CONTACT CATALYSIS. II

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Fractional Combustion

The selective action of the catalytic agent is shown admirably in the fractional combustion of gases, though the data are by no means so complete as one would like. A very interesting study of the effect of platinum on the fractional combustion of gases was made by Henry¹ over ninety years ago; and it is still of fundamental importance.

"Several years have elapsed since the President of the Royal Society [Sir Humphry Davy], in the further prosecution of those researches on flame which had already led him to the most important practical results, discovered some new and curious phenomena in the combustion of mixed gases, by means of fine wires of platinum introduced into them at a temperature below ignition. A wire of this sort being heated much below the point of visible redness, and immersed in a mixture of coal gas and oxygen gas in due proportions, immediately became white-hot, and continued to glow until all that was inflammable in the mixture was consumed. The wire, repeatedly taken out of the mixture and suffered to cool below the point of redness, instantly recovered its temperature on being again plunged into the mixed gases. The same phenomena were produced in mixtures of oxygen with olefiant gas, with carbonic oxide, with cyanogen, and with hydrogen; and in the last case there was an evident production of water. When the wire was very fine, and the gases had been mixed in explosive proportions, the heat of the wire became sufficiently intense to cause them to detonate. In mixtures which were non-explosive from the redundancy of one or other gas, the combination of their bases went on silently, and the same chemical compounds were formed as by their rapid combustion.

¹ Phil. Mag., 65, 269 (1825).

"Facts analogous to these were announced in the autumn of last year by Professor Doebereiner, of Jena, with this additional and striking circumstance—that when platinum in a spongy form is introduced into an explosive mixture of oxygen and hydrogen, the metal, even though its temperature had not been previously raised, immediately glows, and causes the union of the two gases to take place, sometimes silently, at others with detonation. It is remarkable, however, that platinum in this form, though so active on mixtures of oxygen and hydrogen, produces no effect, at common temperatures, on mixtures of oxygen with those compound gases, which were found by Sir Humphry Davy to be so readily acted upon by the heated wire. Carbonic oxide appears indeed, from the statement of M.M. Dulong and Thenard, to be capable of uniting with oxygen at the temperature of the atmosphere, by means of the sponge; but though this is in strictness true, yet the combination, in all the experiments I have made, has been extremely slow, and the due diminution of volume has not been completed till several days have elapsed. On mixtures of olefiant gas, of carburetted hydrogen, or of cyanogen, with oxygen, the sponge does not by any duration of contact exert the smallest action at common temperatures.

"It was this inefficiency of the platinum sponge on the compounds of charcoal and hydrogen in mixture with oxygen, while it acts so remarkably on common hydrogen, and also, though slowly, on carbonic oxide, that suggested to me the possibility of solving by its means some interesting problems in gaseous analysis. I hoped more especially to be able to separate from each other the gases constituting certain mixtures, to the compositions of which approximations only had been hitherto made, by comparing the phenomena and results of their combustion with those which ought to ensue, supposing such mixtures to consist of certain hypothetical proportions of known gases. It might, for instance, be expected that from a mixture of hydrogen and carburetted hydrogen with oxygen, the platinum sponge would cause the removal of the hydrogen, leaving the carburetted hydrogen

unaltered. To ascertain this and a variety of similar facts, I made artificial mixtures of the combustible gases in known volumes; and submitted them, mixed with oxygen, sometimes to contact with the sponge, and sometimes with the balls of clay and platinum, described by Professor Doebereiner.

“When to equal volumes of olefiant gas and an explosive mixture (which is to be understood, whenever it is so named, as consisting of two volumes of hydrogen and one of oxygen gases), one of the platinum balls, recently heated by the blow-pipe, and allowed to cool during eight or ten seconds, is introduced through mercury, a rapid diminution of volume takes place; the whole of the hydrogen and oxygen gases is condensed; but the olefiant gas is either not at all or very little acted upon. In a few experiments when the tube was narrow, and the quantity of mixed gases small, the olefiant gas escaped combustion entirely; but, in general, an eighth or tenth of it was converted into water and carbonic acid. It is difficult, however, to state the precise proportion of any gas which, when added to an explosive mixture, renders the latter insensible to the action of the balls or sponge; for much depends on their temperature when introduced into the gaseous mixture, the diameter of the containing vessel, and other circumstances, which, in comparing different gases, should be so regulated as to be equal in every case.

“When the proportions of the gases are changed, so that the explosive mixture exceeds in volume the olefiant gas, there is a more decided action upon the latter, manifested by an increased production of carbonic acid. Thus, for example, the explosive mixture being to the olefiant as 2.5 to 1, about one-fourth of the olefiant gas was consumed; and by increasing the proportion of the explosive mixture the olefiant gas was still more acted upon. On using oxygen sufficient to saturate both the hydrogen and the olefiant gases, the ball acted much more rapidly: in several instances it became red-hot; all the hydrogen was consumed; and the whole of the olefiant gas was changed into water and carbonic acid. In

this case the use of the sponge is inadmissible, as it kindles the gases, and occasions their detonation.

"When carburetted hydrogen, procured from stagnant water, was added to an explosive mixture, in various proportions between equal volumes, and ten of the former to one of the latter, the action of the hydrogen and oxygen on each other took place as usual, on admitting one of the balls. When, reversing the proportion, the explosive mixture was made to exceed the carburetted hydrogen, but not more than four or five times, the latter gas was entirely unchanged. With a larger proportion of the explosive mixture carbonic acid was always found to have been produced; but still the carburetted hydrogen was very imperfectly consumed; and fully three-fourths of it were generally found to have escaped unburned.

"When to a mixture of hydrogen and carburetted hydrogen, oxygen enough was added to saturate both gases, the effect of the sponge was found to vary with the proportion of the simple hydrogen. In several cases, where the hydrogen did not exceed the carburetted hydrogen more than four times, the latter gas remained unchanged; when in larger proportion, there was a decided action upon the carburetted hydrogen. But it was much more easy to regulate the action of the balls upon such a mixture so as to act upon the hydrogen and oxygen only, than in the case of olefiant gas, which, under similar circumstances, is always more largely converted into water and carbonic acid.

