

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE ROLE PLAYED BY ADSORBED GASES IN INITIATING REACTION CHAINS: THE COMBINATION OF HYDROGEN AND OXYGEN

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Reaction chains initiated in the gas phase, and being broken upon collision with the walls of the containing vessels, have received considerable attention during the past few years. This paper presents a new type of chain mechanism: one in which chains are initiated on a catalytic wall surface, enter into the gas phase, and may eventually return to be broken at the walls.

An equivalent oxygen-hydrogen mixture at about 550° has been found by Thompson and Hinshelwood¹ to exhibit an extremely interesting phenomenon. Between the limits 10 to 100 mm. mercury pressure it explodes; outside these limits it does not. The variation of these limits with temperature is represented by the unbroken line in Fig. 1. At pressures greater than the upper explosion limit B-C a slow measurable reaction occurs, which we shall designate as "the non-explosive reaction." It will be our purpose to develop the evidence which shows that the non-explosive and the explosive reactions differ strikingly from each other, and that factors which accelerate the former retard the latter. A change of a few millimeters' pressure, and the one type of reaction is replaced by its opposing type. For this phenomenon a mechanism will be proposed which involves selective adsorption of gases on the walls of the containing vessel, initiation of chains from these adsorbed gases, and subsequent extension of reaction chains out into the gas phase. Finally it will be shown that such a mechanism can explain other reactions as well, such as the oxidation of carbon disulfide, carbon monoxide and the hydrocarbons.

Explosion Starts from the Walls.—We have been able to demonstrate this by a method described in detail elsewhere.² Two heated porcelain tubes 2 mm. in diameter, at right angles to each other, conducted streams of oxygen and of hydrogen, respectively, into a large iron chamber filled with nitrogen. The gases were pumped off continuously. Suitable devices permitted adjusting the streams so that they exactly crossed each other in an atmosphere of nitrogen, determining their maximum temperature at the point of coincidence within 1° with a thermocouple, and regulating the pressure of the streams by altering the total pressure in the chamber. Under these conditions oxygen and hydrogen were brought together in the absence of walls. An approximately isothermal run was

¹ Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, [A] 122, 610 (1929).

² Alyea and Haber, *Z. physik. Chem.*, [B] 10, 193 (1930).

made by crossing the oxygen and hydrogen initially at 50 to 200 mm. pressure, and following visually through a window in the chamber, or thermally with a thermocouple poisoned to prevent catalytic action, any change which occurred upon lowering the pressure to 10 mm. of mercury. At all pressures the temperature of the crossed streams remained about 20° higher than that of each single stream. The broken-line curves, Fig. 1, represent the thermal observations of seventeen such runs. In none of them is there a sudden increase in temperature when the pressure of the

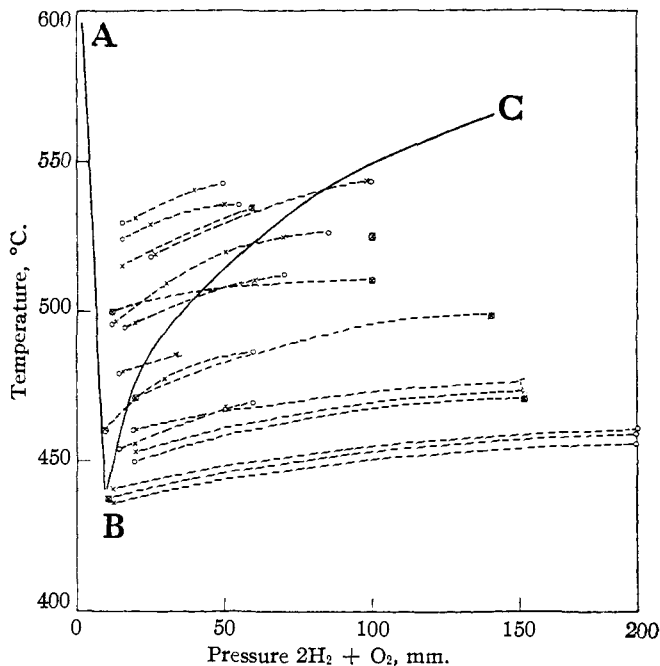


Fig. 1.

gases has fallen to the region where explosion should be occurring. Moreover, there were never any visual indications that explosion had taken place. This means that in the absence of walls no explosion occurs.

