THERMODYNAMICS

Work

Mechanical work = force × displacement = F × d
Electrical work = pot. diff. × quantity of current = E × Q
Gravitational work = gravitational force × height = mg × h
Mechanical Work = pressure × change in volume = -P ×ΔV
For expansion W = –ve ($\because$ $V_2 > V_1$)
For compression W = +ve ($\because$ $V_2 < V_1$)
Units of work 1 cal = 4.184 × 10^7 erg = 4.184 J

Enthalpy :

Enthalpy (H) is defined as the total heat contant of the system at constant pressure,

$H = E + PV$

$\Delta H = \Delta E + \Delta(PV)$

or $\Delta H = \Delta E + (P_2V_2 - P_1V_1)$

$\Delta H = \Delta E + P\Delta V + V\Delta P$

at constant pressure $\Delta H = \Delta E + P\Delta V$

so $\Delta H = \Delta E + \Delta n_g RT$ (For chemical reaction at constant temperature)

First Law of Thermodynamics

Mathematically
$q = \Delta E - w$
or $\Delta E = q + w$
q = heat absorbed or evolved (+ve if absorbed and –ve if evolved)

For Isothermal Process

$dT = 0 \because \Delta E = 0$ $q = -W$ (This is true for ideal gas only)
i.e., heat absorbed is used in work done by the system.

For Adiabatic Process

$\because q = 0$ $\therefore \Delta E = W$
i.e., Internal energy is used up in work done by the system. If work is done on the system. Its internal energy will increase and if work is done by the system its internal energy decreases. In adiabatic process work behave as state function.

For isobaric Process

$\because$ dP = 0 $\quad q_p = \Delta H$

Work done

(1) For irreversible process $W = -P_{ext} \times \Delta V$

(2) For reversible process - $W = -\int_{V_1}^{V_2} PdV$

(3) For reversible isothermal process -

$$W = -2.303\ nRT \log_{10} \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

(4) In adiabatic process $W = \Delta E$

For an ideal gas $W = nC_v(T_2 - T_1)$

or $\quad W = \frac{nR}{(\gamma - 1)}(T_2 - T_1)$

(5) When an ideal gas is freely expand in vacuum then the obtained work done is zero because $P_{ext.} = 0$

(6) Reversible expansion process are more efficient than the irrvesible expansion process.

Entropy

Entropy of a system is a measure of the degree of randomness or disorderness of the system and is denoted by S.

(1) ΔS for reversible isothermal process -

$$\Delta S = \frac{q_{rev.}}{T} = \frac{-W_{rev.}}{T} = \frac{2.303 nRT \log \frac{V_2}{V_1}}{T}$$

$$\Delta S = 2.303\ nR \log \frac{V_2}{V_1} = 2.303\ nR \log \frac{P_1}{P_2}$$

(q_{rev} = heat supplied to a system at temp. TK in a reversible manner)

(2) $\Delta S = S_{products} - S_{reactants}$

(3) $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

$$\Delta S_{total} = \frac{+q}{T_{system}} + \frac{-q}{T_{surroudings}}$$

If $T_{system} < T_{surroundings}$ heat flows from hot region to cold one ΔS_{total} is +ve and heat flow is spontaneous.

If ΔS_{total} is –ve the process is non spontaneous.

(4) ΔS for reversible adiabatic process $\Delta S = \frac{q_{rev.}}{T} = O$

(5) ΔS for reversible isobaric process $= 2.303 nC_P \log \frac{T_2}{T_1}$

(6) ΔS for reversible isochoric process $= 2.303 nC_V \log \frac{T_2}{T_1}$

(7) ΔS for phase transition $q_{rev} = \Delta H_{rev} \Rightarrow \Delta S = \frac{\Delta H_{rev}}{T}$

- Entropy change of fusion , $\Delta S_f = \frac{\Delta H_f}{T}$

  (T = freezing point or melting point)

- Entropy change of vapourization, $\Delta S_v = \frac{\Delta H_v}{T}$ (T = boiling point)

(8) Standard entropy (S°) = entropy of one mole of substance at 1 atm and 25°C

Free Energy

Free energy (G) is a measure of maximum useful work done.