"The addition of one volume of carbonic oxide to two volumes of an explosive mixture produces a distinct effect in suspending the action of the platinum balls, and even of the spongy metal itself. The action of the gases upon each other still, however, goes on slowly, even when the carbonic oxide exceeds the explosive mixture in volume; and after the lapse of a few days the oxygen is found to have disappeared, and to have partly formed water, and partly carbonic acid. I made numerous experiments to ascertain whether the oxygen, under those circumstances of slow combustion, is divided between

the carbonic oxide and the hydrogen in proportions corresponding to the volumes of those two gases. The combustible gases being in equal volumes, and the oxygen sufficient to saturate only one of them, it was found that the oxygen which had united with the carbonic oxide was to that which had combined with the hydrogen as about 5 to 1 in volume. Increasing the carbonic oxide, a still larger proportion of oxygen was expended in forming carbonic acid. On the contrary, when the hydrogen was increased, a greater proportional quantity of oxygen went to the formation of water. But it was remarkable that, when the hydrogen was made to exceed the carbonic oxide four or five times, less oxygen in the whole was consumed than before; the activity of the carbonic oxide appearing to have been diminished, without a corresponding increase in that of the hydrogen.

"In cases where the proportion of the carbonic oxide to the explosive mixture was intentionally so limited that the platinum ball was capable of immediately acting upon the latter, the carbonic oxide was always in part changed into carbonic acid, the more abundantly as its volume was exceeded by that of the explosive mixture. Increasing the oxygen, so that it was adequate to saturate both gases, and causing the hydrogen to exceed the carbonic acid in volume, a speedy action was always exerted by the ball, and the whole of the combustible gases was silently converted into water and carbonic acid. The introduction of the platinum sponge into such a mixture was almost always found to produce detonation. . . .

"It had already been ascertained by Professor Doebereiner that one volume of oxygen diluted with 99 volumes of nitrogen is still sensible, when mixed with a due proportion of hydrogen, to the action of the sponge. Carbonic acid also, even (I find) when it exceeds the explosive mixture ten times, retards only in a slight degree the energy of the sponge. Oxygen, hydrogen, and nitrous oxide gases, when employed to dilute an explosive mixture, are equally inefficient in preventing the mutual action of its ingredients. Ammonia may

be added in ten times the volume of the explosive mixture, and muriatic acid gas in six times its volume, with no other effect than that of rendering the action of the sponge less speedy.

"When mixtures of these gases are exposed to the sponge, the carburetted hydrogen seems to stand entirely neutral. The carbonic oxide is converted into carbonic acid, in the same gradual manner as if it had been mixed with oxygen only; and the carburetted hydrogen remains unaltered.

"In mixtures of these gases, it is of little consequence whether the oxygen be sufficient for the hydrogen and carbonic oxide only, or be adequate to the saturation of all three. The circumstance which has the greatest influence on the results of exposing such mixtures to the sponge, is the proportion which the simple hydrogen bears to the other gases, and especially to the carbonic oxide; for in order that there may be any immediate action, the former should exceed the latter in volume. In that case the hydrogen is converted into water, and the carbonic oxide into carbonic acid; but the carburetted hydrogen, unless the excess of hydrogen be very considerable, remains unaltered. If the proportion of hydrogen be so small that no immediate action is excited by the sponge, the ingredients of the mixture nevertheless act slowly upon each other; and after a few days the whole of the hydrogen and carbonic oxide are found to have united with oxygen, and the carburetted hydrogen to remain of its original volume.

"When the oxygen, in a mixture of these gases, is sufficient to saturate the two first only, and the proportion of hydrogen is so adjusted that the action of the sponge is not very energetic, the hydrogen and carbonic oxide only are acted upon; but if the diminution of volume, which the sponge produces, be rapid and considerable, part of the olefiant gas is converted into water and carbonic acid. This effect on olefiant gas takes place still more readily if the oxygen present be adequate to the saturation of all three combustible gases.

"It is remarkable that, if to a mixture of hydrogen, carbonic oxide, and oxygen, in such proportions that the

sponge would act rapidly in producing combination, olefiant gas be added, the action of the gases on each other is suspended. Thus 20 measures of carbonic oxide, 31 of hydrogen, and 20 of oxygen were instantly acted upon by the sponge; but the addition of 20 measures of olefiant gas to a similar mixture entirely suspended its efficiency. By standing fourteen days, rather more than half the carbonic oxide was acidified, and about one-twelfth of the hydrogen was changed into water, but the olefiant gas remained unaltered.

"In mixtures of these four gases with oxygen, it was found by varying the proportion of hydrogen, that hydrogen and carbonic oxide are most easily acted upon; then olefiant gas; and carburetted hydrogen with the greatest difficulty. When the action of the sponge was moderate, only the hydrogen and carbonic oxide were consumed, or at most the olefiant gas was but partially acted upon. Adding more hydrogen, so as to occasion a more rapid diminution, the olefiant gas also was burned; but the carburetted hydrogen always escaped combustion, unless the hydrogen were in such proportion that the ball or sponge became red-hot.

"From the facts which have been stated, it appears that when the compound combustible gases, mixed with each other, with hydrogen, and with oxygen, are exposed to the platinum balls or sponge, the several gases are not acted upon with equal facility; but that carbonic oxide is most disposed to unite with oxygen; then olefiant gas; and lastly, carburetted hydrogen. By due regulation of the proportion of hydrogen, it is possible to change the whole of the carbonic oxide into carbonic acid without acting on the olefiant gas or carburetted hydrogen. With respect indeed to olefiant gas, this exclusion is attended with some difficulty, and it is generally more or less converted into carbonic acid and water. But it is easy, when olefiant gas is absent, so to regulate the proportion of hydrogen, that the carbonic oxide may be entirely acidified, and the whole of the carburetted hydrogen be left unaltered. This will generally be found to have been accomplished, when the platinum ball has occasioned a diminution of the mixture, at

about the same rate as atmospheric air is diminished by nitrous gas when the former is admitted to the latter in a narrow tube."

Hydrogen is adsorbed by platinum more strongly than ethylene and consequently it tends to burn first. Since ethylene does not burn at all under the same circumstances, it is possible, though not probable, that the combustion in presence of hydrogen may be due to the oxygen passing through some intermediate stage in which it oxidizes the ethylene. That would make this an induced reaction. It seems to me more probable that we are dealing with a case of local heating, the ethylene burning in presence of platinum at the higher temperature thus produced. This is the more probable since more ethylene is burned the greater the ratio of oxy-hydrogen gas and the greater the ratio of oxygen. In fact Henry found that ethylene, when mixed with sufficient oxygen, began to burn in contact with platinum sponge at about 250° and was converted completely into carbon dioxide at about 270° .

Lunge and Harbeck¹ have shown that carbon monoxide is retained very tenaciously by platinum and consequently we should expect it to burn before hydrogen and so it does. Methane is undoubtedly adsorbed much less by platinum than either hydrogen or carbon monoxide and this is in line with the fact that it is burned less readily under these circumstances. Henry found that methane and oxygen begin to react in presence of platinum sponge at temperatures just above 290° . He next studied the behavior of finely divided platinum at high temperatures on those mixtures of gases which are either not decomposed or are decomposed slowly at the temperature of the atmosphere.

