

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 02 (Class XII, Semester - 2)
Module Name/Title	Redox Reactions – Part 1
Module Id	kech_20801
Pre-requisites	Knowledge about Chemical Change, Indicators of chemical reaction, Types of chemical reactions, Balancing of chemical reaction by hit and trial method
Objectives	<p>After going through this module, the learner will be able to:</p> <ul style="list-style-type: none">• Identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously;• Define the terms oxidation, reduction, oxidant (oxidizing agent) and reductant (reducing agent);• Explain mechanism of redox reactions by electron transfer process;• Use the concept of oxidation number to identify oxidant and reductant in a reaction;• Classify redox reaction into combination (synthesis), decomposition, displacement and disproportionation reactions;• Suggest a comparative order among various reductants and oxidants;• Find oxidation number/ oxidation state of a given element.
Keywords	Oxidation, Reduction, Redox, Oxidant, Reductant, Oxidation Number, Oxidation State,

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Introduction

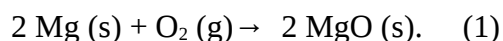
Chemistry deals with varieties of matter and change of one kind of matter into the other. In your lower classes you have studied how to identify that a reaction is occurring by any of the simple observations like:

- Change of temperature
- Evolution of a gas
- Change of colour.

You also learned about transformation of matter from one kind into another through the various types of reactions and classified the reactions as : combination, decomposition, double decomposition, neutralization, oxidation and reduction reactions.

1. Classical Idea of Redox Reactions – Oxidation and Reduction Reactions

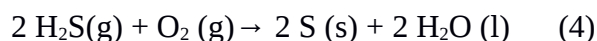
Originally, the term oxidation was used to describe the addition of oxygen to an element or a compound. You have studied oxidation as addition of oxygen as in the following reactions:



In reactions (1) and (2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.

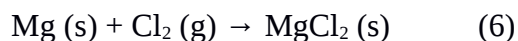


A careful examination of reaction (3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.



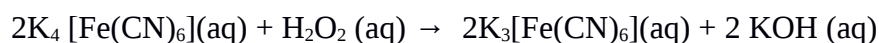
As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (1to4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with

fluorine, chlorine and sulphur etc. occurs according to the following reactions :



Incorporating the reactions (5 to7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as

oxidation. Thus the reaction :



is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide.

To summarise, the term “oxidation” is defined as:

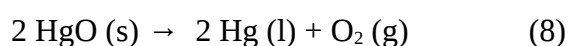
- the addition of oxygen to a substance
- the addition of electronegative element to a substance
- the removal of hydrogen from a substance.
- the removal electropositive element from a substance.

Similarly

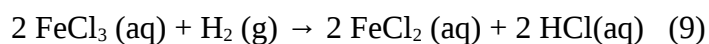
To summarise, the term “reduction” is defined as:

- the addition of hydrogen to a substance
- the addition of electropositive element to a substance
- the removal of oxygen from a substance.
- the removal electronegative element from a substance.

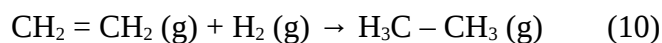
The examples may be:



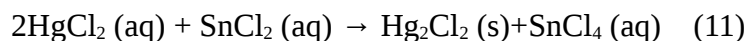
(removal of oxygen from mercuric oxide)



(removal of electronegative element, chlorine from ferric chloride)



(addition of hydrogen)

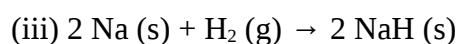
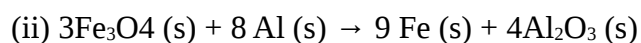
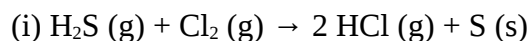


(addition of mercury to mercuric chloride)

A close look at all the reactions (1 to 11) makes us realise that oxidation and reduction do not occur independently these processes always occur simultaneously, hence, the word “redox” was coined for this class of chemical reactions.

