CHAPTER-8
REDOX REACTIONS

oxidation	reduction
1. Addition of oxygen	1. Removal of oxygen
2. Removal of hydrogen	2. Addition of hydrogen
3. Addition of an electronegative element	3. Removal of an electronegative element
4. Removal of an electropositive element	4. Addition of an electropositive element
5. Loss of electron	5. Gain of electron

Oxidation number denotes theoxidation state of an element in a compound ascertained according to a setof rules formulated on the basis thatelectron in a covalent bond belongsentirely to more electronegative element.

Calculation of oxidation number-

1. O. S. of all the elements in their elemental form (in standard state) is taken as zero O. S. of elements in Cl_2, F_2, O_2, P_4, O_3, Fe(s), H_2, N_2, C(graphite) is zero.
2. Common O. S. of elements of group one (1^{st}) is one. Common O. S. of elements of group two (2^{nd}) is two.
3. For ions composed of only one atom, theoxidation number is equal to the chargeon the ion.
4. The oxidation number of oxygen in most compounds is –2.While in peroxides (e.g., H_2O_2, Na_2O_2), eachoxygen atom is assigned an oxidationnumber of –1, in superoxides (e.g., KO_2,RbO_2) each oxygen atom is assigned anoxidation number of –(½).
5. In oxygendifluoride (OF_2) and dioxygendifluoride (O_2F_2), the oxygen is assignedan oxidation number of +2 and +1,respectively.
6. The oxidation number of hydrogen is +1 but in metal hydride its oxidation no. is–1.
7. In all its compounds, fluorine has anoxidation number of –1.
8. The algebraic sum of the oxidation numberof all the atoms in a compound must bezero.
9. In polyatomic ion, the algebraic sumof all the oxidation numbers of atoms ofthe ion must equal the charge on the ion.

Stocknotation:the oxidationnumber is expressed by putting a Romannumeral representing the oxidation numberin parenthesis after the symbol of the metal inthe molecular formula. Thus aurous chlorideand auric chloride are written as Au(I)Cl andAu(III)Cl_3. Similarly, stannous chloride andstannic chloride are written as Sn(II)Cl_2andSn(IV)Cl_4.

Oxidation: An increase in the oxidationnumber
Reduction: A decrease in the oxidationnumber

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Oxidising agent: A reagent which canincrease the oxidation number of an elementin a given substance. These reagents are calledas **oxidants** also.
Reducing agent: A reagent which lowers the oxidation number of an element in a givensubstance. These reagents are also called as**reductants**.
Redox reactions: Reactions which involvechange in oxidation number of the interactingspecies

Balancing of redox reactions:

Oxidation Number Method:

Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite,Na2SO3, in an acid solution to give chromium(III) ion and the sulphate ion.

Step 1: The skeletal ionic equation is:

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Step 2: Assign oxidation numbers forCr and S

+6 –2 +4 –2 +3 +6 –2

$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Step 3: Calculate the increase anddecrease of oxidation number, and make them equal:

+6 –2 +4 –2 +3 +6

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 4: Balance the charge by adding H^+as the reaction occurs in theacidic medium,

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)\ \ 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$$

Step 5: Balance the oxygen atom by adding water molecule.

$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)\ \ 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 4H_2O(l)$$

Half Reaction Method

balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium,wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr^{3+} ions.

Step 1: Produce unbalanced equation for thereaction in ionic form :

$$Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$$

Step 2: Separate the equation into halfreactions:

+2 +3

Oxidation half : $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

+6 –2 +3

Reduction half :$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

Step 3: Balance the atoms other than O andH in each half reaction individually.

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

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Step 4: For reactions occurring in acidicmedium, add H_2O to balance O atoms and $H^+$to balance H atoms.$Cr_2O_7^{2-}$ (aq) +14 $H^+ \rightarrow Cr^{3+}$(aq) + $7H^2O$ (l)

Step 5: Add electrons to one side of the halfreaction to balance the charges. If need be,make the number of electrons equal in the twohalf reactions by multiplying one or both halfreactions by appropriate coefficients.

