ON THE NON-CATALYTIC OXIDATION OF AMMONIA

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The homogeneous non-catalytical oxidation of ammonia has been investigated in quartz reaction vessel. The course of the experiments was followed by analysis. In reaction mixtures containing great amount of ammonia the reaction proceeds slower, than in the presence of small quantity of ammonia and of much oxygen; the rate of the reaction shows between 40—50% ammonia content a sharp spring. The pressure curve of the process has been calculated. The decomposition of the ammonia molecule on the wall was assumed to be the first step of the oxidation as the activation energy of any other elementary reaction between the ammonia and oxygen molecules is so much greater that in the presence of a wall such a homogeneous elementary process cannot take place. The products formed in the heterogeneous decomposition of the ammonia — hydrogen gas and other radicals — drive the reaction to easier steps.

According to earlier experiments ammonia cannot be ignited in the air. If great quantity of ammonia flows from a suitable long tube, although it may be inflamed, its flame is of weak light and readily expires. It burns in oxygen atmosphere with a yellow flame. A quietly burning inverted flame of yellow-green colour can be got, if an oxygen inlet glass tube with upwards bended end is inserted in a bulb filled with ammonia and the oxygen flow ignited [1].

The literature is widely extensive with respect to the catalytic oxidation of ammonia but the homogeneus oxidation of ammonia has, indeed, received much less attention in the research work. There are only quite recently publications of H. WISE, M. F. FRECH [2], E. R. STEPHENS and R. N. PEASE [3], as well as of J. VERWIMP and A. van TIGGELEN [4] dealing with this problem.

Studying the slow non-catalytic reaction between ammonia and oxygen STEPHENS and PEASE have found that the amount of the reacted substance rapidly increases with decreasing initial concentration of the ammonia. Consequently, there are reasons to assume that ammonia itself acts as inhibitor in its own oxidation. With ammonia-rich mixtures the reaction velocity is approximately proportional to the product of the concentration of ammonia and oxygen, while in the case of ammonia-lean mixtures Eq.

$$\frac{dP}{dt} = k \frac{[O_2]^2}{1 + [NH_3]/[O_2]} \tag{1}$$

describes roughly the relation. On conducting the experiments in unpacked, as well as in vessels packed with quartz tubes, no considerable effect of the variation of the surface on the rate of reaction has been found. However, on

covering the surface either of the empty, or that of the packed vessel with potassium chloride they found that while the rate of the oxidation of the ammonia-rich mixtures does not change considerably the rate of those ammonia-lean, *i. e.*, the otherwise rapid reactions considerably decreased. According to the view of the authors, these conclusions must be, however, due to the great experimental difficulties, somewhat provisional.

According to H. WISE and M. F. FRECH the first step of the oxidation reaction of ammonia is the dehydrogenation of the ammonia molecule, which is followed by the oxidation of hydrogen thus formed. Correspondingly, they assume the presence of free hydrogen, as intermediary product.

Examining the same process J. VERWIMP and A. van TIGGELEN have found that between the slow and the rapid reaction a sharp transition exists depending on the ratio of ammonia/oxygen. The apparent activation energy of the reaction is 50 kcal, which agrees to that of the process taking place in the ternary mixture of ammonia-hydrogen-oxygen. Kinetic consideration of the results leads us again only to qualitative conclusions.

The examination of the homogeneous oxidation of ammonia by static methods involved much difficulties. The overall equation of the reaction is

$$4 NH_3 + 3O_2 = 2 N_2 + 6 H_2O$$
$$7 \rightarrow 8$$
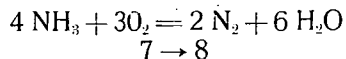
This already shows the source of the main experimental difficulty, that from 7 volums gas becomes only 8 volums and assuming that the reaction will not be completed, there is only a small pressure change to expect. The difficulties are yet increased by the fact that 6 volums are water of the final 8 volums, the condensation of which could not be avoided. Neither the continuous decrease of the temperature of the capillary tube of the vessel has led to the rise in pressure expected, instead the lowering of that set in. Similarly could not made use of the heating of the capillaries outside.

For this very reason, the experiments were arranged as to attain the possible least condensation of water formed. In addition the data of the pressure measurements were completed with analysis.