"When carbonic oxide and hydrogen gases, in equal volumes, mixed with oxygen sufficient to saturate only one of them, were placed in contact with the sponge, and gradually heated in a mercurial bath, the mixture ceased to expand between 150° and 155° , and soon began to diminish in volume. On raising the temperature to 170° , and keeping it some

¹ Zeit. anorg. Chem., 16, 50 (1898).

time at that point, no further diminution was at length perceptible. From the quantity of carbonic acid remaining at the close of the experiment, it appeared that four-fifths of the oxygen had united with the carbonic oxide, and only one-fifth with the hydrogen. When four volumes of hydrogen, two of carbonic oxide, and one of oxygen, were similarly treated, the hydrogen, notwithstanding its greater proportional volume, was still found to have taken only one-fifth of the oxygen, while four-fifths had combined with the carbonic oxide. These facts show that at temperatures between 150° and 170° , the affinity of carbonic oxide for oxygen is decidedly superior to that of hydrogen; as, from the experiments before described, appears to be the case, also, at common temperatures.

"But a similar distribution of oxygen, between carbonic oxide and hydrogen, does not take place, when those three gases are fired together by the electric spark. This will appear from the following table, in which the three first columns show the quantities of gases that were fired, and the two last, the quantities of oxygen that were found to have united with the carbonic oxide and with the hydrogen.

TABLE I

Volumes before firing			Volumes formed	
CO	H ₂	O ₂	CO ₂	H ₂ O
40	40	20	12	28
40	20	20	24	16
20	40	20	10	30

"When equal volumes of carbonic oxide and hydrogen gases, mixed with oxygen sufficient to saturate only one of them, were exposed in a glass tube to the flame of a spirit lamp, without the presence of the sponge, till the tube began to soften, the combination of the gases was effected without explosion, and was merely indicated by a diminution of volume and an oscillatory motion of the mercury in the tube.

At the close of the experiment, out of twenty volumes of oxygen, eight were found to have united with the carbonic oxide, and twelve with the hydrogen—proportions which do not materially differ from the results of the first experiment in the foregoing table. At high temperatures, then, the attraction of hydrogen for oxygen appears to exceed that of carbonic oxide for oxygen: at lower temperatures, especially when the gases are in contact with the platinum sponge, the reverse takes place, and the affinity of carbonic oxide for oxygen prevails.

“Extending the comparison to the attraction of olefiant and hydrogen gases for oxygen at a red heat, I found that when six volumes of olefiant, six of hydrogen, and three of oxygen were heated by a spirit lamp till the tube softened, a slight combination took place as before; all the oxygen was consumed, but only half a volume had been expended in forming carbonic acid, which indicated the decomposition of only one-quarter of a volume of olefiant gas. On attempting a similar comparison between carbonic oxide and olefiant gas, by heating them with oxygen in the same proportions, the mixture exploded as soon as the glass became red-hot, and burst the tube.

“From the fact that carbonic oxide, olefiant gas, and carburetted hydrogen, when brought to unite with oxygen by means of the platinum sponge, assisted by heat, undergo this change at different temperatures, it seemed an obvious conclusion that by exposing a mixture of those gases with each other and with oxygen to a regulated temperature, the correct analysis of such mixtures might probably be accomplished. Mixtures of two or more of the combustible gases were therefore exposed, in contact with oxygen gas and the platinum sponge, in tubes bent into the shape of retorts, which were immersed in a mercurial bath. This bath was gradually heated to the required temperatures, and by proper management of the source of heat was prevented from rising above that degree.

“By subjecting 25 measures of carbonic oxide, 15 of

olefiant gas, and 57 of oxygen, in contact with the sponge, to a heat which was not allowed to exceed 175° till the diminution of volume ceased, all the carbonic oxide was converted into carbonic acid, and the olefiant gas remained in its original volume. By exposing in a similar manner 20 measures of carbonic oxide, 21 of carburetted hydrogen, and 36 of oxygen, to a temperature below 205° , the carbonic oxide was entirely acidified; and on washing out the carbonic acid by liquid potash, the carburetted hydrogen was found unaltered, mixed with the redundant oxygen. A mixture of 10 measures of olefiant gas, 10 of carburetted hydrogen, and 58 of oxygen being heated in contact with the sponge to 265° , the olefiant gas was silently but entirely changed into carbonic acid, while the carburetted hydrogen was not at all acted upon. By acting with the sponge upon 42 measures of carburetted hydrogen, 22 of carbonic oxide, 22 of hydrogen, and 28 of oxygen, first at a temperature of 170° , which was raised gradually to 250° , all the carbonic oxide was changed into carbonic acid, and all the hydrogen into water; but the carburetted hydrogen remained undiminished in quantity, and was found, after removing the carbonic acid, mixed only with the redundant oxygen. In this experiment the diminution of volume had continued some time before there was any perceptible formation of water, the attraction of carbonic oxide for oxygen appearing to prevail over that of hydrogen. The same precedency in the formation of carbonic acid is always apparent when carbonic oxide and hydrogen, mixed even with oxygen enough to saturate both gases, are raised to 175° .

"By thus carefully regulating the temperature of the mercurial bath, the action of oxygen upon several gases (carbonic oxide, olefiant, and carburetted hydrogen, for example) may be made to take place in succession; and by removing the carbonic acid formed at each operation, it may be ascertained how much of each of the two first gases has been decomposed. The carburetted hydrogen indeed always remains unchanged, and its quantity must be determined by

firing it with oxygen by the electric spark. If hydrogen also be present, it is difficult to prevent the olefiant gas from being partially acted upon; but this is of little consequence, as I had shown that it is easy to remove that gas in the first instance by chlorine. It may be remarked that this method of operating on the aeriform compounds of charcoal gives more accurate results than rapid combustion by the electric spark, being never attended with that precipitation of charcoal which is often observed when the gases are exploded with oxygen. A regulated temperature also effects the analysis of such mixtures much more correctly than the action of the sponge or balls, because in the latter case the heat produced is uncertain; and though sometimes adequate to the effect, yet there is always a risk that it may exceed or fall short of that degree which is required for the successful result of the analytic process."

This method of Henry's was afterwards worked out in more detail by Hempel¹ substituting palladium for platinum. A mixture of hydrogen with an excess of oxygen burns completely when passed over palladium. The reaction begins spontaneously at ordinary temperatures but so much heat is evolved that the palladium glows and the gases explode in case they are present in the ratio to form water. When methane and oxygen are passed over palladium at 100° no combination takes place. The reaction starts at about 200°. Thus there was a contraction of 3 cc when a mixture of 29.3 cc methane and 70.6 cc oxygen was passed several times over palladium at about 200°–220°. When a mixture of hydrogen, methane, and air is passed over palladium at ordinary temperatures or at 100°, the hydrogen alone is burned and the methane remains unchanged, provided precautions are taken so that the palladium does not heat up too much.²

If a mixture of hydrogen and methane is passed over copper oxide at 250°, the hydrogen is burned completely while

¹ Ber. deutsch. chem. Ges., 12, 1006 (1879).

