

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 02 (Class XI, Semester - 2)
Module Name/Title	Redox Reactions – Part 2
Module Id	kech_20802
Pre-requisites	Oxidation, Reduction, Redox, Oxidant, Reductant, Oxidation Number/Oxidation State.
Objectives	After going through this module, the learner will be able to: <ul style="list-style-type: none">• Balance chemical equations using oxidation number• Balance chemical equations using half reaction method;• Learn the concept of redox reactions in terms of electrode processes
Keywords	Oxidation, Reduction, Redox, Oxidant, Reductant, Oxidation Number, Oxidation State,

2. Development Team

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Balancing of Redox Reactions

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.

(a) 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. (If you realise that two substances are reduced and nothing is oxidised or vice-versa, something is wrong. Either the formulas of reactants or products are wrong or the oxidation numbers have not been assigned properly).

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.

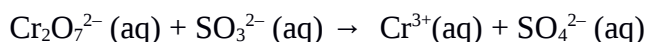
Let us now explain the steps involved in the method with the help of a few problems given below:

Problem 1

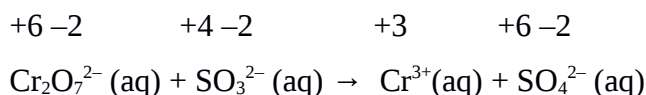
Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite, Na_2SO_3 , in an acid solution to give chromium(III) ion and the sulphate ion.

Solution

Step 1: The skeletal ionic equation is:

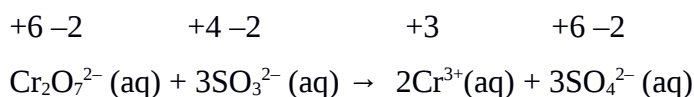


Step 2: Assign oxidation numbers for Cr and S



This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant.

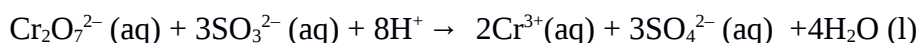
Step 3: Calculate the increase and decrease of oxidation number, and make them equal: from step-2 we can notice that there is change in oxidation state of chromium and sulphur. Oxidation state of chromium changes from +6 to +3. There is decrease of +3 in oxidation state of chromium on right hand side of the equation. Oxidation state of Sulphur changes from +4 to +6. There is an increase of +2 in the oxidation state of sulphur on right hand side. To make the increase and decrease of oxidation state equal, place numeral 2 before chromium ion on right hand side and numeral 3 before sulphate ion on right hand side and balance the chromium and sulphur atoms on both the sides of the equation. Thus we get



Step 4: As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add 8H^+ on the left to make ionic charges equal



Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., $4\text{H}_2\text{O}$) on the right to achieve balanced redox change.



Steps for Balancing by oxidation number Method in alkaline medium:

Step 1: The skeletal ionic equation

Step 2: Assign oxidation numbers to elements in the reaction.

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

Step 4: As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add OH^- ions to make ionic charges equal.

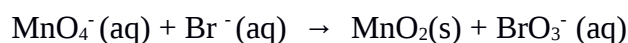
Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., $4\text{H}_2\text{O}$) on the right to achieve balanced redox change.

Problem 2

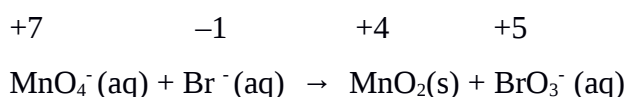
Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

Solution

Step 1: The skeletal ionic equation is :

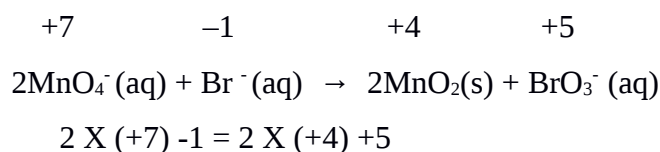


Step 2: Assign oxidation numbers for Mn and Br

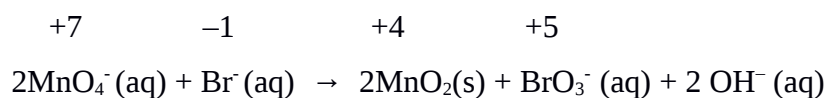


The equation indicates that permanganate ion is the oxidant and bromide ion is the reductant.

