

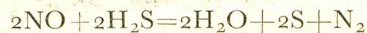
OXIDATION OF SODIUM SULPHIDE WITH NITRIC OXIDE

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SINCE the close of the eighteenth century, several workers have studied the reduction of nitric oxide to nitrous oxide by alkali sulphides¹⁻⁸. However, they did not study the reactions in any great detail. About the year 1929, Dunicliff and co-workers⁹ started a detailed study of the oxidation-reduction systems. In collaboration with Kotwani,¹⁰ Soni and Hamid,¹¹ respectively, Dunicliff studied the oxidation of hydrogen sulphide by chromic acid, potassium dichromate, soluble and insoluble chromates etc. Oxidation of sulphuretted hydrogen was the main purpose of these studies.

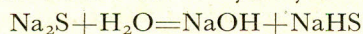
In 1929, Pierce,¹² published a paper entitled "Interaction between nitric oxide and hydrogen sulphide," in which he established that the gases react together with the formation of water, sulphur and nitrogen:



Two years after the publication of this paper Dunicliff, Sardar Mohammad and Jai Kishan¹³ attempted to study the interaction between nitric oxide and hydrogen sulphide in the presence of water, where they detected ammonium sulphide among the intermediate products. They also began a study of the action of nitric oxide on ammonium sulphide, but do not appear to have followed it through. This subject, therefore, has not so far been investigated in any detail and the information about this reaction is sketchy.

In these laboratories the work has been carried out on oxidation of sodium sulphide and polysulphides against potassium permanganate,¹⁴ and later on against potassium dichromate.¹⁵ These reactions were studied in liquid-liquid phase, whereas the present communication deals with the reaction between the nitric oxide (a gas) and sodium sulphide solution.

This reaction differs in many respects from the "interaction between nitric oxide and hydrogen sulphide," already referred to above, in the fact that whereas H_2S is acidic, sodium sulphide is basic due to hydrolysis in solution:



The problem of the oxidation of sodium sulphide is of considerable academic and

theoretical importance. The present investigation attempts to provide quantitative data about the intermediate and final products formed in the liquid as well as in the gaseous phase.

Preparation of Raw Materials

Nitric oxide was prepared by dripping a concentrated solution of sodium nitrite into an acidified solution of ferrous sulphate:



The gas was contaminated with some traces of NO_2 and was, therefore, purified by passing through a concentrated solution of caustic soda and dried over solid sodium hydroxide to free it from nitrogen peroxide and moisture.

Sodium mono-sulphide crystals were taken and washed with distilled water and finally with absolute alcohol. The crystals were filter-pressed and then dried in a vacuum desiccator for 10-15 minutes. Sodium sulphide solution was titrated against standard iodine solution (a known volume of the solution was run into a known excess of standard iodine solution acidified with acetic acid. The excess of iodine was titrated back against standard thiosulphate solution).

Experimental

(a) Quantitative study of the reaction:

The interaction between nitric oxide and sodium sulphide was studied at *room temperature only* (at about 25°C.) and by taking various concentrations of the sulphide solution.

Hydrogen gas was used to provide an inert atmosphere as nitric oxide reacts with atmospheric oxygen to form nitrogen dioxide.

Dunicliff and co-workers¹⁵ used carbon dioxide while studying the reaction between hydrogen sulphide and nitric oxide. In the present investigations, however, carbon dioxide could not be employed as it is absorbed by sodium sulphide solution.

Preliminary experiments showed qualitatively the presence of thiosulphate, sulphate, poly-sulphides, nitrite and ammonium ions in

solution, and sulphur in the precipitate. The colour of sodium sulphide solution underwent various changes, starting from light yellow to deep orange (in the case of strong solution). Finally the solution became quite colourless. At the intermediate stages sulphur decreased in quantity thereby showing the formation of poly-sulphides. At successive stages of change of colour, the solutions were critically examined and analysed so as to trace the course of the reaction.

This gave an approximate idea about the course of reaction. In the initial stages sulphide, thiosulphate, sulphate (traces), nitrite and ammonium along with free sulphur were present, while at the final stage, only sulphate, nitrite, and ammonium were present in the solution and free sulphur in the precipitate, while sulphide and thiosulphate were totally absent. Nitrate was not detectable, even by very delicate tests: tetrathionates were also absent. (Tetra-thionates if formed would be decomposed by the strongly alkaline solution.)

