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The Combination of Hydrogen and Oxygen in Contact with Hot Surfaces

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PHILOSOPHICAL TRANSACTIONS.

I. *The Combination of Hydrogen and Oxygen in Contact with Hot Surfaces.*

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A large number of observations on the rates of chemical reactions in homogeneous systems, *e.g.*, in solutions, has proved that the velocity of a given reaction is determined by its order in accordance with the principle of mass action. It has been frequently assumed that the velocities of gaseous reactions are governed by the same law, although the few measurements which have been so far made hardly justify the assumption. Take, for example, the decomposition of arsine, the velocity of which was determined by enclosing the gas, at atmospheric pressure, in a glass bulb maintained at 310° and recording the pressure at the end of successive time intervals.* The results showed that the velocity of decomposition is directly proportional to the concentration of the arsine. On the assumption that the rate of change was governed by the law of mass action, it was concluded that the decomposition was a monomolecular one. But it is known that at temperatures below about 1000° the vapour of arsenic consists of tetratomic molecules, and, therefore, the equation for the decomposition of arsine at 310° must be written

$$4AsH_3 = As_4 + 6H_2.$$

If so, then assuming that the decomposition takes place in a homogeneous system, its velocity should, according to theory, be proportional to the fourth power of the arsine concentration, and not to the first power as the experiment proves it to be. The discrepancy here indicated has been explained by the further assumption that the reaction really proceeds in stages, as follows :—

(*a*) The monomolecular decomposition of arsine at finite velocity

$$AsH_3 = As + 3H;$$

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* D. M. Kooij, 'Zeit. Phys. Chem.,' 1892, vol. 12, p. 155; J. H. Van 't Hoff, 'Studies in Chemical Dynamics' (1896), p. 2.

(*b*) The subsequent combinations of (1) four arsenic atoms forming the complex As_4, and (2) two hydrogen atoms forming H_2, both combinations taking place with relatively infinite velocities.

The recent determinations of the velocity of the decomposition of ammonia in porcelain vessels at high temperatures by Dr. PERMAN and Mr. ATKINSON* indicate that it is always proportional to the first power of the ammonia concentration. The authors concluded that the decomposition "is monomolecular, proceeding according to the equation $NH_3 = N + 3H$; the union of the atoms to form molecules is probably so quick that it can be neglected when compared with the rate of decomposition of the ammonia molecule" (p. 116).

It may, however, be seriously questioned whether the above assumptions are admissible; whether, in such cases, we are dealing with a chemical change in a homogeneous system to which the principle of mass action can be applied.

In discussing the velocities of gaseous reactions, the catalytic influence of the heated surface to which the gases are exposed, *i.e.*, the walls of the containing vessel, or any solid material with which it may be packed for the purpose of accelerating the reaction, has hitherto not received the attention it deserves. Many workers have investigated the combination of gases in glass vessels at elevated temperatures, and it is generally agreed that, in a large number of cases, the chemical change is mainly, if not entirely, confined to the layer of gas immediately in contact with the surface. We may here recall the many independent attempts of VAN 'T HOFF and VICTOR MEYER to measure the velocity of the interaction of hydrogen and oxygen in glass bulbs, at temperatures below the ignition point. Their efforts were, however, frustrated by the controlling influence of the "surface factor." It would appear, therefore, that whatever may be the mechanism of the "surface action," the gas actually lying on the surface is in a different condition from the main body of the gas, and that this condition is more favourable to chemical interchanges. The system is, therefore, not homogeneous, and the law of mass action does not generally apply to it.

The power possessed by platinum and certain other metals of inducing the combination of hydrogen and oxygen at low temperatures engaged the attention of many eminent investigators during the early part of last century. In 1817 Sir H. DAVY† discovered that a warm spiral of platinum wire will bring about the ignition of hydrogen, and in the next year ERMAN‡ found that electrolytic gas may be fired by such a spiral warmed to 50° only. The subject was, however, first systematically investigated by DULONG and THÉNARD§ and, independently, by DÖBEREINER‖ in the year 1823. DULONG and THÉNARD found that the activity of

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* 'Roy. Soc. Proc.,' 1904, vol. 74, p. 110.

† 'Phil. Trans.,' vol. 107, 1817, p. 77; 'Quart. Journ. of Science,' vol. V., 1818, p. 128.

‡ 'Abhandlungen der Akademie der Wissenschaften in Berlin für 1818–1819,' p. 368.

§ 'Ann. Chim. Phys.,' vol. 23, 440; vol. 24, 380.

‖ 'Schw.,' 34, 91; 38, 321; 39, 159; 42, 60; 63, 465.

platinum is enhanced by immersion in hot nitric acid, followed by a rapid washing with distilled water. The activity thus imparted is lost on exposure to the atmosphere, more quickly in damp than in dry weather, but may be restored either by ignition followed by rapid cooling, or by treatment with nitric acid. Finely divided silver was found to induce the combination of the gases at 150°, thin gold leaves at 260°, whilst fragments of non-metallic substances, such as charcoal, pumice-stone, porcelain, rock crystal and glass exhibited the power at temperatures below 350°. In the case of glass, it was observed that angular pieces were approximately twice as effective as spherical masses of equal surface. DÖBEREINER discovered that freshly prepared platinum black absorbs oxygen from the air, and when thus charged will cause the formation of steam when plunged into a jar of hydrogen. The operation of alternately charging the metal and then burning away the oxygen in hydrogen can, he found, be repeated many times. The platinum thus appeared to act as a carrier of oxygen to the hydrogen.*

This conclusion was, however, criticised by FUSINIERI† in 1825, who, on physical grounds, advocated the view that the function of the platinum is to condense the hydrogen on its surface. This view derived some support from the observation of WILLIAM HENRY‡ that when a platinum ball is immersed in a mixture of equal volumes of electrolytic gas and ethylene, the hydrogen and oxygen alone combine, no combination of the hydrocarbon occuring unless the original mixture contained a much larger proportion of electrolytic gas. This important result was confirmed by GRAHAM in 1829.§

In 1834 FARADAY‖ found that if platinum electrodes are employed in the electrolysis of dilute sulphuric acid, the anode acquires the power of inducing the combination of electrolytic gas to a very high degree, whereas the cathode only becomes feebly active. He attributed the activity of the metal to its power of condensing the hydrogen and oxygen on its surface; the "condensed" gases then combine at the ordinary temperature. This theory was strongly opposed by DE LA RIVE,¶ who revived the idea that the metal acts simply as a carrier of oxygen to the combustible gas, the catalytic process being essentially a series of alternate oxidations and reductions. In support of the "oxygen" theory, he urged the fact that when an alternating current is sent through acidulated water between platinum electrodes, the latter become covered with a fine black powder, produced by the repeated oxidation and reduction of the metal. He further showed that platinum foil rendered active by any of FARADAY'S methods will absorb oxygen but not hydrogen.

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* 'LIEBIG'S Annalen,' XIV. (1835), p. 10.

† 'Giorn. di Fisica,' VII. (1824), pp. 133, 371, 443; VIII. (1825), 259; IX. (1826), p. 46.

‡ 'Annals of Philosophy,' 1825, vol. 25, p. 416.

§ 'N. Quart. Journ. of Science,' vol. 6, p. 354.

‖ 'Experimental Researches in Electricity,' I., p. 165; 'Phil. Trans.,' 1834, Part I., p. 55.

¶ 'Pogg. Annalen,' 46, 489; 54, 386.

We may now consider, *à priori*, the factors which may determine the velocity of an irreversible gaseous reaction of the type $A+B = AB$ in a heterogeneous system. Regarding the matter from the kinetic standpoint, the observed rate of change will, in the absence of other disturbing factors, depend on (1) the actual rate of combination at the surface; (2) the rates at which A and B, respectively, diffuse inwards from the inert atmosphere outside on to the surface; and (3) the rate at which the product AB diffuses outwards. NERNST* has recently advanced a general theory of reactions in heterogeneous systems based on measurements of the rates of solution of salts in water, or of metals and such substances as magnesia, marble and metallic hydroxides in acids. He assumes that, for all practical purposes, the rate at which equilibrium is established at the limiting surface between the two phases (solid-liquid or solid-gas) is infinitely great compared with the rates of diffusion of the reacting substances on to, or of the reaction product away from, the surface. Hence the velocity observed in the system will depend not on the "order" of the reaction, but on the diffusion factors only. Our experiments have proved that this "diffusion" theory is incapable of explaining the facts of the catalytic combination of hydrogen and oxygen. There are clearly other factors which have a determining influence on the course of events.

BODENSTEIN'S *Experiments.*

In the year 1899 M. BODENSTEIN† published the results of experiments on the non-explosive combination of electrolytic gas during its passage through a glazed porcelain tube heated in a lead bath to various temperatures between 482° and 689°. The author was himself conscious of certain inherent sources of error in his experimental method, which influenced the results quite irregularly and often in a very annoying manner ("in oft recht unliebsamer Weise"). In view of this admission it is difficult to say what is the precise significance of his work. Whilst fully recognising that he was dealing with a surface phenomenon entirely, BODENSTEIN concluded that it is impossible to deduce any mathematical expression for his results other than the equation for a reaction of the third order. This, of course, means that, notwithstanding the fact that the reaction was entirely confined to the layer of gas immediately in contact with the walls of the reaction vessel, its velocity was governed by its "order" in accordance with the law of mass action. We shall, however, have no difficulty in proving that this conclusion is wrong.

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* 'Zeit. Phys. Chem.,' 1904, vol. 47, p. 52. In applying the theory to the special case of catalytic gas reactions, NERNST remarks, "Da diese Reaktionen wohl ausschliesslich an der Grenzfläche des Katalysators abspielen, so wird die Geschwindigkeit keineswegs durch den Mechanismus der betreffenden Reaktion, sondern wenn, was allerdings von vornherein nicht sicher ist, der Katalysator während des Reaktionsverlaufes konstante Beschaffenheit behält und zugleich mit praktisch unendlicher Geschwindigkeit die betreffenden Substanzen an der Grenzfläche zur Reaktion bringt, auch hier lediglich durch die Diffusion der reagierenden Stoffe zum Katalysator bedingt werden," p. 55.

† 'Zeit. Phys. Chem.,' 1899, vol. 29, p. 665.

In 1903 BODENSTEIN* published a second paper dealing with the combination of hydrogen and oxygen in contact with a catalysing surface of platinum at the ordinary temperature. The experiments described are divided into two series. In the first series, the platinum surface was kept at the same temperature as the surrounding gas, so that a film of water formed on the surface. Under these conditions, the velocity of the reaction was found to be approximately proportional to the pressure of the electrolytic gas present, any excess of either hydrogen or oxygen merely acting as a diluent. This was explained on the "diffusion" theory by assuming an infinitely great rate of combination at the surface, and that therefore the observed rate depends on the rate of solution of oxygen, or on that of hydrogen when the gas contains an excess of oxygen, in the water film. But whilst the results of the published experiments support this theory, the author admits that others (unpublished) did not.†

In the second series of experiments, the surface of the metal was kept dry by maintaining it at a slightly higher temperature than the surrounding gas. Here the absolute rate of combination was much greater than in the first series of experiments, and it no longer, even approximately, conformed to an equation of the first order. In one experiment, for instance, where "normal" electrolytic gas was employed, the "velocity constant," $\left(k = \frac{1}{t} \log \frac{C_0}{Ct}\right)$, increased from 0·038 to 0·117, or by more than 200 per cent., as the pressure in the apparatus fell from 750 to 24·5 millims. in 14 minutes. In other experiments the values of "k" similarly increased by 100 per cent.

In connection with their researches on the mechanism of hydrocarbon combustion, the authors devised a circulation apparatus which is well adapted for measuring the velocities of catalytic gas reactions, where the product can be quickly removed from the sphere of action either by condensation, or by solution in water or other absorbing liquid. It was therefore decided to make a systematic study of the case of hydrogen and oxygen, in the hope of obtaining sufficiently reliable data to discriminate between the various possible explanations of the action of surface in inducing gaseous reactions. And, in order to avoid the danger of errors arising from a too restricted view of the phenomena, it was decided to examine in detail the action of a great variety of surfaces, including porous porcelain, magnesia, platinum, gold, silver, nickel, copper, and certain easily reducible metallic oxides, such as copper oxide, nickel oxide, and a mixture of ferric and manganous oxides obtained by calcining spathic iron ore. Bartya was also examined, but with less satisfactory results, owing to constant variations in its catalysing power, which seriously affected the velocity measurements.

In the case of an oxidisable metal, or a reducible oxide, it seems necessary to distinguish in principle between the purely "catalytic" combination of the gases

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* 'Zeit. Phys. Chem.,' 1903, vol. 46, p. 725.

† In this connection he remarks, "bei allen späteren (Versuchen) war der Anschluss an die zu Grunde gelegte Gleichung ein merklich schlechterer, und eine ganze Anzahl Beobachtungen wurden gemacht, die zu der Annahme der unendlich grossen Verbrennungsgeschwindigkeit nicht stimmen . . . ." (p. 737).

without any permanent oxidation or reduction of the surface and ordinary chemical processes which do involve such permanent changes. The experiments with reducible oxides, and more particularly those with copper oxide, show that the two kinds of change are quite distinct in character. It is usually not difficult in such cases to find a range of temperature within which the purely catalytic process goes on uncomplicated by the other kind of change, and it is with the mechanism of the former that we are alone concerned in this paper.

Although the research has revealed important minor differences between the action of the various surfaces examined, the results, as a whole, leave no room for doubt but that the catalytic process depends primarily on a condensation of one or other (and, in some cases, possibly both) of the reacting gases on the heated surface. Any purely chemical explanation of the phenomena, such, for instance, as the theory of a rapidly alternating series of oxidations and reductions of the catalysing material, seems quite inadmissible. Equally certain is it that the rate at which the gases combine over a given surface is governed neither by the "order" of the reaction, nor by diffusion factors simply.

The catalysing power of a new surface usually increases up to a steady maximum when successive charges of electrolytic gas are circulated over it. After the attainment of this steady state, the rate of steam formation is always directly proportional to the pressure, provided that the gases are present in their combining ratios, and that the product is rapidly removed from the sphere of action. In other words, the velocity curve for electrolytic gas is always of a "monomolecular" type, after the surface has acquired its "normal" degree of activity. This applies to all the surfaces examined.

When one or other of the reacting gases is present in excess, the rate of combination is nearly proportional to the partial pressure of the hydrogen, which thus becomes the determining factor in any given experiment. The case of copper oxide, and to a certain extent that also of silver, proved to be exceptional in this respect; these cases will be fully discussed later. The whole evidence of the research shows that, except in the case of copper oxide, the hydrogen plays an all important rôle in the catalytic process, being rendered "active" by association with the surface. In the majority of cases the hydrogen is merely "occluded," but in the case of silver there is evidence of chemical combination, that is to say, of the formation of an unstable hydride at the surface. In conformity with this view, the catalysing power of many of the surfaces examined (*e.g.*, porcelain, magnesia, silver, gold, platinum, and nickel) could be stimulated, often in a very high degree, by previous exposure to hydrogen at moderately high temperatures.

In this connection reference must be made to the recent researches of MM. PAUL SABATIER and JEAN SENDERENS,* which have drawn attention to the remarkable

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* 'Comptes Rendus,' (1899), 128, 1173; (1900), 130, 1559, 1761; (1901), 132, 210, 1254; (1901), 133, 321; (1902), 134, 514, 689, 1127; (1902), 135, 87, 225; (1903), 137, 301.

power of many metallic surfaces (and especially nickel) of rendering hydrogen "active" at comparatively low temperatures. In illustration of their results we need only give the following typical instances of direct "*hydrogenations*" effected by passing a mixture of the substance in question with hydrogen over finely divided and freshly reduced nickel. In this way hydrocarbons of the olefine series were quantitatively converted into the corresponding paraffins at 160°, and benzene yielded cyclo-hexane. Nitrobenzene was directly reduced to aniline, whilst nitromethane was converted into methylamine at 150° to 180°, and into methane and ammonia at 350°. The most remarkable results of all, however, were obtained with a mixture of carbon monoxide (1 volume) and hydrogen (3 volumes), which the authors state was completely transformed into methane and steam when passed over finely divided nickel at 250°.