$G = H - TS$,

At constant T & P

$\Delta G = \Delta H - T\Delta S$ (Gibbs - Helmholtz equation)

$\Delta G = G_{products} - G_{reactants}$

(i) $\Delta G^\circ = \Delta G^\circ_{f\ products} - \Delta G^\circ_{f\ reactants}$

(ii) ΔG° for the element = 0

(iii) $\Delta G^\circ = -2.303\ RT \log K$ (K = equilibrium constant)

If ΔG° is –ve, $K > 1$

$\Delta G^\circ = 0, K = 0$

ΔG° is +ve , $K < 1$

Condition for spontaneity of a chemical reaction is ΔG = –ve

ΔH	ΔS	$\Delta H - T\Delta S$	Behaviour
–ve	+ve	$\therefore \Delta G = -ve$	Spontaneous at all temperatures
+ve	–ve	$\therefore \Delta G = +ve$	Non-spontaneous at all temperatures
+ve	+ve	$\Delta G = -ve$ (if $\Delta H < T\Delta S$) $\Delta G = +ve$ (if $\Delta H > T\Delta S$)	Spontaneous Non-spontaneous
–ve	–ve	$\Delta G = -ve$ (if $\Delta H > T\Delta S$) $\Delta G = +ve$ (if $\Delta H < T\Delta S$)	Spontaneous Non-spontaneous

REDOX REACTIONS

1. **Stock notations** Expressing the oxidation state of a metal by Roman numbers like. I ,II, III etc. within parenthesis is called stock notation e.g., $FeSO_4$ = Iron (II) sulphate; Na_2CrO_4 = Sodium chromate (VI) etc.

2. **Valency** of an element is only a number and as such there is no postive or negative sign attached to it. It can neither be zero nor fractional. Oxidation number, on the other hand, refers to charge and hence has either postive or negative sign. It can also be zero or fractional. For example oxidation state of C in CH_2Cl_2 is zero while that of Fe in Fe_3O_4 is $\frac{8}{3}$ and of S in $Na_2S_2O_3$ is 2.0.

3. **Calculation of oxidation state :**

Rules I :

The oxidation state of any atom in its elemental state is zero.

Rules II:

The maximum oxidation state of any atom will be equal to (+group number) and minimum oxidation state will be equal to (group number –8), where group numbers are in roman numerals. For example, Sulphur (S) is member of group VI A and hence its maximum oxidation state is +6 and minimum is = (6–8) = –2

Exception : Cu(IB) : +1, +2
Au (IB) : 1, +3
Xe (0) : +2, +4, +6, +8. etc

Rule III:

The sum of oxidation state of all the atoms in a molecule is zero and for ions, it is equal to the ionic charge.

Rule IV:

The oxidation states of some elements are fixed in all their compounds.

+1: Alkali metals (Li, Na, K, Rb, Cs, Fr) and Ag

+2: Alkaline earth metals (Be. Mg, Ca, Sr, Ba, Ra) and Zn

+3: Al

–1 :F

Rule V:

Oxidation state of hydrogen is +1 in all of its compounds, except the metal hydrides, where it is –1.

Rule VI:

Oxidation state of oxygen is –2 in all of compounds except

(i) Peroxide like Na_2O_2, H_2O_2, BaO_2, etc, where it is –1.

(ii) Superoxides like KO_2, RbO_2, etc, where it is –1/2.

(iii) Some other binary compounds of alkali metals and oxygen like KO_3 (O.S. of O = –1/3), Rb_2O_3 (O.S. of O = –2/3), etc.

(iv) Oxides of fluorine, where it is positive states. For example: O.S. of O in OF_2, O_2F_2, O_3F_2 etc. are +2, +1, +2/3, respectively.

Rule VII:

The charges on different ions commonly used, should be known.