(b) Quantitative analysis of the products of reaction in solution : (1) After the completion of the reaction at each stage, the solution was filtered in order to retain the precipitate of free sulphur, and the filtrate was analysed.

Sulphate—was estimated by precipitating it as barium sulphate in the cold.

Thiosulphate—at the final stage of oxidation thiosulphate was estimated by titration against standard iodine solution. Control experiments showed that if the amount of nitrite in the solution was very small, it did not interfere during the estimation of thiosulphate. Estimation of thiosulphate at the intermediate stages was carried out after removing the sulphide as cadmium sulphide. Thiosulphate was oxidised with bromine to sulphate and estimated along with sulphate remaining behind as barium sulphate. By subtracting the amount of sulphate originally present as such, the quantity of thiosulphate was obtained.

Sulphide: Thiosulphate and sulphide were oxidised by bromine and estimated as barium sulphate along with the sulphate originally present. The amount of sulphate due to sulphide was obtained by subtracting the sulphate due to thiosulphate and sulphate as such.

Ammonium: The reaction solution after the removal of sulphur (by filtration) was heated with strong sodium hydroxide solution and the ammonia evolved was absorbed in 0.1 N sulphuric acid.

Nitrite: (a) By reduction with Devarda's Alloy. The solution was warmed with Devarda's alloy until the evolution of hydrogen ceased and then sodium hydroxide solution was added, the ammonia evolved being absorbed in standard sulphuric acid. By subtracting the amount of ammonia corresponding to the already estimated ammonium, the quantity of nitrite was determined.

(b) Sulphide was removed by CdCO_3 and the 'nitrite' was determined by titration against standard KMnO_4 . Control experiments indicated that thiosulphate in this case did not interfere with the nitrite present.

Free Sulphur: The precipitate of sulphur was washed, dried at 90° and weighed as such.

Results and Discussion

The reaction was studied by passing nitric oxide gas into sodium sulphide solution for various intervals of time and the products were analysed at regular stages. The gaseous products of the reaction were analysed by a modified form of the apparatus used by Milligan¹ and later on by Dunicliff¹⁷ and S. Mohammad for the same purpose.

It has been found that :

- (1) When nitric oxide was passed into sodium mono-sulphide solution of various strengths, sodium poly-sulphides, thiosulphate, sulphate and sulphur along with some ammonium and nitrite ions were formed ;
- (2) In the gaseous phase, the products of the reaction were nitrous oxide and nitrogen, when an excess of nitric oxide was used, and nitrogen only when a strong solution of sodium mono-sulphide was employed ; (Tables No. 5 and 6 respectively).
- (3) Sodium disulphide and trisulphide were also decomposed by nitric oxide giving thiosulphate, sulphate and sulphur along with ammonium and nitrite ions ;
- (4) After the complete oxidation, nearly half the amount of sulphur (calculated on the basis of mono-sulphide) was present as free sulphur, and the remaining half could be accounted for in the sulphate ; (Tables 1 and 2).
- (5) When nitric oxide was passed into sodium disulphide solution of various concentrations, formation of some

higher polysulphides took place, indicated by the decrease in the amount of sulphur and a deep orange colour of the solution, (due to polysulphides);

(6) When sodium tri-sulphide was oxidised by nitric oxide, no decrease in the amount of free sulphur was observed, thus eliminating the possibility of the

TABLE I

TABLE SHOWING THE RELATIVE AMOUNT OF SULPHATE AND FREE SULPHUR PRESENT IN THE SOLUTION AFTER COMPLETE OXIDATION OF $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ BY NITRIC OXIDE

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ dissolved per 500 ml. = 24.006 g. (M/5)

Nitric oxide was passed into M/5 sodium monosulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) solution for 65-75 hours.

The composition of the solution is expressed in g./500 ml.