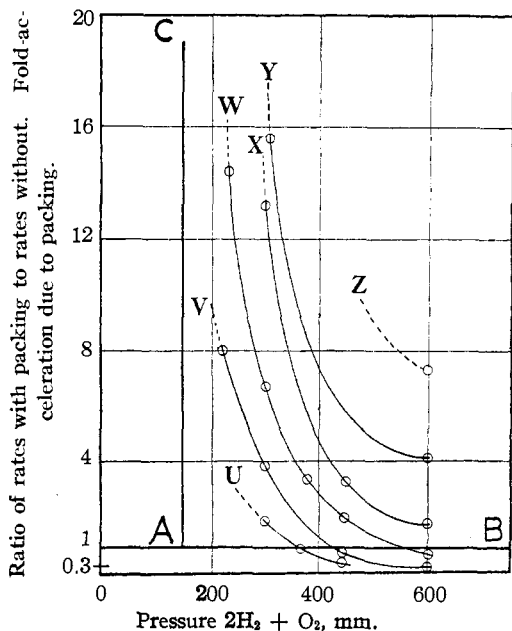
An artificial wall was then supplied: a quartz tube heated from within so that its surface was less than 520° was pushed into the gas stream at 530° and 35 mm., conditions where explosion should have occurred. As if lighted by a match, the gas exploded, and a visible sodium flame immediately appeared, extending from the quartz out into the gas in the direction in which the gas was flowing. The explosion continued until the quartz tube was removed from the gas stream. This could be repeated at will.

These facts clearly indicate that the explosion originates on the walls, and does not take place in their absence.

Unfortunately our experimental method does not give an equivalent oxygen-hydrogen mixture, but instead a portion of the crossed streams contains oxygen-rich mixtures which will explode even at pressures much above the upper explosion limit. This makes it impossible to identify the upper explosion pressure by the use of the quartz rod.

Effect of Different Surfaces.—Rods of glass, porcelain, copper, or iron, initiated explosion just as does quartz. A rod of aluminum, however, was without effect.

Effect of Packing.—The explosion limit is the same in quartz or porcelain vessels, unpacked or filled with crushed quartz or porcelain. This



U, 576°; V, 589°; W, 559°; X, 549°; Y, 529°; Z, 506°.

fact naturally led Hinshelwood,¹ and Semenov and co-workers,³ to believe the reaction to be homogeneous. The experiments described above, and the pretreatment experiments given below, at once disprove the homogeneous mechanisms, which they have postulated, for sudden explosion of oxygen-hydrogen mixtures, and warn against presenting such data as absolute proofs of homogeneity of reaction henceforth.

The non-explosive reaction, on the other hand, is extremely sensitive to the amount of surface present. Hinshelwood and co-workers early data⁴ show that at pressures immediately above the upper explosion limit, the non-explosive reaction is accelerated by filling the vessel with bits of porcelain or silica. It must be pointed out that the retardation due to packing claimed by these authors applies only to their high pressure data; at pressures *immediately* above the explosion limit, packing accelerated, not retarded. This becomes obvious when their results are plotted as in Fig. 2, showing the packing

³ Kopp, Kowalsky, Sagulin and Semenov, *Z. physik. Chem.*, [B] 6, 307 (1930).

⁴ Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, [A] 118, 170 (1928); Gibson and Hinshelwood, *ibid.*, [A] 119, 591 (1928).

effect at different temperatures. In a second paper,¹ however, they present data where, under comparable extent and particle size of packing material, it appears that packing tremendously retards reaction (Table I).