CO_3^{2-}	Carbonate ion	HCO_3^-	Hydrogen carbonate ion
SiO_4^{4-}	Silicate ion	PO_4^{3-}	Phosphate ion
HPO_4^{2-}	Hydrogen phosphate ion	$H_2PO_4^-$	Dihydrogen phosphate ion
HPO_3^{2-}	Phosphite ion	NO_3^-	Nitrate ion
NO_2^-	Nitrite ion	SO_4^{2-}	Sulphate ion
SO_3^{2-}	Sulphite ion	S^{2-}	Sulphide ion
S_2^{2-}	Pyrite ion	$S_2O_7^{2-}$	Disulphate ion
$S_2O_3^{2-}$	Thiosulphate ion	$S_2O_8^{2-}$	Peroxodisulphate ion
ClO^-	Hypochlorite ion	ClO_3^-	Chlorate ion
ClO_2^-	Chlorite ion	ClO_4^-	Perchlorate ion

Rule VIII :

In the complex compound, the overall charge on ligand should be considered in place of considering the charges on individual atoms.

4. Peroxy linkage calculation :

The linkage of the two oxygen atoms i.e. there are the oxygen-oxygen linkages.

(i) $(O.S)_{Cal.} > (O.S)_{max.}$; Peroxy linkage is present

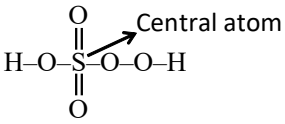
(ii) $(O.S)_{Cal.} = (O.S)_{max.}$: Oxy linkage is present

(ii) $(O.S)_{Cal.} < (O.S)_{max.}$: M–M bond is persent

Calculation of no. of peroxy linkage :

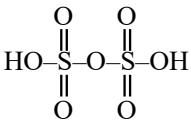
$$n = \frac{(\text{Calculated oxidation state}) - (\text{Maximum oxidation state})}{1 \text{ or } 2}$$

⇒ If two central atom present than divide it by 1
⇒ If one central atom present then divide it by 2
⇒ When 'n' comes out to be fractional then use below formula
$n = [O.S]_{cal.} - [0.S]_{max.} + 1$
Example : H_2SO_5



no. of peroxy linkage = $\frac{8-6}{2} = 1$

Calculated O.S. of S $\rightarrow$ (+8)
Maximum O.S. of S $\rightarrow$ (+6)
i.e. $(O.S.)_{Cal.} > (O.S.)_{max.} \Rightarrow$ Peroxy linkage is present
Example : $H_2S_2O_7$



For sulphur $(O.S)_{max.} = +6$
$(O.S)_{cal.} = +6$
$+2 + 2x - 14 = 0$
$2x = 12$
$x = +6$
Therefore, no peroxy linkage is present.
Example : $H_4P_2O_6$
For phosphorus $(O.S)_{max.} = +5$
$4(+1) + 2x - 12 = 0$
$2x - 8 = 0$
$x = +4$
Therefore, no peroxy linkage is present
As $(O.S)_{max.} > (O.S)_{cal.} \rightarrow$ M – M bond

5. Redox reaction :

Redox reaction are also called electron - transfer reactions since electron are transferred from the reductant to the oxidant.

Type of redox reaction :

These are the reactions involving oxidation as well as reduction.

Examples:

$$\overset{0}{Zn} + 2\overset{+1}{H}Cl \longrightarrow \overset{+2}{Z}nCl_2 + \overset{0}{H_2}$$

(Oxidation = Zn, Reduction = HCl)

1. Disproportionation Reaction:

The redox reaction in which the atoms of same element belonging from the same molecule or ion are oxidised as well as reduced are called disproportionation reaction. Such reaction are also called autoredox or self-redox reaction.

Examples:

$$3\overset{0}{Cl_2} + 6NaOH \longrightarrow 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

Cl–atoms are oxiidised and reduced, both

2. Comproportionation Reaction

These are just the reverse of disproportionation. Atoms of the same element, belonging to the same molecule or ion, oxidise and reduce to give the element in the commom oxidation state.

