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Redox Reactions

☆ Oxidation and Reduction

① Oxidation

Ⓐ Addition of Oxygen

e.g. $C + O_2 \longrightarrow CO_2$

$2Mg + O_2 \longrightarrow 2MgO$

Ⓑ Removal of Hydrogen

e.g.- $\underbrace{H_2S + Br_2 \longrightarrow 2HBr + S}_{\text{Oxidation}}$

$\underbrace{4HCl + MnO_2 \xrightarrow{\Delta} MnCl_2 + Cl_2}_{\text{Oxidation}} + 2H_2O$

Ⓒ Addition of an electronegative radical

e.g.- $4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O$

$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$

Ⓓ Removal of electropositive radical

e.g. $2KI + H_2O_2 \longrightarrow 2KOH + I_2$

$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2K_3[Fe(CN)_6] + 2KCl$

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(E) Loss of Electron

$$Mg(g) \xrightarrow{\Delta} Mg^{+2} + 2e^-$$

$$Na(g) \xrightarrow{\Delta} Na^+ + 1e^-$$

(F) Increase in Oxidation Number

e.g. $2HgCl_2 + \overset{+2}{SnCl_2} \longrightarrow Hg_2Cl_2 + \overset{+4}{SnCl_4}$

Oxidation

Oxidation

$$H_2\overset{-2}{S} + Cl_2 \longrightarrow 2HCl + \overset{0}{S}$$

2. Reduction :

(A) Addition of Hydrogen

e.g.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

Reduction

(B) Removal of Oxygen

e.g. $CuO + H_2 \longrightarrow Cu + H_2O$

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(C) Addition of an electropositive radical

e.g.- $2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

(D) Removal of electronegative radical

e.g.- $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

Reduction

(E) Gain of Electron

$$Cl(g) + 1e^- \longrightarrow Cl^-(g)$$

$$O(g) + 2e^- \longrightarrow O^{2-}(g)$$

(G) Decrease in Oxidation Number

e.g.

$$2\overset{+3}{Fe}Cl_3 + SnCl_2 \longrightarrow 2\overset{+2}{Fe}Cl_2 + SnCl_4$$

Reduction

☆ Oxidising Agent	Reducing Agent
The substances which can bring about oxidation of other substances.	The substances which can bring about reduction of other substances and itself gets oxidized.
Or	Or
Substances that provides oxygen or removes hydrogen.	Substances that provide hydrogen or removes oxygen.

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☆ Oxidation Number

It is also known as oxidation state. The O.N of an element in any species is equal to the charge which its atom appears to have acquired when all other atoms in the species are removed as ions. O.N can have positive, negative or zero values depending upon the state of combination in the compound / ion.

Rules

1. An element in its elemental form has an oxidation number of zero.
2. The Oxidation number of hydrogen is +1 per atom except in metal hydrides.
3. The Oxidation number of oxygen in the combined form except in peroxides and oxyfluorides is −2.

   e.g. Oxide → O^{2-}

   Peroxide → O_2^{2-}

   Superoxide → O_2^{-1}
4. The oxidation number of fluorine in the combined state is −1.
5. The oxidation number of an element in its monoatomic ion is equal to the charge on the ion.
6. The algebraic sum of the oxidation numbers of all the atoms in a neutral molecule is equal to zero.

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e.g. $KMnO_4$

O.N of Mn is x

$\Rightarrow \quad +1 + x + 4(-2) = 0$

$$\boxed{x = +7}$$

$K_2Cr_2O_7$

O.N of Cr is x

$\therefore \quad 2 \times (+1) + 2x + 7(-2) = 0$

$2x = 14 - 2 = 12$

$$\boxed{x = +6}$$

CH_4

$x + 4(+1) = 0$

$$\boxed{x = -4}$$

$CHCl_3$

$x + 1 + 3(-1) = 0$

$x = 3 - 1$

$$\boxed{x = +2}$$

* Oxidation Number	Valency
1. It represents the number of electrons which an atom of an element appears to have gained or lost when in the combined state.	1. It is the number of hydrogen or chlorine atoms or double the no. of oxygen atoms that combine with one atom of the element.
2. Oxidation no. of an element may be different in different compounds.	2. Valency of an element usually remain fixed.
3. O.N of an element may be +ve, -ve or zero.	3. Valency of an element is either +ve or -ve.
4. O.N may have fractional value.	4. Valency is always a whole number.