² Cf. Hempel: Zeit. angew. Chem., 25, 1841 (1912).

the methane is not oxidized at all.¹ This method is said² to be distinctly superior to the fractional combustion of hydrogen by palladium or palladium asbestos because no air or oxygen is added to the combustible gas, which makes it possible to pass the total gas residue through the tube with consequent gain in the accuracy of the analytical results.

In view of the comparative readiness with which methane can be separated from hydrogen by the fractional combustion of the latter gas, it is not surprising that people came to the conclusion that hydrogen always burns more readily than methane. From experiments on the burning of illuminating gas, Landolt³ concluded that in the flame "the gases disappear in the order of their combustibility. Hydrogen burns more readily than any other gas and consequently disappears the soonest in the flame. Marsh gas disappears somewhat more slowly, and the denser hydrocarbons disappear latest, burning chiefly in the upper half of the flame." It has been pointed out by Bone⁴ that Landolt's results are vitiated by the fact that he used a platinum tube of narrow bore, fixed along the vertical axis of the flame for the withdrawal of the partly burned products.

Henry's experiments showed that carbon monoxide was burned before hydrogen when in contact with platinum at relatively low temperatures and that hydrogen burned before carbon monoxide when the gases were exploded by an electric spark. This last result is confirmed by Bunsen's experiments⁵ given in Table II. More hydrogen is burned than carbon monoxide until the ratio of the second to the first is at least six. Henry⁶ is quite explicit that the preferential burning of carbon monoxide in presence of platinum at 150°-170° and the preferential burning of hydrogen when the gases are

¹ Jäger: Jour. Gasbeleuchtung, 41, 764 (1898).

² Dennis: "Gas Analysis," 199 (1913).

³ Pogg. Ann., 99, 411 (1856).

⁴ Phil. Trans., 215, 297 (1915).

⁵ Bunsen: Ges. Abh., 2, 586 (1904).

⁶ Phil. Mag., 65, 277 (1823).

fired by the electric spark is merely a question of temperature. Presumably Bunsen and Landolt held the same view because they do not comment on the low temperature results, which they probably would have done had they considered these results abnormal.

TABLE II

Volumes before firing			Ratio of H ₂ O: CO ₂
CO	H ₂	O ₂	
7.36	2	1	0.85
5.98	2	1	1.08
4.87	2	1	1.28
5.03	2	1	1.29
3.90	2	1	1.53
2.82	2	1	1.83

A new light has been thrown upon the phenomena by Bone¹ and his co-workers. Bone was primarily interested in the way in which a hydrocarbon burns in a supply of oxygen insufficient to oxidize it completely to carbon monoxide, and steam; but, as is usually the case, the scope of the investigations soon became much broader. "The reasons for the selection of methane as the most suitable hydrocarbon for these studies were as follows: (1) it is the simplest saturated hydrocarbon and its molecule contains only one carbon atom; (2) preliminary experiments showed that it can be maintained at 480° to 500° (temperatures considerably higher than those afterwards employed in the oxidation studies) for many days without undergoing the least change; and (3) a mixture of two volumes of methane with one of oxygen is non-explosive. This was the mixture used throughout our experiments.

"In a preliminary series of experiments, the object of which was to determine the most suitable experimental methods for the inquiry, the mixture of methane (2 vols) and oxygen (1 vol) was circulated through a tube containing

¹ Jour. Chem. Soc., 81, 535 (1902) et ff.

fragments of unglazed porcelain maintained at a constant temperature (between 400° and 450°) in a Lothar Meyer furnace. The apparatus involved, however, proved too complicated for experiments which necessarily extended over several days continuously; the results, it may be stated, indicate that a portion of the methane was burnt to carbon monoxide, carbon dioxide, and steam without any liberation of free hydrogen or carbon. We also tried maintaining the mixture at 300° to 350° in contact with palladium black but the 'catalytic' effect of the metal introduced complications which made it difficult for us to follow the real cause of the reaction.

"We finally resorted to the simple expedient of sealing the mixtures of methane and oxygen, under atmospheric pressure, in cylindrical bulbs of boro-silicate glass with capillary ends; the bulbs were afterwards maintained at constant temperatures (between 300° and 400°) for several days in an air-bath until the whole or a part of the oxygen had disappeared. The cooled bulbs were subsequently opened under mercury, any change in volume (always a contraction) noted, and the residual gas withdrawn for analysis. We were thus able to examine the gases at various periods during the oxidation of the methane at any given temperature, and we could hardly fail to detect the formation of a product at any stage of the oxidation which afterwards disappeared before the process was completed.

"The interaction of two such gases as methane and oxygen in glass vessels at low temperatures being a surface phenomenon, the temperature at which its velocity is just appreciable, as well as the velocity at any other given temperature, will, to a certain extent, depend on the character of the surface. In our experiments, 300° was the lowest temperature at which any interaction could be detected after the lapse of two or three weeks. At 325° , however, the velocity was much greater; at 350° , in some instances, the whole of the oxygen disappeared within three or four days, while at 400° the oxidation was always completed in a single

day. But we have so far been unable to measure the relative velocities of the reaction at different temperatures on account of the fact that, except at 400° , when the velocity is considerable the influence of the 'surface factor' may be very different even in two bulbs of the same size, shape, and material. Thus, between 325° and 350° , an appreciable amount of oxidation always occurred within three days, but of a series of similar bulbs filled with the same mixture and heated in the same bath, some exhibited a greater amount of oxidation in two or three days than others did in a week or more. Nor does the 'surface factor' of a given bulb remain constant over two or three successive experiments with the same mixture; whether it would finally become constant after a long series of experiments is a point we are now investigating.

"A series of experiments with bulbs similar to those used in the oxidation studies has shown that steam and carbon monoxide can be maintained at 325° for a fortnight without the slightest change occurring. At 350° no action could be detected within a week, but after ten days some 1.7 percent of carbon dioxide had been formed; at 400° about the same amount of change occurred in a week. On the other hand, mixtures of equal volumes of hydrogen and carbon dioxide showed no signs of change when kept at 325° or 350° for a fortnight or at 400° for a week. . . ."

We have found that moderately dry carbon monoxide and oxygen do not react between 300° and 400° ; the formation of between 0.7 and 1.7 percent of carbon dioxide could usually be detected when the *moist* gases were maintained at 325° , 350° , or 400° for a week. The effects of this possible secondary change in the methane experiments are therefore practically negligible.