Although at the examination of the oxidation reaction the composition of the reaction mixtures varied within a rather wide range ($10\% NH_3 + 90\% O_2 - 90\% NH_3 + 10\% O_2$), there have been only cases examined containing only 60, 50, 40, 30 % NH_3, because with reaction mixtures containing 90, 80, 70 % NH_3 and the corresponding oxygen, besides the oxidation also decomposition of ammonia takes place. Consequently, it interferes with the study. With cases containing 20 and 10 % ammonia the reaction is extraordinary rapid, and due to the small amount introduced into the reaction also the pressure change is small, thus large experimental errors are to be expected. This error still occurs in the analysis. Accordingly we can account for the largest scale of conversion but at the same time — and this is important from the point of view of the analyses — for not very high rate of reaction in cases containing 60, 50, 40, 30 % ammonia. Hence only latter cases were taken into consideration (Fig. 1).
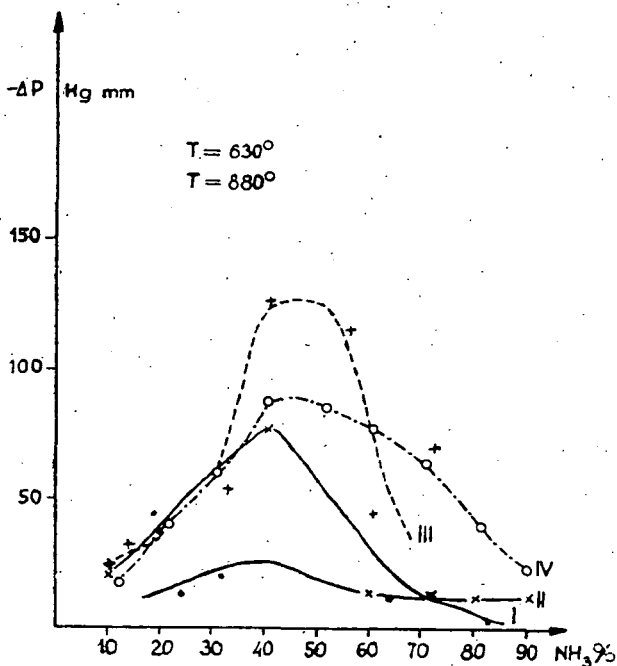
Fig. 1. t = 60 min. I: $P_0 = 130 - 140$ mm Hg (78 — 86), II: $P_0 = 350$ mm Hg (166 — 206),
III: $P_0 = 400$ mm Hg (69 — 77) [I—III.: T = 630° C].
IV: $P_0 = 280$ mm Hg (38 — 47), T = 880° C

    The experiments were carried out in the apparatus used also for exa-
mining the decomposition of ammonia, the vessel was made similarly of
quartz, but it was provided with an outlet tube to which the analysing bulb
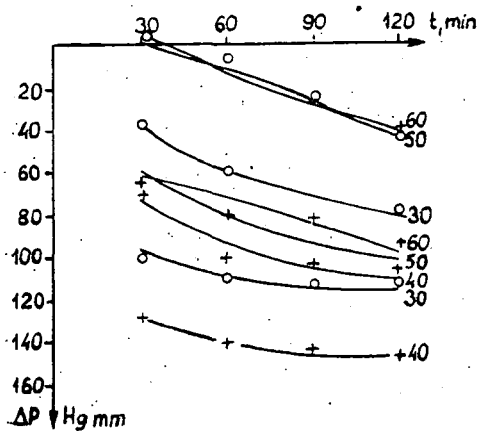with stop cock can be joined.

Fig. 2

The results obtained by
following the pressure change led,
as already mentioned, to rather
much uncertainties. Let us consider
now the agreement between the
data obtained from the pressure
change and from the analysis.
The values of the pressure change
were plotted at different points
of time, further the amount of
water formed was computed on
the basis of the data of the titra-
tions, and the theoretical pressure
values were similarly plotted in
the case if the total amount of
water formed would condense.

Thus we arrived, within the limits of experimental errors — at parallels (Fig. 2) which indicate that the difference between the two amounts of water is constant.

This is a phenomenon striking enough, as with mixtures of different compositions the quantity of water formed varies within a wide range. Should the total amount of water formed really condense the pressure change would vary between 60—140 mm. The pressure change observed cannot thus be the result of the condensation of water formed in a great mol ratio, all the less, as with gradual decreasing of the temperature of the outlet capillary tube it was taken care of the possible retardation of the condensation of water. Accordingly, it must be assumed that the quartz surface, at the high temperatures of the experiments, is able to bind, in some way, a rather great amount of water.

