INTRODUCTION

The simplest and the oldest conception of oxidation was originally designated as processes involving addition of oxygen to or removal of hydrogen from substances in their chemical reactions. Exactly a similar relationship is observed when a non-metallic element, i.e., an electronegative element other than oxygen is added or a metallic element, i.e., an electro-positive element other than hydrogen is removed. But according to the modern concept, the definition has become much broader and denotes:

(i) An increase in the valency of an element in its compounds with electro-negative elements, for example, Cu₂Cl₂ to CuCl₂, FeCl₂ to FeCl₃, SnCl₂ to SnCl₄ and formation of FeS by the direct combination of iron and sulphur where iron from zerovalent state in its elementary form changes to bivalent state.

(ii) A decrease in the valency of an element in its compounds with electro-positive elements, for example, the removal of hydrogen from hydrogen sulphide and the decomposition of gold chloride into its elements involves the oxidation of sulphur and chlorine respectively.

Electrolytic processes can also be termed as oxidation processes, since the metals forming anodes dissolve to form ions and their valencies increase. In fact, the element to
be dissolved loses electrons and thus increases its positive charge or decreases its negative charge.

Oxidation, therefore, may be defined as a process which involves an increase in the positive charge or a decrease in the negative charge on an atom. According to the present day concepts it may be defined as the removal of one or more electrons from the outer shells of the atoms or ions.

The reduction is its reverse, and may be defined as a process involving a diminution in the number of positive charges or an increase in the number of negative charges on an atom. The transformation of ferric iron into ferrous iron and the combination of sulphur with hydrogen, etc., are some of the processes involving reduction.

Both oxidation and reduction occur simultaneously. The element undergoing oxidation loses electrons whereas the other undergoing reduction gains electrons. Therefore, every action involving an exchange of electrons represents an example of oxidation-reduction reaction. For example, in the oxidation of ferrous to ferric by ceric or manganic, the latter ions are reduced to cerous and manganous respectively as:

\[
4^+ + 2^+ = 3^+ + 3^+ \\
\text{Ce} + \text{Fe} = \text{Ce} + \text{Fe}^{3+}
\]

\[
3^+ + 2^+ = 2^+ + 3^+ \\
\text{Mn}^3+ + \text{Fe}^2+ = \text{Mn}^2+ + \text{Fe}^{3+}
\]
arsine and phosphine with various oxidising agents are not unambiguous, since the primary products of reaction further react in chains of reactions with a particular trend towards the formation of final products depending mainly upon the experimental conditions. For example, it is well known that sulphur dioxide and sulphites under definite conditions yield dithionate as well as sulphate both, in free and in combined states (1-8). Much the same is true for the remaining reductants. Futile attempts have been made to clear the mechanism of these reactions.

N-Bromosuccinimide, perborate and persulphate, on the other hand, are fairly strong oxidising agents. When made to react with different reducing agents, they lead to the formation of several products depending upon the nature of the reductants and the experimental conditions. Due to their oxidising character, these compounds are extensively used in industry also.

In the present work a comprehensive and interesting investigation of the mutual interactions of the fore said compounds of the two catagories has been undertaken. For such a purpose, a brief survey of hydrogen sulphide, sulphur dioxide, phosphine and arsine as reducing agents and of N-bromosuccinimide, perborate and persulphate as oxidising agents becomes almost essential.
Hydrogen sulphide as a reducing agent has been known since early nineteenth century. Schönbein (9), and Helbig (10) have reported that hydrogen sulphide in the gaseous as well as aqueous medium reacts with ozone forming sulphur and water. Mailfert (11) has shown oxidation of several metal sulphides into sulphates with ozone.

Thenard (12) obtained sulphur and water when hydrogen sulphide or its aqueous solution was reacted with hydrogen peroxide while Rose (13), by warming a mixture of hydrogen sulphide with chlorine, bromine and iodine respectively, obtained the respective hydrogen halide with the liberation of free sulphur as:

\[ H_2S + X_2 = 2HX + S \]

Similar observations have been made in the interaction of iodine and hydrogen sulphide by other workers also (14, 15).