TABLE I
REACTION RATE DATA

Oxygen-hydrogen pressure, 555°, mm.	Ratio of rates with packing to rates without		
	Early publications		Later publication
600	0.7	0.9	0.08
300	6.7	8.5	.056

The reason for this discrepancy between their early and later results no doubt lies in differences in the washing process or previous history of their packing material. Pease⁵ found that a slight change in the nature of the glass walls, such as is obtained by washing the walls with a solution of potassium chloride, slows down the reaction several thousand fold. This is because the number of chains started is fewer, and the chain-breaking efficiency is increased, on the coated wall, as the work of Taylor and Lavin⁶ on combination of hydroxyl radicals and hydrogen atoms on various surfaces amply confirms.

Effect of the Hydrogen-Oxygen Ratio.—Increasing the ratio accelerates the non-explosive, but is unfavorable to the explosive, reaction. The latter is demonstrated in Thompson and Hinshelwood's results in the first two columns of Table II, where in hydrogen-rich mixtures one must exhaust to lower total pressures before explosion will occur.

TABLE II
REACTION RATE DATA

H ₂ -O ₂ ratio	Mixture explodes below (mm. Hg)	
	Pressure 2H ₂ + O ₂	Pressure H ₂
0.5	129	43
0.67	115	46
1.0	97	49
2.0	99	66
3.0	83	62
4.0	68	56

Attention is directed especially to our calculation in the last column, where it is evident that the hydrogen pressure at which explosion sets in is fairly constant, irrespective of the hydrogen-oxygen ratio.

Pretreatment of the Walls.—Bone and Wheeler⁷ showed that porcelain walls around 500° adsorbed large quantities of hydrogen, but no oxygen. Analogously, when walls were preexposed to hydrogen for some hours, subsequently admitted oxy-hydrogen gas reacted much faster. The surface activity was proportional to the length of pretreatment. Preexpo-

⁵ Pease, *THIS JOURNAL*, **52**, 5106 (1930).

⁶ Taylor and Lavin, *ibid.*, **52**, 1910 (1930).

⁷ Bone and Wheeler, *Phil. Trans.*, [A] **206**, 1 (1906).

sure to oxygen had no effect. It is striking that the increased activity of the surface due to hydrogen pretreatment was still manifest after the walls had been exposed continuously to the oxy-hydrogen mixtures for two hours, *i. e.*, their reaction rate continued to be greater than normal.

For the explosive reaction we have found the reverse is true.² Ten liters per hour, measured at N. T. P., of oxy-hydrogen gas were passed through a porcelain reaction tubing 30 cm. long and 2 mm. in diameter heated at 550° and leading into the large partially evacuated chamber described above. Regulating the pressure in the chamber controls the pressure in the porcelain tube. Normally, if the gas is below 60 mm. pressure it explodes and burns at the mouth of the porcelain tubing; above this it ceases to burn, thus identifying itself with the upper explosion limit discovered by Thompson and Hinshelwood. Procedure was then varied: hydrogen was first passed through the heated tubing at 40 mm. pressure; this was followed by oxy-hydrogen gas at 200 mm., upon lowering the pressure of which, no explosion occurred. Conversely, pretreatment with oxygen seems to favor explosion. A series of consecutive runs carried out in one tubing, Table III, confirm this. Here is evidence that three minutes

TABLE III
DATA OF CONSECUTIVE RUNS

Consecutive pretreatments at 40 mm. with	Time of pre-treatment in minutes	On withdrawing 2H ₂ + O ₂ gas from 200 to 40 mm. it explodes at
H ₂ + O ₂	2	60 mm.
	2	50
	2	55
	2	70
H ₂	5	No explosion
H ₂	2	No explosion
O ₂	2	70
O ₂	3	65
O ₂	1	90
O ₂	1	60
H ₂ + O ₂	1	50
H ₂ + O ₂	2	50
H ₂	3	No explosion
H ₂	2	No explosion
H ₂	1	No explosion
O ₂	5	145
O ₂	2	120
O ₂	2	60
H ₂ + O ₂	1	70
H ₂	6	No explosion
H ₂	1	No explosion
O ₂	0.5	No explosion
O ₂	1.0	110

or longer of hydrogen pretreatment prevents explosion, and that this is counteracted by longer than thirty seconds oxygen pretreatment. We might add that oxy-hydrogen gas may be passed over the hydrogen pretreated surface for several minutes without normal explosion occurring. Four other tubes yielded the same qualitative results, although they required varying lengths of hydrogen pretreatment, up to fifteen minutes, to prevent the explosion. It can be seen in Table III that not even the normal explosion limit could be evaluated accurately.