Example:

$$2H_2\overset{-2}{S} + \overset{+4}{S}O_2 \longrightarrow \overset{0}{S} + 2H_2O$$

6. Methods of Balancing Chemical reactions

1. Oxidation number method

Step I: Select the species undergoing oxidation and reduction and write both the processes, separately

StepII: Balance the atoms of responsible elements (elements responsible for change in oxidation state) by simple counting.

StepIII: Determine the changes in oxidation state of both the process, due to the total number of atoms of responsible elements.

StepIV: Make the changes is oxidation state of both processes, equal by multiplying with suitable numbers. Add both the processes after multiplication.

StepV : If some reaction components are left, write them in proper side and balance them by simple counting.

StepVI: If the reaction is not balanced at step IV or V, add some molecule or ion in the proper side, The species added should be according to the reaction and it should not create a new change in oxidation state.

Example :

$$KMnO_4 + H_2SO_4 + HCl \longrightarrow K_2SO_4 + MnSO_4 + H_2O + Cl_2$$

Solution:

Step I: Oxidation: $\overset{-1}{H}\overset{}{Cl} \longrightarrow \overset{0}{Cl_2}$

Reduction: $K\overset{+7}{M}nO_4 \longrightarrow \overset{+2}{M}nSO_4$

Step II: Oxidation: $2HCl \longrightarrow Cl_2$

Reduction: $KMnO_4 \longrightarrow MnSO_4$

Change is O.S.

Step III: Oxidation: $2\overset{-1}{H}\overset{}{Cl} \longrightarrow \overset{0}{Cl_2}$ 2

Rediuction: $K\overset{+7}{M}nO_4 \longrightarrow \overset{+2}{M}nSO_4$ 5

Change is O.S.

Steep IV: Oxidation: $2HCl \longrightarrow Cl_2$ 2]×5

Reduction: $KMnO_4 \longrightarrow MnSO_4$ 5]×2

$2KMnO_4 + 10\ HCl \longrightarrow 2MnSO_4 + 5Cl_2$

Step V: $2KMnO_4 + 10HCl + 3H_2SO_4 \longrightarrow 2MnSO_4 + 5Cl_2 + K_2SO_4 + 8H_2O$ is the balanced reaction.

2. Ion electron method :

Step I : If the reaction is given in molecular form, convert it in the ionic form. For it, write strong acids, strong bases and all water soluble salts in ionic form and then cancel out the spectator ions (ions common in both sides).

Step II: Select the species undergoing oxidation and reduction and write them separately.

Step III: Balance the atoms of responsible element by simple counting.

Step IV: Balance the atoms of all other elements by adding some molecule or ion in the proper side. The species added should be according to the reaction and it should not create not create any new change in the oxidation state. In most of the reaction, the other elements are hydrogen or oxygen. They are balanced according to medium of the reaction.

In acidic medium:

→ Add one water molecule in the opposite side for each excess of oxygen atom.

→ Add one H^+ ion in the opposite side for each excess of hydrogen atom.

In basic medium:

→ Add one water molecule in the same side and two OH^- ions in opposite side for each excess of oxygen atom.

→ Add one OH^- ion in the same side and one water molecule in the opposite side for each excess of hydrogen atom.

→ Hydrogen and oxygen atoms may also be balanced by balancing them first in acid medium and then replacing the H^+ ions suitably by OH^- ions. For it, add OH^- ions equal in number to the H^+ ions in both the sides and then write the combination of one OH^- ion and one H^+ ion ions as an H_2O molecule. It must be noted that the combination of one H^+ and one OH^- ions, in ionic form of a reaction.

Step V : Balance the charges in both process by addding proper number of electron in the proper side. The number of electrons added and the side, in which they are added, can be checked.

→ In oxidation, electrons will be added in the right side and in the reduction, left side.

→ The number of electrons lost or gained will always be equal to the change in oxidation state.

→ The number of elecrons lost or gained in a particular process in independent to the medium of reaction.

Step VI: Make the total number of electrons lost and gained equal by multiplying with suitable numbers. Add both the processes. It should be balanced reaction in ionic form.

Step VII: If the original reaction was in molecular form, convert the ionic form into molecular form.

