metallurgical processes in which pure metals are obtained from their compounds in ores.

(b) Non-metal displacement: The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water. Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals.

Part IV

Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them .

1. Oxidation Number Method: In writing Equations for oxidation-reduction reactions, Just as for other reactions, the compositions And formulas must be known for the Substances that react and for the products that Are formed. The oxidation number method is Now best illustrated in the following steps:

Step 1: Write the correct formula for each Reactant and product.

Step 2: Identify atoms which undergo change In oxidation number in the reaction by Assigning the oxidation number to all elements In the reaction.

Step 3: Calculate the increase or decrease in The oxidation number per atom and for the Entire molecule/ion in which it occurs. If these Are not equal then multiply by suitable Number so that these become equal.

Step 4: Ascertain the involvement of ions if The reaction is taking place in water, add H^+ Or OH– Ions to the expression on the appropriate Side so that the total ionic charges of reactants and products are equal. If the reaction is Carried out in acidic solution, use H^+ Ions in The equation; if in basic solution, use OH^- Ions.

Step 5 : Make the numbers of hydrogen atoms In the expression on the two sides equal by Adding water (H_2O) molecules to the reactants Or products. Now, also check the number of Oxygen atoms. If there are the same number Of oxygen atoms in the reactants and Products, the equation then represents the Balanced redox reaction.

(b) Half Reaction Method: In this method, The two half equations are balanced separately And then added together to give balanced Equation. Suppose we are to balance the equation Showing the oxidation of Fe2+ 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. The following steps are involved in this task.

Step 1: Produce unbalanced equation for the Reaction in ionic form :

Step 2: Separate the equation into half- Reactions:

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

$$\text{Reduction half : } \overset{+6}{Cr_2}\overset{-2}{O_7^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq)$$

Step 3: Balance the atoms other than O and H in each half reaction individually. Here the Oxidation half reaction is already balanced with Respect to Fe atoms. For the reduction half Reaction, we multiply the $Cr3^+$ by 2 to balance Cr atoms.

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

Step 4: For reactions occurring in acidic Medium, add H_2O to balance O atoms and H^+ To balance H atoms. Thus, we get :

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2\,Cr^{3+}(aq) + 7H_2O\,(l)$$

Step 5: Add electrons to one side of the half Reaction to balance the charges. If need be, Make the number of electrons equal in the two Half reactions by multiplying one or both half Reactions by appropriate number. The oxidation half reaction is thus rewritten To balance the charge:

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

Now in the reduction half reaction there are Net twelve positive charges on the left hand side And only six positive charges on the right hand Side. Therefore, we add six electrons on the left Side.

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

To equalise the number of electrons in both The half reactions, we multiply the oxidation Half reaction by 6 and write as :

$$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$$

Step 6: We add the two half reactions to Achieve the overall reaction and cancel the Electrons on each side. This gives the net ionic Equation as :

$6Fe_2$+(aq) + $Cr_2O_7^{2-}$(aq) + $14H^+$ (aq) → 6 Fe^{3+}(aq) + 2Cr $^{3+}$(aq) + $7H_2O$(l)

Step 7: Verify that the equation contains the Same type and number of atoms and the same Charges on both sides of the equation. This last Check reveals that the equation is fully Balanced with respect to number of atoms and The charges. For the reaction in a basic medium, first Balance the atoms as is done in acidic medium. Then for each H^+ Ion, add an equal number of OH– Ions to both sides of the equation. Where H^+ And OH– Appear on the same side of the Equation, combine these to give H_2O.

[A] MCQ

1) .... is based on the change in the oxidation number of reducing agent and the oxidising agent.

a) Oxidation number method
b) Half Reaction Method
c) Redox reaction Method
d) Half reduction method

Ans- a) Oxidation number method

2) ...is based on splitting the redox reaction into two half reactions.

a) Oxidation number method
b) Half Reaction Method
c) Redox reaction Method
d) Half reduction method

Ans- b) Half reaction method

3) To ascertain the involvement of ions if the reaction is carried out in acidic solution, use ... ions in the equation.

a) OH^-
b) H^-
c) H^+
d) OH^+

Ans- c)H^+

4) To ascertain the involvement of ions if the reaction is carried out in basic solution, use ... ions in the equation.

a) OH^+
b) H^-
c) H^+
d) OH^-

Ans- d) OH^-

5) For the reaction in a basic medium, first balance the atoms as is done in ... medium.

a) Neutral
b) basic

c) acidic
d) All the above

Ans- c) acidic

[B]Short Answers

1) What are two methods are used to balance chemical equations for redox processes.

Ans- Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them .

2) What is half reaction method ?

Ans- In the Half Reaction method, The two half equations are balanced separately And then added together to give balanced Equation. Suppose we are to balance the equation Showing the oxidation of Fe2+ 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.