The results on pretreatment, and the retarding influence of excess hydrogen, make it clear why Thompson and Hinshelwood found that at 550° hydrogen exploded upon streaming into oxygen at 135 mm. or less while oxygen did not explode upon admission to hydrogen unless the pressure of the latter was lower than 84 mm.

Effect of Steam.—Gibson and Hinshelwood⁴ found that the addition of 40% of steam to the oxy-hydrogen mixture speeded up the non-explosive reaction six-fold. That explosion, on the other hand, is completely prevented under these conditions is seen in Table IV. Here our calculations on a few typical measurements by Hinshelwood and co-workers show that the oxy-hydrogen pressure during the course of many of their non-explosive reactions fell into that low pressure region where explosion should have occurred. The steam formed has prevented explosion.

TABLE IV
EXPERIMENTS WITH STEAM

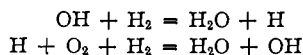
Bulb	Temp., °C.	Initial pressures		P_{steam} preventing explosion at P_E	Should explode below P_E	Non-explosive reaction measd. down to P_{final}
		H ₂	O ₂			
Packed silica	648	200	129	120	150	86
Packed porcelain	582	150	75	46	155	112.5
Empty silica	567	80	51.5	4	126	71.5
Empty silica	549	403	212	356	82	46

P_E and P_{final} are pressures in millimeters from data by Hinshelwood and co-workers.

Effect of Inert Gases.—Nitrogen and argon act in the same way as steam, accelerating the non-explosive reaction, but preventing explosion,^{3,8} since in the absence of inert gases the oxy-hydrogen mixture will explode at higher pressures than in their presence.

Discussion

It is quite certain that we are dealing with chain reactions in both the explosive and the slow reaction,¹ probably involving the mechanism suggested by Bonhoeffer and Haber⁹



⁸ Thompson, *Z. physik. Chem.*, [B] 10, 280 (1930).

⁹ See Farkas, Haber and Harteck, *Naturwiss.*, 18, 266 (1930).

It is clear that the wall breaks the chains by catalyzing the recombination or interaction of H and of OH.

The Non-Explosive Reaction.—But how does the wall initiate chains? The answer was suggested in our introduction: gases adsorbed on its surface release into the gas phase a supply of hydrogen atoms. Bone and Wheeler's results on adsorbed hydrogen were so important as to warrant

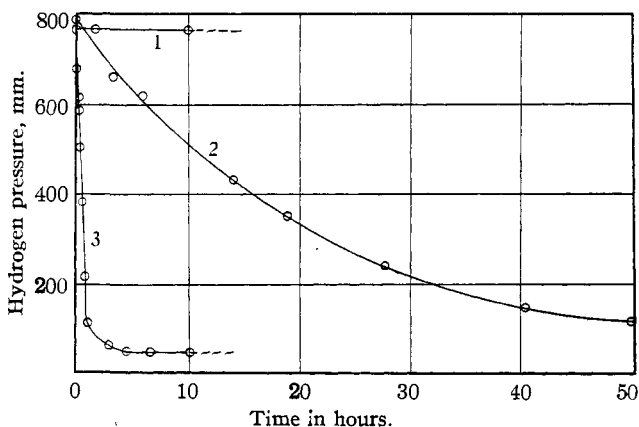


Fig. 3.—Curve 1 at 25°; Curve 2, at 480°; Curve 3, at 530°.