Lunge and Billitz (16) observed that an aqueous solution of hydrogen sulphide is oxidised by hypochlorous acid to form water, sulphuric acid, hydrochloric acid and chlorine. Oxidation of hydrogen sulphide by iodic acid as shown by Feit and Kubierschky (17) yields sulphur, sulphuric acid, iodine and water, while bromic acid forms sulphur, bromine and water and alkali iodates yield sulphur, sulphuric acid, iodine and water. Lunge and Billitz (16) found that alkali bromates yield sulphur, sulphuric acid, bromine and water.
Max Schutze (38) Mas reported oxidation of hydrogen sulphide with iodine pentoxide at room temperature while Bahl and Singh (19) have shown the reaction between para-periodic acid and hydrogen sulphide as:

$$6\text{H}_2\text{I}_6 + 15\text{H}_2\text{S} = 3\text{I}_2 + 2\text{H}_2\text{SO}_4 + 28\text{H}_2\text{O} + 13\text{S}$$

and

$$\text{I}_2 + \text{H}_2\text{S} = 2\text{HI} + 3$$

Murthy and Sanjiva Rao (20) reacted potassium iodate with hydrogen sulphide yielding sulphoxide and sulphur either by decomposing or by reacting with more iodate. Recently Lal and Singh (21) have studied the reaction of hydrogen sulphide on potassium meta-periodate and have represented various stages of the reaction as:

$$6\text{KIO}_4 + 13\text{H}_2\text{S} = 2\text{K}_2\text{SO}_4 + \text{KIO}_3 + \text{KI} + 3\text{I}_2 + 13\text{H}_2\text{O} + 11\text{S}$$

............ (1)

$$\text{KIO}_3 + \text{KI} + \text{H}_2\text{O} + 2\text{S} = \text{K}_2\text{SO}_4 + \text{H}_2\text{S} + \text{I}_2$$

............ (ii)

$$3\text{I}_2 + 3\text{H}_2\text{S} = 6\text{HI} + 3\text{S}$$

............ (iii)

addition of (i), (ii) and (iii) gives

$$6\text{KIO}_4 + 15\text{H}_2\text{S} = 3\text{K}_2\text{SO}_4 + 6\text{HI} + 12\text{H}_2\text{O} + 12\text{S}$$

.... (iv)

or

$$2\text{KIO}_4 + 5\text{H}_2\text{S} = \text{K}_2\text{SO}_4 + 2\text{HI} + 4\text{H}_2\text{O} + 4\text{S}$$

Due to further action of hydrogen sulphide with the reduction
products, the reaction becomes quite complicated. Simultaneously meta-periodate reacts with iodine, one of the products of reaction, in neutral medium (22).

Wagner (23) and Donath (24) independently observed the decomposition of iron free pyrolusite by hydrogen sulphide yielding sulphide which, in a current of carbon dioxide, liberates hydrogen sulphide once again but retains a small amount of sulphur.

Schlagdenhauffen (25) investigated the reaction of hydrogen sulphide on permanganate and noticed that a brown precipitate turning white with excess of permanganate solution was formed. On boiling manganese dioxide with metal sulphides, Donath and Mullner (26) could prepare thiosulphate. Manganese dioxide readily absorbs hydrogen sulphide from a mixture of the gas with hydrogen with the formation of manganese sulphide (27). A mixture of manganese dioxide and iron pyrites when heated at 400° in an inert atmosphere of nitrogen for 20 hours produced manganese sulphate, trimanganese tetroxide (Mn₃O₄), ferroso-ferric oxide (Fe₂O₄), manganese sulphide and traces of sulphur dioxide. At 600° the products obtained were sulphur dioxide (about 20 %), ferroso-ferric oxide, ferric oxide, manganese sesquioxide, manganese oxide and manganese sulphide. No manganese sulphate formation was detected (28).

Dunnicliff and Nijhawan (29) studied the reducing action on permanganate and obtained hydrated manganese dioxide,
sulphate, dithionate, and sulphide. In the presence of large excess of hydrogen sulphide, formation of manganese sulphide, sulphate, thiosulphate, and sulphur was noticed, dithionate being completely absent. Mohammad and Ahluwalia (30) who continued the investigation with silver and calcium permanganates, have reported the formation of sulphate, dithionate, and a complex compound of varying composition represented by the general formula $xR_2O_2 yMnO_3 zMnO_2 nH_2O$ where $R$ denotes the divalent basic metal. They observed that a prolonged passage of hydrogen sulphide gas converted the precipitate into a sand-like mass of greyish colour finally turning pink due to the formation of manganese sulphide, while the solution turned yellow due to the formation of polysulphides. Ultimately, they noticed that dithionate decomposed. The final reaction has been represented as:

$$6Ca(MnO_4)_{2} + 25H_2S \rightarrow 5CaSO_4 + CaS_2O_3 + 12MnS + 25H_2O + 6S$$

Mohammad and Bedi (4), later on, attempted reduction of permanganates of potassium, ammonium, and barium with hydrogen sulphide water under similar conditions and obtained similar products.