[C]Long Answers

1) Explain Oxidation number method.

Ans- Oxidation Number Method: In writing Equations for oxidation-reduction reactions, Just as for other reactions, the compositions And formulas must be known for the Substances that react and for the products that Are formed. The oxidation number method is Now best illustrated in the following steps:

Step 1: Write the correct formula for each Reactant and product.

Step 2: Identify atoms which undergo change In oxidation number in the reaction by Assigning the oxidation number to all elements In the reaction.

Step 3: Calculate the increase or decrease in The oxidation number per atom and for the Entire molecule/ion in which it occurs. If these Are not equal then multiply by suitable Number so that these become equal.

Step 4: Ascertain the involvement of ions if The reaction is taking place in water, add H^+ Or OH^- Ions to the expression on the appropriate Side so that the total ionic charges of reactants and products are equal. If the reaction is Carried out in acidic solution, use H^+ Ions in The equation; if in basic solution, use OH^- Ions.

Step 5 : Make the numbers of hydrogen atoms In the expression on the two sides equal by Adding water (H_2O) molecules to the reactants Or products. Now, also check the number of Oxygen atoms. If there are the same number Of oxygen atoms in the reactants and Products, the equation then represents the Balanced redox reaction.

2) Explain half reaction method suitable example .

Ans- Half Reaction Method: In this method, The two half equations are balanced separately And then added together to give balanced Equation. Suppose we are to balance the equation Showing the oxidation of Fe2+ 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. The following steps are involved in this task.

Step 1: Produce unbalanced equation for the Reaction in ionic form :

Step 2: Separate the equation into half- Reactions:

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

$$\text{Reduction half}: \overset{+6\ -2}{Cr_2O_7^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq)$$

Step 3: Balance the atoms other than O and H in each half reaction individually. Here the Oxidation half reaction is already balanced with Respect to Fe atoms. For the reduction half Reaction, we multiply the $Cr3^+$ by 2 to balance Cr atoms.

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

Step 4: For reactions occurring in acidic Medium, add H_2O to balance O atoms and H^+ To balance H atoms. Thus, we get :

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2\,Cr^{3+}(aq) + 7H_2O\,(l)$$

Step 5: Add electrons to one side of the half Reaction to balance the charges. If need be, Make the number of electrons equal in the two Half reactions by multiplying one or both half Reactions by appropriate number. The oxidation half reaction is thus rewritten To balance the charge:

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

Now in the reduction half reaction there are Net twelve positive charges on the left hand side And only six positive charges on the right hand Side. Therefore, we add six electrons on the left Side.

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

To equalise the number of electrons in both The half reactions, we multiply the oxidation Half reaction by 6 and write as :

$$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$$

Step 6: We add the two half reactions to Achieve the overall reaction and cancel the Electrons on each side. This gives the net ionic Equation as :

$6Fe_2$+(aq) + $Cr_2O_7^{2-}$(aq) + $14H^+$ (aq) → 6 Fe^{3+}(aq) + 2Cr $^{3+}$(aq) + $7H_2O$(l)

Step 7: Verify that the equation contains the Same type and number of atoms and the same Charges on both sides of the equation. This last Check reveals that the equation is fully Balanced with respect to number of atoms and The charges

Part V

Titrations In acid-base systems we come across with a Titration method for finding out the strength of One solution against the other using a pH Sensitive indicator. Similarly, in redox systems, The titration method can be adopted to determine the strength of a reductant/oxidant Using a redox sensitive indicator. The usage of Indicators in redox titration is illustrated below:

i. In one situation, the reagent itself is Intensely coloured, e.g., permanganate ion, MnO_4^- . Here MnO_4^- Acts as the self indicator. The visible end point in this case is Achieved after the last of the reductant (Fe_2^+ Or $C_2O_4^{2-}$) is oxidised and the first lasting Tinge of pink colour appears at MnO_4^- Concentration as low as 10^{-6}mol dm^{-3} (10^{-6} mol L^{-1}). This ensures a minimal 'overshoot' in colour beyond the Equivalence point, the point where the Reductant and the oxidant are equal in Terms of their mole stoichiometry.

ii. If there is no dramatic auto-colour change (as with MnO_4^- Titration), there are Indicators which are oxidised immediately After the last bit of the reactant is Consumed, producing a dramatic colour Change. The best example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but Oxidises the indicator substance Diphenylamine just after the equivalence Point to produce an intense blue colour, Thus signalling the end point.