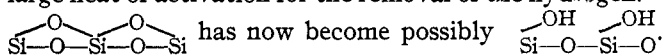
repetition. Their results are confirmed in Table V and Fig. 3. A 500-cc. Pyrex vessel was filled with coarsely powdered new Pyrex tubing, and placed in an oven. Between each run the vessel was exhausted at 500° for about twenty hours with a Cenco oil pump. The greater part of the gas

TABLE V
RESULTS OF EXPERIMENTS

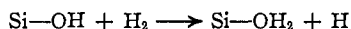
Time in minutes	Pressure of hydrogen, mm.	
	Run I at 530°	Run II at 25°
0.00	700	760
0.50	617	
1	594	
2	553	
3	521	
4	494	
5	471	
10	383	
20	288	
30	227	759
60	113	
120	59	
240	49	
600	47	758
Final total volume of H ₂ adsorbed reduced to N. T. P.	31.6 cc.	0.20

adsorbed could be pumped off and collected again at low pressures, although a small amount was consumed in reducing the Pyrex, which became darkened during the measurements. It is apparent that while no hydrogen was adsorbed at room temperatures, tremendous amounts were taken up at 500°. Oxygen under these conditions was not absorbed at either temperature.

Benton¹⁰ observed the identical phenomenon for hydrogen on nickel. Such a type of curve can only be interpreted as meaning that *at the higher temperature hydrogen is adsorbed in an activated form which it is not at room temperature.* This is also substantiated in the pretreatment phenomena discussed above, where hydrogen being desorbed so slowly indicated a large heat of activation for the removal of the hydrogen. The silica surface



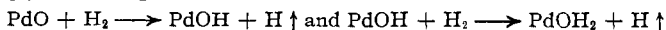
But we shall go one step further to state *that hydrogen in this form on glass is capable of performing reactions which it is unable to effect at room temperature.*¹¹ One possible reaction is



and by such a mechanism our chain reaction is initiated, the hydrogen atom being liberated into the gas phase.

Such a mechanism for the initiation of chains in the non-explosive reaction explains the phenomena discussed previously. Excess of hydrogen, pretreatment with hydrogen, increasing wall surface, would all accelerate the non-explosive reaction and such is found to be the case. The action of inert gases is possibly connected solely with the gas chains, not the initiating of them at the walls. Steam may act by changing the nature of the adsorbed gas layer¹² and breaking the gaseous reaction chains less easily than a dry surface.

In addition to giving us a satisfactory explanation for the hydrogen-oxygen reaction, this idea clarifies numerous other reactions. Polyakov,¹³ passing hydrogen over palladium at 400° obtained an active form of hydrogen which could react with oxygen or recombine further down the tube at a considerable distance from the catalyst. While it is thermodynamically impossible for the palladium to act by shifting the $\text{H}_2 \rightleftharpoons 2\text{H}$ equilibrium and thereby manufacture atomic hydrogen in excess of its exceedingly small equilibrium concentration, the mechanism



is entirely orthodox and made exceedingly likely in this case where a film of oxygen is known to adhere firmly to a palladium surface.

¹⁰ Benton and White, *THIS JOURNAL*, **52**, 2325 (1930).

¹¹ Langmuir, *Trans. Faraday Soc.*, **17**, 607 (1921); Taylor, *THIS JOURNAL*, **53**, 578 (1931).

¹² Elgin and Benton, *ibid.*, **51**, 7 (1929).

¹³ Polyakov, *Naturwiss.*, **16**, 131 (1928); see also *Chem. Abstracts*, **24**, 4434 (1930).

Professor H. S. Taylor has pointed out to me an even more illuminating example: a paper where Mitchell and Marshall¹⁴ demonstrated that hydrogen passed over a platinum catalyst yielded what was undoubtedly monatomic hydrogen only if the gas contained a small amount of oxygen. The hydrogen atoms could reduce copper oxide at 5.5 cm. distance from the catalyst.

Additional applications of this type of reaction, the oxidation of carbon disulfide, of carbon monoxide and of the hydrocarbons are discussed subsequently.

Once the reaction chains have been initiated, what is their course? Thompson and Hinshelwood's data can be best interpreted by assuming that the chains which are set up are both straight and branching, the latter predominating at higher pressures and temperatures. This may be due to a reaction slightly endothermic such as



In an unpacked bulb the rate of reaction, therefore, increases very rapidly with temperature until the chains become so branching that explosion occurs.