Whilst there can be no gainsaying the facts relative to the extraordinary "activity" of hydrogen when it is condensed or occluded by many surfaces, metallic and otherwise, opinions will probably differ as to the cause of the "activity." Many will attribute it to the dissociation of the hydrogen molecule at the moment of occlusion, whilst others will possibly connect it with some influence of hydrogen upon the rate of emission of ions by the surfaces involved. The experiments of Dr. H. A. Wilson on "The Discharge of Electricity from Hot Platinum"* are very suggestive in this connection. He found that hydrogen has an enormous influence on the negative leakage from a clean platinum wire at high temperatures. Thus at 1350°, for a given potential difference, the leakage in hydrogen, at 0·014 millim. pressure, was 25,000 times greater than the corresponding leakage in air. The leakage was, moreover, proportional to the pressure and depended on the hydrogen actually occluded by the metal. These experiments were made at much higher temperatures than any employed in our research, but Professor J. J. Thomson has recently found that the rate of emission of negative corpuscles by alkali metals at the ordinary temperatures is greatly increased whilst they are absorbing hydrogen.† It should also be mentioned that the Reverend P. J. Kirkby, who has qualitatively examined the effects of electrically heating a platinum wire (to *circa* 275°) in electrolytic gas at low pressures (40 millims. and under), concludes that the catalytic combination is "probably connected with the corpuscular discharge which is known to be emitted by platinum."‡ It therefore seems possible that the results obtained by the above investigators and those recorded in this paper may have a common explanation. Whether or not the emission of negative corpuscles by a metal under the influence of hydrogen would induce the combination of the gases immediately in contact with the surface is a question for further investigation.

Our experiments with reducible oxides, and particularly those with copper oxide,

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[*] 'Phil. Trans.,' A, vol. 202, (1903), p. 243.

[†] 'Phil. Mag.,' 6th series, vol. X. (1905), p. 584.

[‡] 'Phil. Mag.,' 6th series, vol. X. (1905), p. 467.

are of special interest in that they prove how inadequate is any purely chemical view of the catalytic process. In the case of ferric and nickel oxides it is possible, within certain temperature limits, to obtain a truly catalytic combination at a rate far in excess of that at which either the surface itself is reduced by hydrogen alone, or the reduced surface reoxidised by oxygen. In the case of copper oxide, it would appear that the catalytic process primarily involves the condensation of "active" oxygen at the surface, and that the film of condensed oxygen actually protects the surface from the attacks of hydrogen; indeed, the substitution of inert nitrogen for the oxygen of electrolytic gas always produces a very remarkable acceleration of the rate at which the hydrogen disappears.

One of the chief difficulties encountered in experiments of the kind under discussion is the reattainment of the state of "normal" activity in a given series of experiments, possibly extending over many days or even weeks together, during the course of which conditions other than temperature are purposely varied. Indeed, the certainty with which the surface can be restored to its "normal" state after a given change of conditions is often a criterion of the value of the series. It is always important, in interpreting the results of a particular set of experiments, to take into account the past history of the surface, and to follow carefully any changes in its catalytic power induced by special circumstances. Throughout the paper, therefore, the experiments with a given surface are described in their chronological order, and the date on which each experiment was performed is indicated in the tabulated results.

An Apparatus for Measuring the Velocities of Catalytic Gas Reactions.

The apparatus employed for measuring the velocity of the catalytic combination of hydrogen and oxygen during this research is shown in Diagram I., fig. 1. It is, however, well adapted for velocity measurements in the case of other catalytic gas reactions when the product can be removed by condensation or absorption by a suitable reagent.

It consists essentially of a closed system in which the reacting gases are circulated, at a uniform rate, over the particular surface under investigation, maintained at a constant temperature, and afterwards through a cooling or absorption arrangement to ensure the rapid removal of the reaction product, in this case steam. The rate of combination is, in the case under discussion, measured by observing the pressure in the apparatus at regular intervals of time. By means of a series of "bye-pass" sampling tubes, samples of the gases can, if necessary, be cut off at intervals during an experiment without altering the pressure in the apparatus, or in any way interfering with either the course or the conditions of the reaction.

Two great advantages may be claimed for this apparatus, namely, (1) that with ordinary electrolytic gas it allows of velocity measurements being made in a single

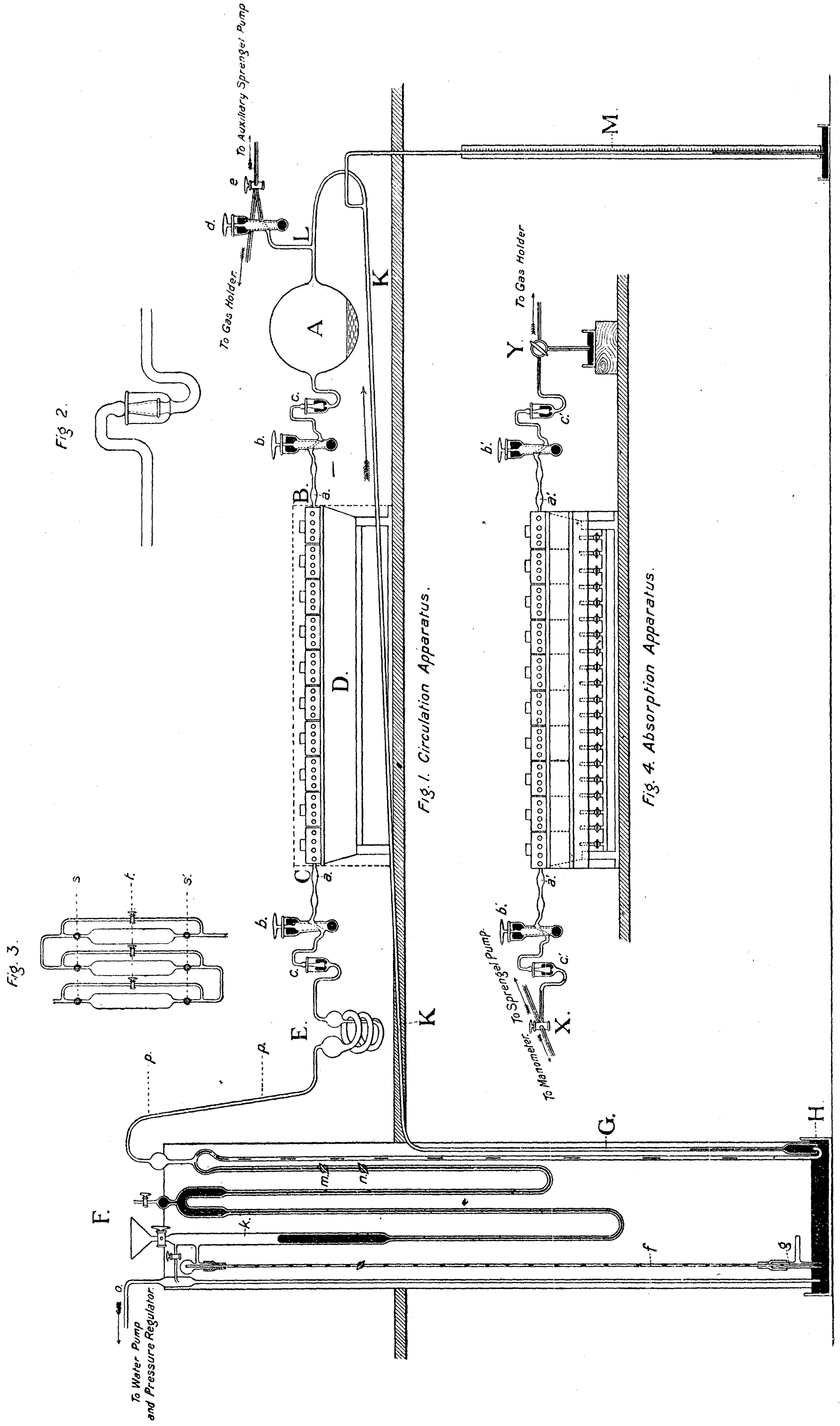

Fig. 1. Circulation Apparatus.

Fig. 4. Absorption Apparatus.

Diagram I.

experiment over a wide range of pressure (from about 500 millims. to as low as 20 millims.), so that practically the whole velocity curve may be determined, and (2) that in cases where the gases are not originally present in their combining ratio, it is possible to follow the variations of the velocity with an ever increasing excess of one of them.

The glass globe A (capacity = about 1200 cub. centims.) serves merely as a reservoir for the reacting gases; it contains a few cubic centimetres of distilled water, so that the gases are kept saturated with aqueous vapour at the room temperature (which is indicated by a thermometer placed with its bulb in contact with the outer wall of the globe).

From the globe the gases are drawn by the automatic Sprengel pump F (the "circulating pump"), at a uniform rate, through the Jena hard glass combustion tube BC, containing the surface under examination, and which is heated in the Lothar Meyer constant temperature furnace D. This furnace is protected from draughts by a thick asbestos hood (indicated by dotted lines in the diagram), at each end of which are arranged suitable screens in order to shield the rest of the apparatus from radiated heat. The gas supply of the furnace is regulated by a Stott's governor, which keeps the temperature constant for, if necessary, many days together.

Each end of the combustion tube is fitted with special glass joints (*aa*) composed of rings of glass of gradually diminishing hardness fused together, ending ultimately in a grade of glass soft enough to allow of its being fused direct on to the mercury cup taps *bb*. The adoption of these special joints obviated the use of any indiarubber connections in the apparatus. The mercury cup taps, *bb*, are in turn connected, by fused glass joints, with the ground glass joints *cc*, each of which works under a mercury seal. An enlarged drawing of one of these joints is shown in the diagram (fig. 2). This device allows of the ready removal of the entire combustion tube, and its transference to similar mercury sealed joints, *c'c'*, in the "absorption apparatus" (fig. 4), to be described later.

On leaving the combustion tube the gases pass through a glass worm, E, surrounded by a water jacket (not shown in the diagram), through which a stream of cold water is constantly maintained, to ensure the rapid cooling of the hot gases and the condensation of steam. The cooled gases then pass onwards to the automatic Sprengel pump F, which delivers them up into the vertical tube, G, standing over mercury in the trough H; thence they pass along the horizontal tube, KK, back again into the globe A, thus completing the circuit.

The apparatus is closed by the mercury cup tap, *d*, sealed into the ⊥-piece L. The other side of *d* is connected, by a fused glass joint, with the three-way tap *e*, through which communication may be made either with the gas-holder containing the experimental mixture, or with an auxiliary automatic Sprengel pump used for the rapid exhaustion of the apparatus as circumstances require. The pressure in the apparatus at any given moment is indicated by the mercurial gauge M, fused into the horizontal tube KK at a point near to the globe A.

It is necessary for the complete success of a given series of experiments that the rate of circulation shall be maintained strictly uniform for, if need be, many days together. This was secured by automatically regulating the suction of the water pump employed to work the Sprengel circulating pump.

The suction of the water pump, applied at *o*, raises mercury from the trough H, a short distance up the tube *f*, which just rests on the surface of the mercury. The mercury is broken up into short threads by the entrance of air (filtered through cotton-wool) through the horizontal arm of the wider **T**-piece *g*, the vertical branch of which reaches to the bottom of the trough H. The force is now sufficient to drive the short threads up to the top of the tube *f*, whence they fall into the reservoir *k*. The circulation of the gases in the apparatus can be adjusted to any desired rate, within considerable limits, by means of the stop-cocks *m*, *n*, which serve to regulate the flow of mercury down the full tube of the circulating pump.*

The capacity of the whole apparatus is about 1500 cub. centims., that of the combustion tube only about 75 to 125 cub. centims., according to the closeness with which it is packed with the catalysing material. In considering the experimental results, it is useful to remember that the dimensions of the apparatus are such that a fall in pressure of, say, x millimetres during a given time interval corresponds to the combination of as nearly as possible $2x$ cubic centimetres of the reacting gases ($2H_2+O_2$).†

Sampling of the Gases during an Experiment.

It was frequently desirable, and sometimes necessary, to check the pressure records by analysing samples of the gas cut off at regular intervals during an experiment. In order to do this without altering the pressure in the apparatus, or interfering with the course of the reaction, the device of "bye-pass" sampling tubes shown in Diagram I., fig. 3, was employed. When required, these tubes were fused into the circulation apparatus, between the worm E and the circulating pump F, at points indicated by the dotted lines *pp*. At the beginning of an experiment the taps *ss* at the ends of each of the tubes were opened, and the taps *tt* in the "bye-passes" closed. It was thus only necessary to close the taps *ss* at each end of one of the tubes and

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[*] The rate of circulation, which is, of course, strictly uniform throughout a given series of experiments, can be varied in different series, so that the gases can be made to complete a circuit in from 30 to about 120 minutes. Such abbreviated expressions as "rate of circulation = 1 in 30 minutes," often used throughout this paper, mean a rate such that the gases completed the circuit once every 30 minutes.

[†] For the purposes of this research two circulation apparatuses were installed in the laboratory. This not only effected a considerable economy of time, but it also permitted of simultaneous examinations of the action of two different surfaces. This plan was so advantageous that during part of the research a third apparatus was requisitioned.

to open the tap *t* in the corresponding "bye-pass" to shut up a sample of the gas at any given moment. At the conclusion of the experiment, after the rest of the apparatus had been exhausted, the contents of each sampling tube could be successively withdrawn through the pump for analysis.*

Preparation of the Gases.

The electrolytic gas employed during the research was prepared by the method recommended by Mr. H. Brereton Baker,† namely, by the electrolysis of a solution of highly purified barium hydroxide. This method ensures its freedom from hydrocarbon impurity, ozone, or hydrogen peroxide, [and repeated careful analyses showed that its constituents were present in exactly their combining ratio.—*February* 10, 1906.]. The gas was collected in a graduated glass holder, fitted with ground-glass joints, over a mixture of equal volumes of pure glycerine and water. From this holder the gas was passed direct into the circulation apparatus, as required. When it was necessary to experiment with mixtures originally containing an excess of one of the reacting gases, the electrolytic gas was mixed in the holder with a known proportion either of hydrogen, prepared electrolytically from a solution of barium hydroxide, or of oxygen, prepared by heating recrystallised potassium permanganate.‡

Experimental Method.

Throughout a given series of experiments the gas supply of the furnace was never interfered with, so that the combustion tube was kept at the desired constant temperature day and night, not only during each experiment, but also during the intervals between two experiments. In this way perfect uniformity of temperature conditions was secured. At the outset of an experiment, the circulation apparatus was thoroughly exhausted by bringing the auxiliary Sprengel pump into action. The experimental mixture was then admitted to the vacuous apparatus, and five minutes later the first pressure reading was taken. Subsequent pressure readings were taken at regular intervals up to the end of the experiment; these readings, corrected for small variations in the room temperature and for the pressure of water vapour, gave a direct measure of the reaction velocity. The time intervals were determined by a chronograph recording stop-watch.

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[*] [It should be stated that all the gas-analyses in connection with the research were carried out over mercury in an improved form of McLeod apparatus described by one of the authors in the 'Proceedings of the Chemical Society,' vol. XIV. (1898), p. 154.—*February* 10, 1906.]

[†] 'Journal of the Chemical Society,' vol. LXXXI. (1902), p. 400.

[‡] The expression "normal electrolytic gas," used throughout this paper, means electrolytic gas *without* any addition of oxygen or hydrogen.

The Absorption Apparatus.