Results of three experiments performed

Experiment No.	Free sulphur g.	Barium sulphate from sulphate g.	Sulphate formed as SO_4'' g.	Sulphur accounted from SO_4'' g.	Total sulphate determined g.	Sulphur theoretical g.	Difference g.
1	1.6795	11.981	4.569	1.5245	3.204	3.206	0.002
2	1.6645	11.2185	4.6185	1.5400	3.245	3.206	0.0015
3	1.6675	11.21275	4.608	1.5360	3.2035	3.206	0.0025

TABLE 2

TABLE SHOWING THE RELATIVE AMOUNT OF SULPHATE AND FREE SULPHUR PRESENT IN THE SOLUTION AFTER COMPLETE OXIDATION OF $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ BY NITRIC OXIDE

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ dissolved per 500 ml. = (M/10) = 12.003 g.

Nitric oxide was passed into M/10 sodium monosulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) solution for 33.5 hours.

The composition of the solution is expressed in g./500 ml.

Results of three experiments

Experiment No.	Free sulphur g.	Barium sulphate from sulphate g.	Sulphate formed as SO_4'' g.	Sulphur accounted from SO_4'' g.	Sulphate sulphur g.	Sulphur theoretical g.	Difference g.
1	0.8420	5.4315	2.2800	0.7592	1.6012	1.6030	0.0018
2	0.8315	5.5965	2.2995	0.7695	1.6010	1.6030	0.0020
3	0.8365	5.5720	2.2920	0.7640	1.6005	1.6030	0.0025

TABLE 3

TABLE SHOWING RELATIVE AMOUNT OF SULPHUR PRESENT IN VARIOUS COMPOUNDS WHEN NITRIC OXIDE WAS PASSED INTO M/5 SODIUM MONOSULPHIDE ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) SOLUTION FOR VARIOUS INTERVALS OF TIME

Amount dissolved per 500 ml. M/5 = 24.066 g.

Hours for which nitric oxide was passed = 65.75 (about)

500 ml. of the solution was taken for the reaction.

The composition of the solution is expressed in gms. /500 ml.

No.	Time in hours	Free sulphur	Sulphate formed as SO_4 "	Thio-sulphate formed as S_2O_3 "	Sulphur Accounted from			Total sulphur determined	Sulphur theoretical	Difference
					SO_4 "	S_2O_3 "	Undecomposed S"			
1.	.79	0.023	Nil	Negligible	Nil	—	3.184	3.204	3.206	0.002
2.	1.833	0.0615	0.0255	0.02097	0.00716	0.012	3.12314	3.2038	3.206	0.0022
3.	3.00	0.1050	0.071	0.13284	0.02366	0.076	2.99834	3.2030	3.206	0.003
4.	6.5	0.1985	0.4967	0.2962	0.1656	0.1695	2.6704	3.2040	3.206	0.002
5.	13.5	0.4652	0.9575	0.41602	0.31916	0.2380	2.18114	3.2035	3.206	0.0025
6.	18.5	0.44272	1.4796	0.52003	0.3932	0.2975	2.0868	3.2047	3.206	0.0013
7.	22.00	0.6685	1.4895	0.76160	0.4965	0.4357	1.6043	3.205	3.206	0.001
8.	33.5	0.9785	2.8474	0.56023	0.89583	0.3205	1.20867	3.203	3.206	0.003
9.	65.75	1.6300	4.7250	Nil	1.5750	Nil	Nil	3.205	3.206	0.001

formation of higher polysulphides (tetra and penta) ;

- (7) Sodium nitrite solution remained unaffected by nitric oxide ;
- (8) Sodium thiosulphate solution was decomposed by nitric oxide giving sulphate and sulphur. Ammonium and nitrite ions were detected in traces; (Table 7).
- (9) When nitric oxide was passed into a mixture of sodium thiosulphate and sodium nitrite solution, the thiosulphate decomposed to give sulphate and sulphur, and a very minute decrease in the amount of 'nitrite' was observed.

The studies on the relative amount of various compounds lead to the conclusion that two different products were formed in the solution:

- (1) The primary products of the reaction in solution were thiosulphate, polysulphides and sulphate, and a precipitation of free sulphur.
- (2) The secondary products of the reaction in solution were nitrite and ammonium ions.

The gaseous products of the reaction were N_2O and N_2 when an excess of nitric oxide was used and the solution of sodium sulphide was weak. When strong solution of sodium sulphide was employed, only nitrogen was evolved.