This assumption could not, however, be evidenced by the oxidation experiments, thus in order to examine it, separate experiments were conducted. The vessel thoroughly evacuated about 900° C was connected through a stop cock with a bulb containing with twice distilled water. Some 20—30 mm water vapour was introduced into the vessel. After waiting a longer time, and closing the stop cock the bulb was weighed. The difference of the two measurements gave the quantity of water disappeared during the course of the experiment. Knowing the volume and temperature of the system the quantity of water could be calculated, which fills the vessel and joined capillaries in form of saturated vapour. This quantity of water was subtracted from the loss in weight but still remained a quantity more or less (in the first experiments 4—5 mg, further less and less, 1—2 mg) the disappearance of which could only be interpreted assuming that water can be found by quartz surface at such a high temperature. Quantitative conclusions could, however, not be drawn from the experiments, since our apparatus was not for such purposes built, thus we worked with rather large experimental errors. It should be noted that from 10—150 mm Hg ammonia and from about the same amount of oxygen introduced during the oxidation experiments, only as much water has been formed, as much disappeared during the course of the former experiments with water, also in the case if the reaction is brought to completion. Accordingly, under such conditions no exact data might be expected from the results of pressure measurements, it is more adequate to control the advancement of the reaction by analysis.

The initial total pressure of the experiments was 330—350 mm Hg, temperature 620—630° C. On determining the amount of ammonia left in the reaction mixture frozen in at 30′, 60′, 90′ and 120′ respectively, the results obtained are summarized in Table I.

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Table I.

No.	Temperature °C	p_0 mm Hg	NH$_3$ %	Remaining NH$_3$ %	Consumed NH$_3$ mm Hg	Time min.
165.	625	343,9	90,3	76,74	—	30
166.	630	336,5	89,6	75,40	—	60
167.	625	357,0	87,2	72,82	—	90
168.	625	354,7	85.6	72,37	—	120
169.	630	340,0	78,1	75,49	—	30
170.	625	340,3	78,2	73,27	—	60
171.	625	355,7	77,7	70,00	—	90
172.	625	336,4	80,3	71,84	—	120
173.	625	339,6	67,4	68,03	—	30
174.	625	332,6	71,5	72,23	—	60
177.	625	343,3	67,7	70,98	—	90
176.	625	333,1	71,1	65,08	—	120
178.	620	338,3	59,4	74,50	51,1	30
179.	625	343,7	57,4	68,13	63,4	60
180.	620	333,6	62,0	67,46	66,7	90
181.	625	331,2	60,5	62,61	75,3	120
182.	620	337,3	51,4	73,07	46,3	30
183.	630	349,5	50,3	62,83	65,9	60
184.	625	340,4	50,2	58,62	70,7	90
185.	625	345,2	46,3	50,11	79,7	120
189.	620	334,6	39,7	22,68	102,6	30
188.	630	337,8	38,8	14,03	112,8	60
191.	625	339,0	40,5	15,76	115,5	90
192.	625	344,8	39,9	14,27	117,8	120
193.	630	335,8	31,0	22,93	80,1	30
194.	625	319,7	33,6	18,59	87,4	60
195.	625	354,5	30,3	14,52	91,8	90
196.	620	347,6	30,1	14,29	89,6	120
197.	630	335,6	19,7	24,05	—	30
200.	630	344,6	20,4	17,69	—	60
206.	620	325,2	21,0	16,50	—	90
198.	620	352,7	19,7	16,89	—	120
216.	620	345,8	10,4	19,14	—	5
217.	620	347,5	9,8	15,42	—	10
218.	620	340,5	9,3	10,83	—	15