Problem 1

In the reactions given below, identify the species undergoing oxidation and reduction:



Solution

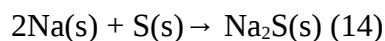
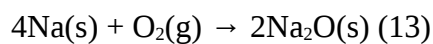
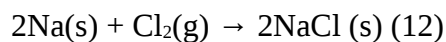
(i) H_2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed from S). Chlorine is reduced due to addition of hydrogen to it.

(ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide (Fe_3O_4) is reduced because oxygen has been removed from it.

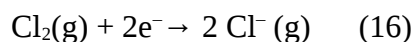
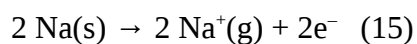
(iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced. Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

2. Redox Reactions in Terms of Electron Transfer Reactions

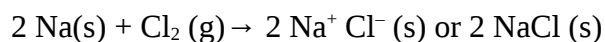
According to the discussions above we understand that the following reactions are redox reactions:



Let us write reaction 12 in terms of loss and gain of electrons from our previous knowledge and break the reaction into two steps :



Each of the above two steps(15,16) is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction :



Now convert reaction 13 and 14 also into half reactions for practice. The half reactions that involve loss of electrons are called oxidation half reactions. Similarly, the half reactions that involve gain of electrons are called reduction half reactions.

To summarise, we may mention that-

Oxidation: Loss of electron(s) by any species.

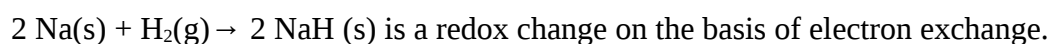
Reduction: Gain of electron(s) by any species.

Oxidising agent : Acceptor of electron(s).

Reducing agent : Donor of electron(s).

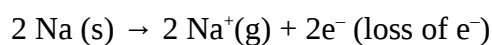
Problem 2

Justify that the reaction :

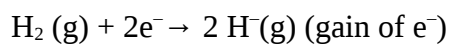


Solution

Since in the above reaction the compound formed is an ionic compound, which may also be represented as $\text{Na}^+\text{H}^-(\text{s})$, this suggests that one half reaction in this process is :



and the other half reaction is:



Thus we can see that sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change.

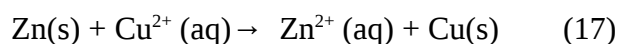
2.1 Competitive Electron Transfer Reactions

In your previous classes you have studied about reactivity series and its use to explain displacement and double displacement reactions. Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 1,

for about one hour. After some time the iron strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of Zn^{2+} ions among the products can easily be judged when the blue colour of the solution due to Cu^{2+} has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing Zn^{2+} ions, appearance of white zinc sulphide, ZnS can be seen on making the solution alkaline with ammonia.

The reaction between metallic zinc and the

aqueous solution of copper nitrate is :



In reaction (17), zinc has lost electrons to form Zn^{2+} and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons, something must be reduced, accepting the electrons lost by zinc. Copper ion is reduced by gaining electrons from the zinc.

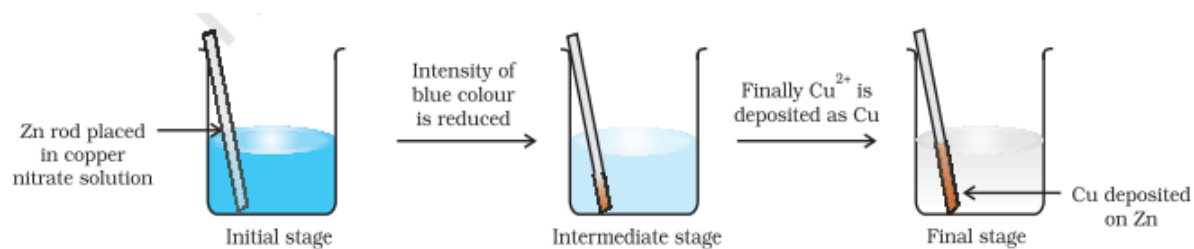
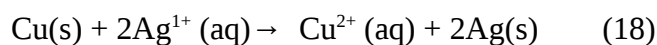


Fig. 1 Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.

Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 2. The solution develops blue colour due to the formation of Cu^{2+} ions on account of the reaction:



Here, Cu(s) is oxidised to $\text{Cu}^{2+}(\text{aq})$ and $\text{Ag}^+(\text{aq})$ is reduced to Ag(s) .

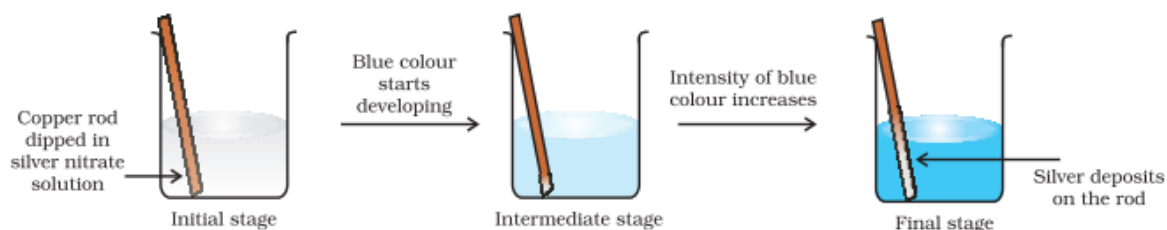


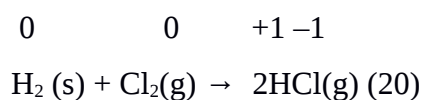
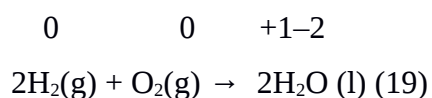
Fig. 2 Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker.

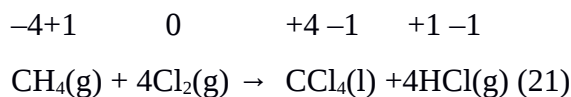
By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order: $\text{Zn} > \text{Cu} > \text{Ag}$. We can make our list more vast and design a metal activity series or electrochemical series. This would help us to design a class of cells, named as Galvanic cells in which electrical energy is produced by virtue of chemical reactions.

3. Oxidation Number

It is easy for us to understand a redox reaction in terms of electron gain and loss for reactions involving electrovalent compounds. Let us understand how to recognize redox for reactions with covalent compounds and molecules.

In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electronegative atom. For example, we show charge on each of the atoms forming part of the following reactions :





It may be emphasised that the assumption of electron transfer is made for theoretical purpose only and it leads to the simple description of redox reactions.

Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron pair in a covalent bond belongs entirely to more electronegative element.

It is not always possible to remember or make out easily in a compound/ion, which element is more electronegative than the other. Therefore, a set of rules has been formulated to determine the oxidation number of an element in a compound/ion.

Let us state the rules for the calculation of oxidation number. These rules are:

1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H_2 , O_2 , Cl_2 , O_3 , P_4 , S_8 , Na, Mg, Al has the oxidation number zero.
2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion, +2, Fe^{3+} ion, +3, Cl^- ion, -1, O_2^{2-} ion, -2; and so on.
3. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds.
4. In all its compounds, fluorine has an oxidation number of -1.
5. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and CaH_2 , its oxidation number is -1.
6. The oxidation number of oxygen in most compounds is -2.

But for the case of peroxides, superoxides and compounds with fluorine:

Peroxides (e.g., H_2O_2 , Na_2O_2), each oxygen atom is assigned an oxidation number of -1

Superoxides (e.g., KO_2 , RbO_2) each oxygen atom is assigned an oxidation number of $-(1/2)$. **Oxygen bonded to fluorine** e.g., oxygen difluoride (OF_2) and dioxygendifluoride (O_2F_2), the oxygen is assigned an oxidation number of +2 and +1, respectively.

7. Other halogens (Cl, Br, and I) show an oxidation number of -1, when they occur as halide ions in their compounds. In rest of their compounds oxidation states may be worked out by the fixed oxidation states as of other elements as stated in points 3 to 6.

8. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion. Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion, $(\text{CO}_3)^{2-}$ must equal -2 .
9. The atoms of transition elements usually display several positive oxidation states. The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the long form of periodic table) for the other groups. Thus, it implies that the highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table. In the third period, the highest value of oxidation number changes from 1 to 7

Group	1	2	13	14	15	16	17
Element	Na	Mg	Al	Si	P	S	Cl
Compound	NaCl	MgSO ₄	AlF ₃	SiCl ₄	P ₄ O ₁₀	SF ₆	HClO ₄
Highest oxidation number state of the group element	+1	+2	+3	+4	+5	+6	+7

Now let us apply above rules, to find out the oxidation number of the desired element in a molecule or in an ion. A term that is often used interchangeably with the oxidation number is the oxidation state. Thus in CO_2 , the oxidation state of carbon is $+4$, that is also its oxidation number and similarly the oxidation state as well as oxidation number of oxygen is -2 . This implies that the oxidation number denotes the oxidation state of an element in a compound.

2.4 Stock notation

The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as Stock notation. According to this, the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl_3 . Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl_2 and Sn(IV)Cl_4 . This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised form or reduced form. Thus, $\text{Hg}_2(\text{I)Cl}_2$ is the reduced form of Hg(II)Cl_2 .

Problem 3

Using Stock notation, represent the following compounds :HAuCl₄, Tl₂O, FeO, Fe₂O₃, CuI, CuO, MnO and MnO₂.

Solution

By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows:

HAuCl₄ → Au has 3

Tl₂O → Tl has 1

FeO → Fe has 2

Fe₂O₃ → Fe has 3

CuI → Cu has 1

CuO → Cu has 2

MnO → Mn has 2

MnO₂ → Mn has 4

Therefore, these compounds may be represented as:

HAu(III)Cl₄, Tl₂(I)O, Fe(II)O, Fe₂(III)O₃, Cu(I)I, Cu(II)O, Mn(II)O, Mn(IV)O₂.

The idea of oxidation number has been invariably applied to define oxidation, reduction, oxidising agent (oxidant), reducing agent (reductant) and the redox reaction.

To summarise, we may say that:

Oxidation: An increase in the oxidation number of the element in the given substance.

Reduction: A decrease in the oxidation number of the element in the given substance.

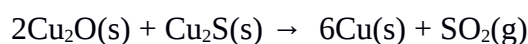
Oxidising agent/ oxidant: A reagent which can increase the oxidation number of an element in a given substance.

Reducing agent/ reductant :A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as

Redox reactions: Reactions which involve change in oxidation number of the interacting species.

Problem 4

Justify that the reaction:



is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant and which acts as a reductant.

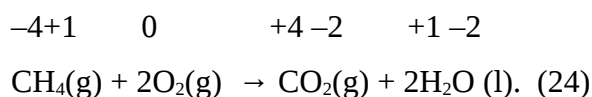
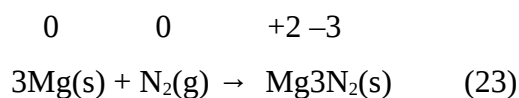
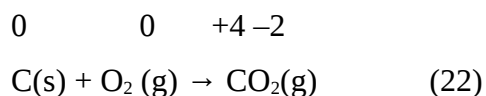
4. Types of Redox Reactions

4.1. Combination reactions

A combination reaction may be denoted in the manner:



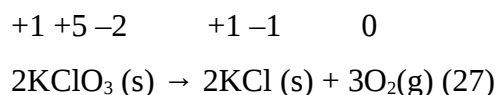
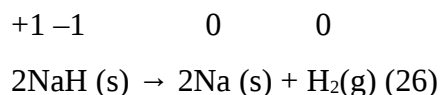
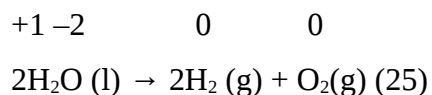
Some examples of this category are:



It may carefully be noted that there is no change in the oxidation number of hydrogen in methane.