TABLE 4

TABLE SHOWING THE RELATIVE AMOUNT OF SULPHUR CONTAINED AS DIFFERENT COMPOUNDS WHEN NITRIC OXIDE WAS PASSED INTO M/SODIUM MONOSULPHIDE ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) SOLUTION FOR DIFFERENT INTERVALS OF TIME

Amount dissolved/500 ml. = 12.003 g.

Time for which the gas was passed = 33.5 hours.

500 ml. of the solution was taken for the reaction.

The composition of the solution is expressed in g./500 ml.

No.	Time in hours	Free sulphur	Sulphate formed as SO_4''	Thio-sulphate formed as $\text{S}_2\text{O}_3''$	Sulphur accounted from			Total sulphur determined	Sulphur Theoretical	Difference
					SO_4''	$\text{S}_2\text{O}_3''$	Undecomposed			
1.	3.0	.98	.9369	.10400	.03123	.595	1.40633	1.5950	61.603	.00794
2.	4.5	.216	.1830	.15120	.0610	.0865	1.2385	1.6020	1.603	.001
3.	7.5	.1995	.4968	.33124	.16516	.1895	1.04094	1.5951	1.603	.0079
4.	13.5	.3895	.96375	.39417	.32125	.2255	0.65905	1.5953	1.603	.0077
5.	22.00	.7575	1.370	.34086	.5035	.1950	0.1408	1.5968	1.603	.0062
6.	33.50	.8045	2.3817	Nil	.7939	Nil	Nil	1.5984	1.603	.0046

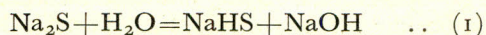
TABLE 5

ANALYSIS OF THE GASEOUS PRODUCTS OF THE REACTION BETWEEN NITRIC OXIDE AND SODIUM SULPHIDE SOLUTION

Results of three experiments

No.	Volume of the gas. cc.	Volume of hydrogen cc.	Volume after combustion cc.	Contraction cc.	Nitrogen cc.	Composition	
						Nitrous oxide %	Nitrogen %
1.	14.0	26.6	36.0	4.6	9.4	32.85	67.15
2.	14.7	27.1	36.8	5.0	9.7	34.00	67.00
3.	15.0	28.3	37.4	5.9	9.1	37.3	62.70

Sodium sulphide got hydrolyzed and then reacted with the gas, because it was found that N/10 solution (sodium mono-sulphide) was more than 86.4% hydrolyzed in water according to the equation :



The reaction between nitric oxide and sodium sulphide proceeded according to the stages mentioned below.

TABLE 6

ANALYSIS OF THE GASEOUS PRODUCTS OF REACTION BETWEEN NITRIC OXIDE
AND AN EXCESS OF SODIUM SULPHIDE SOLUTION

Results of three experiments

No.	Volume of the gas cc.	Volume of hydrogen cc.	Volume after combustion cc.	Contraction cc.	N ₂ cc.	N ₂ O %	N ₂ %
1.	23.3	34.1	57.3	0.1	23.2	0.0	100
2.	25.1	36.6	61.5	0.0	25.1	0.0	100
3.	22.5	35.9	58.4	0.0	22.5	0.0	100

TABLE 7

TABLE SHOWING THE DECOMPOSITION OF N/10 (Na₂S₂O₃ 5H₂O) SODIUM THIOSULPHATE SOLUTION BY NITRIC OXIDE WHEN NITRIC OXIDE WAS PASSED FOR 10 (TEN) HOURS THROUGH 500 ML. OF THE SOLUTION

THE REACTION SOLUTION WAS ANALYSED AT INTERMEDIATE INTERVALS

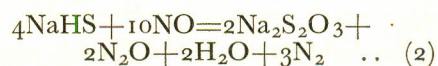
The composition of the solution is expressed in g./500 ml.