Nitric acid reacts with an aqueous solution of hydrogen sulphide under certain conditions and produces to sulphur, sulphuric acid, nitric oxide and ammonia (16).
Reduction of potassium chromate (31), chromic acid (32), ammonium chromate (33), lead chromate (34), potassium dichromate (35), mercurous chromate (36) and barium chromate (37) has been studied in detail and chromium has never been found to be converted into sulphate completely.

Bendall and co-workers (38) have reported oxidation of hydrogen sulphide and sodium sulphide by chloramine-T to sulphuric acid and sulphur respectively.

With sulphur dioxide, hydrogen sulphide yields various thionates and thiosulphate depending upon the conditions (39-43).

Thenard (44) and Meyer (7) oxidised sulphurous acid and sulphites by hydrogen dioxide and obtained sulphates. Nabl (45) represented the reaction with hydrogen peroxide as:

$$2\text{H}_2\text{SO}_3 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{H}_2\text{S}_2\text{O}_6$$

followed by

$$\text{H}_2\text{S}_2\text{O}_6 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_4$$

According to Kastle and Loevenhart (46) when sulphur dioxide is oxidised by hydrogen peroxide, a labile oxide, $\text{H}_3\text{O}_2(\text{O}_2)\text{H}_3$, as an intermediate, is first formed. Henville (47) has also reported similar oxidation of sulphur dioxide by hydrogen peroxide whereas Hammick (48) has tried various metal oxides for oxidation of sulphur dioxide and has shown that two types of reactions are involved in it. The first
In which sulphur dioxide gets oxidised to trioxide and the second in which both sulphide and sulphate with a probable intermediate formation of sulphite are formed.

Jullien (49) has reported the oxidation of moist sulphur dioxide by chlorine. An aqueous solution of sulphur dioxide reduces chlorine giving hydrochloric and sulphuric acids (50). Oxidation of sulphur dioxide by bromine has been reported by Mayr and Peyfuss (61). They have shown the reaction as:

$$\text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HBr}$$

According to Bunsen (52) the reaction between sulphurous acid, only in less than 0.04 per cent concentration, and iodine is complete and represented as:

$$\text{SO}_2 + 2\text{H}_2\text{O} + \text{I}_2 = \text{H}_2\text{SO}_4 + 2\text{HI}$$

Higher concentration of sulphurous acid, however, reverses the reaction. In a similar reaction, Macaulay (53) has shown quantitative oxidation of sulphurous acid to sulphuric acid by 0.1 n iodine and, in a moderately concentrated solution, he has shown the formation of an intermediate product $\text{SO}_2\text{HI}$. Exactly identical results have been reported by Witekowa and Witek (54) and represented as:

$$\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}$$

$$\text{HI} + \text{SO}_2 = \text{HI}_2\text{SO}_2$$
The reaction between chlorates and sulphur dioxide under different experimental conditions has been attempted by quite a number of research workers (55-61). Formation of chlorine dioxide has invariably been detected in these reactions. Feit and Kubierschky (17) found that sulphurous acid is completely oxidised to sulphuric acid by bromic acid. Hendrixson (62) oxidised sulphurous acid by bromates in acidic solution and reported the formation of sulphate and dithionate. Landolt (63) has given the mechanism of oxidation of sulphurous acid by iodic acid. Lal and Kaushik (64) have investigated the oxidation of sulphurous acid by an aqueous solution of potassium meta-periodate. They have shown the formation of sulphuric acid, hydriodic acid and potassium sulphate and have represented the reaction as:

$$2\text{HIO}_4 + 3\text{H}_2\text{SO}_3 = 7\text{H}_2\text{SO}_4 + 2\text{HI} + \text{K}_2\text{SO}_4$$

Oxidation of sulphur dioxide by manganese dioxide, present in low grade ores of manganese, has been reported by Bock et al (65). They have shown the formation of sulphate, dithionate and free sulphuric acid. Cavicchi (66) could affect 49 per cent oxidation of sulphite to dithionate in an attempt to oxidise sulphite by manganese dioxide. Formation of sulphate and dithionate by oxidation of sulphur dioxide by manganese dioxide was observed by Gay Lussac and Welter (5). In their investigation: Heeren (67) and Spring and Bourgeois (6)
have obtained manganese dithionate and manganese sulphate representing the reaction as:

\[ \text{MnO}_2 + 2\text{H}_2\text{SO}_3 = \text{MnS}_2\text{O}_6 + 2\text{H}_2\text{O} \]

with a simultaneous reaction:

\[ \text{MnO}_2 + \text{SO}_2 = \text{MnSO}_4 \]