Fe^{2+} (aq) → Fe^{3+} (aq) + e–

$Cr_2O_7^{2-}$ (aq) + $14H^+$ (aq) + 6e– → $2Cr^{3+}$(aq) +$7H_2O$ (l)

$6Fe^{2+}$ (aq) →6 Fe^{3+} (aq) +6 e–

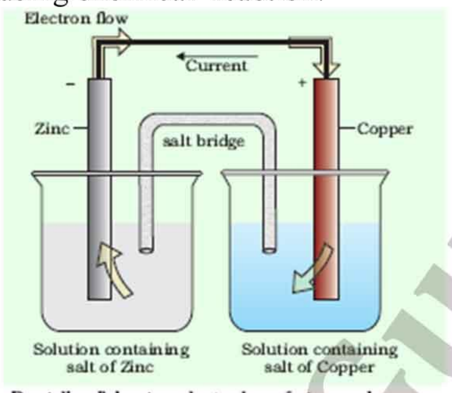
Step 6: We add the two half reactions toachieve the overall reaction and cancel theelectrons on each side. This gives the net ionicequation as :

$6Fe^{2+}$(aq) + $Cr_2O_7^{2-}$ (aq) + $14H^+$(aq) → 6 Fe^{3+}(aq) +2Cr $^{3+}$(aq) + $7H_2O$(l)

A **redox couple** is defined as havingtogether the oxidised and reduced forms of asubstance taking part in an oxidation orreduction half reaction.

Represented as Zn^{2+}/Zn and Cu^{2+}/Cu.

❖ Electrochemical cells are the devices which are used to get electric current by using chemical reaction.



Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

The potential associated with eachelectrode is known as **electrode potential**. Ifthe concentration of each species taking partin the electrode reaction is unity (if any gasappears in the electrode reaction, it is confinedto 1 atmospheric pressure) and further thereaction is carried out at 298K, then thepotential of each electrode is said to be the**Standard Electrode Potential**.

- SHE is used to measure electrode potential and its standard electrode potential is taken as 0.00 V.

ONE MARK QUESTIONS

1. Define oxidation and reduction in terms of oxidation number.
   Ans Increase in Oxidation Number is Oxidation and decrease in Oxidation Number is called reduction.
2. What is meant by disproportionation? Give one example.
   Ans : In a disproportionation reaction an element simultaneously oxidized and reduced.
   $P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^-$
3. What is O.N. of sulphur in H_2SO_4?Ans: +6

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4. Identify the central atom in the following and predict their O.S.
   HNO_3
   Ans: central atom:- N; O.S. +5
5. Out of Zn and Cu which is more reactive?
   Ans: Zn.
6. What is galvanization?
   Ans: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.
7. How is standard cell potential calculated using standard electrode potential?
   Ans: $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
8. What is O.S. of oxygen in H_2O_2?
   Ans: - -1.
9. The formation of sodium chloride from gaseous sodium and gaseous chloride is a redox process justify.
   Ans: Na atom get oxidize and Cl is reduced.

TWO MARKS QUESTIONS

1. Write the balanced redox reaction .
   (I) $MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$ [acidic medium]
   (II) $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$ [Acidic medium]

   Ans:- (i) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}$
   (ii) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
2. Identify the strongest & weakest reducing agent from the following metals: .Zn, Cu, Na, Ag, Sn
   Ans: Strongest reducing agent: Na, weakest reducing agent: Ag.
3. Determine the oxidation no. of all the atoms in the following oxidants:$KMnO_4$, $K_2Cr_2O_7$ and $KClO_4$
   Ans :
   In $KMnO_4$ K = +1, Mn = +7, O = -2
   In $K_2Cr_2O_7$K = +1, Cr = +6, O = -2
   In $KClO_4$K = +1, Cl = =+7, O = -2
4. Determine the oxidation no. of all the atoms in the following species:Na_2O_2 and OF_2.
   Ans: In Na_2O_2Na = +1, O = -1
   InOF_2, F = -1, O = +2

5. Is it possible to store :
   (i) H_2SO_4 in Al container?(ii) CuSO4 solution in Zn vessel?
   Ans : (i) yes. (ii) No.
6. Calculate the standard e.m.f. of the cell formed by the combination of $Zn/Zn^{2+} || Cu^{2+}/Cu$.
   Solution- : $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
   $=0.34 - (-0.76) = 1.10V.$
7. Identify the oxidizing and reducing agents in the following equations:

(i) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}$
(ii) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

Ans : (i) O.A. = MnO_4^- ; R.A.= Fe^{2+}
(ii)O.A.=$Cr_2O_7^{2-}$; R.A.= Fe^{2+}

8. Predict all the possible oxidation states of Cl in its compounds.
   Ans:- 0, -1, +1, +3, +5, +7
9. Formulate possible compounds of 'Cl' in its O.S.is: 0, -1, +1, +3, +5, +7
   Ans: Cl_2, HCl, HOCl, HOClO, $HOClO_2$, $HOClO_3$ respectively.
10. List three measures used to prevent rusting of iron.
    Ans: (i) galvanization(coating iron by a more reactive metal)
    (ii) greasing/oiling
    (iii) painting.

