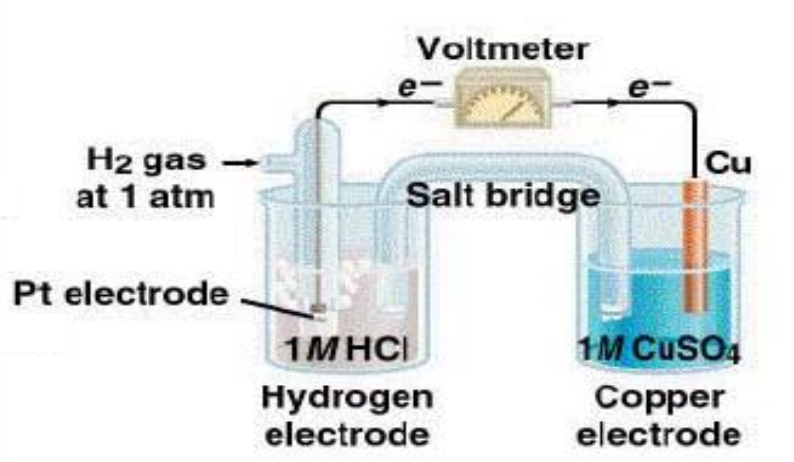
T = absolute Temp. (°C + 273)

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



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

Properties of Oxidizing Agents

1. Potassium permanganate ($KMnO_4$)
2. Potassium dichromate ($K_2Cr_2O_7$)
3. Iodine (I_2) Potassium iodate (KIO_3)
4. Bromate-bromide mixture

1. Potassium permanganate ($KMnO_4$)

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

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

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

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 $Na_2S_2O_3$

- Titrations involving iodine (I_2)

1. Iodimetry
2. Iodometry

- Titrations that create or consume I_2 are widely used in quantitative analysis.

Iodimetry: Direct titration of reducing substances with iodine

- The reducing substances ($E^\circ < +0.54$ 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

1. The oxidizing substance ($E^\circ > +0.54$ V)is treated with excess iodide salt:

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O$$
$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

2. The liberated Iodine is titrated with standard sodium thiosulphate (starch as indicator)

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

Iodimetry

a) A reducing analyte

b) One step

c) Standard solution: Iodine (I_2)

Iodometry

a) An oxidizing analyte

b) Two steps

c) Standard solution: Sodium thisoufate

Potassium iodate (KIO_3)

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

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$ (in 0.1 N HCl) Eq.wt = m.wt/5

$IO_3^- + 2I_2 + 6H^+ \rightarrow 5I^+ + 3H_2O$ (in 4-6 N HCl) Eq.wt = m.wt/4

$IO_3^- + 2I^- + 6H^+ \rightarrow 3I^+ + 3H_2O$ Eq.wt = m.wt/4

Andrew's Reaction

- KIO_3, when used as an oxidising agent was itself reduced to elemental iodine.
- However, if the reagent is used in the presence of an excess of concentrated HCl, the reduction product is not I2 but iodine monochloride (ICl), where iodine is formally in the +1 oxidation state.

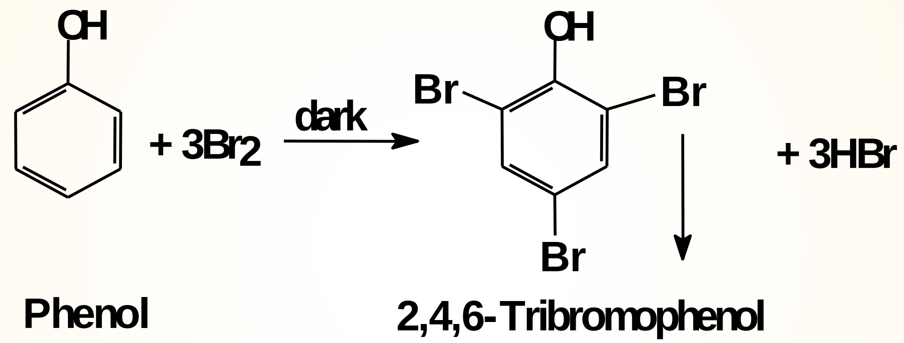
$$IO_3^- + 6HCl + 4e^- \rightarrow \underset{\text{pale yellow}}{ICl} + 5Cl^- + 3H_2O$$

4. 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:

$$Br_2 + 2I^- \rightarrow I_2 + 2\ Br^-$$

$$I_2 + 2\ Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2\ I^-$$

- ❑ 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 ($KMnO_4$):

$$KMnO_{4\ (violet)} + Fe^{2+} + H^{+} \rightarrow Mn^{2+}_{\ (colourless)} + Fe^{3+}.$$

- 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.

Detection of End Point in Redox Titrations

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+}

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

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

Detection of End Point in Redox Titrations

3. Internal Redox Indicator

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

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

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

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

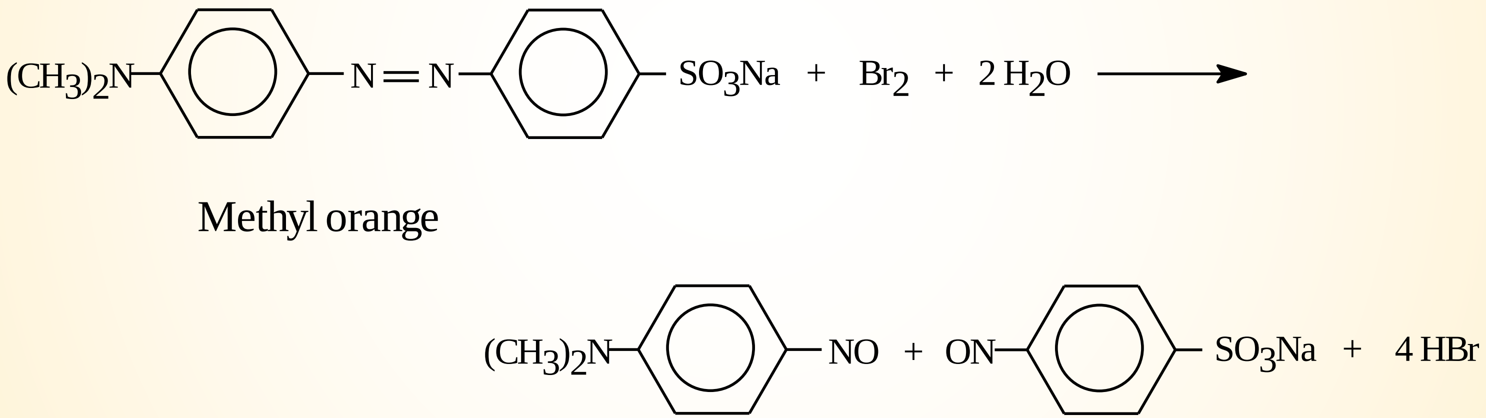
When $[In_{ox}] = [In_{red}]$, and $E = E°$

Detection of End Point in Redox Titrations

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

Redox indicators

Indicator	Color: Oxidized	Color: Reduced	E°
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