"In 1895 V. Meyer and Raum¹ published the results of an investigation on the combination of the elements of electrolytic gas in glass bulbs, very similar to those used by us, at temperatures between 300° and 518° . At 300° , the formation

¹ Ber. deutsch. chem. Ges., 28, 2804 (1895).

of water could just be detected after 65 days; in the case of four out of five bulbs maintained at 350° for 5 days, a very small amount of combination occurred (between 0.5 and 1.9 percent only of the original gas had disappeared), while in the fifth bulb as much as 16.4 percent of the gases had combined.¹ At 448° , the combination was still very slow. We have carefully repeated these experiments, using bulbs which had previously been employed for heating the mixtures of methane and oxygen. At 335° we have never been able to detect the slightest formation of water from electrolytic gas within a week; at 350° , in six bulbs no combination took place in a week, although in the case of a seventh bulb, in which the glass had become devitrified at one end, the formation of water could be distinctly seen. At 400° three bulbs exhibited no signs of change after three days; after a week, water could be distinctly seen in one bulb (nearly 40 percent of the mixture had combined) but none could be detected in the other two. Professor Dixon informs us that some years ago he maintained bulbs filled with electrolytic gas at 350° for several weeks, but was unable to detect any formation of water. Our own experience shows that hydrogen and oxygen, even when mixed in combining proportions and undiluted with other gases, do not within a week or two combine at 350° to any appreciable extent provided the glass surface with which the gases are in contact remains perfectly smooth. At 400° , however, we are on the border line where the formation of water may be recognized within a week but hardly within three days. In our experiments with methane at this temperature, the whole of the oxygen always disappeared within a single day.

"We have also found that the following pairs of gases have no mutual action at temperatures between 350° and 400° (within a week or two): methane and carbon dioxide;

¹ Judging from our own experiments at this temperature, we are inclined to attribute this relatively large formation of water to some roughness of the inner surface of the bulb either present originally or caused by a partial devitrification of the glass during heating.

methane and steam; carbon monoxide and hydrogen; it may therefore be taken for granted that no appreciable complication arising from possible secondary change enters into our experiments on the oxidation of methane.

"We have found that between 300° and 400° methane combines with oxygen with an enormously greater velocity than does hydrogen itself under the same conditions."

In a later paper Bone¹ says that "under similar conditions ethane burns much more rapidly than methane, and in borosilicate glass bulbs both hydrocarbons are oxidized at temperatures much below the limiting temperature (about 400°) at which, under similar conditions, steam is formed appreciably from electrolytic gas."

In a lecture before the Royal Institution Bone² showed an experiment "designed to illustrate the infinitely greater affinity of acetylene and ethylene as compared with that of hydrogen for oxygen at the high temperature of flames. I have here two bulbs containing mixtures of each of these hydrocarbons with hydrogen and oxygen corresponding to $C_2H_2 + 2H_2 + O_2$ and $C_2H_4 + H_2 + O_2$, respectively, and I will ask you to contrast the behavior of these with that of the equimolecular mixture of ethane and oxygen $C_2H_6 + O_2$ which was exploded a few minutes ago. It should be noted that while all three mixtures contain the same relative proportions of carbon, hydrogen, and oxygen, they differ in respect of the proportions between the combined carbon and hydrogen. Asking you to bear in mind how the equimolecular mixture of ethane and oxygen on explosion gave rise to a black cloud of carbon and a considerable formation of water, I will now fire the other two mixtures. You will observe that in neither case has there been any deposition of carbon, and an inspection of the cold bulbs will show that little or no steam formation has occurred. In fact the hydrocarbon has been burnt to carbonic oxide and hydrogen, leaving the hydrogen absolutely untouched by the oxygen.

¹ Jour. Chem. Soc., **85**, 694 (1904).

² Proc. Roy. Inst., **19**, 82 (1908).

"These experiments have an important bearing on the chemistry of flames. Hydrogen is usually considered as one of the most combustible of gases, but here we see it pushed to one side by the all-powerful hydrocarbon, as though it were so much inert nitrogen. This at once raises another question which has lately been occupying my attention. Ever since Davy's experiments on flame, the combustibility of hydrogen has been considered to be superior to that of methane; this, however, cannot be true in regard to slow combustion, since it can be easily proved that between 300° and 400° methane is oxidized at a far faster rate than hydrogen. Nevertheless I have recently observed facts which incline me to think that it may possibly be true in regard to flames. If further investigation confirms this opinion, it will be necessary to enquire into the cause of the peculiar relative inertness and stability of methane as compared with other gaseous hydrocarbons when subjected to the action of oxygen at high temperatures."

Later work showed that even at high temperatures methane is burned preferentially.¹ "The possibility of deducing from our bomb experiments a direct comparison between the relative affinities of methane and hydrogen in explosions arose from the fact that the primary oxidation of methane involves a direct transition from $\text{CH}_4 + \text{O}_2$ to $\text{CH}_2(\text{OH})_2$, which latter breaks up ultimately into $\text{CO} + \text{H}_2 + \text{H}_2\text{O}$ without any deposition of carbon. Whence it follows that if mixtures, $\text{CH}_4 + \text{O}_2 + x\text{H}_2$, be exploded, the division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (i. e., direct oxidation) may be deduced from the proportion of the original methane found intact in the final products, provided always that there is no separation of carbon, which in fact is never observed in such circumstances.

"The experimental method consisted therefore in exploding a series of mixtures, $\text{CH}_4 + \text{O}_2 + x\text{H}_2$, in which the hydrocarbon and oxygen were initially present in as nearly as

¹ Bone: *Phil. Trans.*, 215, 298 (1915).

possible equimolecular proportions, but in which x (the volume ratio of H_2 to CH_4) was varied between 2 and 3, and determining from the percentage of the original methane remaining intact in each case (1) the oxygen distribution when $x = 2$ and (2) the influence upon such distribution of successive equal increments of x up to 8. And in order to determine the possible influence of the walls of the explosion vessel upon the results, parallel series of experiments were carried out in each of the two bombs, A (capacity about 103 cc) and B (capacity about 275 cc). In each case the mixture exploded with a distinctly audible sound, which diminished in intensity as the proportion x of hydrogen increased, until with the mixture $CH_4 + O_2 + 8H_2$ only a faint puff was heard. In no case was there any separation of carbon. The mean results of the experiments, so far as the distribution of oxygen between methane and hydrogen is concerned, are summarized in Table III.