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Conventional and Stock Notation

Some metals form two monatomic cations exhibiting different O.S. These oxidation states are distinguished by using the suffix -ous and -ic.
The suffix -ous is used for the cation having lower O.N while the suffix -ic is used for the cation having higher O.N.

e.g.- $Cu^{+1} \rightarrow$ cuprous ion
$Cu^{+2} \rightarrow$ cupric ion

Stock Notation

Cu^{+} is indicated as $Cu(I)$

Types of Redox Reactions

① Combination Redox Reactions

The reaction in which two substances combine together to form a new compound

$$A + B \longrightarrow C$$

e.g.- $\overset{0}{C} + \overset{0}{O_2} \longrightarrow \overset{+4}{C}\overset{-2}{O_2}$

$$\overset{-4}{C}\overset{+1}{H_4} + 2\overset{0}{O_2} \longrightarrow \overset{+4}{C}\overset{-2}{O_2} + 2\overset{+1}{H_2}\overset{-2}{O}$$

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② Decomposition Redox Reactions

The reaction in which a compound breaks up into two or more substances atleast one of which is in elemental form.

e.g- $2\overset{+1}{H_2}\overset{-2}{O} \xrightarrow{\text{electricity}} 2\overset{0}{H_2} + \overset{0}{O_2}$

$\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3} \xrightarrow{\Delta} 2\overset{+1}{K}\overset{-1}{Cl} + 3\overset{0}{O_2}$

③ Displacement Redox Reaction

$AB + C \longrightarrow AC + B$

The reaction in which an atom or ion in a compound is displaced by an ion (or atom) of another element.

Ⓐ Metal displacement Reaction

e.g- $Zn(s) + CuSO_4 \longrightarrow ZnSO_4 + Cu$

Ⓑ Non-metal displacement Reaction

e.g- $2\overset{0}{Na} + 2\overset{+1}{H_2}\overset{-2}{O} \longrightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} + \overset{0}{H_2}$

④ Disproportionation Reaction

The reaction which involve simultaneous oxidation and reduction of an element in one oxidation state.

e.g. $2\overset{+1}{H_2}\overset{-1}{O_2} \longrightarrow 2\overset{+1}{H_2}\overset{-2}{O} + \overset{0}{O_2}$

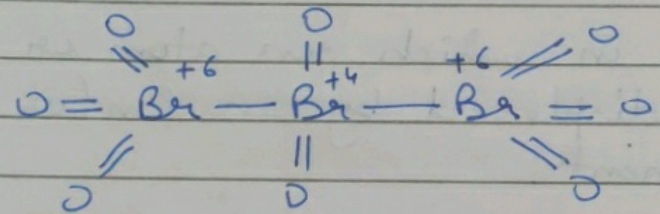
$\overset{0}{P_4} + 3OH^- \xrightarrow{+3H_2O} \overset{-3}{P}H_3 + 3H_2\overset{+1}{P}O_2^-$

☆ The Paradox of Fractional O.N

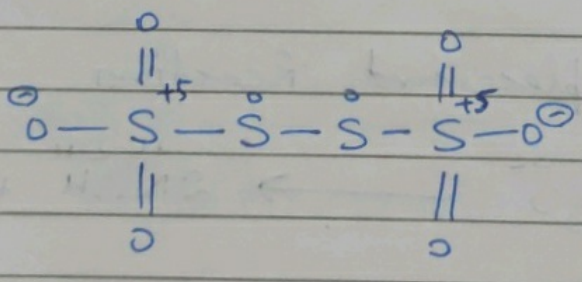
e.g. ① $C_3O_2 \longrightarrow$ O.N of $C = 4/3 = 1.33$

$$O = \overset{+2}{C} = \overset{0}{C} = \overset{+2}{C} = O$$

② $Br_3O_8 \longrightarrow$ O.N of $Br = \frac{16}{3} = 5.33$



③ $S_4O_6^{2-} \longrightarrow$ O.N of $S = \frac{10}{4} = 2.5$



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* Balancing of Redox Reaction

e.g. $Fe^{+3} + H_2S \longrightarrow Fe^{+2} + S + H^+$

Step-I Calculate the O.N of each element

Oxidation

$$Fe^{+3} + H_2S^{2-} \longrightarrow Fe^{+2} + S^{0} + H^+$$

Reduction

Step-II Divide in two Oxidation and Reduction half

Oxidation half	Reduction half
$H_2S^{-2} \longrightarrow S^{0}$	$Fe^{+3} \longrightarrow Fe^{+2}$