Whenever it was necessary to test the power of a given surface to absorb hydrogen (or oxygen) at higher temperatures than could be obtained with the Lothar Meyer furnace of the circulation apparatus, the combustion tube containing the catalysing material was transferred to the "absorption apparatus" shown in Diagram I., fig. 4. This consisted of a high-temperature furnace, properly screened by an asbestos hood and placed symmetrically with regard to the two ground-glass mercury cup joints *c′c′*, into which the combustion tube exactly fitted. One of these joints was fused on to the three-way tap X, through which connection could be made either with an automatic Sprengel pump or a syphon manometer. The other joint was similarly fused to the tap Y, which served to connect the apparatus with the gas-holder containing the hydrogen (or oxygen). In making an experiment, the combustion tube was first of all thoroughly exhausted and heated to the desired experimental temperature (usually about 650°), which was kept constant by the employment of a Stott's governor in connection with the gas supply of the furnace. The gas under examination was then admitted from the holder, and the absorption (if any) followed by taking pressure readings every few minutes. When the material was fully charged, the furnace was turned out and the unabsorbed gas pumped out in the cold. Finally, the combustion tube was again heated to the experimental temperature and any occluded gas pumped out and collected for examination. In this way the rapidity and extent to which a given surface occluded the gas was measured, and, by afterwards transferring the combustion tube with its contents back again to the circulating apparatus, the influence of repeated occlusions on its catalysing power was determined.

PART I.—EXPERIMENTS WITH POROUS PORCELAIN.

In these experiments the combustion tube of the apparatus was closely packed with fragments of unglazed porous porcelain which had been previously heated to 1000° in a muffle furnace. The material was perfectly white in colour and presented a large surface to the reacting gases. Its average composition was as follows:—

	Per cent.		Per cent.
Silica	75·75	Calcium oxide	1·45
Alumina	21·30	Magnesium oxide	0·35
Ferric oxide	0·05	Sodium and potassium oxides	0·70

During the course of the research, altogether five different surfaces of this material were employed. The results obtained with all five surfaces were the same in three important particulars, namely (1) that with normal electrolytic gas the rate of combination was always proportional to the pressure of the dry gas; (2) that with an excess of either of the two reacting gases the rate of combination was always mainly, if not entirely, proportional to the partial pressure of the hydrogen; and (3) that the catalysing material occluded hydrogen, but not oxygen, at dull red heat.

First Series.—Normal Electrolytic Gas with Surface A *at* 450°.

The following two experiments were made at the outset of the research with the object of testing BODENSTEIN'S statement that the rate of combination in contact with porcelain is in accordance with the equation for a reaction of the third order (*loc. cit.*). The material was less porous than that used in most of the subsequent experiments, and the rate of circulation considerably slower, namely, a complete circuit in about two hours. The temperature of the combustion tube was 450° throughout each experiment, and pressure records were taken every twelve hours. In the following tables:—

t = time in hours from the beginning of each experiment;
T = temperature of the combustion tube;
P = corrected pressure of the dry gas in the apparatus;
k_1, k_2 and k_3 are the "constants" calculated from the equations for reactions of the first, second and third orders respectively.

EXPERIMENT I. October 29 to November 2, 1903. T = 450°. Rate of circulation = 1 in 120 minutes.					EXPERIMENT II. November 4 to 9, 1903. T = 450°. Rate of circulation = 1 in 120 minutes.				
t.	P.	k_1.	$k_2 \times 10^6$.	$k_3 \times 10^8$.	t.	P.	k_1.	$k_2 \times 10^6$.	$k_3 \times 10^8$.
hours.	millims.				hours.	millims.			
0	469·4	—	—	—	0	465·6	—	—	—
12	330·4	0·0127	75	19	12	324·0	0·0131	78·2	20
24	229·0	0·0129	93	30	24	228·6	0·0129	92·8	30
36	167·2	0·0124	107	43	36	163·9	0·0126	109·8	45
48	120·9	0·0123	128	67	48	116·1	0·0125	134·7	72
60	89·4	0·0120	151	100	60	84·6	0·0123	161·2	112
72	66·2	0·0118	180	155	72	60·7	0·0123	199·0	185
84	48·3	0·0117	221	252	84	42·9	0·0123	251·9	321
96	36·0	0·0116	267	400	96	28·6	0·0126	341·8	634
108	27·8	0·0113	313	597	108	20·6	0·0125	429·5	1088
120	21·0	0·0112	379	943	120	14·6	0·0125	552·7	1931

The pressure curve for Experiment II., which is reproduced in Diagram II., Curve A, shows how regular was the rate of combination throughout the five days over which the observations extended.

These results prove conclusively that with normal electrolytic gas the rate of

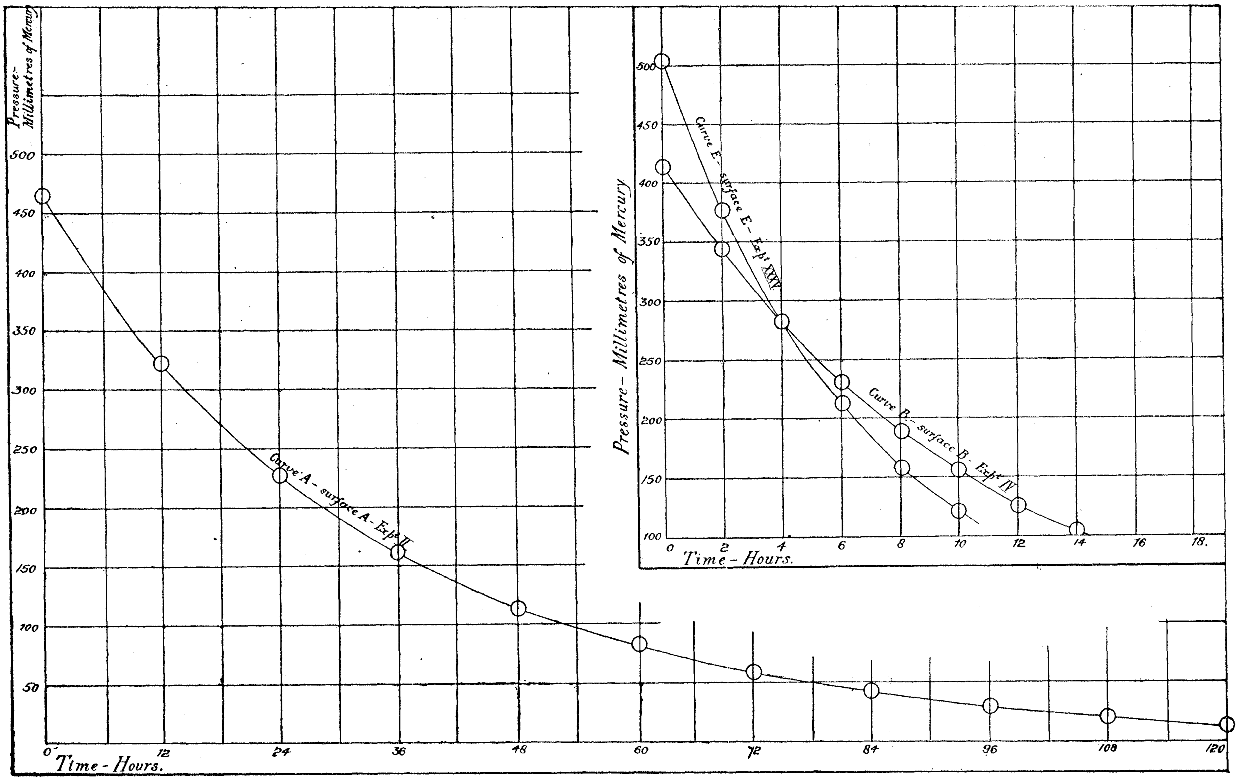

Diagram II. Experiments with porcelain. Pressure curves for normal electrolytic gas.

combination is proportional to the pressure of the dry gas, the values of "k_1," calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$, being remarkably constant throughout each experiment, even though the total pressure varied over a wide range.

Second Series.—Experiments with Surface B at 430°.

This surface had been previously used for experiments on the catalytic combination of carbon monoxide and oxygen, during the course of which it had settled down to a very steady condition as regards its catalysing power. Before being packed into the combustion tube of the apparatus, the material was thoroughly burnt out at red heat in a current of air. Neither the tube nor its packing was changed throughout the whole of the following series of experiments (III. to XX. inclusive), which may be sub-divided into three groups, according to the special objects in view in each case.

1*st Group.—With Normal Electrolytic Gas.*

This group comprised two experiments with normal electrolytic gas. In Experiment III. the rate of circulation was 1 in 20 minutes, and in IV. 1 in 30 minutes, otherwise the conditions were the same. As might be expected, the absolute rate of combination was greater in III. than in IV. The values of "k_1" given in the following table are calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$; it will be seen that in each experiment the rate of combination varied directly with the pressure of the dry gas.*

Experiment III. March 7, 1904. T = 430°. Rate of circulation = 1 in 20 minutes.			Experiment IV. March 14, 1904. T = 430°. Rate of circulation = 1 in 30 minutes.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	406·7	—	0	411·8	—
2	322·5	0·0503	2	343·3	0·0395
4	259·4	0·0486	4	283·5	0·0405
6	203·0	0·0501	6	230·3	0·0420
8	159·6	0·0507	8	188·5	0·0424
10	125·5	0·0510	10	155·6	0·0422
12	97·1	0·0519	12	126·2	0·0424
14	76·1	0·0520	14	106·0	0·0422
16	58·7	0·0526			

The pressure curve for Experiment IV. is shown in Diagram II., Curve B, p. 15. The gas remaining in the apparatus at the end of Experiment IV. was withdrawn and analysed; it contained

$$H_2 = 66{\cdot}1, \quad O_2 = 33{\cdot}2, \quad \text{and} \quad N_2 = 0{\cdot}7 \text{ per cent.}†$$

The nitrogen would correspond to rather less than 0·2 per cent. in the original gas.

2nd Group.—*Showing the Influence of Excess of either Hydrogen or Oxygen respectively on the Rate of Combination.*

The primary object of these experiments was to test the validity of the "diffusion" theory. If the observed rate of change in a heterogeneous gas system is determined by diffusion factors only, it must, at any given moment, depend on the rate at which the gas in defect at the surface diffuses on to it from the outside inert atmosphere.

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* That the combination was entirely a surface phenomenon was proved by a "blank" experiment in which the catalysing material was removed and normal electrolytic gas continuously circulated at a pressure of 478 millims. through the empty combustion tube at 430° for 6 hours. There was, however, no fall in pressure. This blank experiment, therefore, shows also that the glass surface of the combustion tube had no appreciable influence at 430° on the course of events.

† [*Added February* 10, 1906.—Since nothing but steam was produced in the above experiments, this analysis proves that the gas obtained by the electrolysis of a solution of pure barium hydroxide contains hydrogen and oxygen in exactly equivalent proportions.]

Now since the rate of diffusion of hydrogen is four times that of oxygen, it follows, assuming the rate of combination at the surface to be infinite, that with normal electrolytic gas there will always be an excess of hydrogen at the surface. The rate of steam formation would, therefore, be determined by the rate of diffusion of the oxygen. This conclusion is obviously not incompatible with the results of the previous experiments with the normal gas. Applying the same argument to cases in which the gases are not present in their combining proportions, it follows that so long as the hydrogen exceeds one-third of the total volume its rate of diffusion will maintain it in excess at the surface, and the rate of steam formation should depend on the partial pressure of the oxygen only. As soon, however, as the hydrogen falls below this limit, the rate should depend on the partial pressure of the hydrogen only.

In tabulating the results of these experiments it will be necessary to record in separate columns the partial pressures of both hydrogen and oxygen, as well as the constants calculated from each set of partial pressures. In this way the influence of each gas on the rate of change can be seen at a glance. In the following tables, therefore :—

t = time in hours from the beginning.

P = total pressure of the dry gas (corr.) in the apparatus.

P_{H_2} = the partial pressure of the hydrogen.

P_{O_2} = the partial pressure of the oxygen.

$$k_{H_2} = \frac{1}{t} \log \frac{P_{0H_2}}{P_{tH_2}}.$$

$$k_{O_2} = \frac{1}{t} \log \frac{P_{0O_2}}{P_{tO_2}}.$$

T = temperature of the combustion tube.

EXPERIMENT V.

March 21, 1904.

Original mixture = $3H_2+O_2$ nearly. The rate of circulation was rapid, and [32·5 per cent. of the original oxygen disappeared during the first two hours.—*February* 10, 1906.] T = 430°.

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	411·8	311·8	100·0	—	—
2	314·2	246·7	67·5	0·0509	0·0853
4	243·4	199·5	43·9	0·0485	0·0894
6	184·9	160·5	24·4	0·0481	0·1021
8	144·2	133·4	10·8	0·0461	0·1208
10	117·4	115·5	1·9	0·0431	0·1721

In a comparative experiment (VI.) made, three days later, with normal electrolytic gas, under precisely the same conditions, [only 21·5 per cent. of the oxygen initially present disappeared during the first two hours, the values of "k_1" varying between 0·0572 and 0·0532 as the pressure in the apparatus fell from 429·6 to 116·6 millims. in 12 hours.—*February* 10, 1906.]

These two experiments bring to light the significant fact that where an excess of hydrogen is initially present, the rate of combination does not depend on the partial pressure of the oxygen, as the diffusion theory demands, but rather on that of the hydrogen. The increasing excess of hydrogen in Experiment V. steadily accelerated the disappearance of the oxygen.

In the next three experiments (VII. to IX. inclusive), the influence of rather a large excess of hydrogen or oxygen respectively on the initial rate of change was studied. The rate of circulation was the same in all three experiments, but it was purposely made slower than in the two preceding experiments, in order that the reaction might be extended over 8 or 10 hours in each case. In Experiment VII. (April 7, 1904), the mean value of the reaction constant "k_1" for normal electrolytic gas was found to be 0·0195.

In Experiments VIII. and IX., original mixtures corresponding nearly to $9H_2+O_2$ and H_2+6O_2, respectively, were employed, with the following results:—

EXPERIMENT VIII. April 8, 1904. Original mixture = $9H_2+O_2$ nearly. T = 430°.					EXPERIMENT IX. April 15, 1904. Original mixture = H_2+6O_2 nearly. T = 430°.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	377·9	41·9	—	—	0	48·7	296·3	—	—
2	351·1	28·5	0·0159	0·0837	2	44·1	294·6	0·0216	0·0018
4	328·5	12·2	0·0152	0·0960	4	39·7	291·8	0·0222	0·0017
6	311·1	8·5	0·0141	0·1154	6	35·5	289·7	0·0229	0·0016
8	297·7	1·8	0·0129	0·1708	12	26·7	285·3	0·0217	0·0014
					18	19·6	281·8	0·0218	0·0012
					24	12·9	278·5	0·0240	0·0011

The rates of change observed in the three experiments may be best compared by considering the percentage of the original electrolytic gas which disappeared during the first two hours in each case. In Experiments VII. and IX., with "normal" gas and excess of oxygen respectively, these percentages were practically the same, namely, 9·1 and 9·4 respectively. The corresponding figure in Experiment VIII., however, with excess of hydrogen, was no less than 32 per cent., a very clear proof of the accelerating influence of excess of hydrogen.

The conclusion that the rate of change is proportional to the partial pressure of the hydrogen, was finally confirmed by the two following experiments, in which the original mixtures corresponded to approximately H_2+O_2 and $3H_2+O_2$ respectively. The rate of circulation, which was the same in both, was somewhat faster than in the three preceding experiments (VII. to IX.).

EXPERIMENT X.

April 26, 1904.
Original mixture = H_2+O_2. T = 430°.

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	398·0	196·0	202·0	—	—
2	358·0	169·2	188·8	0·0320	0·0148
4	329·5	150·2	179·3	0·0289	0·0130
6	294·0	126·5	167·5	0·0317	0·0136
8	268·4	109·5	158·9	0·0316	0·0131
12	228·3	82·7	145·6	0·0312	0·0119
24	156·9	35·1	121·8	0·0311	0·0092
28	142·1	25·3	116·8	0·0318	0·0085
32	129·0	16·5	112·5	0·0335	0·0080

EXPERIMENT XI.

April 29, 1904.
Original mixture = $3H_2+O_2$. T = 430°.