TABLE III
Explosion of mixtures $CH_4 + O_2 + xH_2$

$x =$	2	4	6	8
Bomb A	%	%	%	%
O_2 to CH_4	95.3	81.0	54.9	31.4
O_2 to H_2	4.7	19.0	45.1	68.6
Bomb B				
O_2 to CH_4	97.1	91.0	72.6	—
O_2 to H_2	2.9	9.0	27.4	—

"It is at once evident from the results with the mixture $CH_4 + O_2 + 2H_2$ that the affinity of methane is at least twenty to thirty times greater than that of hydrogen for oxygen in explosions. The actual distribution of oxygen when a particular mixture is exploded is undoubtedly influenced to some extent by the walls of the containing vessel but not by the absolute initial pressure. The influence of the containing walls would presumably disappear after a certain limiting ratio of area to volume is attained, and, had the resources at our disposal permitted, it would have been interesting to have made

further experiments with a still larger bomb than B. An examination of the summarized results in Table III leads to the important conclusion that *the influence of successive increases in x , the volume ratio of H_2 to CH_4 in the mixture exploded, upon the actual oxygen distribution for a given vessel is proportional to x^2* . This can hardly mean other than that in explosion flames hydrogen is directly burned to steam as the result of trimolecular impacts, $2H_2 + O_2 = 2H_2O$.

"The success of the experiments described in the preceding section led us to make a similar attempt to determine the division of oxygen between methane and carbon monoxide when mixtures of the general composition $CH_4 + O_2 + xCO$ are exploded under pressure. In this we were not completely successful, owing to a slight separation of carbon in the explosions whenever x exceeded 3.0 or thereabouts. Provided, however, the x did not exceed this limit, no carbon was deposited during the explosion, and such experiments may be given in detail as quite reliable so far as the question of the oxygen distribution between the two inflammable constituents is concerned." When the mixture $CH_4 + O_2 + 3CO$ was exploded in bomb A, 91-92 percent of the oxygen reacted with the methane and only 8-9 percent with the carbon monoxide. With the mixture $CH_4 + O_2 + 6CO$ in bomb A about 20 percent of the oxygen reacted with the carbon monoxide and only 16-17 percent with the same mixture in bomb B. These values of 20 percent in bomb A and 17 percent in bomb B for carbon monoxide correspond with 45.1 percent and 27.4 percent for hydrogen. When the mixture $CH_4 + O_2 + 2CO$ was exploded in bomb B 4.7 percent oxygen reacted with the carbon monoxide as against 2.9 percent reacting with the hydrogen in the corresponding experiment of Table III. At low concentrations ($x = 2$) a little more carbon monoxide is oxidized than hydrogen but it is very much the other way when $x = 6$.

"It is important to compare the results obtained with the foregoing $CH_4 + O_2 + xCO$ mixtures not only among themselves, but also with the results of the corresponding experi-

ments with $\text{CH}_4 + \text{O}_2 + x\text{H}_2$ mixtures. In the first place, it is evident that the affinities of either hydrogen or carbon monoxide are greatly inferior to that of methane for oxygen in explosion flames; thus it may be inferred from the experiments with $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$ that the ratio of the affinities [really reaction velocities] $\text{CH}_4 : \text{H}_2$ is of the order 20 or 30 to 1 at least, and probably higher if the influence of the walls of the containing vessel could be eliminated. Owing to the uncertainty of our knowledge as to the precise mechanism of the combustion of carbon monoxide in explosions, that is to say, as to the extent and character of the intermediary action of steam, it is perhaps difficult to assign, even approximately, any numerical relation between the affinities of methane and carbon monoxide for oxygen in flames. Nevertheless, it may be pointed out, without laying undue stress on the fact, that when the mixtures, initially containing methane, hydrogen, or carbon monoxide, and oxygen in stoichiometrical proportions (i. e., $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$ and $\text{CH}_4 + \text{O}_2 + 2\text{CO}$) were exploded under similar conditions in bomb B, the carbon monoxide was apparently more effective than hydrogen in pulling away oxygen from the predominating affinity of the hydrocarbon. [The reverse is true if one starts with $\text{CH}_4 + \text{O}_2$ and 6H_2 or 6CO .] From the theoretical standpoint it would probably be well worth while to undertake a further extended study of the matter in larger explosion vessels than we have employed, although it would be both a costly and a laborious enterprise.

"Whereas, in the case of hydrogen, the influence of successive increments in x , the volume ratio of the other combustible constituent to methane in the mixture exploded, upon the actual oxygen distribution is proportional to x^2 in the case of carbon monoxide, it is more nearly proportional to x . This points to some fundamental difference between the modes of combustion of the two gases in flames; thus whilst the evidence is strongly in favor of the supposition that hydrogen is burnt directly to steam as the result of trimolecular collisions $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, the results with mixtures $\text{CH}_4 + \text{O}_2 + \text{CO}$ seem to require some different supposition, such, for instance, as an intermediary action of steam."

From the experiments of Henry, Landolt, and Bone, we see that hydrogen burns before methane at low temperatures in contact with platinum and at high temperatures when the gases are drawn off through a platinum tube. We see also that methane burns before hydrogen at moderate temperatures in borosilicate glass bulbs and also when the gases are fired by an electric spark. It is quite clear that a surface phenomenon is an important factor in changing the results. In Henry's experiments the platinum is unquestionably the cause of the preferential burning of the hydrogen and it seems probable that this is also true for Landolt's experiments. The existence of the water-gas equilibrium with hydrogen as one of the constituents is fairly strong evidence that hydrogen is more stable than methane. Bone's results may therefore be considered as approaching at high temperatures the results due to free burning away from a surface. This is the more probable because he always finds a greater relative oxidation of methane in the larger bomb where the ratio of surface to volume is less. The existence of a surface is also shown by Bone's observation that about 80 percent combustion of hydrogen occurs when the mixture $\text{CH}_4 + \text{O}_2 + 2\text{H}_2$ is passed over chamotte¹ at 500°. I do not know enough about the adsorbing properties of chamotte to know just why it acts as it does; but this is a very striking reversal.

Since we can get almost complete preferential burning either of hydrogen or methane at moderate temperatures depending on the nature of the surface, it is probable that a more extended study of different surfaces would give us all the intermediate values for the distribution of oxygen between methane and hydrogen just as Sabatier and Mailhe² have found all sorts of gradations between the reactions $\text{CH}_3\text{CH}_2\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$ and $\text{CH}_3\text{CH}_2\text{OH} = \text{CH}_3\text{CHO} + \text{H}_2$ when alcohol is passed over different heated metals or oxides. While I have not been able to find any definite studies along

¹ Bone: *Ber. deutsch. chem. Ges.*, **36**, 12 (1913).

² *Ann. Chim. Phys.*, [8] **20**, 341 (1910).

this line, there are some indications that special results might be obtained with special solids.