Example :

$KMnO_4 + H_2SO_4 + HCl \rightarrow K_2SO_4 + MnSO_4 + Cl_2 + H_2O$

Solution:

Step I: Ionic form of the given reaction is

$K^+ + MnO_4^- + 2H^+ + SO_4^{2-} + H^+ + Cl^- \longrightarrow 2K^+ + SO_4^{2-} + Mn^{2+} + SO_4^{2-} + Cl_2 + H_2O$

or $MnO_4^- + H^+ + Cl^- \longrightarrow Mn^{2+} + Cl_2 + H_2O$

Step II: Oxidation: $Cl^- \longrightarrow \overset{0}{Cl_2}$

Reduction: $\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+}$

Step III: Oxidation: $2Cl^- \longrightarrow Cl_2$

Reduction: $MnO_4^- \longrightarrow Mn^{2+}$

Step IV: Oxidation: $2Cl^- \longrightarrow Cl_2$

Reduction: $MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$

Step V: Oxidation: $2Cl^- \longrightarrow Cl_2 + 2e^-$

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

Step VI: Oxidation: $2Cl^- \longrightarrow Cl_2 + 2e^-] \times 5$

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

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

It is balanced reaction in ionic form.

Step VII: $2KMnO_4 + 10\ HCl + 3H_2SO_4 \longrightarrow 2MnSO_4 + 8\ H_2O + 5Cl_2 + K_2SO_4$ is the balanced reaction.

7. Equivalence weight (E) :

In general, Eq. wt. (E) = $\frac{\text{Atomic weight or Molecular weight}}{\text{valency factor(v.f)}} = \frac{\text{Mol. wt.}}{\text{n-factor}} = \frac{M}{x}$

Number of Equivalents = $\frac{\text{mass of species}}{\text{eq. wt. of that species}}$

For a solution, Number of equivalents = N_1V_1, where N is the normality and V is the volume in litres

- Equivalent mass is a pure number which, when expressed in gram, is called gram equivalent mass.
- The equivalent mass of a substance may have different values under different conditions.
- There is no hard and fast rule that equivalent weight will be always less than the molecular mass.

(a) The equivalent weight of an element is that weight of the element that will combine with or replace directly or indirectly 1.0 gm of H, 35.5 gm of Cl or 8.0 gm. of O or 108 gm of Ag.

(b) In the reaction $Mg + Cl_2 \rightarrow MgCl_2$

1 atom of Mg loses 2 electrons to become Mg^{2+} ion. If we start with 1 mole or 24 gm of Mg, we have N_A (6.023×10^{23}) number of Mg atoms which would lose $2N_A$ number of electrons and form N_A number of Mg^{2+} ions. Therefore, we get $2N_A$ number of electrons from 24 gm of Mg.

So, N_A number of electrons can be obtained from $\frac{24}{2}$ = 12 gm of Mg. Thus the equivalent weight of Mg = 12.

Thus equivalent weight of an element is that weight of the element which loses or gained Avogadro number (N_A) of electrons.

Valency factor/n-factor calculation :

For Elements : Valency factor = valency of the element.

For Acids : Valency factor = number of replaceable H^+ ions per acid molecule.

v. f. for acid is the number of OH^- replaced from the base by each molecule of acid.

Example :

n factor of HCl = 1

n factor of CH_3COOH = 1

n factor of H_2SO_4 = 2

For Bases :

Valency factor = number of replacable OH^- ions per base molecule.

Example :

n factor of NaOH = 1

n factor of $Ca(OH)_2$ = 2

n factor of $Al(OH)_3$ = 3

n factor of $B(OH)_3$ = 1 (because it is a mono basic acid)

Salts :

(i) When no atom undergoes change in oxidation state

The n-factor for such salts isdefined as the totalmoles of cationic/anionic charge present in 1 mole of the salt. For the reaction

$2Na_3PO_4 + 3BaCl_2 \rightarrow 6NaCl + Ba_3(PO_4)_2$

n-factor of Na_3PO_4 in this reaction is 3

n-factor of $BaCl_2$ in this reaction is 2

n-factor of NaCl in this reaction is 1

n-factor of $Ba_3(PO_4)_2$ in this reaction is 6

(ii) When only one atom undergoes change in oxidation state and goes in only one product

The n-factor of such salts is defined as the number of moles of electrons exchanged (lost or gained) by one mole of the salt.