Balance the charge both sides

$H_2S \longrightarrow S + 2e^-$	$Fe^{+3} + 1e^- \longrightarrow Fe^{+2}$

Balance atoms other than C & H

$H_2S \longrightarrow S + 2e^-$ —①	$Fe^{+3} + 1e^- \longrightarrow Fe^{+3}$ —②

Acc. to electroneutrality principle

① + 2×②

$$H_2S + 2Fe^{+3} \longrightarrow S + 2Fe^{+3} \cancel{+2H^+}$$

Balance Hydrogen using H^+

$$H_2S + 2Fe^{+3} \longrightarrow S + 2Fe^{+3} + 2H^+$$

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✰ Redox Titrations

The ~~red~~ reaction in which oxidation and reduction take place simultaneously is called redox reaction.
Volumetric titrations based upon simultaneous oxidation and reduction reactions are termed as redox titrations.
The redox system having higher (more positive or less negative) E° value, will show greater tendency for reduction.

→ Redox Pairs in redox titrations

A titration involving two redox pairs, one getting reduced, whereas the other getting oxidised is known as oxidation - reduction titration.

e.g-	Reducing Agent	Oxidising agent	Medium
1.	$FeSO_4$	$KMnO_4$	Acidic
2.	$FeSO_4$	$K_2Cr_2O_7$	Acidic
3.	$FeSO_4.(NH_4)_2SO_4.6H_2O$	$KMnO_4$	Acidic
4.	$FeSO_4.(NH_4)_2SO_4.6H_2O$	$K_2Cr_2O_7$	Acidic
5.	$(COOH)_2$	$KMnO_4$	Acidic
6.	$Na_2S_2O_3$	I_2	Neutral

→ Equivalent mass of an oxidising agent

The number of parts of mass of the substance which contains 8 parts by mass of reactive oxygen or reacts with 1.008 parts by mass of hydrogen, is equal to the equivalent

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mass of the oxidising agent.

e.g- $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$2(39 + 55 + 64)$ $\qquad$ 5×16

$= 316$ parts $\qquad$ $= 80$ parts

80 parts of O is liberated from 316 parts of $KMnO_4$

8 parts of O $= \frac{316}{80} \times 8$

eq. mass of $KMnO_4 = 31.6$

→ Equivalent Mass of Reducing Agent

The number of parts by mass of a substance which contain 1.008 parts by mass of reactive hydrogen or reacts with 8 parts by mass of oxygen, is equal to the equivalent mass of reducing agent.

$CuO + H_2 \longrightarrow Cu + H_2O$

$(63.5 + 16)$ $\qquad$ 2×1.008

79.5 $\qquad$ 2.016

* Electronic concept of Equivalent Mass

Equivalent mass $= \dfrac{\text{Molecular mass}}{\text{No of } e^- \text{ involved in the reaction}}$

e.g $2MnO_4^- + 6H^+ + 10e^- \longrightarrow 2Mn^{+2} + 3H_2O + 5[O]$

$2Mn^{+7} + 10e^- \longrightarrow 2Mn^{+2}$

$1Mn^{+7} + 5e^- \longrightarrow Mn^{+2}$

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Eq. mass of $KMnO_4$ = $\frac{\text{Mol. mass of } KMnO_4}{5}$

$= \frac{(39+55+4\times16)}{5} = 31.6$

✶ Redox Indicators

A redox indicator is a substance which exhibits different colours in the oxidised and reduced forms. Change in the colour of each redox indicator takes place at a definite potential. In $KMnO_4$ titrations, $KMnO_4$ acts as a self-indicator.

e.g.

$KMnO_4$ → self indicator — colourless - Pink

$K_2Cr_2O_7$ → diphenylamine — colourless - deep blue

N- Phenylanthranilic acid — Yellowish - green - purple red

Q- Why is only dil. H_2SO_4 used for acidifying $KMnO_4$?