The data obtained were turned into mm Hg. With the aid of this it could be calcutated what rise in pressure should have obtained in the case if water took part in the building up of total pressure, with a pressure corresponding to the temperature of the experiment ($\Delta p =$ mm Hg ammonia decreased/4). Since the initial total pressure could not be equally chosen in some of the experiments, and at the same time, because of the small pressure changes relative small deviations may cause great errors, in the total pressure change and rate-curves calculated on the basis of titration, always reduced values (divided by initial total pressure) were plotted.
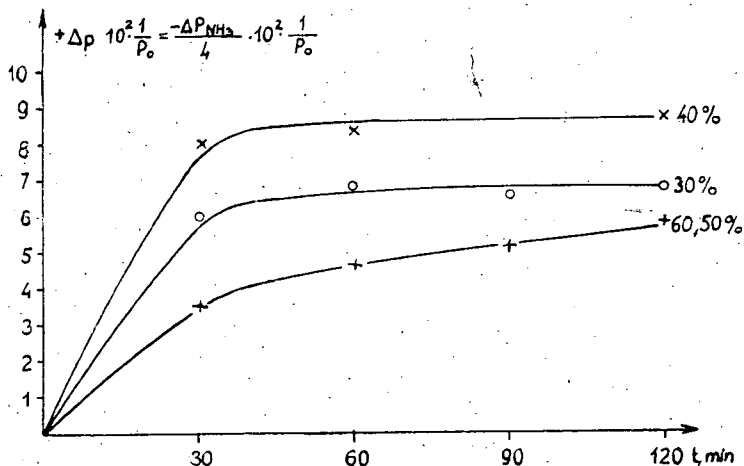

Fig. 3

In the cases dealing with 60 and 50 percent, as it is seen, the curves roughly cover each other. The greatest change observable was found in the case of the composition concerned, at 40 percent.

Fig. 4 represents the rate curves calculated on the basis of the above data, similarly in form of reduced values.

Fig. 5 illustrates the variation of the pressure of ammonia with time. As the curves show, the concentration of ammonia decreases most sharply in the first 30', thereafter only smoothly. The reaction runs most rapidly with the 30 per cent mixture. The character of our measurements permits only rough approximation for the order of reaction; the order for ammonia was found to be of second. It is supported by the mathematical treatment, too, carried out with curve p_{NH_3}, as a result of which the curves may be best represented by Eq.

$$p_{NH_3} = \frac{p_{0NH_3}}{1 + c p_{0NH_3} t} ,\tag{2}$$

where $p_0 =$ initial pressure of ammonia, $p_{NH_3} =$ actual pressure of ammonia at the time $t, c =$ constant. This equation is the substance formula of a second order reaction. From this equation was determined the value of c for the mixtures of different percentages and for four experimental points (30', 60',
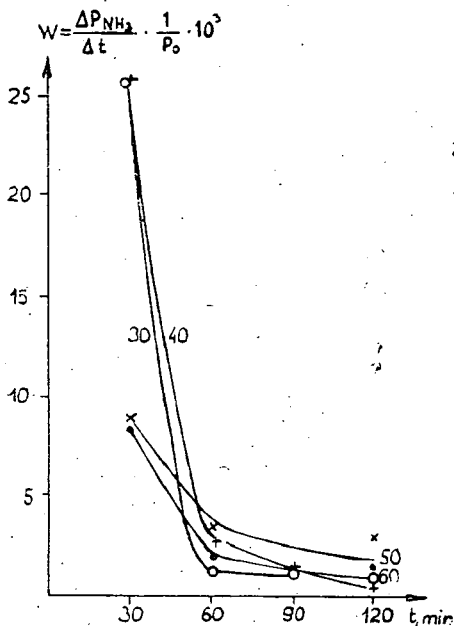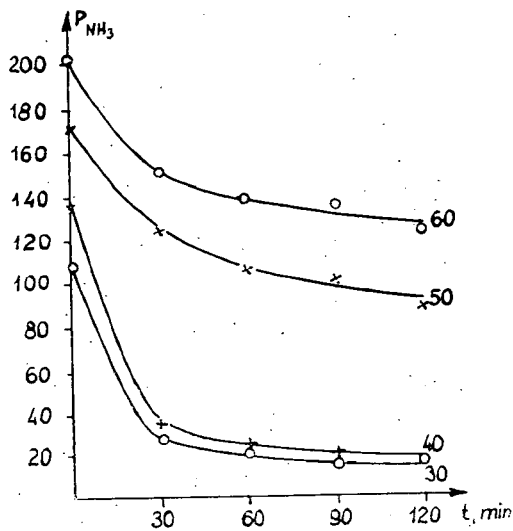
Fig. 4

Fig. 5

90', 120'). The average values of c obtained for the 4 points of time were applied in each experiment to determine the most proper values of c. This was carried out by the method of the least squares. Following tables summarize the data obtained dealing with 60, 50, 40, 30 percent ammonia and the corresponding oxygen.