For example, let us calculate the n-factor $KMnO_4$ for the given chemical change.

$KMn^{+7}O_4 \xrightarrow{H^+} Mn^{+2}$

In this reaction, oxidation state of Mn changes from +7 to +2. Thus, $KMnO_4$ is acting as oxidising agent, since it is reduced

$\therefore$ n-factor of $KMnO_4 = |1 \times (+7) - 1 \times (+2)| = 5$

Similarly

(a) $KMn^{+7}O_4 \xrightarrow{H_2O} Mn^{+4}$

n-factor of $KMnO_4 = |1 \times (+7) - 1 \times (+4)| = 3$

(b) $KMn^{+7}O_4 \xrightarrow{OH^-} Mn^{+6}$

n–factor of $KMnO_4 = |1 \times (+7) - 1 \times (+6)| = 1$

It can be seen that in all above chemical changes, $KMnO_4$ is acting as oxidising agent, yet its n-factor is not same in all reactions. Thus, the n-factor of a compound is not fixed, it depends on the type and the extent of reaction it undergoes.

(iii) When only one atom undergoes change in oxidation state but goes in two products with the same oxidation state

In such case, the n-factor is calculated in the same manner as in case (ii).

For example, let us calculate the n-factor of $K_2Cr_2O_7$ for the given chemical change.

$Cr_2O_7^{2-} \rightarrow Cr^{3+} + Cr^{3+}$

In this reaction, state of Cr changes from +6 to +3 in both products.
$\therefore$ n-factor of $K_2Cr_2O_7 = |2 \times (+6) - 2 \times (+3)| = 6$

(iv) When only one atom undergoes change in oxidation state but goes in two products with different oxidation state

Consider a chemical change, $2Mn^{7+} \rightarrow Mn^{4+} + Mn^{2}$
Out of the two moles of Mn^{7+}, one mole Mn^{7+} changes to Mn^{+4} bygaining 3 moles of electrons and the other mole of Mn^{7+} changes to Mn^{2+} by gaining 5 mole of electrons, so in all 8 mole of electrons are gained by 2 mole of Mn^{7+}. So each mole of Mn^{7+} has gained 8 / 2 = 4 mole of electrons. Thus, 4 would be the n-factor of Mn^{7+} in this reaction.

If the reaction would have been
$3Mn^{7+} \rightarrow 2Mn^{2+} + Mn^{4+}$

Out of 3 moles of Mn^{7+}, two moles of Mn^{7+} changes to Mn^{2+} by gaining 10 mole of electrons and one mole of Mn^{7+} changes to Mn^{4+} by gaining 3 mole of electrons. Thus each mole of Mn^{7+} have gained 13 / 3 mole of electrons. Therefore, the n-factor of Mn^{7+} in this reaction would be 13 / 3.

Note that n-factor can be a fraction because it is not the number of electrons exchanged but it is the number of moles of electrons exchanged which can be a fraction.

Now, if the reaction would have been $3Mn^{7+} \rightarrow Mn^{2+} + 2Mn^{4+}$. Thus, each mole of Mn^{7+} have gained 11 / 3 mole of electron. Therefore, n-factor of Mn^{7+} in this reaction would be 11 / 3. Salts which react in a fashion that only one atom undergoes change in oxidation state but goes in two products with different state (in one product with same oxidation state and in other with different state than in the reactant).

For such reactions also, the n-factor calculation is not possible without the knowledge of balanced chemical reaction because n-factor of reactant would depend on the fact that how much of reactant under went change to different oxidation state +y and how much of reactant remained in the same oxidation state +x.