Halving the pressure will cut down the reaction rate many-fold; this effect will be most pronounced at high temperatures, where branching predominates. This is confirmed in Gibson and Hinshelwood's results where the ratio of reaction rate, time for half change, at 600 mm. to the rate at 300 mm. of $2\text{H}_2 + \text{O}_2$ gas mixture is 3.7 at 529° but 18.9 at 569° . In fact this result seems to indicate that there is little if any branching at 529° , so that one must distinguish between the branching-chain, high-temperature explosion at $>570^\circ$, and the low-pressure explosion at 500° , which as pointed out subsequently may consist only of a very large number of straight chains.

In the packed bulb, chains are broken too soon to permit much branching. The reaction increases less slowly with temperature. Explosion is delayed until much higher temperatures, representing maximum branching. Halving the pressure hardly affects the reaction rate until very high temperatures are reached. Gibson and Hinshelwood found that in a packed vessel the rate at 600 mm. was the same as that at 300 mm. at 529° , and 1.8 faster at 569° .

The retarding effect of packing should be greater under those conditions favoring branching chains, *i. e.*, high temperature and pressure. Actually it becomes so great as to counterbalance the catalytic effect of walls initiating chains; the reaction is less in the packed vessel.

Temp., °C.	Ratio of rate with porcelain to rate without	
	at 600 mm.	at 300 mm.
529	4.1	15.6
569	0.3	8.1

¹⁴ Mitchell and Marshall, *J. Chem. Soc.*, 123, 2448 (1923).

Change of Adsorbed Gas Layer at the upper Explosion Pressure.— At the beginning of the paper we mentioned the curious abruptness with which the explosive reaction replaces the non-explosive, as one passes the upper explosion limit. Why does the latter, which is becoming slower and slower as the pressure is lowered, suddenly become explosive?

The answer is that there is a sudden change in the adsorbed gas layer responsible for the initiation of the reaction chains.

At this point we wish to draw an analogy with experiments by Langmuir.¹⁵ Hydrogen and oxygen do not react on a tungsten filament at 1500°K. There is, instead, a unimolecular film of oxygen which shields the tungsten surface and prevents it from dissociating the hydrogen as it normally does in the absence of oxygen. The oxygen forces are directed inward toward the tungsten, WO_3 forms and distils off, and the oxygen is gradually consumed. At the point where less than a unimolecular film of oxygen remains, it can no longer ward off the hydrogen, the hydrogen gets in and "making a flank attack on the oxygen" rapidly reacts with it to form steam, and almost instantaneously sweeps the surface bare of oxygen. Thereafter, the normal dissociation of hydrogen into atoms on the tungsten surface sets in.

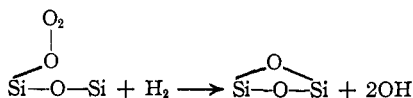
In our case, with a silica vessel, at 500° and pressures of several hundred millimeters, the gas layer is reversed and the walls are covered with hydrogen, to the exclusion of oxygen. When the pressure is lowered some of the hydrogen is desorbed. This, as well as the branching effects discussed above, slows down the non-explosive reaction. We know this from adsorption measurements such as those presented in Table V, and by analogy with desorption of hydrogen on nickel. However, there is still enough hydrogen to prevent the oxygen from entering the surface layer, just as the oxygen layer on tungsten warded off the hydrogen.

The upper explosion pressure limit is reached. Further reduction in pressure results in the hydrogen sheath losing its power to exclude oxygen from the surface. This may be caused either by a small desorption of hydrogen, or a large stepwise desorption similar to that found by Benton and White,¹⁰ where a small reduction of hydrogen pressure resulted in the sudden desorption from nickel of a third of all the adsorbed hydrogen. In this way the hydrogen sheath is broken open to a flank attack by the oxygen, excess hydrogen swept from the surface and the surface exposed to equal bombardment by oxygen as well as hydrogen.