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	387·4	292·5	94·9	—	—
2	339·4	260·5	78·9	0·0253	0·0401
4	294·4	230·5	63·9	0·0259	0·0429
6	258·0	206·2	51·8	0·0253	0·0438
8	227·6	185·9	41·7	0·0246	0·0447
10	200·4	167·8	32·6	0·0241	0·0464
12	176·4	151·8	24·6	0·0237	0·0488
14	154·4	137·1	17·3	0·0235	0·0528
16	134·0	123·6	10·4	0·0240	0·0600
18	115·8	111·4	4·4	0·0233	0·0741

3rd Group.—Experiments Showing the Stimulating Influence of Hydrogen upon the Catalysing Power of the Surface.

The fact that the rate of combination throughout a given experiment is always proportional to the partial pressure of the hydrogen, can hardly have any other meaning than that the formation of steam is an indirect process, dependent on a primary change, induced by the surface, in which the hydrogen is concerned. This led us to investigate the separate influence of hydrogen and oxygen respectively at 430°, and also of hydrogen at red heat, upon the catalysing power of the surface.

At 430°.

The general plan of this series of seven experiments (XII. to XVIII. inclusive), all made with normal electrolytic gas at 430°, under precisely the same conditions as regards rate of circulation, was briefly the following :—

Before each experiment (except the first, which was simply made to determine the "normal" value of the reaction constant "k_1" for the series), either hydrogen or oxygen was circulated over the surface at 430° for a period of time varying from 24 to 72 hours. The gas was then rapidly withdrawn from the apparatus by means of the auxiliary Sprengel pump, the action of which was continued for about 15 or 20 minutes after the manometer had indicated a "moist" vacuum. A charge of electrolytic gas was immediately admitted, and the rate of combination determined over a period of 8 or 10 hours in the usual manner. Finally, the apparatus was again thoroughly exhausted. The furnace was never turned down during the whole of the five weeks over which the series of experiments extended, and the apparatus was kept exhausted during the intervals between each experiment. The rate of circulation in each experiment was 1 in 35 minutes.

Experiment XII.—In this experiment, in which electrolytic gas was admitted to the apparatus without any preliminary treatment of the surface with either hydrogen or oxygen, the mean value for "k_1" was found to be 0·0363.

In two of the three following experiments (namely, XIII. and XV.), the surface was subjected to a preliminary treatment with hydrogen at 430° for 24 and 40 hours respectively, and in the third (XIV.) to the action of oxygen for 24 hours. The results are tabulated below :—

Experiment XIII. May 3 and 4, 1904. Preliminary treatment with hydrogen at 430° for 24 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			Experiment XIV. May 7 and 8, 1904. Preliminary treatment with oxygen at 430° for 24 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			Experiment XV. May 9 to 11, 1904. Preliminary treatment with hydrogen at 430° for 40 hours. Rate of circulation = 1 in 35 minutes. T = 430°.		
t.	P.	k_1.	*t.*	P.	k_1.	*t.*	P	k_1.
hours.	millims.		hours.	millims.		hours.	millims.	
0	397·4	—	0	388·4	—	0	347·9	—
2	313·5	0·0515	2	337·6	0·0305	2	264·8	0·0592
4	252·5	0·0492	4	297·0	0·0291	4	203·5	0·0582
6	211·4	0·0457	6	257·5	0·0291	6	155·1	0·0584
8	177·4	0·0438	8	228·0	0·0287	8	120·8	0·0578
10	149·4	0·0425				10	89·0	0·0592

The catalysing power of the surface was, therefore, greatly stimulated by previous exposure to hydrogen at 430°, the stimulus being the more marked and enduring the longer the surface had been subjected to the action of the gas. Moreover, the great contrast between the rates observed, according as the surface had been previously treated with hydrogen or oxygen, is very striking. The stimulus imparted by the 40 hours' preliminary treatment with hydrogen in Experiment XV. gradually wore away when successive charges of electrolytic gas were circulated over the surface, until finally it was restored to its normal condition.

In the next three experiments (XVI. to XVIII. inclusive), the stimulating influence of hydrogen was very marked. In Experiment XVI., after a preliminary treatment of the surface with oxygen at 430° for 48 hours, the rate of combination observed was almost exactly normal (compare Experiment XII.). In Experiment XVIII., the usual procedure was somewhat modified in that after the 24 hours' preliminary treatment with hydrogen the apparatus was continuously exhausted for 18 hours, the combustion tube being kept at 430° the whole time. It is evident from the results that the imparted "stimulus" survived this long exhaustion.

EXPERIMENT XVI. May 12 to 14, 1904. Preliminary treatment with oxygen at 430° for 48 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			EXPERIMENT XVII. May 16 to 19, 1904. Preliminary treatment with hydrogen at 430° for 72 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			EXPERIMENT XVIII. May 30 to 31, 1904. Preliminary treatment with hydrogen at 430° for 24 hours. Rate of circulation = 1 in 35 minutes. T = 430°.		
t.	P.	k_1.	*t*.	P.	k_1.	*t*.	P.	k_1.
hours.	millims.		hours.	millims.		hours.	millims.	
0	412·7	—	0	405·2	—	0	298·8	—
2	347·5	0·0373	2	304·3	0·0622	2	233·8	0·0543
4	289·5	0·0385	4	225·4	0·0637	4	181·3	0·0542
6	244·0	0·0380	6	175·8	0·0604			
8	208·7	0·0370	8	138·0	0·0585			

The ratio hydrogen/oxygen in the gas withdrawn from the apparatus at the end of Experiment XVII. was 2·138, a circumstance which certainly indicates some occlusion of hydrogen in the pores of the porcelain during the long preliminary treatment. The stimulus caused by the hydrogen in this experiment gradually wore away as successive charges of electrolytic gas were circulated over the surface during the next 18 hours, until finally it was restored to its normal condition.

At Red Heat.

Whilst the preceding experiments leave no room for doubt but that the catalytic action of porcelain is connected with a preliminary change in which the hydrogen is chiefly concerned, they do not discriminate between a chemical and a physical explanation of the process. If the stimulating effect of hydrogen at 430° is due to a chemical reduction of the catalysing material, we should expect a greatly enhanced and more permanent effect after long treatment with hydrogen at red heat. But, on the other hand, if the stimulus in question is due to a physical change in the hydrogen within the cavities of the material, subsequent long exhaustion at red heat should materially diminish, if not entirely obliterate it. This was the issue we attempted to decide in the next two experiments, which were carried out in the following manner :—

Before each experiment the combustion tube containing the porcelain was transferred to an ordinary combustion furnace and connected, through fused glass joints, at the one end with a supply of pure dry hydrogen, and at the other end with a Sprengel pump and manometer. The tube was heated to bright redness in a slow current of hydrogen for from 36 to 48 hours, and subsequently exhausted at dull red heat for 20 hours. The stop-cocks at each end of the tube were then closed, and it was transferred back again to the circulation apparatus, when the rate of combination for normal electrolytic gas at 430° was once more determined, the rate of circulation being precisely the same as in the preceding experiments of the series. The results of the two experiments are tabulated below :—

EXPERIMENT XIX. June 3 to 6, 1904. Preliminary treatment with hydrogen at red heat for 48 hours, followed by exhaustion at red heat for 20 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			EXPERIMENT XX. June 8 to 11, 1904. Preliminary treatment with hydrogen at red heat for 36 hours, followed by exhaustion at red heat for 12 hours. Rate of circulation = 1 in 35 minutes. T = 430°.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	398·8	—	0	383·6	—
1	364·9	0·0386	2	325·6	0·0356
2	336·8	0·0368	4	283·3	0·0329
3	311·3	0·0359	6	243·2	0·0330
6	246·1	0·0349	10	179·2	0·0330
7	225·0	0·0355	12	154·2	0·0330

These rates show very decisively that the surface had not been stimulated by the long exposure to hydrogen at red heat. The values of "k_1" are practically the same as the value obtained in Experiment XII., namely 0·0363, with the surface in a "normal" condition, and with the same rate of circulation. Hence the peculiar action of hydrogen in the catalytic process cannot be ascribed to a chemical reduction of the surface.

Absorption of Hydrogen by Porous Porcelain at Red Heat.

It was now necessary to ascertain whether or not hydrogen is occluded to any appreciable extent by porous porcelain at high temperatures. The combustion tube containing material used in the preceding experiments was transferred to the "absorption apparatus" (see Diagram I., fig. 2), where, after a preliminary thorough exhaustion at 700°, pure hydrogen, which had been just previously passed over red hot copper, was admitted, and the subsequent absorption of the gas by the red hot porcelain was followed by pressure readings at frequent time intervals. In three different experiments the following records were obtained :—

t	0	1	2	3	4	5	10	15	20	30	60 minutes
(1) P . . .	720	664	645	636	628	621	597	585	575	561	532 millims.
(2) P . . .	740	—	688	677	—	668	646	637	630	621	— ,,
(3) P . . .	766	706	693	686	680	674	665	657	650	633	— ,,

The gas absorbed at red heat was very obstinately retained when the apparatus was exhausted at the ordinary temperature. In the third of the above experiments, for instance, it was not removed after 10 hours' continuous pumping. As soon, however, as the tube was again heated to redness, the occluded gas could always be completely removed after two or three hours' pumping.

3*rd*, 4*th and* 5*th Series.—Experiments with Surfaces C, D and E.*

Whilst the behaviour of these three surfaces resembled that of the surface B in the three important respects already referred to on pp. 13 and 14, certain differences were observed which must not be overlooked in constructing a theory of the catalytic process.

Surface C.

The activity of this surface was stimulated by long exposure to hydrogen at the ordinary temperature, but not when the treatment was repeated at 450°. The stimulating influence of hydrogen at the ordinary temperature is illustrated by the results of the following series of experiments, at 430°, with normal electrolytic gas :—

Normal electrolytic gas. T = 430°. Rate of circulation = 1 in 45 minutes.

Experiment.	Date.	Condition of surface.	k_1 for time interval 0 to 2 hours.
XXI.	February 17, 1905	Normal	0·0175
XXII.	„ 19, 1905	„	0·0165
XXIII.	March, 1, 1905	After exposure to hydrogen in the cold for one week	0·0299
XXIV.	„ 3, 1905	After two days' exhaustion at 430°	0·0201
XXV.	„ 4, 1905	Normal	0·0170
XXVI.	„ 14, 1905	After exposure to hydrogen in the cold for ten days	0·0328

Another interesting feature about the behaviour of this surface was that in every experiment with mixtures containing an excess of oxygen, the activity was initially rapidly stimulated up to a fairly high limit, after which the rate of combination depended on the partial pressure of the hydrogen only. But whilst this enhanced activity was undoubtedly due to the excess of oxygen, it ceased as soon as all the hydrogen had disappeared. In other words, the surface was not stimulated under the influence of oxygen alone, either at 450° or at dull red heat, but only by an excess of oxygen in presence of hydrogen, and whilst the gases were actually combining. This peculiarity is well illustrated by the results of the following series of experiments at 450°:—

(*a*) With normal electrolytic gas:—

$T = 450°$. Rate of circulation = 1 in 60 minutes.

Experiment XXVII.	Surface normally active	$k_1 = 0·0250$
,, XXVIII.	Surface after exposure to hydrogen at 450°	$k_1 = 0·0220$
,, XXIX.	,, ,, oxygen ,,	$k_1 = 0·0218$

(*b*) With mixtures originally corresponding to $3H_2 + O_2$ and $H_2 + 4O_2$ respectively:—

Experiment XXX. June 2, 1905. Original mixture = $3H_2 + O_2$. $T = 450°$. Rate of circulation = 1 in 60 minutes.					Experiment XXXI. June 20, 1905. Original mixture = $H_2 + 4O_2$. $T = 450°$. Rate of circulation = 1 in 60 minutes.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	370·7	123·1	—	—	0	99·3	397·4	—	—
1	357·4	116·4	0·0168	0·0242	2	81·5	389·0	0·0428	0·0046
2	343·6	109·6	0·0164	0·0252	4	66·5	381·5	0·0435	0·0044
4	315·6	95·6	0·0174	0·0274	6	54·6	375·7	0·0432	0·0041
6	293·8	84·7	0·0168	0·0271	8	44·6	370·7	0·0434	0·0038
8	271·3	73·4	0·0169	0·0281	10	36·4	366·6	0·0436	0·0035
12	235·2	55·3	0·0165	0·0289	18	16·5	356·8	0·0433	0·0026
16	207·2	41·3	0·0158	0·0296	22	11·9	353·7	0·0420	0·0023
20	184·0	29·8	0·0152	0·0308	26	7·5	351·5	0·0431	0·0021

The surface had the power of occluding hydrogen (but not oxygen) at dull red heat. In one experiment with pure hydrogen, carried out at 650° in the absorption apparatus, the pressure fell from 704 to 594 millims. during 30 minutes; this represented the occlusion of between 6 and 7 cub. centims. of gas, measured at 0° and 760 millims.

The results of the fourth series of experiments with surface D merely confirmed those obtained with C, and need not, therefore, be further described.

Surface E.

This surface had been previously used for experiments on the slow combustion of acetylene, and in its raw condition displayed a peculiar susceptibility to the stimulating influence of oxygen. Indeed, its activity was affected by previous exposure to hydrogen or oxygen at 450° in exactly the opposite sense to that observed with the surface B. This is shown by the results of the following series of experiments with normal electrolytic gas at 450°. The rate of circulation was 1 in 60 minutes throughout.

Experiment.	Date.	Condition of surface.	k_1 for time interval 0 to 1 hour.	Remarks.
XXXIV.	June 24, 1905	Normal	0·0636	Rate of combination proportional to pressure throughout each experiment.
XXXV.	,, 25, 1905	,,	0·0636	
XXXVII.	,, 27, 1905	After exposure to hydrogen at 454° for fourteen hours	0·0382	
XXXVIII.	,, 29, 1905	After two days' continuous exhaustion. Normal	0·0612	
XL.	July 1, 1905	After exposure to oxygen at 450° for sixteen hours	0·0879	Stimulus rapidly wore off. Surface again normal after five hours.
XLI.	,, 2, 1905	After further exposure to oxygen at 450°	0·0976	

In experiments with an excess of either of the two reacting gases, the surface was always more than normally active, and, after an initial period of acceleration, the rate of combination always remained proportional to the partial pressure of the hydrogen. This is shown by the results of the two following experiments with mixtures originally corresponding to $3H_2+O_2$, and H_2+3O_2, respectively. In the latter case, the rate of combination after the first hour was about 2·5 times normal, and the results are best analysed by calculating two sets of values for "k_{H_2}," the one set for the whole experiment, the other for the course of events after the first hour.

EXPERIMENT XXXVI.

June 26, 1905.
Original mixture = $3H_2+O_2$. T = 450°.
Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	380·4	130·7	—	—
2	304·3	92·6	0·0485	0·0748
3	269·1	75·0	0·0501	0·0804
4	239·7	60·3	0·0501	0·0840
5	215·1	48·0	0·0495	0·0870
6	190·7	35·8	0·0500	0·0937
7	169·1	25·0	0·0503	0·1026
9	134·5	7·7	0·0502	0·1366

EXPERIMENT XXXIX.

June 30, 1905.
Original mixture = H_2+3O_2. T = 450°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.		k_{O_2}.
hours.	millims.	millims.			
0	131·0	391·3	—	—	—
1	107·0	379·3	0·0779	—	0·0136
2	70·5	361·1	0·1345	0·181	0·0174
3	48·1	349·9	0·1450	0·174	0·0162
4	31·5	341·5	0·1547	0·177	0·0148
5	21·9	336·7	0·1554	0·172	0·0131
6	15·5	333·5	0·1545	0·168	0·0116
7	11·0	331·3	0·1504	0·165	0·0104

After the above experiments were concluded, the combustion tube containing the catalysing material was transferred to the "absorption apparatus," where its power of occluding hydrogen at dull red heat (*circa* 650°) was tested. In one experiment the pressure fell from 764 to 648 millims., and in another from 765 to 657 millims., or by about one-seventh, during 30 minutes. Corresponding experiments with oxygen gave negative results.