Time in hours	1	2	4	6.5	10
Thiosulphate taken as (Na ₂ S ₂ O ₃)	..	12.410	12.410	12.410	12.410	12.410	12.410
Thiosulphate taken as (S ₂ O ₃ "	..	5.6060	5.6060	5.606	5.606	5.606	5.606
Thiosulphate left as (S ₂ O ₃ "	..	5.33093	5.16836	4.62472	3.42502	2.0068	
Thiosulphate decomposed as (S ₂ O ₃ "		0.27507	0.43764	.98128	2.18098	3.59920	
Sulphate formed as BaSO ₄	..	0.2300	0.5500	1.2650	2.6200	3.9000	
Sulphate formed as SO ₄ "	..	0.09465	0.22634	0.5200	1.07822	1.60498	

First Stage : To start with, medium of the reaction was alkaline, therefore, the oxidation of sulphide solution took place with the formation of thiosulphate (S₂O₃"), a product which is in the lower state of oxidation, because the oxidising power of nitric oxide (and also that of other oxidising agent) is low in the alkaline medium (due to the low oxidising potential).

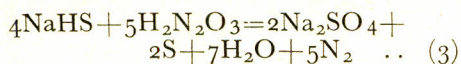
Sodium hydrosulphide produced from the

reaction (1) reacted with nitric oxide to give thiosulphate according to the equation :



This change was also confirmed by the analysis of the gaseous products of the reaction, where nitrous oxide and nitrogen were obtained. Nitric oxide on long contact with water gave

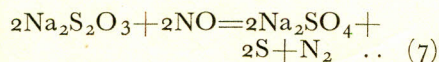
nitro-hydroxylammic acid (Angeli's acid).¹⁸
This acid reacted with sodium hydrosulphide according to the equation



Second Stage : The sulphur which was set free during the first stage of the reaction combined with the unreacted sulphide to give polysulphides.

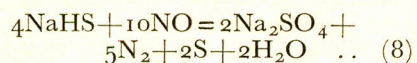


Third Stage : Due to the greater dissolution of nitric oxide in solution, the medium became less alkaline consequently the thiosulphate was decomposed by nitric oxide according to the equation :



During the initial stages nitrogen and nitrous oxide (cf. equation (2) above) were present as the gaseous products of the reaction, but towards the final stage nitrogen was the only product formed.

Fourth Stage : Sulphide, polysulphide and thiosulphate were completely decomposed to give sulphate and sulphur. The total reaction under all the four steps above may be summed up as follows :—



This equation is based on the quantitative data recorded in tables 1 to 4 where it has been shown that half the amount of sulphur accounted from sulphide was precipitated as free sulphur, while the remaining half was present in the sulphate formed at the final stage of oxidation. The analysis of the gaseous products at various stages indicated that nitric oxide was ultimately reduced to nitrogen though initially nitrous oxide was also formed as an intermediate product.

The course of reaction as studied in the case of sodium disulphide was found to be identical with that in the case of mono-sulphide except that the quantity of the various products formed was higher due to the presence of greater amount of sulphur in the compound. However in the case of the trisulphide, some deviations from the usual course of reaction were observed.

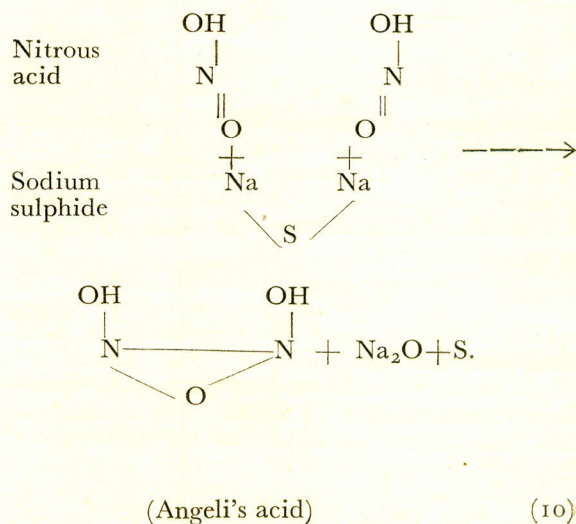
Reaction Mechanism

The by-product such as nitrite and ammonium ions were also studied in order to ensure their formation and to elucidate the mechanism of the reaction.