THREE MARK QUESTIONS

1. Write short notes on :
   (a) Electrochemical series(b) redox reactions (c) oxidizing agents
   Ans :(a) Electrochemical series :- arrangement of metals(non-metals also) in increasing order of their reducing power or vice versa.
   (b) Reactions in which both Oxidation and reduction take place simultaneously are REDOX REACTIONS.
   (c)oxidizing agents : chemical specie which can oxidize the other one or can reduce itself.
2. Calculate O. S. of sulphur in the following oxoacids of 'S' :
   H_2SO_4 ,$H_2SO_3$$H_2S_2O_8$and $H_2S_2O_7$
   Ans : +6, +4, +6 and +6 respectively.
   (calculate by considering x of 'S' and taking +1 of H, -2 0f "O" and -1 of "O" in peroxide bond.)
3. Explain role of salt bridge in Daniell cell.
   Ans : (a) it completes the electric circuit in the cell.
   (b) it maintains the electric neutrality in the cell.

4. Account for the followings :
   (i) sulphur exhibits variable oxidation states.
   Ans. Due to the presence of vacant 'd' orbitals in 'S'
   (ii) Fluorine exhibits only -1 O.S.
   Ans . It is most electronegative element
   (iii) oxygen can't extend its valency from 2.
   Ans. Small size/unavailabilityof vacant 'd' orbitals in O
5. Balance the equation $MnO_4^- + I^- \rightarrow Mn^{2+} + I_2 + H_2O$by ion electron method in acidic medium.
   Ans :<u>Step-I</u> Balancing of reduction half reaction by adding protons and electrons on LHS and more water molecules on RHS:
   $8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O$

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<u>Step-II</u> Balancing of oxidation half reaction by adding electrons on RHS:
$2I^- \rightarrow I_2 + 2e^-$
Step-III To multiply the OHR by 5; RHR by2 andto add OH & RH reactions to get overall redox reaction(cancellation of electrons of RH & OH reactions):

$$[8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$$

$$[2I^- \rightarrow I_2 + 2e^-] \quad \times \quad 5$$

$$MnO_4(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}$$

6. complete and balance the following equations:

(i) $H^+ + Cr_2O_7^{2-} + Br^- \rightarrow 2Cr^{3+} + Br_2 +$ -----

(ii) $H_2O_2 + Cl^- \rightarrow OH^- + Cl_2$

(iii) $Zn + Cu^{2+} \rightarrow$?

Ans :(i) $14H^+ + Cr_2O_7^{2-} + 6Br^- \rightarrow 2Cr^{3+} + 3Br_2 + 7H_2O$

(ii) $H_2O_2 + 2Cl^- \rightarrow 2OH^- + Cl_2$

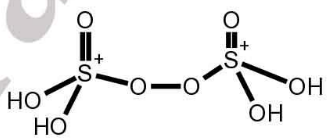
(ii) $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

7. Identify the oxidizing and reducing agents in the following equations:
   (i) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
   (ii) $H_2 + Cl_2 \rightarrow 2HCl$
   (iii) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$
   Ans :(i) O.A. $= H_2SO_4$; R.A.= Fe
   (ii) O.A. $= Cl_2$; R.A.$=H_2$
   (iii)O.A. $= MnO_2$; R.A. =HCl
8. . Arrange the following in increasing order of their reducing power:

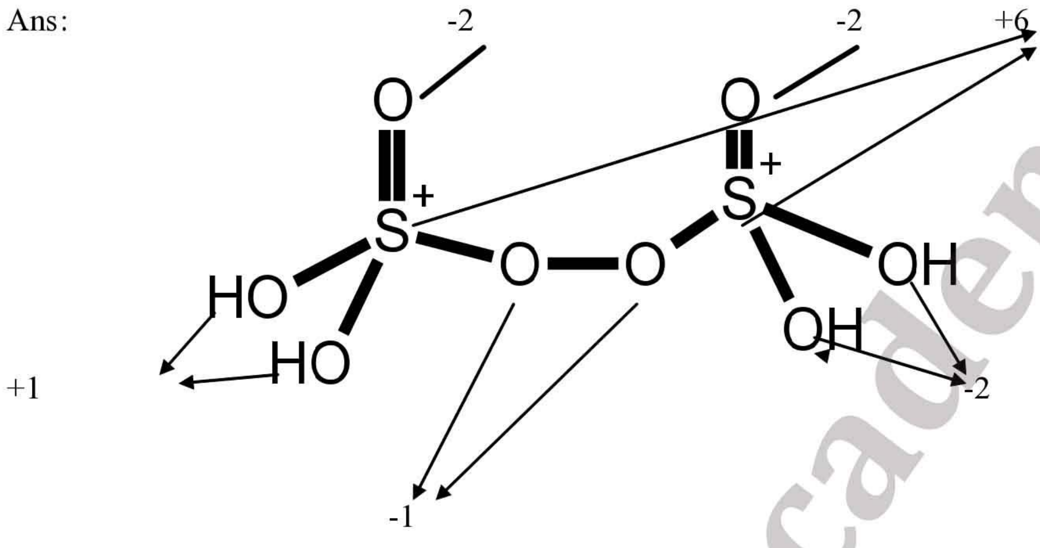
Cu, Ag, Au, Zn, Fe, Al, Na, Mg, Pt(SHE), Hg, Ca, K

Ans : Au, Hg, Ag, Cu, Pt(SHE), Fe, Zn, Al, Mg, Na, Ca, K

9. Indicate O.S. of each atom present in given structure of peroxodisulphuric acid



Ans:



10.What is SHE? What is its use?

Ans :Standard Hydrogen Electrode (SHE) has beenselected to have zero standard potential at alltemperatures. It consists of a platinum foilcoated with platinum black (finely dividedplatinum) dipping partially into an aqueous solution in which the activity (approximateconcentration 1M) of hydrogen ion is unity andhydrogen gas is bubbled through the solutionat 1 bar pressure.The potential of the other half cell is measuredby constructing a cell in which reference electrode is standard hydrogen electrode. The potential of the other half cell is equal to thepotential of the cell.

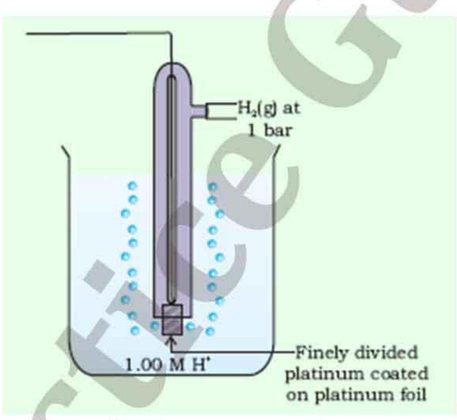


Fig: SHE

HOTS QUESTIONS

1. Is rusting of iron an electrochemical phenomenon? How ?explain.

Ans : Yes. Rusting of iron is an electrochemical phenomenon because this is possible due to formation of a small electrochemical cell over rough surface of iron and the following redox reaction takes place there in that cell-

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Oxidation $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

Reduction $O_2 + 4H^+ \ \ 4e^- \rightarrow 2H_2O$

$e- + \frac{1}{2} O_2 + 2H_2O + 2Fe^{2+} \rightarrow Fe_2O_3 + 4H^+$

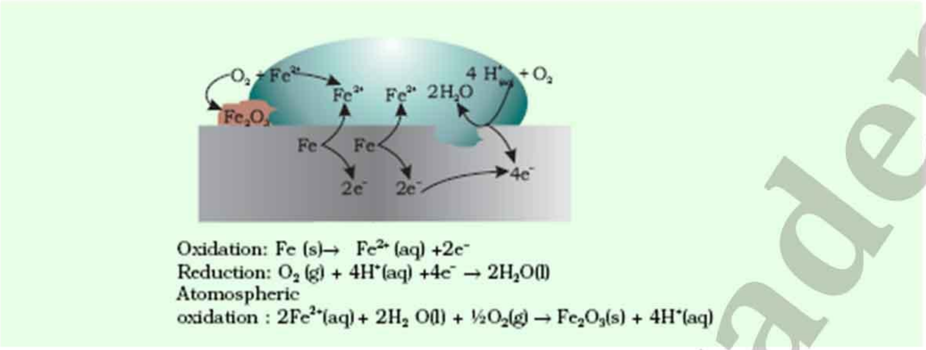

Fig. 5.14 Corrosion of iron in atmosphere.

2. We expand croreof Rupees and even thousands of lives every year due to corrosion. How can be preventing it. Explain.

Ans : (i) By Galvanization: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.

(ii) By greasing /oiling (to keep away the object from the contact of air & moisture.)

(iii)By painting (to keep away the object from the contact of air & moisture.)

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