The catalysing power of the surface, as well as its susceptibility to any stimulus by oxygen, underwent a marked alteration as the result of the repeated occlusions of hydrogen, followed by prolonged exhaustion, at dull red heat. Its activity was now much reduced, the new "normal" value for "k_1" at 450° being only 0·033 as compared with the 0·063 obtained in previous experiments. It is, however, significant that the new value was almost identical with that obtained in Experiment XXXVII., namely, 0·0382, after the surface had been exposed to hydrogen at 450°.

In its new condition of reduced activity, the surface had completely lost its susceptibility to stimulus by oxygen; indeed, prolonged exposure to oxygen at 450° now actually diminished its catalysing power. On the other hand, it had acquired the power of responding, to a slight degree, to the stimulating influence of hydrogen at 450°. In short, its behaviour now approximated to that of surface B, a circumstance which proves how profoundly the action of porcelain may be affected by its past history.

Summary.

Reviewing now the results obtained with the five surfaces as a whole, it is clear that the rate of steam formation is governed neither by the "order" of the reaction, as Bodenstein asserted, nor by diffusion factors simply, as Nernst has suggested. Nor is the theory of a rapidly alternating series of oxidations and reductions of the catalysing surface admissible. The evidence is, on the contrary, altogether in favour of the view that the catalytic action of porcelain is primarily due to the condensation, or occlusion, of one, and possibly both, of the reacting gases on its surface. The fact that whenever one or other of the gases is present in excess, the rate of combination is proportional to the partial pressure of the hydrogen, and that the material absorbs hydrogen at red heat, indicates that occluded hydrogen is an all important factor in the process. It would also seem, from the results obtained with surfaces C and E, that occluded oxygen also may exercise an accelerating influence on the process; otherwise it is difficult to account for the fact that in several of the experiments with an excess of oxygen a surface proved more than normally active, and that surface E, before it had been subjected to the treatment with hydrogen at red heat, could be stimulated by previous exposure to oxygen at 450°. Another significant circumstance is that, whilst excess of hydrogen always produced a *continuous* acceleration throughout a given experiment, any acceleration due to an excess of oxygen was only manifested during the initial stages. These facts suggest the following view of the catalytic process. 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.

PART II.—EXPERIMENTS WITH A BASIC SURFACE OF CALCINED MAGNESITE.

The primary object of these experiments was to ascertain whether a surface composed of basic and non-reducible oxides behaves in the same way towards electrolytic gas as does the acidic porcelain. The material selected was a specimen of magnesite containing considerably less than 1 part of iron in 100,000; it was thoroughly calcined at 1000° in a muffle furnace, and then packed into the combustion tube of the circulation apparatus.* The packed tube was heated to dull redness in a current of dry air for several hours; it was then cooled, and connected with the circulation apparatus, where it was thoroughly exhausted at 430° for 24 hours.

Several successive charges of normal electrolytic gas were then circulated in the apparatus, during which the catalysing power of the surface gradually increased up to a steady maximum, after which it remained practically constant. This steady state was regarded as the "normal" condition of the surface.

The following series of nine experiments was then made under precisely the same conditions as regards temperature (430°) and rate of circulation (namely, 1 in 60 minutes). In the first experiment, the rate of combination for normal electrolytic gas was shown to be directly proportional to the pressure of dry gas. In the second, where a mixture of approximately $3H_2+O_2$ was employed, it was found to be nearly proportional to the partial pressure of hydrogen.

After Experiment II., hydrogen was circulated over the surface at 430° for 16 hours, and on redetermining the rate of combination for normal electrolytic gas over the "hydrogenised" surface in Experiment III., it was found to be abnormally high. At the conclusion of Experiment III., the apparatus was exhausted at 430° for 16 hours, and on subsequently circulating a fresh charge of electrolytic gas over the surface, it was finally restored to its normal condition (Experiment IV.). The results of these four experiments are tabulated below :—

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* The calcined material had the following percentage composition :—$MgO = 87 \cdot 00$, $CaO = 12 \cdot 42$, $Al_2O_3 = 0 \cdot 33$, $SiO_2 = 0 \cdot 25$.

EXPERIMENT I. July 6, 1904. Normal electrolytic gas. Surface in "normal" condition.			EXPERIMENT II. July 7, 1904. Original mixture $3H_2+O_2$ nearly.				
t.	P.	k_1.	*t*.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.		hours.	millims.	millims.		
0	369·8	—	0	252·3	85·9	—	—
1	268·8	0·1386	1	200·5	60·0	0·0997	0·1558
2	206·3	0·1268	2	165·4	42·5	0·0917	0·1528
3	151·0	0·1296	3	136·0	27·8	0·0895	0·1633
4	110·5	0·1312	4	110·8	15·1	0·0894	0·1890
5	77·8	0·1354	5	94·2	6·8	0·0856	0·2203
6	52·6	0·1413	5½	87·5	3·5	0·0836	0·2527
8	25·2	0·1458	6	83·3	1·4	0·0802	0·2980

EXPERIMENT III. July 8, 1904. Normal electrolytic gas over "hydrogenised" surface.			EXPERIMENT IV. July 9, 1904. Normal electrolytic gas after prolonged exhaustion at 430°.		
t.	P.	k_1.	*t*.	P.	k_1
hours.	millims.		hours.	millims.	
0	425·8	—	0	390·0	—
1	267·2	0·2024	1	257·2	0·1809
2	150·2	0·2262	2	178·0	0·1704
3	79·8	0·2424	3	125·8	0·1638
4	36·7	0·2661	4	91·3	0·1576
5	14·2	0·2954			

The ratio H_2/O_2 in the residual gas from Experiment I. was exactly 2·0. For the residual gas in Experiment III. the ratio was, however, 2·2, a clear indication that hydrogen had been occluded by the catalysing material during the treatment to which it had been subjected between Experiments II. and III.

At the conclusion of Experiment IV., oxygen was circulated over the surface at 430° for 36 hours in order to completely "dehydrogenise" it. After pumping the residual oxygen out of the apparatus, the rate for normal electrolytic gas was now found to be very little more than half the normal value, as follows:—

Experiment V.

July 11, 1904.

Normal electrolytic gas after oxygen. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.	*t*.	P.	k_1.
hours.	millims.		hours.	millims.	
0	400·0	—	6	147·6	0·0723
1	340·0	0·0706	7	123·2	0·0731
3	248·8	0·0687	8	103·2	0·0735
4	205·8	0·0721	9	86·0	0·0740
5	180·8	0·0690			

The pressure curves for Experiments I., II., and V., which are reproduced in Diagram III., show very clearly the effects of "hydrogenation" and "dehydrogenation" respectively on the activity of the surface.

The results of the last four experiments of the series may be discussed together. Starting with the surface in the condition in which it had been left after Experiment V., a mixture originally containing an excess of hydrogen ($3H_2+O_2$) was circulated over it (Experiment VI.). Its activity was at once stimulated, and the rate of steam formation as the experiment proceeded was always as nearly as possible proportional to the partial pressure of the hydrogen. The residual hydrogen from VI. was circulated over the surface at 430° for 16 hours. It was then pumped out of the apparatus, and, on redetermining the rate for normal electrolytic gas over the "hydrogenised" surface (Experiment VII.), it was found to be so abnormally active that no less than 41·67 per cent. of the original electrolytic gas disappeared during the first hour, and, moreover, the stimulus outlasted the four hours over which the experiment extended.

At the conclusion of Experiment VII., the combustion tube of the apparatus was transferred to a high temperature furnace and exhausted at dull red heat for 16 hours, during which all the hydrogen occluded by the catalysing material was extracted. The tube was then cooled and refitted into the circulation apparatus. The rate for normal electrolytic gas was afterwards redetermined (Experiment VIII.). The values of "k_1" now showed that the stimulus imparted by the hydrogen had practically disappeared, the material being in the same "normal" condition as in Experiment I. Clearly, therefore, the enhanced activity of the surface after exposure to hydrogen at 430° in Experiment III. cannot be attributed to any chemical reduction of the material composing it.

Finally, in Experiment IX., a mixture containing excess of oxygen was circulated over the surface. The rate of combination observed was strictly proportional to the partial pressure of the hydrogen throughout, and the values "k_{H_2}" showed that the surface was no more than normally active. The results of the four experiments are tabulated on the next page.

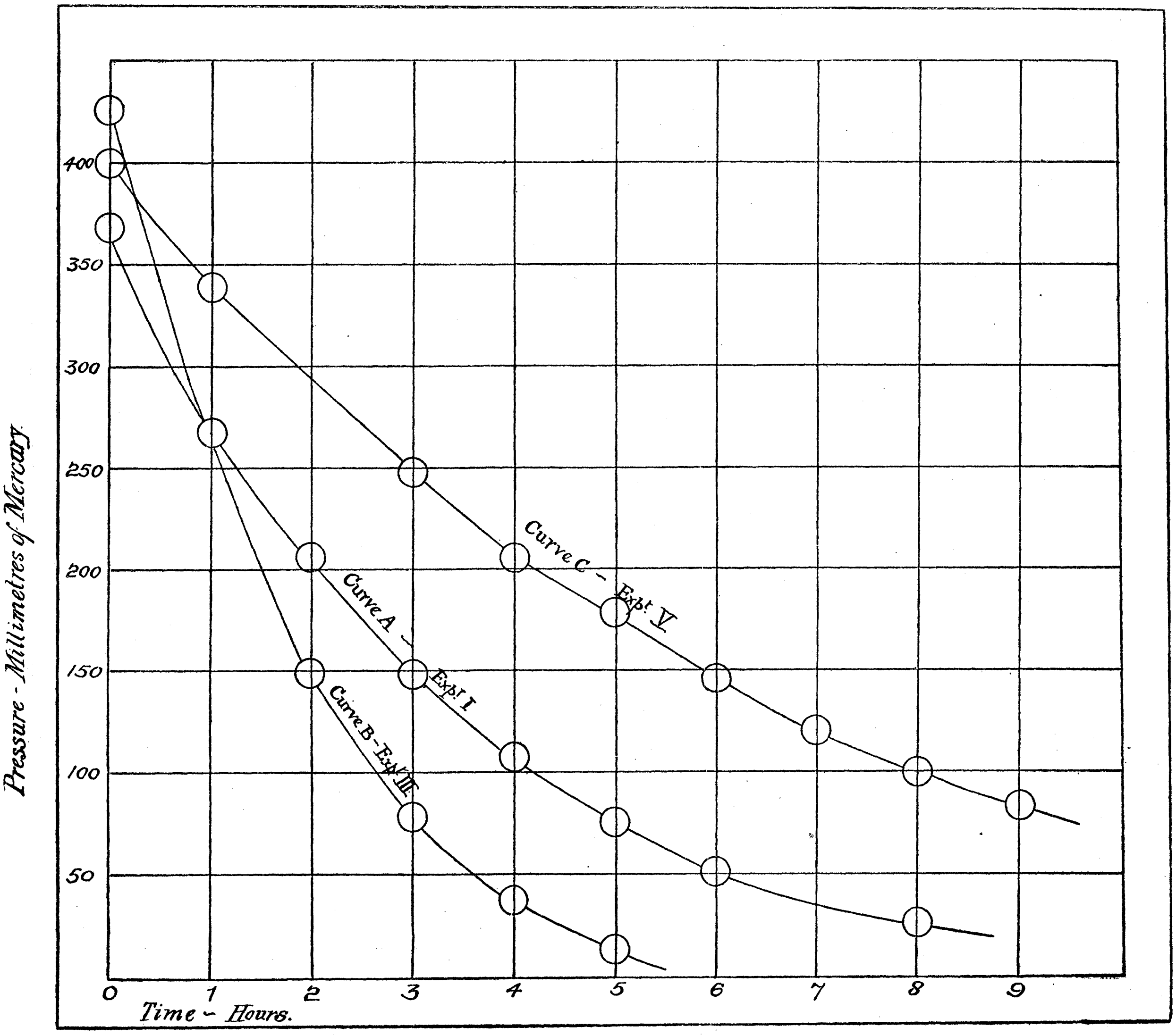

Diagram III. Experiments with magnesia. Pressure curves for normal electrolytic gas.

Curve A. Surface in "normal" condition.
„ B. "Hydrogenised" surface.
„ C. Surface "dehydrogenised" by exposure to oxygen.

Experiment VI.

July 15, 1904.
Original mixture $3H_2+O_2$ nearly. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	299·4	99·5	—	—
1	260·8	80·2	0·0600	0·0936
2	220·1	59·8	0·0663	0·1105
3	184·9	42·2	0·0698	0·1242
4	157·1	28·3	0·0700	0·1365
5	126·7	13·1	0·0747	0·1761
7	102·1	0·8	0·0668	0·2992

Experiment VII.

July 16, 1904.
Normal electrolytic gas over the "hydrogenised" surface. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	395·3	—
1	230·7	0·2339
2	138·4	0·2278
3	80·3	0·2307
4	46·3	0·2328

Experiment VIII.

July 27, 1904.
Normal electrolytic gas. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	401·2	—
1	291·3	0·1390
2	210·4	0·1402
3	151·4	0·1411
4	109·6	0·1408
5	78·6	0·1416

Experiment IX.

July 29, 1904.
Original mixture H_2+O_2. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	134·1	266·5	—	—
1	97·9	248·4	0·1366	0·0305
2	71·3	235·1	0·1371	0·0272
3	52·8	225·9	0·1349	0·0239
4	37·6	218·2	0·1380	0·0217
6	18·8	208·9	0·1422	0·0176
8	10·3	204·6	0·1395	0·0143
10	5·3	202·1	0·1403	0·0120

Absorption of Hydrogen at Red Heat.

That the basic material had the power of absorbing hydrogen at red heat was proved by transferring the combustion tube containing it to the "absorption apparatus." The tube was exhausted at red heat until no more gas could be withdrawn from it. Pure hydrogen was then admitted up to 763 millims. pressure. The gradual absorption of the gas is shown by the following pressure records :—

t	0	1	2	5	10	20	30 minutes
P. . . .	763	744	738	719	706	691	682 millims.

The apparatus was then cooled and thoroughly exhausted at the ordinary temperature. It was again heated to redness, when about 5 cub. centims. of hydrogen were extracted. Experiments on the absorption of oxygen at red heat gave entirely negative results.

Summarising now the above results, it is evident that (1) with normal electrolytic gas the rate of combination is proportional to the pressure of the dry gas, (2) when an excess of either of the reacting gases is present, the rate is determined mainly by the partial pressure of the hydrogen, and (3) the catalysing power of the material is, on the one hand, greatly stimulated by hydrogen, but, on the other hand, diminished by oxygen. These considerations, together with the fact that the material occludes hydrogen but not oxygen at red heat, show that its catalytic action must be referred to its power of occluding hydrogen.

Part III.—Experiments with Silver.

In selecting silver as the first metallic surface for investigation, we had in view two considerations, namely (1) the instability of its oxides above 350°,* and (2) its relationship to sodium and copper, which suggest the possibility of its forming a hydride at high temperatures.† For most of the experiments, the metal was employed in the form of a gauze of 23 strands per centimetre, each strand having a diameter of 0·18 millim.;‡ a final series of experiments was, however, made with foil prepared from "assay" silver.

First Series with Silver Gauze at 400°.

Throughout the first series of six experiments, the temperature of the combustion tube was 400°, and the rate of circulation 1 in 60 minutes. The weight of silver gauze employed was 62 grammes, and the area exposed to the reacting gases would be about 430 sq. centims.

At the outset of the series, successive charges of normal electrolytic gas were continuously circulated over the heated gauze for 12 hours, its catalysing power gradually increased, by about 30 per cent., up to a steady maximum, which was considered to represent the "normal" condition. The rate of combination was then determined as follows:—

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* According to Carnelly and Walker ('Trans. Chem. Soc.,' 1888, vol. 53, p. 79), the decomposition of Ag_2O, which is rapid between 270° and 300°, is quite complete between 300° and 430°.