Column 3 of the tables contains the values of p_i calculated by applying the values of c listed in column 6. Column 4 contains the values of c calculated on the basis of Eq. (2), and column 5 the mean values of them, column 6 those calculated by the method of the least squares.

Table II.

Time	$c \cdot 10^5$			p_{NH_3}	
	On basis of Eq. (2)	Mean	Calculated	Found	Calculated
30'	5,6			150,2	168,7
60'	3,8	3,6	3,2	137,9	145,1
90'	2,7			134,6	127,4
120'	2,4			126,0	113,5

60 % NH$_3$

Table III.

| Time | $c \cdot 10^5$ | | | p_{NH_3} | |
	On basis of Eq. (2)	Mean	Calculated	Found	Calculated
30'	7,3			123,7	134,3
60'	6,2	5,6	5,2	104,1	111,0
90'	4,7			99,3	94,6
120'	4,3			9,3	82,5

50 % NH₃ (annotation): 50 % NH_3

Table IV.

| Time | $c \cdot 10^4$ | | | p_{NH_3} | |
	On basis of Eq. (2)	Mean	Calculated	Found	Calculated
30'	7,9			32,0	37,97
60'	6,4	5,9	6,3	21,8	26,45
90'	4,9			19,1	15,59
120'	4,3			16,8	12,03

40 % NH_3

Table V.

| Time | $c \cdot 10^4$ | | | p_{NH_3} | |
	On basis of Eq. (2)	Mean	Calculated	Found	Calculated
30'	9,8			25,7	29,63
60'	7,4	8,0	8,1	18,4	17,23
90'	6,8			14,0	12,14
120'					9,38

30 % NH_3

The data of the tables show that the agreement between the calculated and the empirical values of p_i is, with mixtures containing 40 and 30 per cent of ammonia, better than with those containing 60 and 50 per cent. It should be noted that in the case of 30 % only the calculated value of p_i was taken at 120', being the empirical value obviously incorrect. Thus on calculating c, here only three points were taken into account, while the fourth p_{NH_3} based on the foregoing examples, was calculated theoretically. The variation of c with the composition can be seen in the following Table.

The values of c may be, as it is shown, sharply divided, in two parts; the first contains mixtures of 50 and 60 per cent ammonia, while to the other belong those of 40 and 30 per cent. It is another striking observation that, as shown by the curves of Fig. 4, the reaction rate sharply breaks between the composition of 40 and 50 per cent. The rate increases to a great extent.

Table VI.

NH$_3$ %	$c \cdot 10^4$
60	0,32
50	0,52
40	6,3
30	8,1

With mixtures of 30 per cent, the rate is still greater but relating to that of 40 % does not increase considerably. In the case of mixtures containing 10, 20 and to a certain extent 30 per cent ammonia the reaction runs so rapid that already after 5' reaction time a rather small amount of ammonia is left which does not differ much from that remaining after 30'. Here one must account for rather large experimental errors being the least amount of ammonia to be determined 0,2—0,3 mg only. Consequently, in the case of such a small concentration of ammonia the determination of the initial rates is, with our measuring methods, not possible. It might be assumed that with different compositions, two kinds of mechanism should be taken into account, which would result in such a great change of rate. However, the fact that although the rates are rather different and the values of c are also separated in two parts, but the equation of the pressure curve holds in both cases,
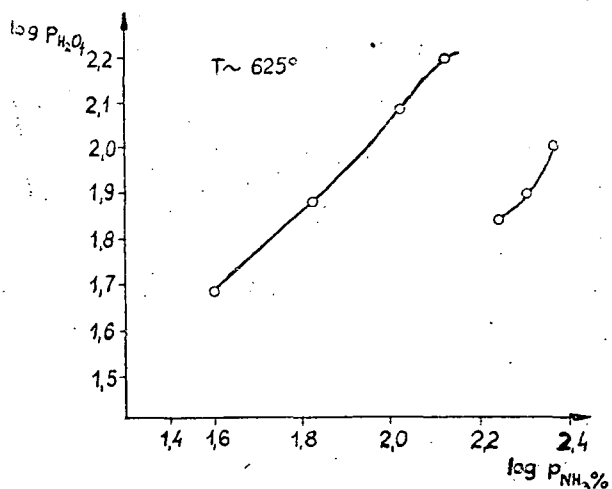