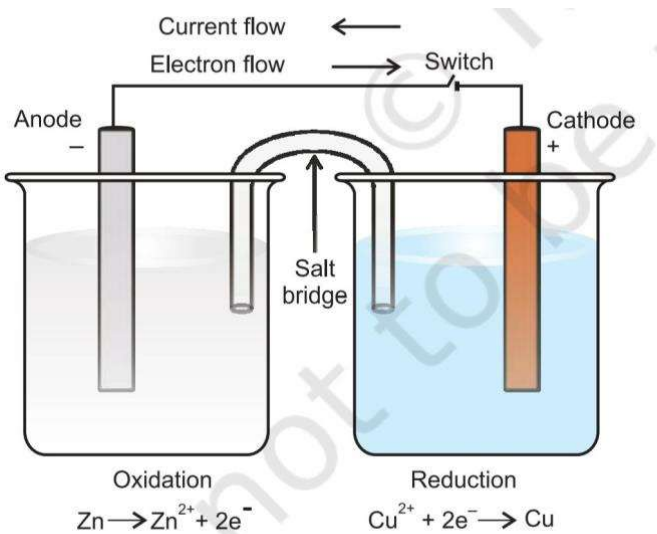
iii. There is yet another method which is Interesting and quite common. Its use is Restricted to those reagents which are able To oxidise I^- Ions, say,

for example, Cu(II): $2\ Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$

Limitations of Concept of Oxidation Number, The concept of redox processes has been Evolving with time. This process of evolution Is continuing. In fact, in recent past the Oxidation process is visualised as a decrease In electron density and reduction process as An increase in electron density around the Atom(s) involved in the reaction.

The experiment corresponding to reaction , can also be observed if zinc rod is Dipped in copper sulphate solution. The redox Reaction takes place and during the reaction, zinc is oxidised to zinc ions and copper ions Are reduced to metallic copper due to direct Transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now We modify the experiment in such a manner That for the same redox reaction transfer of Electrons takes place indirectly. This Necessitates the separation of zinc metal from

Copper sulphate solution. We take copper Sulphate solution in a beaker and put a Copper strip or rod in it. We also take zinc Sulphate solution in another beaker and put A zinc rod or strip in it. Now reaction takes Place in either of the beakers and at the Interface of the metal and its salt solution in Each beaker both the reduced and oxidized Forms of the same species are present. These Represent the species in the reduction and Oxidation half reactions. A redox couple is Defined as having together the oxidised and Reduced forms of a substance taking part in An oxidation or reduction half reaction. This is represented by separating the Oxidised form from the reduced form by a Vertical line or a slash representing an Interface (e.g. solid/solution). For example In this experiment the two redox couples are Represented as $Zn2^+/Zn$ and $Cu2^+/Cu$. In both Cases, oxidised form is put before the reduced Form. Now we put the beaker containing copper sulphate solution and the beaker Containing zinc sulphate solution side by side. We connect solutions in two Beakers by a salt bridge (a U-tube containing a solution of potassium chloride or Ammonium nitrate usually solidified by Boiling with agar agar and later cooling to a Jelly like substance). This provides an electric Contact between the two solutions without Allowing them to mix with each other. The Zinc and copper rods are connected by a metallic Wire with a provision for an ammeter and a Switch. The set-up as shown in figure is known As Daniell cell.



When the switch is in the off Position, no reaction takes place in either of The beakers and no current flows through the Metallic wire. As soon as the switch is in the On position, we make the following Observations:

a) The transfer of electrons now does not take Place directly from Zn to Cu^{2+} but through The metallic wire connecting the two rods As is apparent from the arrow which Indicates the flow of current.
b) The electricity from solution in one beaker To solution in the other beaker flows by the Migration of ions through the salt bridge. We know that the flow of current

is possible Only if there is a potential difference Between the copper and zinc rods known As electrodes here.

The potential associated with each Electrode is known as electrode potential. If The concentration of each species taking part In the electrode reaction is unity and further the Reaction is carried out at 298K, then the Potential of each electrode is said to be the Standard Electrode Potential. By Convention, the standard electrode potential The Electrode potential value for each electrode Process is a measure of the relative tendency Of the active species in the process to remain In the oxidised/reduced form. A negative E° Means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A Positive E° Means that the redox couple is a Weaker reducing agent than the H^+/H_2 couple. The standard electrode potentials are very Important and we can get a lot of other useful Information from them.

[A] MCQ

1) The potential associated with each electrode is known as ...

a) electrode potential
b) oxidation potential
c) reduction potential
d) None of above

Ans- a) electrode potential

2) If the concentration of each species taking part in the electrode reaction is unity and further the reaction is carried out at 298K, then the potential of each electrode is said to be the…

a) Normal Electrode Potential
b) Standard Electrode Potential
c) Critical Electrode Potential
d) None of above

Ans- b) Standard Electrode Potential.