† The recent experiments of Leduc ('Comp. Rend.,' 1902, vol. 135, p. 1332, and 1903, vol. 136, p. 1254) have shown that copper forms a stable hydride at temperatures below red heat, where the tension of dissociation only becomes appreciable at temperatures when the metal rapidly absorbs oxygen from the air.

‡ The gauze, which was kindly supplied by Messrs. Johnson and Matthey, was made of the purest obtainable wire. We made a careful chemical analysis of about 10 grammes of the gauze, but were unable to detect the presence of any impurity. Both copper and bismuth were specially tested for.

EXPERIMENT I.

July 25, 1904.
Normal electrolytic gas. T = 400°. Surface in "normal" condition.
Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	447·5	—
1	325·5	0·1381
2	241·4	0·1341
3	166·7	0·1429
4	115·8	0·1468
5	82·4	0·1469
6	58·5	0·1473
7	41·4	0·1477

The values of "k_1," calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$, show that, as in the cases of porous porcelain and magnesia, the rate of steam formation is directly proportional to the pressure of the dry gas, and, therefore, that the process is a surface phenomenon entirely. In the next three experiments (II. to IV. inclusive), the influence of oxygen on the catalysing power of the surface was studied. In Experiment II., a mixture originally corresponding to H_2+2O_2 was employed, with the following results :—

EXPERIMENT II.

July 25, 1904.
Electrolytic gas + excess of oxygen. The original mixture corresponded to H_2+2O_2.
T = 400°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	130·7	261·4	—	—
1	103·5	248·0	0·1013	0·0228
2	82·1	237·1	0·1009	0·0212
3	60·7	226·5	0·1110	0·0207
4	44·9	218·6	0·1160	0·0194
5	28·9	210·5	0·1310	0·0188
5½	22·9	207·7	0·1376	0·0180
6	17·9	205·1	0·1439	0·0175
7	12·1	202·1	0·1476	0·0159
8	8·9	200·7	0·1458	0·0144
9	6·1	199·2	0·1478	0·0131

These numbers show that, initially, the rate of steam formation was proportionately rather slower than with normal gas in the previous experiment; it was, however, gradually accelerated as the experiment proceeded, until after the fourth hour it had attained a steady maximum. From this point onwards the rate remained nearly proportional to the partial pressure of the hydrogen. The significance of these results will be considered later.

At the conclusion of Experiment II., successive determinations were made of the rate for normal electrolytic gas (1) after the surface had been subjected to the action of oxygen at 450° for 36 hours, and (2) after the apparatus had been further exhausted during 12 hours. The results of these two experiments, which are tabulated below, show that oxygen *per se* has no stimulating influence on the activity of the surface, but rather, owing to its "dehydrogenising" action, the reverse. The long exhaustion which intervened between the two experiments completely restored the surface to its normal condition.

EXPERIMENT III. July 27, 1904. Normal electrolytic gas after treatment with oxygen 36 hours. T = 400°. Rate of circulation = 1 in 60 minutes.			EXPERIMENT IV. July 28, 1904. Normal electrolytic gas. Surface in "normal" condition. T = 400°. Rate of circulation = 1 in 60 minutes.		
t.	P.	k_1.	*t.*	P.	k_1.
hours.	millims.		hours.	millims.	
0	470·4	—	0	467·3	—
1	357·4	0·1193	1	336·2	0·1430
2	256·6	0·1316	2	240·7	0·1441
3	167·8	0·1492	3	170·3	0·1462
4	112·6	0·1552	4	120·6	0·1471
5	71·2	0·1640			

The results of the last two experiments of the series (V. and VI.) are chiefly interesting in that they point to a theory of the catalytic process. Starting with the surface in the "normal" condition, a mixture containing an excess of hydrogen was admitted to the apparatus, and the rate of combination observed until nearly the whole of the oxygen had disappeared (Experiment V.). During the interval between Experiments V. and VI., hydrogen was circulated over the gauze at 400° for 18 hours and then pumped out of the apparatus. Immediately afterwards the rate for normal electrolytic gas over the "hydrogenised" surface was determined (Experiment VI.). The results of the two experiments are tabulated below :—

EXPERIMENT V. August 3, 1904. Original mixture = $3H_2+O_2$ (nearly). T = 400°. Rate of circulation = 1 in 60 minutes.					EXPERIMENT VI. August 4, 1904. Normal electrolytic gas over "hydrogenised" surface. T = 400°. Rate of circulation = 1 in 60 minutes.		
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k.
hours.	millims.	millims.			hours.	millims.	
0	286·0	98·7	—	—	0	358·4	—
1	202·1	56·7	0·1508	0·2407	1	218·8	0·2143
1½	170·5	41·0	0·1498	0·2544	2	133·1	0·2151
2	145·2	28·3	0·1472	0·2712	3	78·4	0·2200
3	118·8	15·1	0·1272	0·2718	4	47·6	0·2192
3½	110·9	11·2	0·1176	0·2700	5	25·0	0·2313

The immediate effect of the excess of hydrogen in Experiment V. was a marked stimulation of the surface, which increased up to nearly the end of the second hour, when, it would appear, the surface had become fully hydrogenised. In conformity with this idea, the rate of steam formation was, during the interval 0 to 2 hours, nearly proportional to the partial pressure of the hydrogen; afterwards, however, it was largely governed by the oxygen pressure.

The stimulation of the surface by hydrogen is not only well marked, but is also shown to be very enduring, in Experiment VI.

Second Series with Silver Gauze at 400°.

At the outset of this series of experiments, the gauze was taken out of the combustion tube and heated to a temperature just short of the melting-point. A marked change took place both in its outward appearance and mechanical properties. The metal had lost its original elasticity and become exceedingly brittle; its surface had assumed a beautiful frosted appearance, and was covered with minute pits and excrescences, as will be seen from the photomicrograph B of it reproduced on p. 37. This should be compared with A, which shows the original condition of the surface. The whole behaviour of the metal suggested the breaking up of a hydride, and recalled the experiments of BEILBY and HENDERSON on the action of ammonia on metals at high temperatures.* In the case of silver, they found that "at 800° the polished surface of fine silver wire acquired a frosted appearance, and when examined with the microscope the wire was found to be coated all over with minute rounded blisters or bubbles, whilst there was very distinct evidence of 'spitting.' The elasticity of the metal was also very greatly reduced." They attributed the change

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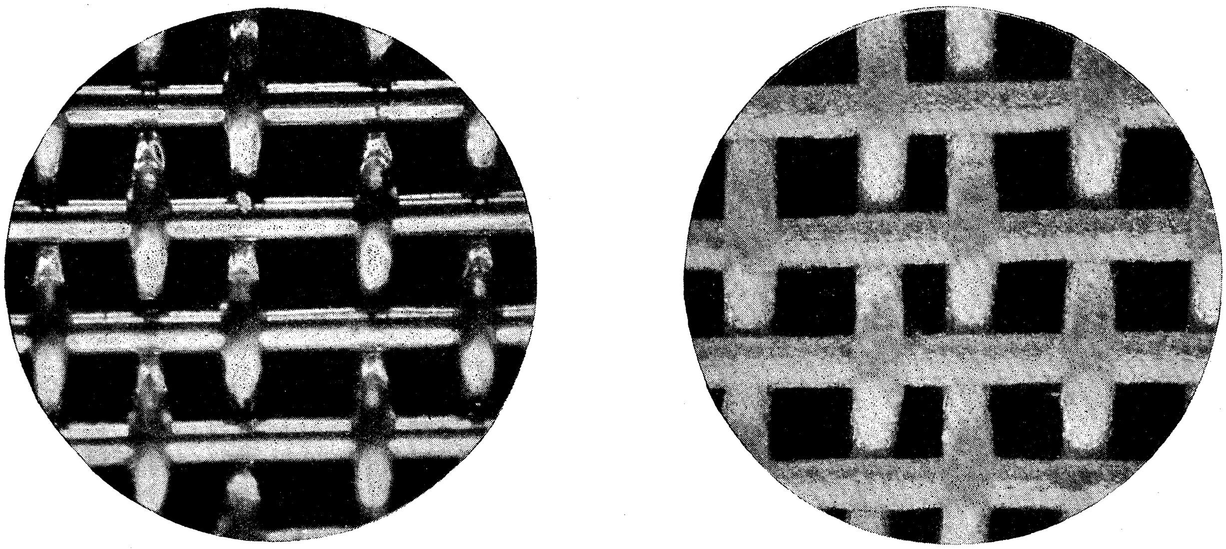
* 'Trans. Chem. Soc.,' 1901, vol. 79, p. 1245.

to the rapid formation and decomposition of an unstable nitride. Graham also noticed a very similar effect in his experiments on the occlusion of hydrogen by metals. He records that 108·8 grammes of silver wire occluded 0·211 vol. of hydrogen (2·2 cub. centims.) when heated to redness and slowly cooled in the gas, and that "the metal acquired a beautiful frosted appearance on the surface, and by repeated heating it became highly crystalline and brittle."*



A. In its original condition.

B. After first series of experiments at 400° and subsequent heating (*vide* p. 36).

Photomicrographs of the silver gauze.

In view of the greatly increased surface area of the metal, consequent upon the treatment referred to above, we were not surprised to find that its catalysing power had increased something like threefold (as compared with the "normal" rate in the previous series), when the rate for normal electrolytic gas was re-determined (Experiment VII.), as under :—

Experiment VII.

September 11, 1904.

Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 65 minutes.

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$ hours.
P	337·8	148·2	45·2	18·6 millims.
k_1	—	0·7154	0·8735	0·8394

That the enhanced catalysing power of the gauze was really due to its increased surface area was proved by rubbing off part of the frosted surface (it was obviously

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* 'Phil. Trans.,' 1866, vol. 156, p. 435; also 'Chemical and Physical Researches,' pp. 275–277.

impossible to remove it in places where the strands of wire overlapped) with a chamois leather, and subsequently re-determining the rate of combination for normal gas in the two following experiments :—

EXPERIMENT VIII. September 20, 1904. Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 65 minutes.			EXPERIMENT IX. September 21, 1904. Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 65 minutes.		
t.	P.	k_1.	*t.*	P.	k_1
hours.	millims.		hours.	millims.	
0	397·6	—	0	367·4	—
$\frac{1}{2}$	246·6	0·4150	$\frac{1}{2}$	222·9	0·4342
1	153·2	0·4142	1	141·4	0·4148
$1\frac{1}{2}$	97·8	0·4062	$1\frac{1}{2}$	90·6	0·4054
2	58·6	0·4158	2	55·0	0·4124
$2\frac{1}{2}$	36·8	0·4134	$2\frac{1}{2}$	33·8	0·4146
3	22·9	0·4132	3	20·2	0·4199

In the next experiment, a mixture initially corresponding to $3H_2+O_2$, nearly, was employed. The residual hydrogen was subsequently circulated over the gauze at 400° for 16 hours, after which it was pumped out, and the rate for "normal" electrolytic gas re-determined (Experiment XI.).

EXPERIMENT X. September 21, 1904. Electrolytic gas plus excess of hydrogen, $3H_2+O_2$. T = 400°. Rate of circulation = 1 in 65 minutes.					EXPERIMENT XI. September 22, 1904. Normal electrolytic gas over "hydrogenised" surface. T = 400°. Rate of circulation = 1 in 65 minutes.		
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	*t.*	P.	k_1.
hours.	millims.	millims.			hours.	millims.	
0	298·1	100·9	—	—	0	370·4	—
$\frac{1}{2}$	223·1	63·5	0·2516	0·4018	$\frac{1}{2}$	158·2	0·7388
1	156·7	30·3	0·2792	0·5223	1	59·4	0·7949
$1\frac{1}{2}$	129·1	16·4	0·2422	0·5260	$1\frac{1}{2}$	19·3	0·8554
2	114·9	9·2	0·2070	0·5199			
$2\frac{1}{2}$	106·9	5·4	0·1781	0·5085			

The results of Experiment X. confirm those of the corresponding experiment of the previous series (Experiment V.) with the mixture $3H_2+O_2$. Up to a certain condition of maximum "hydrogenation," the rate of steam formation largely depended on the partial pressure of the hydrogen, afterwards, however, on that of the oxygen. In

Experiment XI. the further stimulation of the surface by hydrogen is again well marked. Moreover, it proved very enduring in character, hardly fading at all during several successive experiments with normal electrolytic gas, and, indeed, subsequent complete "dehydrogenation" of the surface by oxygen at 400° only reduced the value of "k_1" for normal electrolytic gas to 0·6554. It is evident, therefore, that the stimulating action of hydrogen was partly due to the surface becoming "hydrogenised," and partly also to the permanent increase in the surface area when this condition was removed. This was very clearly shown in the next two experiments (XII. and XIII.). Starting with the gauze in its completed "dehydrogenised" condition, hydrogen was again circulated over it at 400° for 16 hours, and afterwards rapidly withdrawn from the apparatus. The rate for normal electrolytic gas was at once re-determined, as follows:—

Experiment XII.

Normal electrolytic gas over "hydrogenised" gauze. T = 400°.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1 hour.
P	371·1	203·4	115·1	66·6	36·6 millims.
k_1	—	1·0488	1·0168	0·9944	1·006

The increase in the value of "k_1" from 0·65 to 1·04 must be ascribed to the direct influence of hydrogen, that is to say, to the association of hydrogen with the surface.

The combustion tube containing the gauze was now transferred to a high-temperature furnace and exhausted, first in the cold, and afterwards at red heat. About 9 cub. centims. of hydrogen were extracted during four hours at red heat, and the exhaustion was continued for a full hour after the gas had ceased to be evolved. The gauze was cooled *in vacuo*, and the tube afterwards transferred back to the circulation apparatus, where the rate for normal electrolytic gas was finally re-determined (Experiment XIII.). The complete removal of the hydrogen had left the gauze in an extremely "active" condition, owing to the large increase in its surface area and porosity.

Experiment XIII.

September 26, 1904.
Normal electrolytic gas. T = 400°.

t	0	$\frac{1}{4}$	$\frac{1}{2}$ hour.
P	327·6	36·6	2·6 millims.
k_1	—	3·80	4·20

The Absorption of Hydrogen by Silver.—At Dull Red Heat.

It now became necessary to obtain some further evidence concerning the absorption of hydrogen by silver at high temperatures. Accordingly the combustion tube (capacity = 135 cub. centims.) containing the 62 grammes of silver gauze employed in the preceding experiments was transferred to the "absorption" apparatus, where it was thoroughly exhausted at dull red heat (*circa* 650°) during several hours. Pure hydrogen was then admitted up to a pressure of 744 millims. A rapid absorption of the gas at once began, the pressure falling to 381 millims. in 25 minutes, as follows:—

t . .	0	2	4	6	8	10	15	20	25 minutes
P .	774	689	610	547	499	464	414	395	381 millims.

The tube was next allowed to cool, and was subsequently exhausted at the room temperature until the whole of the unabsorbed gas (about 25 cub. centims.) had been extracted. The temperature was thereupon again raised to dull red heat, and the exhaustion continued for 15 hours longer. During the whole of this time hydrogen was very slowly evolved (about 7·5 cub. centims. were collected within the first three hours), and a mirror of silver appeared near the cool end of the combustion tube, a circumstance which suggested the decomposition of a hydride rather than the mere giving off of "condensed" or "occluded" gas.

In order to completely "dehydrogenise" the surface, pure oxygen was now admitted to the red hot tube up to a pressure of 763 millims. During the next minute the pressure rapidly fell to 683 millims., and water condensed in the cool ends of the tube. There then followed a very slow fall in pressure (29 millims. during the next 14 minutes), probably due to a small absorption of oxygen. The pressure records during this treatment with oxygen were as follows:—

t . . .	0	1	2	3	4	5	10	15 minutes
P . . .	763	686	680	675·5	672	669	662·5	657 millims.
	H_2O formed							

The tube was next continuously exhausted at dull red heat for 14 hours, after which pure hydrogen was once more admitted up to a pressure of 747 millims. There followed a very rapid absorption, the pressure falling to 432 millims. within the first five minutes, and to 180 millims. by the end of an hour. During the first minute there was a slight condensation of moisture in the cool ends of the tube, due to the burning out of the small amount of residual occluded oxygen. The pressure records during the absorption of hydrogen were as follows :—

t. . . .	0	1	2	3	4	5	10	15	20	30	60	120	150 minutes.
P . . .	747	639	571	516	472	432	334	275	244	210	181	157	155 millims.
	some H_2O formed												

The tube was finally exhausted (1) at the room temperature for an hour for the removal of any unabsorbed gas, and (2) at dull red heat for 40 hours, during which no less than 26 cub. centims. of hydrogen were very slowly extracted.