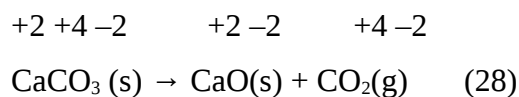
4.2. Decomposition reactions

A decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are:



It may carefully be noted that there is no change in the oxidation number of potassium in potassium chlorate in reaction (27). This may also be noted here that all decomposition reac-

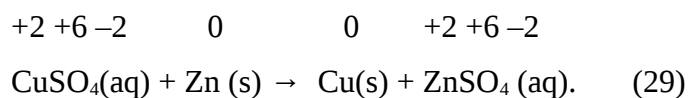
tions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.



4.3. Displacement reactions

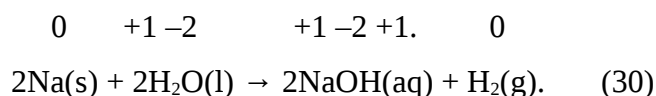
Displacement reactions fit into two categories: metal displacement and non-metal displacement.

(a) Metal displacement: A metal in a compound can be displaced by another metal in the uncombined state. An examples is:

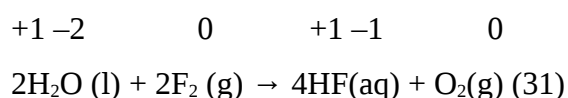


The reducing metal (Zn in this case) is a better reducing agent than the one that is being reduced (Cu) which evidently shows more capability to lose electrons as compared to the one that is reduced.

(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.



The power of halogen elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :

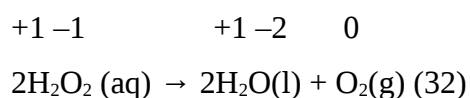


It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution .

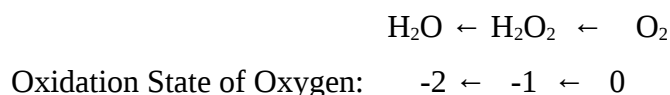
Disproportionation reactions

Disproportionation reactions are a special type of redox reactions in which a same element in one oxidation state is simultaneously oxidised and reduced.

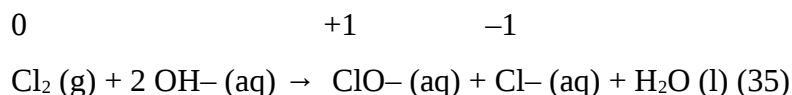
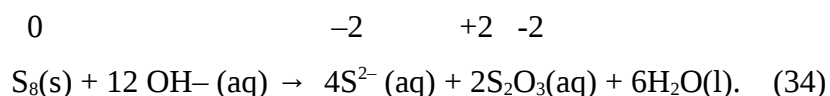
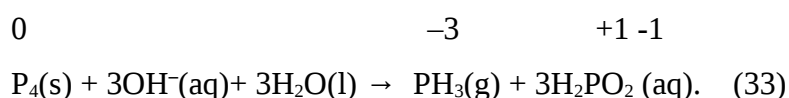
Let us understand by an example of the decomposition of hydrogen peroxide, where oxygen experiences disproportionation.



Here the oxygen of peroxide, which is present in -1 state, is converted to zero oxidation state in O_2 and decreases to -2 oxidation state in H_2O .



Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :



The reaction (8.48) describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds. It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (35), fluorine shows deviation from this behavior, can you tell why?

This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. Thus fluorine does not show a disproportionation tendency.

Problem 5

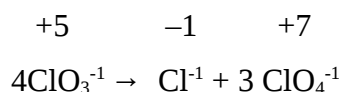
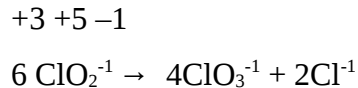
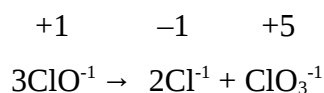
Which of the following species, do not show disproportionation reaction and why?



Also write reaction for each of the species that disproportionates.