3) A negative E° means that the redox couple is a ... reducing agent than the H^+/H_2 couple.

a) Equal
b) Weaker
c) stronger
d) Either a) or b)

Ans- c) stronger

4) A positive E° means that the redox couple is a ... reducing agent than the H^+/H_2 couple.

a) Equal

b) Weaker
c) stronger
d) Either a) or c)

Ans- b) weaker

5) A ... is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.

a) redox potential
b) redox efficiency
c) redox couple
d) redox reaction

Ans- c) redox couple

[B]Short Answers

1) What are the observation if switch is on position of Daniell cell ?

Ans- The following observations listed when the switch is in the on position.

1. The transfer of electrons now does not take Place directly from Zn to Cu^{2+} but through The metallic wire connecting the two rods As is apparent from the arrow which Indicates the flow of current.
2. The electricity from solution in one beaker To solution in the other beaker flows by the Migration of ions through the salt bridge. We know that the flow of current is possible Only if there is a potential difference Between the copper and zinc rods known As electrodes here.

2) Explain limitations of Concept of Oxidation Number.

Ans- The concept of redox processes has been Evolving with time. This process of evolution Is continuing. In fact, in recent past the Oxidation process is visualised as a decrease In electron density and reduction process as An increase in electron density around the Atom(s) involved in the reaction.

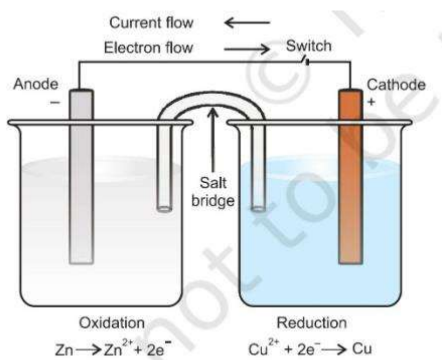
3) Write short note on standard electrode potential .

Ans- If The concentration of each species taking part In the electrode reaction is unity and further the Reaction is carried out at 298K, then the Potential of each electrode is said to be the Standard Electrode Potential. By Convention, the standard electrode potential The Electrode potential value for each electrode Process is a measure of the relative tendency Of the active species in the process to remain In the oxidised/reduced form. A negative E° Means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A Positive E° Means that the redox couple is a Weaker reducing agent than the H^+/H_2 couple.

[C]Long Answers

1) Explain the set up of Daniell cell .

Ans- Take copper Sulphate solution in a beaker and put a Copper strip or rod in it. We also take zinc Sulphate solution in another beaker and put A zinc rod or strip in it. Now reaction takes Place in either of the beakers and at the Interface of the metal and its salt solution in Each beaker both the reduced and oxidized Forms of the same species are present. These Represent the species in the reduction and Oxidation half reactions. A redox couple is Defined as having together the oxidised and Reduced forms of a substance taking part in An oxidation or reduction half reaction. This is represented by separating the Oxidised form from the reduced form by a Vertical line or a slash representing an Interface (e.g. solid/solution). For example In this experiment the two redox couples are Represented as Zn2+/Zn and Cu2+/Cu. In both Cases, oxidised form is put before the reduced Form. Now we put the beaker containing copper sulphate solution and the beaker Containing zinc sulphate solution side by side. We connect solutions in two Beakers by a salt bridge (a U-tube containing a solution of potassium chloride or Ammonium nitrate usually solidified by Boiling with agar agar and later cooling to a Jelly like substance). This provides an electric Contact between the two solutions without Allowing them to mix with each other. The Zinc and copper rods are connected by a metallic Wire with a provision for an ammeter and a Switch. The set-up as shown in figure is known As Daniell cell.



2) Give the usage of indicators in redox titration.

Ans- The usage of Indicators in redox titration is illustrated below:

i. In one situation, the reagent itself is Intensely coloured, e.g., permanganate ion, MnO_4^- . Here MnO_4^- Acts as the self indicator. The visible end point in this case is Achieved after the last of the reductant (Fe_2^+ Or $C_2O_4^{2-}$) is oxidised and the first lasting Tinge of pink colour appears at MnO_4^- Concentration as low as 10^{-6}mol dm^{-3} (10^{-6} mol L^{-1}). This ensures a minimal 'overshoot' in colour beyond the

Equivalence point, the point where the Reductant and the oxidant are equal in Terms of their mole stoichiometry.

ii. If there is no dramatic auto-colour change (as with MnO_4^- Titration), there are Indicators which are oxidised immediately After the last bit of the reactant is Consumed, producing a dramatic colour Change. The best example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but Oxidises the indicator substance Diphenylamine just after the equivalence Point to produce an intense blue colour, Thus signalling the end point.

iii. There is yet another method which is Interesting and quite common. Its use is Restricted to those reagents which are able To oxidise I^- Ions, say,

for example, Cu(II): $2\,Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$