Ans:- For acidification in $KMnO_4$ titrations, only sulphuric acid is suitable whereas the other mineral acids like HCl and HNO_3 are not. In $KMnO_4$ titrations, HCl is not used because $KMnO_4$ oxidises HCl to chlorine gas and thus interferes in the quantitative estimation of the reducing agents

$$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{+2} + 8H_2O + 5Cl_2$$

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HNO_3 cannot be used because it itself is a strong oxidising agent and can oxidise the reducing agent, thereby introducing an error in the results.

→ Normality Equation

$$N_1 \times V_1 = N_2 \times V_2$$

where N_1 & N_2 are normalities of soln 1 & 2
V_1 & V_2 are volumes of soln 1 & 2

→ Molarity eqn

$$z_1 M_1 V_1 = z_2 M_2 V_2$$

where M_1 & M_2 are molarities of soln 1 & 2
V_1 & V_2 are volumes of soln 1 & 2
z_1 & z_2 are the no of equivalents

✱ Electrode reaction and the concept of Half-Cell

A galvanic cell consists of two electrodes dipping into the same or two different electrolytes. When the two electrodes of a galvanic cell are joined by a conducting wire, certain chemical reaction take place at each electrode. During these reactions, electron transfer from/to the electrode takes place. The electron-transfer reactions which take place at the electrodes are called electrode reactions.

These electrodes reactions take place in such a way that one of the electrode supplies electrons, while the other electrode sucks up the electrons continuously. This flow of electrons causes oxidation at one electrode (called anode) and reduction on the other electrode (called cathode). Therefore, the reaction at each electrode is called half-cell reaction. Thus, each galvanic cell is a combination of two half-cells. These half-cells are called anodic half-cell and cathodic half cell.

→ Anode is the -ve electrode, and oxidation occurs at the anode.

→ Cathode is the +ve electrode, and reduction occurs at the cathode.

Oxidation

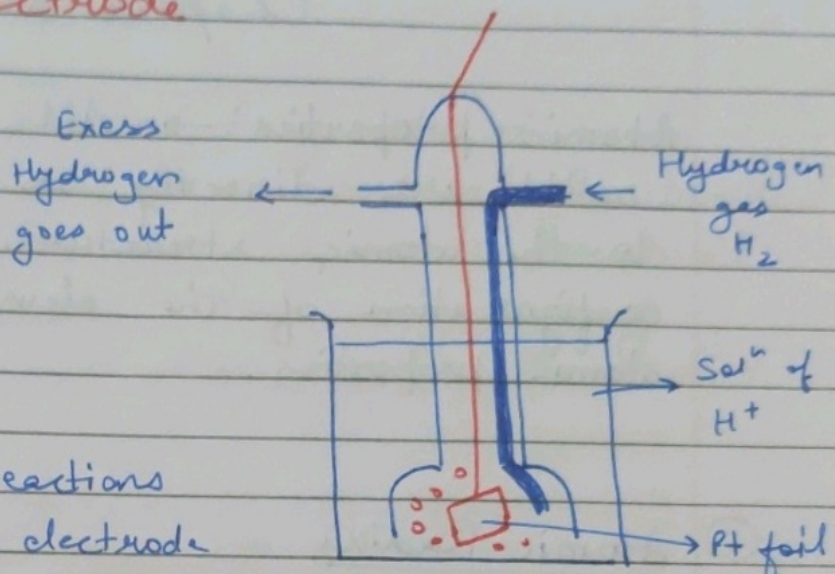
$$Zn + Cu^{+2} \longrightarrow Cu + Zn^{+2}$$

Reduction

Half-reaction at anode: $Zn \longrightarrow Zn^{+2} + 2e^-$

Half-reaction at cathode: $Cu^{+2} + 2e^- \longrightarrow Cu$

✗ Hydrogen electrode



The electrode reactions for a hydrogen electrode are,

$$H^+(aq) + e^- \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \frac{1}{2} H_2(g)$$

The emf of hydrogen electrode depends

ⓐ Concentration of H^+ ions in the solution.

ⓑ Pressure of the hydrogen gas.

✗ Standard Hydrogen Electrode

A hydrogen electrode in which pressure of hydrogen gas is maintained at 1atm and the conc. of H^+ ions in the solution is 1mol/L is called a standard hydrogen electrode (SHE). The emf of a standard hydrogen electrode is 0.00 V at all temperature. It is used as primary reference electrode.