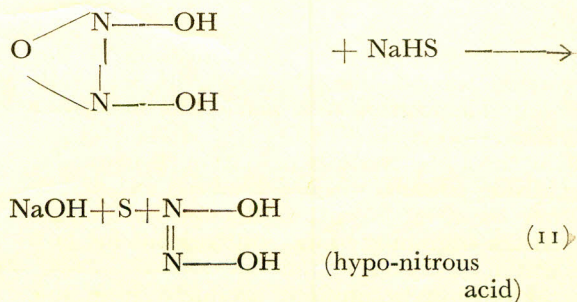
According to L. Moser,¹⁹ F. J. Joss,²⁰ and S. Zimmermann²¹ nitric oxide cannot be preserved over water without any change owing to the hydrolysis :

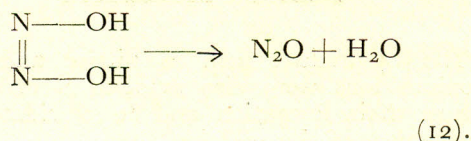


Zimmerman²¹ also said that nitric oxide on long contact with water gives nitro-hydroxylaminic acid (Angeli's acid). The formation of Angeli's acid from nitrous acid and Na_2S can be explained as below :—



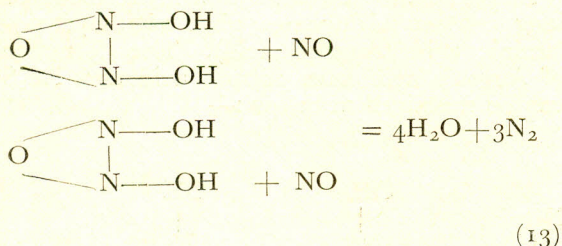
This acid then reacted with NaHS to give hyp-nitrous acid which decomposed to give nitrous oxide and H_2O .



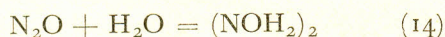


It appears that the starting point in the whole mechanism is hyponitrous acid and nitrous acid.

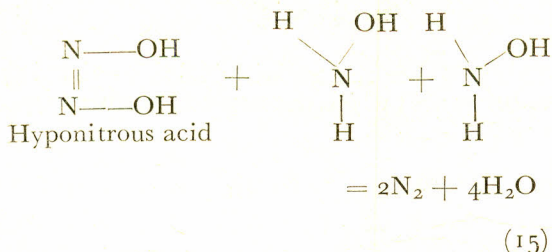
With the passage of time the quantity of Angeli's acid increased with the result that it started decomposing gradually as shown by the equation:



The evidence of the hydration of nitrous oxide to give hyponitrous is also given by Nichols and Derbigny.²² The mechanism of the final product of reduction is thought to depend upon the formation of hyponitrous acid.



(Hyponitrous acid has been discussed by L.H. Milligan and G.R. Gillete,²³ W.D. Bancroft,²⁴ N.R. Dhar,²⁵ and M. Coblens and J.K. Bernstein.²⁶) Accordingly the formation of nitrogen in the final stage of oxidation can be explained by

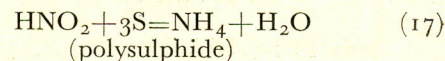


The formation of nitrite can be explained thus :—

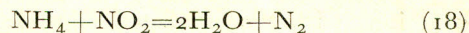


In the beginning of the experiment, the nitrite was in excess but its amount decreased later as the medium became less alkaline.

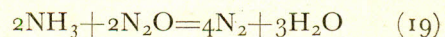
The formation of ammonium can be explained by the reaction :



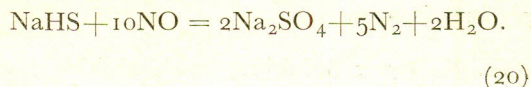
Towards the end interaction takes place and N_2 is produced according to the equation :



Nitrous oxide also reacts with NH_3 to give nitrogen.



To sum up, the above experiments lead us to the conclusion, that sodium sulphide is oxidised by nitric oxide to give sulphate and sulphur in the final stage of the reaction through the intermediate formation of polysulphides, thiosulphate, a small amount of NH_4^+ and NO' ions. Nitric oxide is reduced to nitrogen via nitrous oxide. Sulphate is virtually the end product in solution, sulphur in the precipitate, and nitrogen in the gaseous products of the reaction, thus



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