Oxidation - Redution

For B. Sc. II Year

I paper (Inorganic Chemistry)

By-

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Oxidation is defined as

- Addition of oxygen
- Addition of electronegative element
- Loss of proton
- Loss of electronegative element
- Loss of electron
- Increase in oxidation state

Reduction is defined as

- Gain of Hydrogen
- Gain of electropositive element
- Loss of Oxygen
- Loss of electronegatve element
- Gain of electron
- Dicrease in oxidation state

Oxidation Number

The oxidation number of an element is defined as the charge which an atom of element appears to have when the electron on the atom are counted according to following arbitrary rules:

- Electrons shared between two like atoms are divided equally between the sharing atoms.
- Electrons shared between two unlike atom are counted with more electronegative element.

Based on the above conventions the following operational rules have been derived which permit easy calculation of oxidatio numbers:

- The oxidation number of each element in the uncombined state is zero
- The oxidation number of an ion is the same as its charge.
- The sum of the oxidation number of all the atoms in the fomula for a neutral compound is zero.
- In all hydrogen compounds (except hydrides of active metals) the oxidation number of hydrogen per atom is +1.
- In all oxygen compounds (except hydrgen peroxides and other peroxides and superoxides) the oxidation number of oxygen per atom is -2.

Single Electrode Potential

- The tendency of an electrode to lose or gain electrons when it is in contact with its own ion in solution, is called electrode potential.
- Tendency to gain electrons means also the tendency to get reduced, this tendecy is called reduction potential.
- Tendency to lose electron means the tendency to get oxidised. Hence it is called oxidation potential.

Note : It is not possible to determine experimentally the potential of a single electrode. It is only the difference of potentials betwen the two electrodes taht we can measure by combining them to give a complete cell.

Sign of Electrode Potential

- According to latest convention adopted by IUPAC the electrode potential is given positive sign if electrode reaction involves reduction when connected to standard hydrogen electrode and a negative sign if the electrode reaction involve oxidation when connected to the standard hydrogrn electrode when potential is taken arbitrarily as zero

Standard Electrdoe Potentials. The Electrochemical Series

The potential of an electrode at a given temperature depends upon concentration of the ions in the solution. If the concentration of the ions is unityand the temperature is 250c, the potential of the electrode is termed as the Sttandard electrode potential E0el

- The standrad electrode potetial of a number of electrodes are given in table. These values are said to be on hydrogen scale since in these determination of of the potential of the standard hydrogen electrode used as rhe reference electrode, has been taken as zero. The values are arranged in the dicreasing order as shown is called the Electrochemical series.

Sr. No.	Electrode	Reduction Half reaction Oxidising agent → Reducing agent	E^0 (volts)At 25
1	$F^- \| F_2 \| Pt.$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87
2	$Au^+ \| Au$	$Au^+ + e^- \rightarrow Au$	+1.68
3	$Ce^{4+}, Ce^{3+} \| Pt.$	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
4	$Au^{3+} \| Au$	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
5	$Cl^- \| Cl_2 \| Pt$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
6	$Pt^{2+} \| Pt$	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.20
7	$Br^- \| Br_2 \| Pt$	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
8	$Hg^{2+} \| Hg$	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.854
9	$Ag^+ \| Ag$	$Ag^+ + e^- \rightarrow Ag$	+0.799
10	$Hg_2^{2+} \| Hg$	$Hg_2^{2+} + 2e^- \rightarrow Hg_2$	+0.790
11	$Fe^{3+}, Fe^{2+} \| Pt.$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
12	$I^- \| I_{2(s)} \| Pt$	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
13	$Cu^{2+} \| Cu$	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
14	$Pt \| Hg \| Hg_2Cl_2 \| Cl^-$	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.242
15	$Ag \| AgCl_{(s)} \| Cl^-$	$AgCl + e^- \rightarrow Ag + Cl^-$	+0.222
16	$Cu^{2+} \| Cu^+$	$Cu^{2+} + e^- \rightarrow Cu^+$	+0.153
17	$Sn^{4+}, Sn^{2+} \| Pt$	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
18	$H^+ \| H_2 \| Pt$	$2H^+ + 2e^- \rightarrow H_{2(g)}$	0.0 (Definition)
19	$Pb^{2+} \| Pb$	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
20	$Sn^{2+} \| Sn$	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
21	$Ni^{2+} \| Ni$	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.257
22	$Co^{2+} \| Co$	$Co^{2+} + 2e^- \rightarrow Co$	-0.280
23	$Cd^{2+} \| Cd$	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
24	$Fe^{2+} \| Fe$	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440

Application Of Electrochemical Series

- **(i) Reactivity of metals**: The activity of the metal depends on its tendency to lose electron or electrons, i.e., tendency to form cation . This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active. The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series.
- (a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.
- (b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.
- (c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

- (ii) **Electropositive character of metals** :The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups
- (a) Strongly electropositive metals : Metals having standard reduction potential near about – 2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.
- (b) Moderately electropositive metals : Metals having values of reduction potentials between 0.0 and about – 2.0 volt are moderately electropositive Al, Zn, Fe, Ni, Co, etc., belong to this group.

- [The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.]
- **(c) Displacement of hydrogen from dilute acids by metals :** The metal which can provide electrons to ions present in dilute acids for reduction, evolve hydrogen from dilute acids.
- The metal having negative values of reduction potential possess the property of losing electron or electrons.
- Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.
- The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

- **(d) Displacement of hydrogen from water :** Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series. Alkali and alkaline earth metals liberate hydrogen

(iii) Displacement reactions

- (a) To predict whether a given metal will displace another, from its salt solution: A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.
- (b) Displacement of one nonmetal from its salt solution by another nonmetal: A non-metal higher in the series (towards bottom side), i.e., having high value of reduction potential will displace another non-metal with lower reduction potential, i.e., occupying position above in the series. The non-metal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential,. Thus, can displace bromine and iodine from bromides and iodides.

(iv) Reducing power of metals: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases, as the standard reduction potential becomes more and more negative. Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron. (decreasing order of reducing nature)
Alkali and alkaline earth metals are strong reducing agents.

(v) Oxidising nature of non-metals : Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. Thus, oxidising nature increases from top to bottom in the electrochemical series. The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

(Fluorine) is a stronger oxidant than and , (Chlorine) is a stronger oxidant than and

(vi) Thermal stability of metallic oxides : The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.

- **(vii) Extraction of metals :** A more electropositive metal can displace a less electropositive metal from its salt’s solution. This principle is applied for the extraction of Ag and Au by cyanide process. Silver from the solution containing sodium argento cyanide, , can be obtained by the addition of zinc as it is more electro-positive than Ag and Au.
- Weakly electropositive : The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group