The original hydrogen-covered surface released hydrogen atoms into the gas phase at a slow rate such that the ensuing reaction was non-explosive. We cannot predict the new type of surface reaction which will be suddenly produced below the exposure pressure. The nature of the adsorbed gas has been radically altered, and there is no objection to assuming that it

¹⁵ Langmuir, *THIS JOURNAL*, **38**, 2271 (1916).

might initiate chains much faster than the hydrogen-covered surface, in fact so fast that explosion occurs. A possible reaction is



where the energy necessary to produce 2OH from $\text{H}_2 + \text{O}_2$ (only 14 cal.) is supplied by the formation of the Si-O bond. This cannot happen of course if the Si-O is covered with hydrogen, *i. e.*, Si-OH, at higher pressures.

The Lower Explosion Limit.—Professor Haber² has already suggested as the cause of the lower explosion limit, AB, Fig. 1, an insufficiency of triple collisions at low pressure to carry on the chain step $\text{H} + \text{O}_2 + \text{H}_2 \longrightarrow \text{H}_2\text{O} + \text{OH}$, which explains why, below the identical lower pressure limit, neither the thermal explosion^{1,3} nor the spark explosion¹⁶ occurs.

Explanation of Factors Influencing Explosion.—In addition to what has already been said explaining phenomena connected with the non-explosive reaction, such a mechanism satisfies explosive characteristics as well. The upper explosion limit is independent of packing in such similar surfaces as quartz, glass and silica, because it marks the pressure at which oxygen first gains admission to the surface, independent of the amount of surface present. Surfaces of iron and copper give the same qualitative results. Aluminum was expected to be ineffective in causing the explosion, and indeed such was found to be the case. Professor Taylor has called my attention to the similarity between an alumina surface and Langmuir's oxygen-coated tungsten filament.¹⁵ In both instances the covering of oxygen atoms is so tightly bound, chemically, to the metal surface that activity in catalyzing the combination of hydrogen and oxygen is completely paralyzed. No explosion results.

Pretreatment with hydrogen saturates the walls and thereby delays explosion. Of course, the hydrogen may also prevent explosion by poisoning the surface with excess steam.

Excess of hydrogen naturally means one must exhaust to lower total pressures of oxy-hydrogen gas before the hydrogen sheath is broken. The significance of the last column in Table II now becomes apparent: it is the hydrogen pressure below which oxygen gains access to the silica surface.

Other Reactions.—There is every reason to expect that a great many other chain reactions may be initiated at the walls and extend into the gas phase by such a mechanism as we have proposed above. Moreover, in addition to the normal non-explosive reaction, there is always a possibility in each of these cases of sudden change in the nature of the adsorbed gas layer, and a corresponding sudden alteration in reaction velocity upon lowering the pressure. The explosion characteristics of the hydrogen-

¹⁶ Kowalsky, *Z. physik. Chem.*, [B] 11, 56 (1930).

oxygen reaction are probably to be met with in numerous reactions. Several such reactions in the field of oxidations are given.

Oxidation of Carbon Disulfide.—It has already been confirmed by H. W. Thompson^{8,17} that this reaction simulates the hydrogen-oxygen reaction. Reaction chains are initiated at above 150° at a wall doubtless covered with carbon disulfide, which by a mechanism analogous to that postulated above for the generation of hydrogen atoms liberates oxygen atoms into the gas phase. These will react with carbon disulfide in the gas phase, as Kopsch and Harteck¹⁸ have shown, and the reaction chain be propagated as usual. As the pressure is lowered explosion sets in at 200 mm. This would be interpreted to mean that the carbon disulfide is sufficiently desorbed from the glass surface at this point to permit oxygen to gain access to the surface layer, giving rise to a new explosive surface reaction. Carbon disulfide and oxygen flowing from two concentric tubes explode at a much lower temperature¹⁹ (107°) than under the usual static⁸ measurements (140°). This is to be expected because the surface of the oxygen tube should undoubtedly be relatively free from adsorbed carbon disulfide, and, therefore, favorable to initiate explosion at much lower than the normal temperatures.