Reaction between manganese dioxide and sulphurous acid in cold has been studied by Meyer (7) also. The end products in this case are sulphate and dithionate and they are suggested to be formed as a result of the decomposition of manganic sulphite, an intermediate product as:

\[ 2\text{MnO}_2 + 3\text{H}_2\text{SO}_3 = \text{Mn}_2(\text{SO}_3)_3 + 3\text{H}_2\text{O} + \text{O} \]

\[ \text{Mn}_2(\text{SO}_3)_3 = \text{MnSO}_4 + \text{MnS}_2\text{O}_6 \]

\[ \text{MnS}_2\text{O}_6 + \text{O} = \text{MnSO}_4 \]

Lunge and Smith (68) could obtain 86 per cent conversion of sulphur dioxide into sulphuric acid with permanganate. They attributed the loss to the volatilisation of sulphur dioxide during the experiment whereas Dymond and Hughes (2) could adequately explain this loss due to the formation of dithionate and represented the reaction as:

\[ 17\text{H}_2\text{SO}_3 + 6\text{KMnO}_4 = 2\text{K}_2\text{S}_2\text{O}_6 + \text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 6\text{H}_2\text{SO}_4 + 11\text{H}_2\text{O} \]

They further observed that the changes in temperature and concentration did not affect various products of this reaction and when sulphurous acid was poured into excess of
permanganate solution, sulphuric acid was the only product. From this, they concluded that in the reduction of $\text{Mn}_2\text{O}_7$ of permanganate to $\text{MnO}_2$, oxidation of sulphurous to sulphuric acid was complete. Chevillot and Edwards (69) obtained the alkali and manganese sulphates when sulphurous acid was oxidised by permanganate in aqueous solution. Later on, Honig and Zatsek (70) detected that oxidation of alkali sulphites to sulphates by permanganate solution in neutral or alkaline medium was complete, the concentration of permanganate solution, of course, showed a considerable effect on the composition of the precipitate. Lal et al. (71) have studied oxidation of sulphur dioxide and sulphites by permanganates in acidic and alkaline media. They have shown the formation of a complex compound represented by the general formula $x\text{R}_2\text{O}$, $y\text{MnO}$, $z\text{MnO}_2$ along with sulphate and dithionate, the latter being formed only in the acidic medium.

Oxidation of sulphur dioxide to sulphur trioxide with nitric oxide (72) and reduction of nitric acid to nitric oxide with sulphur dioxide at 50-60° (73) are also well known.

Hodkinson and Young (57) have also studied the action of dry sulphur dioxide on chromates and dichromates and have shown that the reaction yields always chromium sulphate along with some other metal sulphates. They have
observed the reaction to be identical with the one with permanganates. Lal and Kaushik (74) have recently reported that the reduction of wet chromates of lead, silver and barium with sulphurous acid is very slow. Chromic acid, first set free as a result of double decomposition, reacts with sulphur dioxide with the formation of chromium sulphate and chromium dithionate. The metal sulphites, with the exception of barium, which gets converted into sulphate, remain as such.

Wardlaw and co-workers (75-81) have studied the reactions of sulphur dioxide very extensively. They have reported that sulphur dioxide reduces most readily in very low acidic medium and oxidises most readily in strongly acidic medium. This behaviour may be explained on the ionic basis by which oxidation is represented by the surrender of positive charges and reduction by the transference of negative charges. In an aqueous solution sulphur dioxide is regarded as a weak acid, ionising into H⁺, HSO₃⁻ and SO₃²⁻ ions and thus it functions as a reducing agent, for example:

\[
\begin{align*}
2\text{Fe}^3+ + 2\text{SO}_3^- + \text{H}_2\text{O} & = 2\text{Fe}^2+ + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\end{align*}
\]

In strongly acidic solution, however, the concentration of \text{SO}_3⁻ ion would be reduced and, therefore, its reducing power be diminished. They have represented the reaction with
copperous and ferrous chlorides as:

\[ 2Cu_2Cl_2 + S_2 + 4HCl = 4CuCl_2 + 2H_2O + S \] (80)

and

\[ 4FeCl_2 + S_2 + 4HCl = 4FeCl_3 + 2H_2O + S \] (79)

Oxidation of arsine by oxygen has been reported by Lockemann (82) as:

\[ 4AsH_3 + 3O_2 = 4As + 6H_2O \]

Spontaneous oxidation of arsine by oxygen, at room temperature, results in the liberation of metallic arsenic and water (83). Complete oxidation of arsine was affected by Beckleben and Lockemann (84) by shaking the gas with 3-30 per cent hydrogen dioxide for over 3 hours.