(v) Salts or compounds which undergoes disproportionation reaction

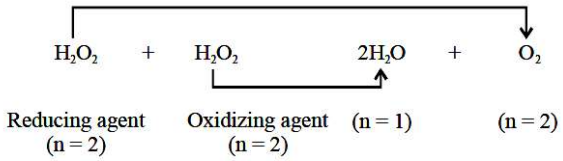
Disproportionation reactions can be divided into two types.

(a) Disproportionation reactions in which moles of compound getting oxidised and reduced are same i.e. moles of oxidising agent and reducing agent are same. The n-factor for such compounds is calculated by either the number of mole of electrons lost or gained by one mole of the compound because in such a case, n-factor of the compound acting as oxidizing agent or as reducing agent would be same.

For example, $2H_2O_2 \rightarrow 2H_2O + O_2$
Out of 2 mole of H_2O_2 used in reaction, one mole of H_2O_2 gets oxidised to O_2 (oxidation state of O changes from –1 to –2). When 1 mole of H_2O_2 gets oxidised to O_2, the half - reaction would be $O_2^{2-} \rightarrow O_2^0 + 2e^-$ and when 1 mole of H_2O_2 gets reduced to H_2O,

the half-reaction would be $O_2^{2-} + 2e^- \rightarrow 2O^{2-}$

Thus, it is evident that one mole of H_2O_2 (which is either getting oxidised or reduced) will lose or gain 2 mole of electrons. Therefore, n-factor of H_2O_2 as oxidizing as well as reducing agent in this reaction is 2. Thus



Or when the reaction iswritten as
$2H_2O_2 \rightarrow 2H_2O + O_2$
Where, H2O2 is not distinguished as howmuch of it functions as oxidizing agent and howmuch as reducing agent, then n-factor calculation can be done in the followingmanner. Find the number of electrons exchanged (lost or gained) using the balanced equation and divide it by the number ofmoles H_2O_2 involved in the reaction.Thus, then-factor of H_2O_2 when the reactioniswrittenwithout segregating

Oxidising and reducing agent is $\frac{2}{2}$

$$\underset{(n=1)}{2H_2O_2} \rightarrow \underset{(n=1)}{2H_2O} + \underset{(n=2)}{O_2}$$

(b) Disproportionation reactions inwhichmoles of compound getting oxidised and reduced are not same.
$6Br_2 + 12OH^- \rightarrow 10Br^- + 2BrO_3^- + 6H_2O$

In this reaction, themole of electrons lost by the oxidation of some of themoles of Br2 are same as the number ofmole of electrons gained by the reduction of rest of the moles of Br_2 of the 6 moles of Br_2 used, onemole is getting oxidized, loosing 10 electrons (as reducing agent) and 5 moles of Br_2 are getting reduced and accepts 10moles of electron (as oxidizing agent)

$$Br_2 \longrightarrow 2Br^{+5} + 10\,e^-$$
$$5Br_2 + 10e^- \longrightarrow 10Br^-$$

$$Br_2 + 5Br_2 \longrightarrow 10\,Br^- + 2\,Br^{+5}$$

Reducing agent (n = 10) Oxidizing agent (n = 2) (n = 1) (n = 5)

Thus, n-factor of Br_2 acting as oxidizing agent is 2 and that Br_2 acting as reducing agent has n-factor 10.
Or when the reaction is written as
$6Br_2 \rightarrow 10Br^- + 2Br^{5+}$
where, Br_2 is not distinguished as how much of it function as oxidizing agent and how much as reducing agent, then for calculating n-factor of compound in such reactions, first find the total number of electrons exchanged (lost or gained) using the balanced equation and divide it with the number of mole of Br2 involved in the reaction to get the number of mole electrons exchanged by one mole of Br_2. In the overall reaction, the number of mole of electrons exchanged (lost or gained) is 10 and the moles of Br_2 used in the reaction are 6.

Thus, each mole of Br_2 has exchanged 10/6 or 5/3 mole of electrons. Therefore , the n-factor of Br_2 when the reaction is written without segregation oxidising and reducing agent is 5/3.

$$\underset{(N = 5/3)}{6Br_2} \rightarrow \underset{(N = 1)}{10Br^-} + \underset{(N = 5)}{2Br^{5+}}$$