Oxidation of Carbon Monoxide.—This proceeds at about 650°, presumably initiated on the walls by reaction with adsorbed carbon monoxide. Even at these high temperatures oxygen is still not appreciably adsorbed in an active state.⁷ However, if the chains are initiated by the release of oxygen atoms into the gas phase, the oxidation reaction would proceed by subsequent interaction with water, and not by direct reaction with gaseous carbon monoxide.²⁰ As the pressure of the gases at 650° is lowered to 100 mm., the same phenomenon appears as in the hydrogen-oxygen reaction: due to the possible desorption of carbon monoxide the surface is suddenly bared to attack by oxygen and explosion results.⁸

Oxidation of Hydrocarbons.—Pease²¹ has demonstrated that the oxidation rate of propane decreases several-fold as the temperature is raised from 300 to 425°, but that above this temperature it explodes. The presence of hydrogen has no effect at the lower temperatures, but above 425° it completely inhibits explosion. It is possible that at 300° the surface is covered with propane. As the temperature is raised, propane is desorbed, and the measurable reaction between oxygen and adsorbed propane decreases. At 425° the propane sheath becomes permeable to oxygen and with the new type of adsorbed gas layer explosion occurs.

¹⁷ Thompson, *Naturwiss.*, **18**, 531 (1930).

¹⁸ Kopsch and Harteck, *Z. Elektrochem.*, **36**, 714 (1930).

¹⁹ Dixon, *Rec. trav. chim.*, **44**, 305 (1925).

²⁰ Jackson and Kistiakowsky, *THIS JOURNAL*, **52**, 3471 (1930); Farkas, Goldfinger and Haber, *Naturwiss.*, **12**, 266 (1930).

²¹ Pease, *THIS JOURNAL*, **51**, 1839 (1929).

The hydrogen inhibits only above 425° because below this temperature it is not appreciably adsorbed. Our measurements, Table V, Fig. 3, make it probable that above 425° , however, it would effectively poison the surface and prevent propane explosion.

Post-Explosion.—Farkas, Haber and Harteck²² observed that if, within two minutes after an oxygen–hydrogen mixture has been exploded by a spark, a fresh supply of gas is admitted to the reaction vessel, explosion occurs even at $420, 20^{\circ}$ lower than the lowest normal explosion temperature. It is possible that the spark explosion removes adsorbed hydrogen from the walls, leaving them accessible to oxygen and in a still highly activated state sufficient to catalyze the explosion of the newly admitted gas.

The author wishes to thank Professor H. S. Taylor for his sympathetic interest in, and criticisms of, this paper.

Summary

1. The adsorption of hydrogen on glass increases tremendously above 450° . It is, therefore, adsorbed in a highly activated form not possible at lower temperatures.

2. This gas layer initiates reaction chains which extend out into the gas phase in the combination of hydrogen and oxygen at 500° .

3. Analogously, other chain reactions may be initiated from a layer of gas adsorbed on glass or metallic surfaces, as in the oxidations of carbon disulfide, carbon monoxide and the hydrocarbons.

4. The reaction rate of a hydrogen–oxygen mixture diminishes as the pressure is lowered. Below a certain pressure, however, it explodes. It is shown that the non-explosive and the explosive reactions differ strikingly from each other. The former is extremely sensitive to increase of reaction surface; the latter, not. Pretreatment of the walls with hydrogen, excess hydrogen in the gas mixture, steam and inert gases all accelerate the non-explosive reaction but prevent explosion.

5. These characteristics can be attributed to the controlling influence of the adsorbed layer of hydrogen gas. Explosion occurs at that pressure below which the surface ceases to be completely protected by the hydrogen.

6. Desorption of carbon disulfide or carbon monoxide may similarly account for the sudden explosion of these gases in oxygen below a critical pressure, or for phenomena in the oxidation of the hydrocarbons.

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²² Farkas, Haber and Harteck, *Z. Electrochem.*, **36**, 711 (1930).