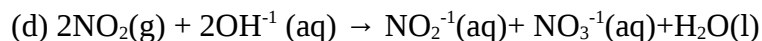
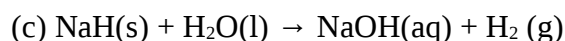
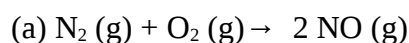
Solution

Among the oxoanions of chlorine listed above, ClO_4^{-1} does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is, +7. The disproportionation reactions for the other three oxoanions of chlorine are as follows:



Problem 6

Suggest a scheme of classification of the following redox reactions

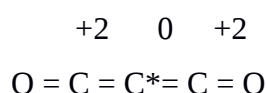


The Paradox of Fractional Oxidation Number

Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:

C_3O_2 [where oxidation number of carbon is $(4/3)$], Br_3O_8 [where oxidation number of bromine is $(16/3)$] and $Na_2S_4O_6$ (where oxidation number of sulphur is 2.5).

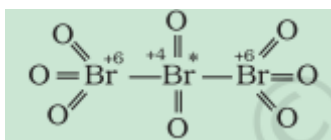
We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C_3O_2 , Br_3O_8 and $S_4O_6^{2-}$ reveal the following bonding situations:



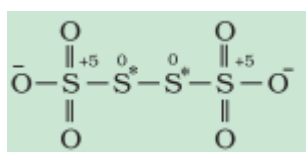
Structure of C_3O_2
(carbon suboxide)

The Carbon marked with asterisk is combined with carbon atoms only so its oxidation number is taken as '0'.

This reveals that in C_3O_2 , two carbon atoms are present in +2 oxidation state each, and the average is $4/3$. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon.



Structure of Br_3O_8 (tribromooctaoxide)



Structure of $S_4O_6^{2-}$ (tetrathionate ion)

Likewise in Br_3O_8 , each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is $16/3$.

In the same fashion, in the species $S_4O_6^{2-}$, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of

sulphurs of the $S_4O_6^{2-}$ is 2.5, whereas the reality being +5, 0, 0 and +5 oxidation number respectively for each sulphur.

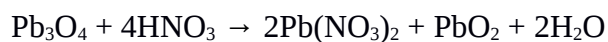
We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only.

Problem 7

Why do the following reactions proceed differently ?



and



Solution

Pb_3O_4 is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO_2 .

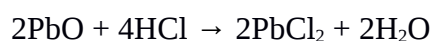
In PbO_2 , lead is present in +4 oxidation state, whereas the stable oxidation state of lead in PbO is +2. PbO_2

acts as an oxidant and, therefore, can oxidise Cl^- ion of HCl into chlorine. Whereas

PbO which is a basic oxide gives a neutralization reaction with acid HCl . Therefore, the reaction



can be splitted into two reactions namely:

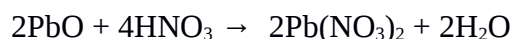


(acid-base reaction)



(redox reaction)

Since HNO_3 itself is an oxidising agent therefore, it is unlikely that the reaction may occur between PbO_2 and HNO_3 . However, the acid-base reaction occurs between PbO and HNO_3 as:



5. Summary

Oxidation may be summarised as:

Oxidation:

- Loss of electron(s) by any species
- An increase in the oxidation number of the element in the given substance.

Reduction:

- Gain of electron(s) by any species
- A decrease in the oxidation number of the element in the given substance.

Oxidising agent/ oxidant:

- A reagent which can increase the oxidation number of an element in a given substance.
- Acceptor of electron(s)

Reducing agent/ reductant :

- A reagent which lowers the oxidation number of an element in a given substance.
- Donor of electron(s)

Redox reactions: Reactions which involve change in oxidation number of the interacting species.

Redox reactions form an important class of reactions in which oxidation and reduction occur simultaneously. Three tier conceptualisation viz, classical, electronic and oxidation number, which is usually available in the texts, has been presented in detail. Oxidation, reduction, oxidising agent (oxidant) and reducing agent (reductant) have been viewed according to each conceptualisation. Oxidation numbers are assigned in accordance with a consistent set of rules.

Oxidation State/oxidation number may be found by remembering the rules as:

1. An element, in the free state, bears an oxidation number of zero.
2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion.
3. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds.
4. In all its compounds, fluorine has an oxidation number of -1.
5. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds

-
6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero.
 7. The highest value of oxidation number exhibited by an atom of an element is equal to the number of valence electrons.

Redox reactions are classified into four categories: combination, decomposition displacement and disproportionation reactions.