Berzelius (85) bubbled chlorine into arsine and found that each bubble produced a flame with the formation of hydrochloric acid and a brown cloud of arsenic. Similar results were obtained by other workers (86,87). With excess of chlorine, arsenic trichloride is formed. The oxidation of arsine by chlorine water has been shown as:

\[ AsH_3 + 3Cl + 4H_2O = H_3AsO_4 + 8HCl \] (84)

Stock (88) has studied action of liquid chlorine on arsine at -140° and obtained reddish products possibly forming unstable intermediate products, arsenic dihydrochloride.
(AsH₂Cl) and arsenic hydrodichloride (AsHCl₂). According to Simon (89), arsine is oxidised by an aqueous solution of bromine and the products formed are arsenic trioxide, arsenic acid and hydrobromic acid. Ogier (90) has shown the formation of arsenic and hydrobromic acids only when oxidation of arsine is done by excess of bromine. Similar observation has been made by Reckleben and Lockemann (84). Oxidation of arsine, slow in cold and rapid in hot, by iodine has shown the formation of iodides of arsenic and hydrogen (87). In presence of water, the action of iodine on arsine has been represented as:

$$\text{AsH}_3 + 4\text{I}_2 + 4\text{H}_2\text{O} = \text{H}_3\text{AsO}_4 + 8\text{HI} \quad (84).$$

Thoms and Hess (91) represented the same reaction to be taking place in two stages. The first stage of the reaction in neutral medium is represented as:

$$\text{AsH}_3 + 3\text{I}_2 + 3\text{H}_2\text{O} = \text{H}_3\text{AsO}_3 + 6\text{HI}$$

and the second as:

$$\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_3\text{AsO}_4 + 2\text{HI}$$

Balard (92) oxidised arsine with chlorine monoxide and obtained arsenic pentoxide and hydrogen chloride as the products. Formation of some chlorine is also detected if arsine is not in excess. Reckleben and Lockemann (84) have oxidised arsine with a solution of sodium hypochlorite or calcium hypochlorite. The reaction with sodium
hypochlorite has been represented as:

\[ \text{AsH}_3 + 4\text{NaOCl} = \text{H}_3\text{AsO}_4 + 4\text{NaCl} \]

Oxidation of arsine by chloric acid, in neutral medium, forms arsenic and metal chloride whereas in the acidic medium no reaction takes place (93). Acidified solution of potassium chlorate oxidises arsine in presence of silver nitrate, a catalyst, as:

\[ \text{AsH}_3 + 3\text{HClO}_3 = \text{As(OH)}_3 + \text{HCl} \]

whereas the reaction with bromic acid proceeds as:

\[ 5\text{AsH}_3 + 8\text{HBrO}_3 = 5\text{H}_3\text{AsO}_4 + 4\text{Br}_2 + 4\text{H}_2\text{O} \] (84).

Parsons (93) stated that iodic acid oxidises arsine with the formation of free iodine and arsenic trioxide. He represented the reaction as:

\[ 5\text{AsH}_3 + 6\text{HIO}_3 = 5\text{H}_3\text{AsO}_4 + 3\text{I}_2 + 3\text{H}_2\text{O} \]

Reckleben and Lockemann (84) have also studied the oxidation of arsine with iodic acid. They have represented the reaction as:

\[ 5\text{AsH}_3 + 8\text{HIO}_3 = 5\text{H}_3\text{AsO}_4 + 4\text{I}_2 + 4\text{H}_2\text{O} \]

Same workers have also reported the oxidation of arsine by periodic acid as:

\[ \text{AsH}_3 + 4\text{HIO}_4^- = \text{H}_3\text{AsO}_4 + 4\text{HIO}_3 \]
Gay Lussac and Thenard (96) and Soubeiran (87) while heating sulphur with arsine have shown the formation of hydrogen sulphide, arsenic and later on arsenic sulphide. Ame (96) showed that arsine with sulphur trioxide produces sulphur dioxide and arsenic which is further oxidised to trioxide. With sulphur dioxide, arsine produces arsenic and its tri-sulphide (93).

According to Stromeyer (86), arsine is oxidised by nitrogen peroxide and arsenic is set free. Parsons (93) has found that arsine with nitrous acid and also with a solution of potassium hydroxide containing some potassium nitrite (97) forms a grey crust of arsenic. Similar reaction was reported with nitric acid by Stromeyer (86).

Soubeiran (87) observed that solution of many heavy metal salts decompose the gas and the metal arsenide and water are formed. Reckleben and co-workers (98), Sketchly (99), Freis (100), Brukl (101) and Carmelo Russo (102) have described details of the action of arsine on silver nitrate under various experimental conditions.