Calvert¹ showed that oxygen adsorbed by boxwood charcoal oxidizes ethylene to carbon dioxide and water at ordinary temperatures. This is not surprising because charcoal adsorbs ethylene strongly. Since charcoal has little or no effect in causing hydrogen and oxygen to combine,² it is probable that we should get a preferential burning of ethylene in case a mixture of ethylene, hydrogen, and oxygen were brought in contact with charcoal. While this experiment seems not to have been tried, we do know that charcoal does seem to promote oxidation of carbon compounds.

In the form of wood ashes charcoal is often used in out-houses and elsewhere to eliminate unpleasant odors. The charcoal first adsorbs the odoriferous substances and then accelerates their oxidation, by oxygen which is adsorbed from the air. This dual function of the charcoal was pointed out clearly by Stenhouse³ in 1854. "The powerful effects of freshly burned charcoal, especially when coarsely powdered, in absorbing gases and vapors, have long been known. Hence the limited extent to which charcoal has occasionally been employed to sweeten fetid water, and animal substances in the incipient stages of putrefaction. Sufficient attention has not, I think, however, been bestowed hitherto upon a second and still more important effect which charcoal exerts upon those complex products of decomposition; viz., that of oxidizing them rapidly, and resolving them rapidly into the simplest combinations they are capable of forming. . . .

"My attention was particularly drawn to the importance of charcoal as a disinfecting agent by my friend, John Turnbull, Esq., of Glasgow, the well-known extensive chemical manufacturer. About nine months ago Mr. Turnbull placed the bodies of two dogs in a wooden box, on a layer of charcoal powder of a few inches in depth, and covered them with a

¹ Jour. Chem. Soc., 20, 293 (1867).

² See, however, Craig: Chem. News, 90, 109 (1904).

³ Pharm. Jour., 13, 454 (1854).

quantity of the same material. Though the box was quite open and was kept in his laboratory, no effluvia were ever perceptible. On examining the bodies of the animals at the end of six months, scarcely anything remained of them except their bones. Mr. Turnbull sent me a portion of the charcoal powder which had been most closely in contact with the bodies of the dogs. I submitted it for examination to one of my pupils, Mr. Turner, who found it contained comparatively little ammonia, not a trace of sulphuretted hydrogen, and very appreciable quantities of nitric and sulphuric acid, with acid phosphate of lime. About three months ago, Mr. Turner subsequently buried two rats in about two inches of charcoal powder, and a few days afterward the body of a full grown cat was treated similarly. Though the bodies of these animals are now in a highly putrid state, not the slightest odor is perceptible in the laboratory.

“From this short statement of facts, the utility of charcoal powder, as a means of preventing noxious effluvia from churchyards and from dead bodies in other situations, such as on board ship, is sufficiently evident. Covering a churchyard to the depth of from two to three inches with coarsely powdered charcoal would effectually prevent any putrid exhalations ever finding their way into the atmosphere. Charcoal powder also greatly favors the rapid decomposition of the dead bodies with which it is in contact, so that in the course of six or eight months little is left except the bones.

“In the modern systems of chemistry, such, for instance, as the last edition of ‘Turner’s Elements,’ charcoal is described as possessing antiseptic properties, while the very reverse is the fact. Common salt, nitre, corrosive sublimate, arsenious acid, alcohol, camphor, creosote, and most essential oils, are certainly antiseptic substances, and, therefore, retard the decay of animal and vegetable matters. Charcoal, on the contrary, as we have just seen, greatly facilitates the oxidation—and consequently the decomposition—of any organic substances with which it is in contact. It is, therefore, the very opposite of an antiseptic.”

Shenstone invented a respirator¹ filled with powdered wood charcoal "to destroy any miasmata or infectious particles present in the air in the case of fever and cholera hospitals, and of districts infected with ague, yellow fever, and similar diseases. The object in view is, by filtering the air through such a porous substance as wood charcoal, to intercept the miasmata which may have got mixed with it. These, I think, cannot fail to be absorbed by the pores of the charcoal, where they will be rapidly oxidized and destroyed by the condensed oxygen with which they will be brought into the most intimate contact. The probability of this expectation being realized is greatly strengthened by the results of repeated trials with the respirator on certain noxious and offensive gases, such as ammonia, sulphuretted hydrogen, hydrosulphate of ammonia, and chlorine. I have found that air, strongly impregnated with these gases, and which could not be respired for any length of time under ordinary circumstances, may be breathed with impunity when the charcoal respirator is worn, the odor of these gases being rendered almost, if not altogether, imperceptible. Any other highly porous substance, such for instance as spongy platinum, or pounded pumice-stone, might probably be found to answer perfectly well for filling the respirator, but I have selected charcoal as the cheapest and most easily available material.

"While the filtration of water through charcoal powder and other porous substances has been advantageously practised for many centuries, the object in view being to deprive the water of numerous impurities diffused through it, which produce injurious effect on the animal economy, it is certainly somewhat remarkable that the very obvious application of a similar proceeding to the lighter fluid in which we live, viz., air, which not infrequently contains even more noxious impurities floating in it than are usually present in water, should have been overlooked so unaccountably up to the present time."

The combined deodorizing and oxidizing action of char-

¹ The first of the modern gas masks.

coal accounts for a fact which has puzzled some campers, that there is no apparent relation between the amount of wood ashes needed and the number of people using an out-house.

In this case there may well be a special catalytic action because Shenstone¹ has pointed out that "the absorbent power of charcoal is comparatively much greater than its capacity for inducing chemical combination. In this respect charcoal presents a remarkable contrast to spongy platinum, which, though inferior as an absorbent for some gaseous substances—such, for instance, as ammonia, of which spongy platinum absorbs only 30 volumes, while charcoal absorbs 90—is, nevertheless, immensely more effective, both as an oxidizer, and as a promoter of chemical combination generally. As it is desirable for some purposes, while retaining the absorbent power of charcoal unimpaired, to increase its oxidating influences, it struck me that this important object might be easily effected by combining the charcoal with minutely divided platinum. In this way, a combination is produced to which I have given the name of platinized charcoal, which possesses the good properties of both of its constituents. In order to platinize charcoal, nothing more is necessary than to boil the charcoal, either in coarse powder or in large pieces, in a solution of bichloride of platinum, and when the charcoal has become thoroughly impregnated with the platinum, which seldom requires more than ten minutes or a quarter of an hour, to heat it to redness in a closed vessel—a capacious platinum crucible being very well adapted for this purpose. When 150 grains of charcoal were impregnated with nine grains of platinum by the process just described, the charcoal was found to have undergone no change in its external appearance, though its properties had been altered very essentially. When a few grains of this platinized charcoal were passed up into a mixture of dry oxygen and hydrogen in the proportions to form water, over mercury, the two gases combined rapidly in the course of a few minutes, precisely

¹ Jour. Chem. Soc., 8, 105 (1856).