[*Third Series with Silver Gauze at* 500°.

In a series of experiments with normal electrolytic gas at this temperature, it was proved that the rate of combination, although very fast, still remained proportional to the partial pressure, and that, as at 400°, the catalysing power of the surface was stimulated, in a marked degree, by previous exposure to hydrogen.—*January* 31, 1906.]

Fourth Series with Silver Foil at 400°.

In order to ascertain whether the catalytic process is materially influenced by the physical character of the surface, a final series of experiments was made at 400° with pure silver foil. A piece of pure "assay" silver was rolled out into a thin ribbon (40 centims. long and 1·5 centims. broad), and after its surface had been slightly etched by momentary immersion in cold dilute nitric acid, followed by a thorough washing with hot distilled water, it was wound spirally round a glass rod. The extremities of the rod were provided with small glass projections, so that it would rest inside the combustion tube of the circulation apparatus without the foil touching the glass walls. The area of the foil exposed to the reacting gases was 60 sq. centims.

Successive charges of normal electrolytic gas were circulated over the foil at 400°, until the rate of combination, which was at first rather slow, had attained a steady maximum. The values of "k_1" increased from 0·0310 to 0·0770 during this period, after which the rate of combination remained proportional to the pressure of the dry gas. This is shown in Experiment XXII., which gives the normal value of "k_1" for the series.

EXPERIMENT XXII.

April 7, 1905.
Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 70 minutes.

t.	P.	k_1.
hours.	millims.	
0	560·2	—
1	468·3	0·0779
2	388·1	0·0795
3	325·1	0·0788
5	234·2	0·0758
6	194·0	0·0767
7	162·6	0·0767
9	115·9	0·0760
11	82·1	0·0758
12	70·5	0·0750
23	10·7	0·0747

In the next experiment (XXIII.), a mixture corresponding very nearly to $3H_2+O_2$ was employed. The surface was immediately stimulated, and the rate of charge was much more proportional to the partial pressure of the hydrogen than to that of the oxygen throughout the experiment. The results were as follows:—

EXPERIMENT XXIII.

April 8, 1905.
$3H_2+O_2$. T = 400°. Rate of circulation = 1 in 75 minutes.

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	394·8	297·2	97·6	—	—
$\frac{1}{2}$	364·8	277·2	87·6	0·0606	0·0938
1	332·4	255·6	76·8	0·0656	0·1040
$1\frac{1}{2}$	298·0	232·6	64·5	0·0710	0·1158
2	266·3	211·4	54·9	0·0740	0·1249
$2\frac{1}{2}$	238·2	192·6	45·6	0·0754	0·1322
$3\frac{1}{2}$	189·9	160·4	29·5	0·0764	0·1484
4	171·0	147·8	23·2	0·0778	0·1562
$4\frac{1}{2}$	147·6	132·2	15·4	0·0782	0·1782

The residual hydrogen was then circulated over the foil at 400° for 22 hours, after which the apparatus was exhausted (1 hour), and a fresh charge of electrolytic gas admitted. The rate of combination observed (Experiment XXIV.) was extremely rapid, no less than 66·8 per cent. of the original gas disappearing within an hour as compared with only 16·5 per cent. in Experiment XXII., when the foil was in a condition of "normal" activity. The rapidly diminishing values of "k_1" indicated a fading away of the stimulus as the experiment proceeded. In order to completely "dehydrogenise" the foil, air was circulated over it at 400° for 22 hours. The apparatus was again exhausted, and finally the rate for normal electrolytic gas was re-determined in Experiment XXV. The results of this experiment prove that the "dehydrogenised" foil had become comparatively inactive; as the experiment proceeded, however, its catalysing power gradually increased, until finally it attained the "normal" value. The striking difference between the course of events in Experiments XXIV. and XXV. proves how completely the catalytic process depends on the association of the metal with hydrogen. The rate of circulation in these two experiments was 1 in 75 minutes.

Experiment XXIV. April 9, 1905. T = 400°. Normal electrolytic gas over "hydrogenised" foil.			Experiment XXV. April 11, 1905. T = 400°. Normal electrolytic gas over "dehydrogenised" foil.		
t.	P.	k_1.	*t.*	P.	k_1.
hours.	millims.		hours.	millims.	
0	521·0	—	0	479·6	—
$\frac{1}{4}$	334·0	0·7776	$\frac{1}{2}$	464·7	0·0272
$\frac{1}{2}$	257·2	0·6138	1	440·6	0·0367
$\frac{3}{4}$	207·0	0·5344	2	376·8	0·0523
1	173·0	0·4788	3	328·8	0·0546
$1\frac{1}{2}$	120·0	0·4250	4	285·3	0·0564
2	82·6	0·4000	5	240·1	0·0601
			6	209·3	0·0600
			22	21·1	0·0616

At the conclusion of Experiment XXV., the combustion tube containing the foil was removed to the absorption apparatus, where it was subjected to the prolonged action of hydrogen at dull red heat (650°). After the metal had become fully "hydrogenised," the tube was cooled and the unabsorbed gas withdrawn. The tube was again transferred back to the circulation apparatus, where the rate for normal electrolytic gas was re-determined (Experiment XXVI.). The metal was now found to be extraordinarily active, so much so that pressure records had to be taken every few minutes; by the end of half an hour no less than 83 per cent. of the original gas had disappeared. The values for "k_1" are, for purposes of comparison with the previous experiments of the series, referred to the hour as the unit of time.

EXPERIMENT XXVI.

April 15, 1905.
Normal electrolytic gas over surface previously treated with hydrogen at 650°.
T = 400°. Rate of circulation = 1 in 75 minutes.

t.	P.	k_1.	t.	P.	k_1.
minutes.	millims.		minutes.	millims.	
0	497·2	—	15	185·2	1·716
5	355·2	1·754	20	138·2	1·668
10	254·2	1·749	30	80·2	1·585

The remarkable influence of hydrogen on the activity of the metal is strikingly illustrated by the four pressure curves, for normal electrolytic gas, reproduced in Diagram IV., p. 45. Curve A was obtained with the surface in its "normal" condition, and C after complete "dehydrogenation" with oxygen. Curves B and D show the influence of "hydrogenation" at 400° and 650° respectively.

During the course of the experiments just described, a bright mirror of silver had formed along the whole length of the glass rod round which the ribbon had been wound, and the inner surface of the combustion tube had become completely coated with a thin brown film, suggestive of the decomposition of a volatile compound of silver.

Summarising now the results of the four series of experiments, it is evident (1) that with normal electrolytic gas the rate of combination is proportional to the pressure of the dry gas; (2) that the activity of the surface is always greatly stimulated by previous treatment with hydrogen, but not with oxygen; (3) that an "active" surface absorbs hydrogen both at 400° and at dull red heat; and (4) that the behaviour of the "hydrogenised" metal suggests the formation of a hydride rather than the mere occlusion or condensation of the gas. The theory of the catalytic action of the metal indicated by the facts is that it essentially involves the rapid formation and oxidation of a hydride, or at least of a film of "hydrogenised" silver. Two independent velocities, namely, that of "hydrogenation" (V_1) and that of the oxidation of the "hydrogenised" metal (V_2), therefore come into play during the process, and the relative values of the two will, in any particular case, depend on the condition of the surface as regards its power of combining with hydrogen. In the experiments with the gauze, for example, it is evident that V_1 was faster than V_2, for with mixtures containing excess of hydrogen the catalysing power of the surface was quickly stimulated up to a certain limit of complete "hydrogenation," after which the velocity of steam formation was nearly proportional to the partial pressure of the oxygen (*vide* Experiments V. and X.). In the case of the foil, however, it is evident from the results of Experiment XXIII. that V_1 was slower than V_2, for the velocity of steam formation was nearly proportional to the partial pressure of the hydrogen throughout.

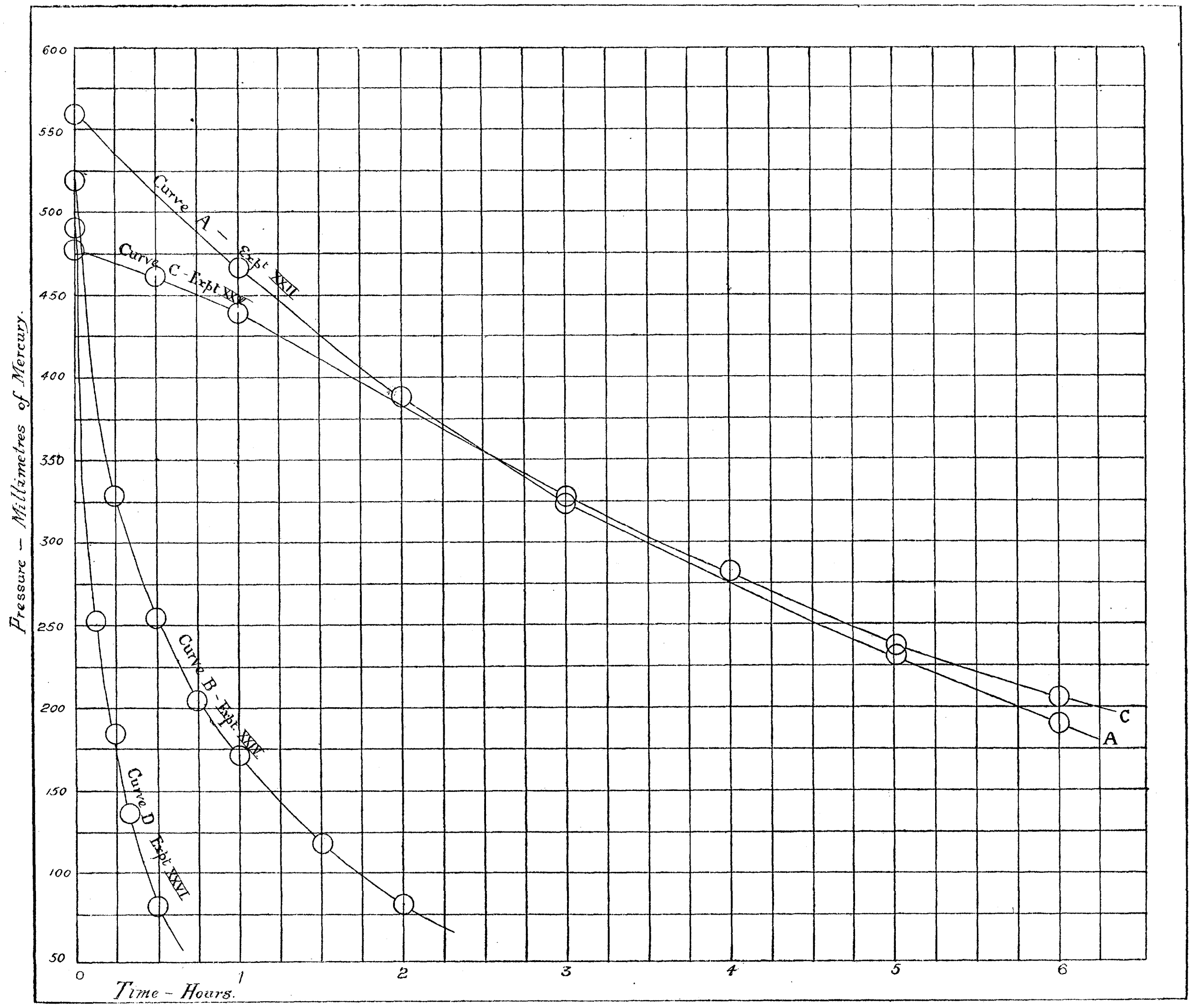

Diagram IV. Experiments with silver foil. Pressure curves for normal electrolytic gas.
Curve A, surface in "normal" condition. Curve C, surface "dehydrogenised" by oxygen.
,, B, surface "hydrogenised" at 400°. ,, D, surface "hydrogenised" at 650°.

PART IV.—EXPERIMENTS WITH GOLD GAUZE.

In order that a series of experiments might be carried out with a gold surface under as nearly as possible the same conditions as the preceding experiments with silver, Messrs. JOHNSON, MATTHEY & Co. very kindly prepared a gauze of fine gold wire containing 22 strands (each 0·15 millim. diameter) per centimetre. A rectangular piece of this gauze, measuring 23·3 by 9·25 centims., and weighing 52·9 grammes, was employed for the experiments. The surface exposed to the reacting gases would be approximately 447 sq. centims.

After a preliminary series of experiments with normal electrolytic gas, at different temperatures between 250° and 400°, in which the rate of combination was always found to be proportional to the pressure of the dry gas, we adopted 250° as the best experimental temperature for the investigation of the influence of an excess of each gas, respectively, on the catalytic process. The following three experiments were then made with normal electrolytic gas. In Experiments V. and VI., the gauze was in its "normal" condition, but before Experiment VII., oxygen had been circulated over it at 250° for two days.

EXPERIMENT V.			EXPERIMENT VI.			EXPERIMENT VII.		
November 25, 1904. Surface in "normal" condition. Normal electrolytic gas. T = 250°. Rate of circulation = 1 in 45 minutes.			November 27, 1904. Surface in "normal" condition. Normal electrolytic gas. T = 250°. Rate of circulation = 1 in 45 minutes.			December 1, 1904. Surface after exposure to oxygen at 250° for 2 days. Normal electrolytic gas. T = 250°. Rate of circulation = 1 in 45 minutes.		
t.	P.	k_1.	*t*.	P.	k_1.	*t*.	P.	k_1.
hours.	millims.		hours.	millims.		hours.	millims.	
0	355·5	—	0	348·6	—	0	339·3	—
1	275·5	0·1107	1	270·9	0·1096	1	257·8	0·1193
2	215·8	0·1084	2	218·6	0·1014	2	204·8	0·1097
3	175·8	0·1019	3	173·6	0·1010	3	166·9	0·1027
4	141·1	0·1003				4	135·9	0·0993
5	112·2	0·1001				5	107·3	0·1000
6	89·3	0·1000				6	84·1	0·1009
7	70·1	0·1007						

It is again evident that the rate of combination is proportional to the pressure of the dry gas, although in all three experiments the amount of change during the first hour was proportionally rather larger than during any of the succeeding hours. From the results of Experiment VII. it is clear that oxygen *per se* has no stimulating influence on the catalysing power of the surface.

In the next two experiments (VIII. and IX.), the influence of an excess of oxygen and hydrogen, respectively, on the rate of combination was studied. The rate of circulation was the same in each experiment (namely, complete circuit in 45 minutes), and during the interval between the two experiments the apparatus stood vacuous.

EXPERIMENT VIII.

December 4, 1904.
Original mixture = H_2+2O_2 nearly. Rate of circulation = 1 in 45 minutes. T = 250°.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	116·6	244·1	—	—
1	85·0	228·4	0·1374	0·0289
2	65·0	218·3	0·1269	0·0242
3	52·3	212·0	0·1161	0·0204
4	43·6	207·6	0·1068	0·0176
5	37·8	204·7	0·0979	0·0153
6	30·8	201·4	0·0964	0·0139
8	19·9	195·7	0·0960	0·0120
10	14·4	192·9	0·0908	0·0102

EXPERIMENT IX.