Oxidation of arsine by potassium permanganate as:

\[ 10 \text{AsH}_3 + 16\text{KMnO}_4 \rightarrow 5\text{K}_3\text{AsO}_4 + \text{K}_2\text{MnAsO}_4 + 2\text{Mn}_3(\text{AsO}_4)_2 + 9\text{Mn(OH)}_2 + 6\text{H}_2\text{O} \] (103)

has been reported without any confirmatory evidence. Parsons (93) has shown the reaction as:

\[ 6\text{KMnO}_4 + 4\text{AsH}_3 \rightarrow 3\text{Mn}_2\text{O}_2(\text{OH})_2 + 2\text{As}_2\text{O}_3 + 6\text{KOH} \]
and Jones (104) as:

\[ 2\text{KMnO}_4 + \text{AsH}_3 = \text{Mn}_2\text{O}_3 + \text{K}_2\text{HAsO}_4 + \text{H}_2\text{O} \]

while Reckleben and Lockemann (84) found the oxidation of arsine by neutral or acidic solution of permanganate to be slow and incomplete.

Bendall and co-workers (38) have shown that arsine is rapidly oxidised by chloramine-T to arsenic acid irrespective of the proportion of the reactants. The initial oxidation to arsenious acid is, however, slower than oxidation of the latter to arsenic acid.

Due to almost insoluble character of phosphine in water, very little work has been done to study the oxidation of phosphine. Most of the attempts made have been proved to be futile and, therefore, a very little work in this field is available in literature.

Stock (88) has shown that phosphine reacts with chlorine at a low temperature. Balard (105) has attempted the reaction with bromine and has reported the decomposition of phosphine with the formation of phosphorus and hydrogen bromide. Hofmann (106) observed that purified phosphine inflames on coming in contact with bromine water while Thomson (107) has shown that it reacts with iodine forming phosphorus and hydrogen iodides. Balard (105) has noticed that hypochlorous acid oxidises phosphine with the formation of phosphoric and hydrochloric acids. Similar results were
obtained with calcium hypochlorite by Dalton (94). Moser and Brukl (103) have represented the reaction with a solution of iodic acid as:

$$2\text{HI}_3 + 5\text{PH}_3 = 5\text{H}_3\text{PO}_4 + 4\text{I}_2 + 4\text{H}_2\text{O}$$

While Bose (108) found that phosphine when passed over dried sulphur trioxide at ordinary temperature gave red phosphorus and sulphur dioxide. Cavazzi (109) has shown the action of sulphurous acid and phosphine by the equation:

$$\text{PH}_3 + 2\text{H}_2\text{SO}_3 = \text{H}_3\text{PO}_4 + 2\text{H}_2\text{O} + 2\text{S}$$

Dalton (94) again found that phosphine at ordinary temperature reduces nitric oxide to nitrous oxide, slowly, in a few hours time. Kulisch (110) reacted phosphine with solutions of heavy metal salts and obtained either the metal or its phosphide. In some cases both the metal and its phosphide, are produced. With cupric sulphate, as in the case of other heavy metal salts, the probable reaction may be represented as:

$$8\text{CuSO}_4 + \text{PH}_3 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 4\text{H}_2\text{SO}_4 + 4\text{Cu}_2\text{SO}_4$$

and cuprous sulphate reacts further as:

$$3\text{Cu}_2\text{SO}_4 + 2\text{PH}_3 = 3\text{H}_2\text{SO}_4 + 2\text{Cu}_3\text{P}$$

and

$$4\text{Cu}_2\text{SO}_4 + \text{PH}_3 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 4\text{H}_2\text{SO}_4 + 8\text{Cu}$$

With excess of silver nitrate Moser and Brukl (103) have shown the reaction as:
Be duction of gold salts in solution by phosphine to metallic gold or gold phosphide is quite well-known since early times. A solution of gold chloride in dry ether reacts with phosphine as:

\[ \text{AuCl}_3 + \text{PH}_3 = \text{AuP} + 3\text{HCl} \]  

Winter (112) has shown that phosphine reduces solution of ammonium molybdate to a blue solution which becomes colourless on warming or allowing to stand.