Step 3: Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease.



Step 4: As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add 2OH^- ions on the right to make ionic charges equal.

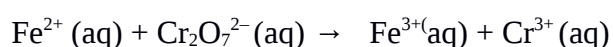


Step 5: Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one H_2O molecule) on the left side to achieve balanced redox change.

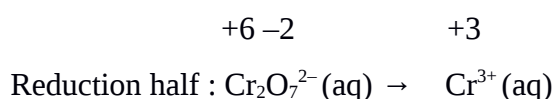
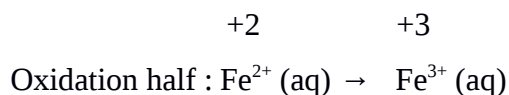


(b) **Half Reaction Method:** In this method, the two half equations are balanced separately and then added together to give balanced equation. Suppose we are to balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(\text{Cr}_2\text{O}_7)^{2-}$ in acidic medium, wherein, $(\text{Cr}_2\text{O}_7)^{2-}$ ions are reduced to Cr^{3+} ions. The following steps are involved in this task.

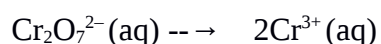
Step 1: Produce unbalanced equation for the reaction in ionic form :



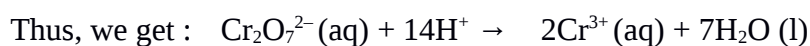
Step 2: Separate the equation into half reactions:



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 Cr^{3+} by 2 to balance Cr atoms.



Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.



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:



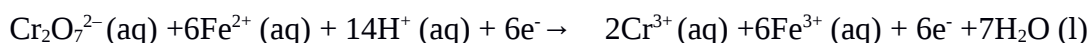
Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.



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



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 :



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 .

Thus we can summarise the Steps for Balancing by ion-electron (Half Reaction Method) in acidic medium:

Step 1: Write the skeletal ionic equation

Step 2: Divide the equation into two half-reactions as Oxidation half and Reduction half

Step 3: Balance the atoms undergoing change of oxidation states in the two half reactions separately.

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.

Step 5: Add electrons to one side of the half reaction to balance the charges. Electrons will be added to product side in oxidation half and reactant side in case of reduction half.

Step 6: Equalise the number of electrons in both the half reactions by multiplying by the suitable whole number. Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation.

Steps for Balancing by ion-electron (Half Reaction Method) in alkaline medium:

Step 1: Write the skeletal ionic equation

Step 2: Divide the equation into two half-reactions as Oxidation half and Reduction half

Step 3: Balance the atoms undergoing change of oxidation states in the two half reactions separately.

Step 4: Balance the O atoms in the half reactions, by adding water molecules. Balance the H atoms, by adding H^+ ions. As the reaction takes place in a basic solution, therefore, add same number of OH^- ions to both sides of the Equation as the number of H^+ ions. Where H^+ and OH^- appear on the same side of equation, combine these to give H_2O .

Step 5: Balance the charges of the two half-reactions by adding electrons. Electrons will be added to product side in oxidation half and reactant side in case of reduction half.

Step 6: Equalise the number of electrons in both the half reactions by multiplying by the suitable whole number. Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

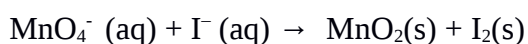
Step 7: Do a final verification that the equation is balanced in respect of the number of atoms and charges on both sides.

Problem 3

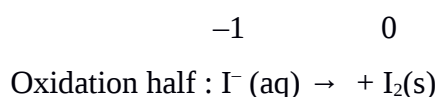
Permanganate (VII) ion, MnO_4^- in basic solution oxidises iodide ion, I^- to produce molecular iodine (I_2) and manganese (IV) oxide (MnO_2). Write a balanced ionic equation to represent this redox reaction.