Fig. 6

renders likely the assumption that in spite of the great differences these are only in degree. The observation of J. VERWIMP and A. van TIGGELEN [4] too, who examining the same reaction at different temperature and under different experimental conditions, although similarly found the break in rate with about 50 per cent ammonia content, the activation energy of the reaction was in all of the cases 49 500 cal. Corresponding to Fig. 6 of their publication the logarithm of the formed amount of water was plotted, under our experimental conditions, against the logarithm of the initial pressure of ammonia (Fig. 6). Though our experiments were carried out at a temperature higher by 100° we obtained a curve of rather similar shape. The exact composition, where the rate changes, was not determined, it was only observed that the change takes place somewhere between 40 and 50 per cent content of ammonia.

STEPHENS and PEASE give account in their paper [3] dealing with the oxidation of ammonia on the experiment, in which they observed that the increase of the surface of the vessel (packed with quartz fragments) did not influence the rate of the reaction. On the contrary, the covering of the surface of the vessel either packed or unpacked, with potassium chloride, with mixtures containing a small amount of ammonia, consequently, where the reaction would proceed most rapidly, the rate considerably decreased. For its interpretation it was assumed that the reaction starts on the walls and the chain breaks down at the same place.

In this relation we carried out experiments, and observed that no reaction takes place in a new reaction vessel fully heated out. In order to justify this observation the evacuated reaction vessel was kept at 1000° for three days, then introduced a mixture of ammonia÷oxygen (1:1). No reaction took place. On reproducing the reaction already a sligh pressure change (2—3 mm Hg) could be observed. On the occasion of the third filling the reaction run usually. These experiments are in agreement with those of F. BERNREUTHER and M. BODENSTEIN [5] carried out in order to study the formation of hydrochloric acid. These authors attributed the phenomenon to the complete lack of adsorbed substance on the carefully heated and evacuated surface. Thus the lack of reaction at the first admission of hydrogen both and chlorine made waterfree at very low temperature is owing to the annihilation of the chlorine atom formed — the active centres — on the walls. On the course of further experiments, however, as the hydrochloric acid end product, which is adsorbed more readily than the chlorine atom, saturated more and more the walls, so decreased the possibility of the recombination of the chlorine atoms on the walls, the reaction rate continuously increased up to the fourth experiment, which led to explosion.

Based on the similarity, also from our experiments it could be concluded that the active centres of the reaction break down on the clean waterfree walls, therefore the reaction fails to set in at the first admission. Further on, however, the adsorption of the end products — first of all that of water — decreases the rate of recombination of the active centres, thus the reaction sets in with a continuously increasing rate. This seems, however, to contradict the mentioned conclusions of STEPHENS and PEASE. The contradiction perhaps might be solved assuming that the active centres formerly formed in one of the steps of the reaction (presumably OH and O) collide with the NH_2 and

NH radicals, respectively, with ammonia on the walls, while other intermediates (presumably OH and O again) break down on the walls. Consequently, the walls play, during the course of the reaction, a very important and varying role.

Based on our experiments carried out in order to study the non catalytic oxidation of ammonia the following establishments could be made.

The activation energy of any elementary process between ammonia and oxygen molecule is so great that no elementary reaction of such a nature can be set in presence of the wall, since the products deriving from the decomposition of ammonia on the wall — hydrogen gas and other radicals — offer to the reaction easier ways to develop.

The two possible forms of the primary acts are:

$$\nearrow \text{NH} + \text{H}_2$$
$$\text{NH}_3$$
$$\searrow \text{NH}_2 + \text{H}$$
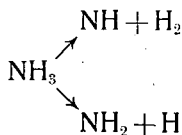
the first one of which is more likely rendering possible to understand why some authors have found in the system hydrogen too. Presumably also $\text{NH} + \text{O}_2 = \text{NO} + \text{OH}$, and parallel with it, due to the high temperature of the reaction, runs $\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \rightarrow \text{O} + \text{OH}$ too. The effect obtained through covering the surface with potassium chloride points to the presence of oxygen atoms.

Consequently, the above establishments mean certain limits from the point of view of the role of the oxygen molecule in the primary acts and of the extent of activation energies required, as well.

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