With potassium permanganate, phosphine undergoes chemical reactions as:

\[ 6\text{KMnO}_4 + 4\text{PH}_3 = 3\text{Mn}_2\text{O}_3 + 2\text{K}_2\text{HPO}_3 + 2\text{KH}_2\text{PO}_3 + 3\text{H}_2\text{O} \]  

\[ 2\text{KMnO}_4 + \text{PH}_3 = \text{K}_2\text{HPO}_4 + \text{H}_2\text{O} + 2\text{MnO}_2 \] and

\[ 2\text{KMnO}_4 + \text{PH}_3 = \text{K}_2\text{HPO}_4 + \text{H}_2\text{O} + \text{Mn}_2\text{O}_3 \]  

In presence of 96 per cent sulphuric acid, oxidation of
phosphine with potassium permanganate has been represented by the equation:

$$5\text{PH}_3 + 8\text{KMnO}_4 + 12\text{H}_2\text{SO}_4 = 5\text{H}_3\text{PO}_4 + 8\text{MnSO}_4 + 4\text{K}_2\text{SO}_4 + 12\text{H}_2\text{O}$$ (114)

Oxidation of phosphine by 0.1 n potassium dichromate in presence of dilute sulphuric acid has been reported by Seil (115) as:

$$\text{PH}_3 + 2\text{O}_2 = \text{H}_3\text{PO}_4$$

Bendall and co-workers (38) have shown the interaction of phosphine and chloramine-T showing thereby that with excess of phosphine hypophosphorous and phosphorous acids are obtained. When chloramine-T is taken in excess complete but slow oxidation to phosphoric acid takes place, the slow intermediate stage being the oxidation of hypophosphorous to phosphorous acid.

So far the reducing character of hydrogen sulphide, sulphur dioxide, arsine and phosphine only has been dealt with. A little survey of the oxidising character of N-bromosuccinimide, perborate and persulphate is also equally important.

During the last decade, the study of oxidation by organic compounds has attracted chemists to a considerable extent. Oxidation of cholic acid and its derivatives to yield methyl cholate and the corresponding cholate respectively by...
N-bromosuccinimide has been reported earlier (116). Various products have been obtained by the oxidation of thio-ethers with N-bromosuccinimide, in carbon tetrachloride, under suitable experimental conditions (117).

Berka and Zyka (118) have studied the oxidative action of N-bromosuccinimide. They have reported quantitative reduction with some substances in the acidic medium and with some in the bicarbonate medium. They have further concluded that the oxidation by N-bromosuccinimide is not always quantitative and with many substances, there is no success at all. The oxidation properties have been shown to be equal to those of bromate and hypobromite in reactions where oxidation is quantitative but its use as a volumetric reagent is limited due to its less stability.

Gröbel (119) oxidised some disulphides with N-bromosuccinimide under certain experimental conditions with the formation of certain new disulphides.

Due to the decomposition of perborates with the production of oxygen at high temperature and to some extent even at low temperature, they have been used in industry as oxidizing agents. Starek (120) employed perborate as a bleaching agent in textile. Goffert (121) studied the action of perborate on S-H group of the skin and found the reversibility of the reaction with S-H groups to varying extents in the three layers of skin.
Chaban (122) has recommended the addition of 10 per cent solution of an alkali salt of hydrated perborate such as NaBO$_2$.H$_2$O$_2$.3H$_2$O to a polymerised chloro-substituted ethylene to improve the resistance of the finished product towards light, heat, weather and aberration. Vanselow and Quirk (123) have said that perborate may be used in the bath for the latensification of photographic images. Due to its oxidising nature, it has been used as a bleaching agent for teeth (124). Sanchez (125) used sodium perborate as an oxidising agent in the colorimetry of strychnine. Chlorine dioxide was prepared by Koninklijke et al (126) by treating sodium chlorate dissolved in sulphuric acid at 60° with sodium perborate while air was being bubbled through the solution. The reaction was complete in 25 minutes. Mehta and Vakilwala (127) have reported that azo compounds from aniline are formed in greater yield with sodium perborate-acetic acid than hydrogen peroxide-acetic acid. Mehta and Iyer (128) have employed sodium perborate as an oxidising agent in presence of ferrous sulphate and acetic acid. They have studied the graded oxidation of polyhydric alcohols. They have further reported that the yields of osazones and hence of the aldehydes formed, was less with sodium perborate than with hydrogen peroxide but the former has other advantages.
Oxygen is evolved when a saturated solution of bleaching powder is added to perborate as:

\[ \text{NaBrO}_3 + \text{CaOCl}_2 + \text{H}_2\text{O} \rightarrow \text{NaH}_2\text{BO}_3 + \text{CaCl}_2 + \text{O}_2 \]  
(129)

Sodium perborate precipitates metallic gold from gold solutions according to the equation:

\[ 2\text{AuCl}_3 + 6\text{NaBrO}_3 + 9\text{H}_2\text{O} \rightarrow 2\text{Au} + 6\text{NaCl} + 6\text{H}_3\text{BO}_3 + 9\text{O} \]  
(130)

Potassium persulphate reacts with hydrogen peroxide in aqueous solution probably as:

\[ \text{H}_2\text{O}_2 + \text{K}_2\text{S}_2\text{O}_8 \rightarrow 2\text{KHSO}_4 + \text{O}_2 \]  
(131)

In presence of silver ions as catalyst the reaction between hydrogen peroxide and potassium persulphate is considerably fast and is represented as:

\[ \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O}_2 \]

but in the absence of the catalyst, the reaction is slow (132). The reaction between hydrogen peroxide and potassium persulphate has been studied quite thoroughly by several other workers as Palme (133) and Friend (134).