Solution

Step 1: First we write the skeletal ionic equation, which is



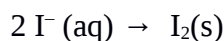
Step 2: The two half-reactions are:



Reduction half: $\text{MnO}_4^- (\text{aq}) \rightarrow \text{MnO}_2(\text{s})$

↓

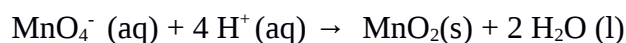
Step 3: To balance the I atoms in the oxidation half reaction, we rewrite it as:



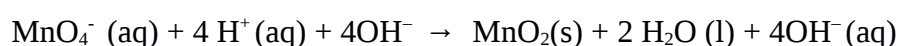
Step 4: To balance the O atoms in the reduction half reaction, we add two water molecules on the right:



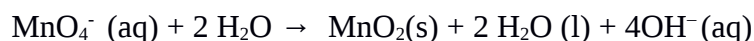
To balance the H atoms, we add four H^+ ions on the left:



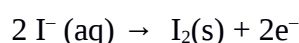
As the reaction takes place in a basic solution, therefore, for four H^+ ions, we add four OH^- ions to both sides of the equation:



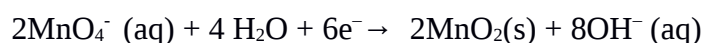
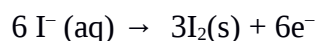
Replacing the H^+ and OH^- ions with water, the resultant equation is:



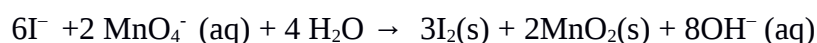
Step 5: In this step we balance the charges of the two half-reactions in the manner depicted as:



Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.



Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.



Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

Redox Reactions as the Basis for 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 $\text{C}_2\text{O}_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as $10^{-6} \text{ mol dm}^{-3}$ ($10^{-6} \text{ mol L}^{-1}$). 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 $\text{Cr}_2\text{O}_7^{2-}$, 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): $2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow \text{Cu}_2\text{I}_2(\text{s}) + \text{I}_2(\text{aq})$ (8.59) This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions ($\text{S}_2\text{O}_3^{2-}$), which too is a redox reaction: $\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ (8.60) I_2 , though insoluble in water, remains in solution containing KI as KI_3 . On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only

3.4 Limitations of Concept of Oxidation Number

As you have observed in the above discussion, 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 spare electron density around the atom(s) involved in the reaction.

4. Redox Reactions and Electrode Processes

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 Zn^{2+}/Zn and Cu^{2+}/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:

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.

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 (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) 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 (E^0) of hydrogen electrode is 0.00 volts. 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^0 means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive E^0 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. The values of standard electrode potentials for some selected electrode processes (reduction reactions) are given in Table.

Table 1: The Standard Electrode Potentials at 298 K

Ions are present as aqueous species and H₂O as liquid; gases and solids are shown by g and s respectively.

	Reaction (Oxidised form + ne^- → Reduced form)	E^\ominus / V	
↑ Increasing strength of oxidising agent	$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
	$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
	$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$	1.78
	$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$	1.51
	$Au^{3+} + 3e^-$	$\rightarrow Au(s)$	1.40
	$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$	1.33
	$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
	$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$	1.23
	$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
	$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$	0.97
	$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$	0.92
	$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
	$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
	$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
	$I_2(s) + 2e^-$	$\rightarrow 2I^-$	0.54
	$Cu^+ + e^-$	$\rightarrow Cu(s)$	0.52
	$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
	$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$	0.22
	$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$	0.10
	$2H^+ + 2e^-$	$\rightarrow H_2(g)$	0.00
	$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	-0.13
	$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	-0.14
	$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$	-0.25
	$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	-0.44
	$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	-0.74
	$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	-0.76
	$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-$	-0.83
	$Al^{3+} + 3e^-$	$\rightarrow Al(s)$	-1.66
	$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$	-2.36
	$Na^+ + e^-$	$\rightarrow Na(s)$	-2.71
	$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	-2.87
	$K^+ + e^-$	$\rightarrow K(s)$	-2.93
	$Li^+ + e^-$	$\rightarrow Li(s)$	-3.05

1. A negative E^\ominus means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
2. A positive E^\ominus means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

5. Summary

We can summarize through this module that:

- Oxidation number and ion-electron method both are useful means in writing equations for the redox reactions.
- The equation has to be balanced by making the electron released and accepted to be equal.

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- The equation should be balanced keeping in mind the medium to be acidic or basic.
 - Different redox couple can be used to create a cell.
 - Potential associated with each electrode is known as electrode potential.
 - Different electrodes are assigned the with H^+/H_2 couple having electrode potential assigned as 0.00V