in the same way as when a clay ball of spongy platinum is employed. When, however, a fragment of charcoal containing a considerably larger proportion of platinum was passed up into a similar mixture, the gases combined instantly with explosive violence, just as if platinum black had been used. If pieces of cold platinized charcoal are held in a jet of hydrogen, they speedily become incandescent, and inflame the gas. Platinized charcoal, when slightly warmed, likewise rapidly becomes incandescent in a current of coal gas, but the jet of gas is not inflamed, owing to the very high temperature, a white heat, which is required for this purpose. In the vapor of alcohol or wood-spirit, platinized charcoal becomes red-hot and continues so till the supply of vapor is exhausted. In the course of a few hours, spirits of wine, in contact with platinized charcoal and air, are converted into vinegar. I find that 2 percent of platinum is sufficient to platinize charcoal for most purposes. Charcoal containing this small amount of platinum causes a mixture of oxygen and hydrogen to combine perfectly in about a quarter of an hour, and this is the strength of platinized charcoal that seems best adapted for charcoal disinfectant respirators. Charcoal containing 1 percent of platinum causes a mixture of oxygen and hydrogen to combine in about two hours; and charcoal containing the extremely small quantity of $\frac{1}{4}$ percent platinum produces the same effect in from 6 to 8 hours."

Of course it is not certain that the effect of charcoal on the dead dogs was exclusively an oxidizing action due to oxygen adsorbed by the charcoal. Some part of the result may very well have been due to micro-organisms which Stenhouse could not be expected to know about.

It is interesting to note that Bone's experiments on surface combustion led him to the conclusion that adsorption played an important part in the phenomenon. Bone¹ began by a study of the combination of hydrogen and oxygen in contact with hot surfaces of porcelain, magnesia, silver, gold, platinum, nickel, calcined spathic iron ore (containing 79.0

¹ Phil. Trans., 206A, 1 (1906).

percent ferric oxide and 14.5 percent manganous oxide), nickelous oxide, and copper oxide. With each of these surfaces the rate is proportional to the pressure of the dry gas when electrolytic gas is used, is approximately proportional to the partial pressure of hydrogen when either gas is present in excess, and is increased by a previous treatment with hydrogen. In the case of porcelain Bone decides that "porous porcelain occludes or condenses both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. In general, however, whereas in the case of oxygen the process is extremely rapid and the surface layer is soon saturated, the occlusion of hydrogen is slower and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen."

The behavior of magnesium, "together with the fact that the material occludes hydrogen but not oxygen at red heat, shows that the catalytic action must be referred to the power of occluding hydrogen." The catalytic action of the four metals examined is due primarily "to an association of the surface with hydrogen—in the case of silver probably to the formation of an unstable hydride, in the other three cases to an occlusion of the gas. The evidence in favor of the 'occlusion' theory is particularly strong in the case of nickel, where the 'normal' condition of activity can be reduced almost to the vanishing point by prolonged exhaustion at a comparatively low temperature. Moreover, the subsequent recovery of activity can be demonstrated by circulating successive charges of electrolytic gas over the surface under conditions which entirely preclude any chemical action of either of the reacting gases on the metal." "Considering the results obtained with the three different reducible oxides as a whole, they seem to be quite incompatible with any purely chemical explanation of the catalytic process. In the case of copper oxide it would appear to involve the condensation of a film of 'active' oxygen

on the surface, and that this film actually protects the catalyzing oxide from the attacks of the hydrogen, which would otherwise reduce it energetically. At low pressures the film becomes too attenuated to ensure complete protection, and in consequence, the formation of steam is accelerated by reason of hydrogen penetrating through onto the oxide and reducing it. In conformity with this idea, the rate of steam formation when the gases are not present in combining ratios was found to be proportional to the partial pressure of the oxygen.

"In the cases of the other reducible oxides examined, the fact that the gases combined at moderate temperatures, without permanently altering the surface, and at rates always far in excess of the rates at which either the surface was reduced by hydrogen, or the reduced surface reoxidized, does not harmonize with the purely chemical theory. It is difficult to resist the conclusion that in these cases also the catalytic action is due primarily to a physical condensation of one or other of the reacting gases at the surface. Since the rate of combination was always proportional to the partial pressure of the hydrogen in all experiments where the gases were not present in combining ratios, it would appear to be the hydrogen which is condensed and so rendered active."

The fact that the catalytic combustion depends on an intimate contact of the reacting gases with the surface is shown by the appearance of a piece of silver gauze before and after it had acted as catalytic agent for hydrogen and oxygen at 400°. The wires were originally very smooth but after using they became quite rough. Bone¹ points out that at very high temperatures the specific nature of the solid seems to be relatively unimportant. At such temperatures one would get practically no displacement of equilibrium by the catalytic agent because the reaction in the gas phase takes place so rapidly that the final equilibrium is that of the gas phase and not that of the catalytic agent.

¹ Ber. deutsch. chem. Ges., 46, 14 (1913).

The general conclusions to be drawn from this paper are:

1. At low temperatures the nature of the catalytic agent may determine which of two combustible gases will burn the more rapidly.

2. As might be expected hydrogen burns more readily than methane or ethylene in presence of platinum.

3. From Landolt's experiments the same seems to be true in the flame provided a platinum tube is inserted; but these experiments should be repeated.

4. In presence of copper oxide at 250° all the hydrogen in a mixture of hydrogen and methane can be burned without any of the methane being decomposed.

5. In presence of chamotte at 500° hydrogen burns much more readily than methane. So little is known about the adsorption by chamotte that this result could not have been predicted.

6. In borosilicate glass bulbs at 300° – 400° methane, ethane, ethylene, and acetylene are oxidized much more rapidly than hydrogen or carbon monoxide.

7. When mixtures of methane, oxygen, and hydrogen or carbon monoxide are exploded by an electric spark the methane burns much more rapidly than either the hydrogen or the carbon monoxide.

8. Depending on conditions either hydrogen or carbon monoxide will burn the more readily.

9. Since charcoal causes ethylene to be oxidized to carbon dioxide and water, and since charcoal has very little effect on a mixture of hydrogen and oxygen, it is probable that charcoal would cause preferential burning of ethylene in a mixture of ethylene and hydrogen.

10. By suitable selection of the catalytic agent it should be possible to get all intermediate stages from complete burning of methane to complete burning of hydrogen.

11. Since relatively more methane was burned in the explosion experiments the larger the bulb, it seems probable

that methane burns more readily than hydrogen at high temperatures and in the absence of solid catalytic agents.

12. At very high temperatures the specific effect of the solid catalytic agent must become negligible because the reaction will take place so rapidly in the gas phase that the equilibrium reached will be that of the gas phase and not that of the catalytic agent.

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