Free persulphuric acid and its salts are very powerful oxidising agents and react with hydrochloric acid solution and even chlorides forming chlorine; with bromides and iodides forming bromine and iodine respectively. Marshall (135) has shown that potassium iodide reacts with persulphate giving
Iodine which is oxidised further to iodic acid at the later stage of the reaction. Stages of this reaction have also been discussed by Price (136). He has not supported the assumption put forth by Mark (137) regarding formation of various products through different routes. Effect of various catalysts on the acceleration of this reaction has also been studied quite thoroughly (138-141). Dittrich and Bollenbach (142) have shown that alkali chlorides, bromides and iodides are oxidised to chlorates, bromates and iodates respectively when heated with a solution of persulphate in nitric acid in presence of silver nitrate. Muller and Jacob (143) have examined the interaction of persulphate and iodates resulting in the formation of sulphates and periodates.

Hydrogen sulphide reacts with persulphate, on warming, giving a turbid solution (144) whereas sulphur trioxide is absorbed by persulphate losing some of its active oxygen and forming perpyrosulphate as:

\[ K_2S_2O_8 + 2SO_3 = K_2SO_4 \cdot 2S_2O_6 \]  

Investigations of Marshall (146) have shown that persulphate, in slight excess, when reacts with thiosulphate, a tetra-thionate is formed in accord with:

\[ 2M_2S_2O_3 + M_2S_2O_8 = 2M_2SO_4 + M_2S_4O_6 \]

and the reaction is quite exothermic. In case thiosulphate
is in excess, trithionate is formed owing to the removal of sulphur from tetrathionate by the excess of thiosulphate or its decomposition products since the solution becomes faintly acidic. Sorum and Edwards (147) have reinvestigated the oxidation of thiosulphate by persulphate.

Levi and co-workers (148) have shown that selenium, tellurium and arsenic pass into solution as anions when they are treated with solution of potassium persulphate while antimony and bismuth form their insoluble oxides. Bringhenti (149) and Levi and co-workers (150) have examined the action of persulphate in solution on metals as copper, silver, gold, magnesium, zinc, cadmium, mercury, aluminium, titanium, tin, lead, arsenic, antimony, bismuth, chromium, selenium, tellurium, uranium, manganese, iron, nickel, cobalt, pladium, platinum and have shown that, except gold and platinum, the metals either pass directly into solution or remain undissolved in the form of oxides or basic salts. The nature of the end products very much depends upon the metallic character of the elements, the less metallic forming anions and the more metallic cations.

Vitali (151) has shown the decomposition of metal salts in solution by persulphate forming sulphuric acid, the metal sulphate and oxygen; of metal chlorides forming hydrochloric acid which is further attacked by nascent oxygen and liberates chlorine. In some cases even metal peroxides are produced.
Barium and strontium salts react with persulphate precipitating their sulphates with quantitative liberation of oxygen (151). Cerous salts are oxidised to ceric salts (when heated), lead salts precipitate lead dioxide if medium is alkaline, chromium salts are converted into chromates, manganese to manganese dioxide, ferrous to ferric and cobalt to cobalt peroxide when oxidised by persulphate (152). Oxidation of Mn(II) by persulphate, using silver ions as catalyst, in acidic medium, yields manganese dioxide and permanganate as the end products (153).

Catalytic oxidation of oxalate by persulphate in acidic medium in presence of silver ions has been reported by Gupta and Ghosh (154).

In view of the literature cited above, it appears that the reduction of N-bromosuccinimide, potassium persulphate and sodium perborate by hydrogen sulphide, sulphur dioxide, arsine and phosphine, as proposed in the present work, would be an interesting project to undertake for investigations.

The concentrations of various reactants, i.e., the reductants and the oxidants, have been selected of required suitabilities. The order of investigations has also been adjusted adequately. All experiments have been done at room temperature. While taking the amounts of the reactants, their solubility, rate of reaction and the nature of the products have been taken into account.

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