December 8, 1904.
Original mixture = $3H_2+O_2$ nearly. Rate of circulation = 1 in 45 minutes. T = 250°.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims	millims.		
0	295·7	95·0	—	—
1	251·1	72·8	0·0709	0·1156
2	210·9	52·6	0·0734	0·1283
3	177·8	36·0	0·0736	0·1404
4	150·3	22·4	0·0735	0·1569
5	127·1	10·7	0·0733	0·1897
6	113·7	3·9	0·0692	0·2311

These experiments prove that the rate of combination is mainly determined by the partial pressure of the hydrogen. Throughout Experiment IX., with excess of hydrogen, the values of "k_{H_2}" are remarkably constant, but in VIII., with excess of oxygen, they gradually diminish as the combination proceeds. These conclusions were afterwards confirmed by the results of Experiments XI. and XIV. It would appear that a steadily increasing excess of oxygen has a slight retarding influence.

The stimulating influence of hydrogen, so well marked in IX., was further proved by circulating hydrogen over the gauze at 250° for 4 days, and afterwards re-determining the rate of combination for normal electrolytic gas, as follows:—

EXPERIMENT X.

December 12, 1904.
Normal electrolytic gas after exposure of the surface to hydrogen at 250° for 4 days. T = 250°.

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	4 hours.
P	324·6	257·3	212·8	182·0	157·3	138·9	125·9	103·1 millims.
k_1	—	0·2018	0·1834	0·1674	0·1573	0·1474	0·1371	0·1245.

In this experiment no less than 34·5 per cent. of the original gas disappeared within the first hour, as compared with 22·5 per cent. in Experiments V. and VI. The stimulus was, however, very transient and was hardly noticeable after the first hour.

The foregoing conclusions were confirmed by the following group of four experiments, made under precisely the same conditions as regards temperature and rate of circulation as those just described.

In Experiment XI., an original mixture corresponding very nearly to $3H_2+O_2$ was employed. The rate of combination was again proportional to the partial pressure of the hydrogen; the values "k_{H_2}," it will be observed, are almost identical with those obtained in the corresponding Experiment IX.

In Experiment XII., the rate for "normal" electrolytic gas was determined after hydrogen had been continuously circulated over the gauze at 250° for 5 days, and had then been withdrawn as rapidly as possible from the apparatus.

Experiment XIII. shows the rate for "normal" gas after the gauze had been completely "dehydrogenised" by circulating oxygen over it at 250° for 16 hours. The great difference between the rates observed in these two experiments is a further striking proof of the stimulating influence of hydrogen. Finally, in Experiment XIV., a mixture H_2+2O_2 was employed after the gauze had been completely "dehydrogenised" by circulating oxygen over it for 36 hours at 250°.

EXPERIMENT XI.

December 14, 1904.
Original mixture = $3H_2+O_2$ nearly. T = 250°. Rate of circulation = 1 in 45 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	305·7	100·6	—	—
1	258·4	77·0	0·0730	0·1160
2	218·3	56·9	0·0731	0·1237
3	184·9	40·2	0·0728	0·1328
4	155·5	25·5	0·0734	0·1490
5	134·3	14·9	0·0710	0·1659
6	115·9	5·7	0·0702	0·2078

EXPERIMENT XII.

December 19, 1904.
Normal electrolytic gas over "hydrogenised" gauze. T = 250°. Rate of circulation = 1 in 45 minutes.

t.	P.	k_1.
hours.	millims.	
0	406·9	—
$\frac{1}{4}$	325·1	0·3900
$\frac{1}{2}$	275·5	0·3388
$1\frac{1}{2}$	161·0	0·2685
2	137·4	0·2357
$2\frac{1}{2}$	119·8	0·2124
3	101·8	0·2006

EXPERIMENT XIII.

December 20, 1904.
Normal electrolytic gas over "de-hydrogenised" surface. T = 250°. Rate of circulation = 1 in 45 minutes.

t.	P.	k_1.
hours.	millims.	
0	399·2	—
$\frac{1}{2}$	355·3	0·1013
1	317·0	0·1002
2	255·9	0·0966
3	200·1	0·1000
4	161·3	0·0984
5	127·4	0·0992

EXPERIMENT XIV.

December 22, 1904.
Original mixture = $H_2 + 2O_2$ nearly. T = 250°. Rate of circulation = 1 in 45 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	109·3	218·7	—	—
1	96·3	212·2	0·0550	0·0132
2	88·1	208·1	0·0468	0·0108
3	81·6	204·8	0·0423	0·0095
5	70·2	199·2	0·0385	0·0081
7	60·0	194·0	0·0372	0·0074
9	50·7	189·4	0·0370	0·0069
11	43·5	185·8	0·0364	0·0064

The Absorption of Hydrogen by the Gold Gauze at 600°.

The results of the foregoing experiments led us to try the action of hydrogen upon the gauze at 600° in the absorption apparatus.* The fall in pressure in each of two experiments amounted to from 30 to 40 millims. out of 760 millims. during the first hour, and in the third experiment the total fall in pressure was 105 millims. during 20 hours. The occluded gas was retained in a vacuum at the ordinary temperature, but could be readily extracted at dull red heat. A microscopic examination of the gauze revealed no signs of disintegration, or of the formation of a hydride, as in the corresponding experiment with silver. The immediate cause of the catalytic action would, therefore, seem to be a merely superficial occlusion, or condensation, of hydrogen, rather than the formation of a hydride or any deep action of the gas. The following re-determination of the rate of combination for normal electrolytic gas at 250°, after the treatment with hydrogen at 600°, showed how greatly the catalysing power of the surface had been stimulated.

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* In speaking of his experiments on the action of hydrogen upon gold at red heat, GRAHAM remarks: "The power of this metal to occlude hydrogen is very sensible." In one experiment it occluded 0·48 of its own volume of the gas ('Phil. Trans.,' 1866, vol. 156, p. 433; 'Chemical and Physical Researches,' p. 275).

Experiment XV.

January 12, 1905.
Normal electrolytic gas over "hydrogenised" gold. T = 250°.
Rate of circulation = 1 in 45 minutes.

t	0	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{2}$	2 hours
P . . .	364·7	189·7	138·3	108·1	62·6	36·4 millims.
k_1 . . .	—	0·5676	0·5612	0·5281	0·5101	0·5004

The influence of hydrogen on the catalysing power of the surface is illustrated in the three pressure curves shown in Diagram V., below. Curve A is for the gauze in its "normal" condition, B shows the transient stimulus imparted by previous exposure to hydrogen at 250°, whilst C shows the more permanent effect of "hydrogenation" at 600°.

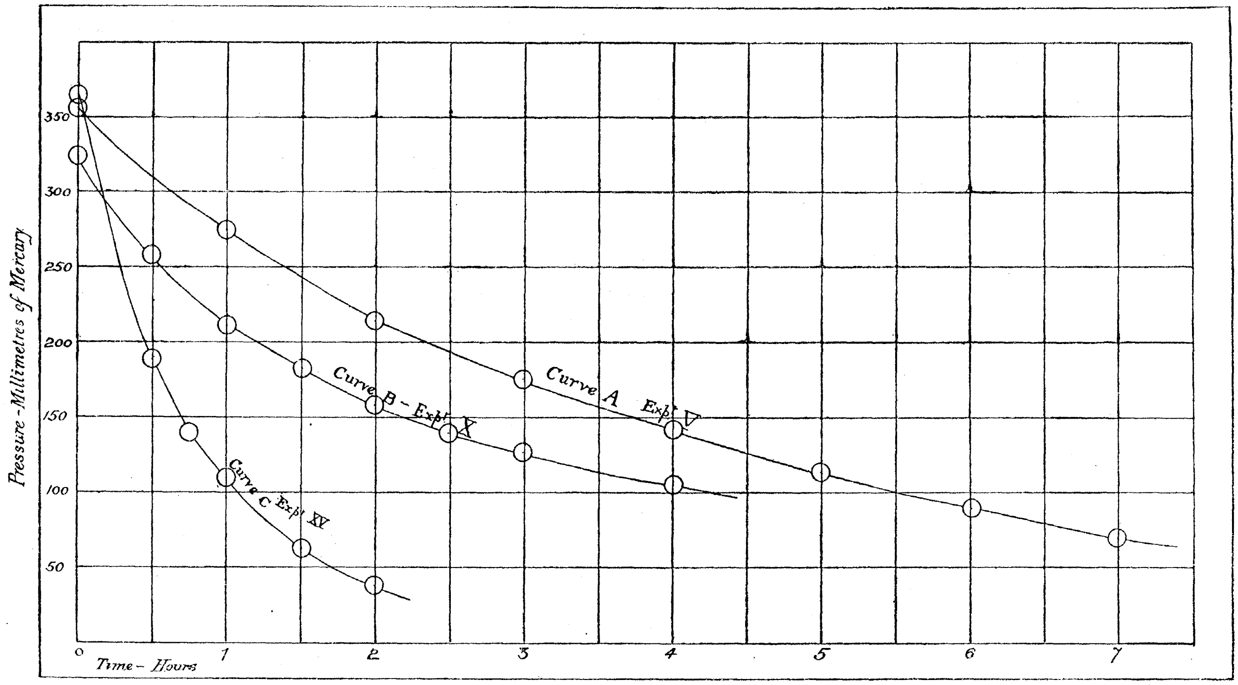

Diagram V. Experiments with gold gauze. Pressure curves for normal electrolytic gas. Curve A, surface in "normal" condition. Curve B, surface "hydrogenised" at 250°. Curve C, surface "hydrogenised" at 600°.

Part V.—Experiments with Platinum.

Bodenstein (*loc. cit.*), from his experiments on the combination of hydrogen and oxygen over a *dry* platinum surface at ordinary temperatures, concluded that whereas an excess of hydrogen has no marked influence on the velocity of the reaction, excess of oxygen produces a considerable acceleration. We cannot entirely endorse this conclusion, at least so far as higher temperatures are concerned, since the following experiments, which were carried out at 160°–170°, show that the action of platinum is not materially different from that of the other metals examined. In the following experiments a piece of platinum gauze (18 strands, each 0·12 millim. in diameter, per centimetre), 7·5 centims. long and 2·7 centims. broad, weighing 2·67 grammes, was employed. The area exposed to the reacting gases would, therefore, be approximately 27·5 sq. centims. The rate of circulation was the same in all experiments, namely, 1 in 65 minutes, but the temperature varied somewhat in different experiments between the above limits.

Experiment I., which gives the "normal" value of "k_1" for the series, proves that with normal electrolytic gas the rate of combination is proportional to the pressure. In Experiment II., where the original mixture corresponded very nearly to H_2+2O_2, the rate was throughout proportional to the partial pressure of the hydrogen, although the values of "k_{H_2}" indicate that the gauze was more than normally active. Experiment III. gives the rate for normal electrolytic gas after the residual oxygen from II. had been circulated over the gauze for 16 hours; there was no evidence of any stimulation. Experiment IV. merely confirms the results of II.

In Experiment V. the value of "k_1" for normal electrolytic gas was re-determined, and in VI. an original mixture corresponding to $3H_2+O_2$ was employed. The rate of combination was again nearly proportional to the partial pressure of the hydrogen throughout. The residual hydrogen was afterwards circulated over the gauze at 165° for 16 hours and finally quickly withdrawn from the apparatus. On re-determining the rate for normal electrolytic gas over the "hydrogenised" surface (Experiment VII.) it was found to be abnormally active. The stimulus, however, rapidly wore away as the experiment proceeded, entirely disappearing after 30 minutes.

EXPERIMENT I.			EXPERIMENT II.						EXPERIMENT III.		
November 26, 1904. Normal electrolytic gas. T = 165–8°. Rate of circulation = 1 in 65 minutes.			November 27, 1904. Original mixture = H_2+2O_2 nearly. T = 169–173°. Rate of circulation = 1 in 65 minutes.						November 28, 1904. Normal electrolytic gas after oxygen. T = 170–2°. Rate of circulation = 1 in 65 minutes.		
t.	P.	k_1.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k_1.
hours.	millims.		hours.	millims.	millims.			hours.	millims.	
0	308·8	—	0	123·7	248·5	—	—	0	368·9	—
1	236·6	0·1157	1	68·9	221·1	0·2541	0·0508	½	326·3	0·1066
2	191·5	0·1038	1½	50·1	211·7	0·2617	0·0464	1	286·9	0·1091
3	155·4	0·0994	2½	25·9	199·6	0·2716	0·0381	1½	252·3	0·1101
4	124·5	0·0987	3	18·9	196·2	0·2719	0·0342	2	214·8	0·1174
5	99·9	0·0980	3½	13·9	193·7	0·2712	0·0310	2½	183·5	0·1212
6	77·6	0·0999	4	10·3	191·8	0·2699	0·0281	3	162·6	0·1186
7	56·6	0·1052	4½	7·3	190·3	0·2730	0·0259			
8	40·7	0·1100								

EXPERIMENT IV.

December 5, 1904.
Original mixture = H_2+2O_2 nearly. T = 169–171°. Rate of circulation = 1 in 65 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	115·8	229·1	—	—
1	83·8	213·1	0·1405	0·0314
2	53·0	197·7	0·1697	0·0319
3	36·8	189·6	0·1659	0·0274
4	25·8	184·1	0·1630	0·0237
5	19·8	181·1	0·1538	0·0204
6	14·6	178·5	0·1502	0·0180

EXPERIMENT V.

December 14, 1904.
Normal electrolytic gas. T = 161–2°. Rate of circulation = 1 in 65 minutes.

t.	P.	k_1.
hours.	millims.	
0	400·2	—
1	317·2	0·1010
2	250·4	0·1019
3	182·0	0·1141
4	137·2	0·1163
5	101·2	0·1194
6	73·1	0·1231

EXPERIMENT VI.

December 20, 1904.
Original mixture = $3H_2+O_2$. T = 164–5°. Rate of circulation = 1 in 65 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	241·6	80·5	—	—
1	208·0	63·8	0·0650	0·1010
2	182·0	50·8	0·0615	0·1000
3	160·0	39·6	0·0597	0·1027
4	140·4	30·0	0·0590	0·1072
5	123·8	21·7	0·0581	0·1138
6	110·0	14·7	0·0570	0·1229
7	97·2	8·3	0·0565	0·1409
8	86·1	2·6	0·0560	0·1863

EXPERIMENT VII.

December 21, 1904.
Normal electrolytic gas over "hydrogenised" gauze. T = 164–5°.
Rate of circulation = 1 in 65 minutes.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	1	2	3 hours.
P	275·6	234·0	214·9	189·4	151·5	129·0 millims.
k_1	—	0·2840	0·2160	0·1628	0·1299	0·1100

PART VI.—EXPERIMENTS WITH NICKEL.

The nickel was employed in the form of a rectangular piece of gauze, containing 10 strands per centimetre, and measuring 15 by 14 centims. The surface exposed to the reacting gases was approximately 330 sq. centims. The metal proved to be a very efficient catalyser, although its catalysing power was rather sensitive to comparatively small changes in temperature. Thus in three preliminary experiments (Nos. I. to III. inclusive) at 200°, 220°, and 240°, the rate of circulation being 1 in 40 minutes, the mean values of "k_1" obtained were 0·010, 0·045, and 0·350 respectively.

The ratio H_2/O_2 for the residual gas from Experiment II. was found to be exactly 2·0, and in the case of Experiment III. it was 2·2. Apparently, therefore, the prolonged action of the gases at 240° caused a slight oxidation of the metal, which, however, did not occur at 220°, the temperature chosen for all the succeeding experiments.

At 220°.

On circulating successive charges of normal electrolytic gas over the gauze at 220°, its catalysing power increased up to a point such that from 12 to 15 per cent. of the gas always disappeared during the first hour of a given experiment. After this point had been reached, however, the values of "k_1" increased regularly during each experiment, as though the activity of the surface was being continually stimulated as the combination proceeded. This induced activity almost entirely disappeared during the interval between two successive experiments, when the apparatus was continuously exhausted. This is shown by the two following experiments with normal electrolytic gas. The rate of circulation for these, as well as all the other experiments of the series, was 1 in from 35 to 40 minutes.

EXPERIMENT IV. May 29, 1905. Normal electrolytic gas.			EXPERIMENT V. May 31, 1905. Normal electrolytic gas.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	514·7	—	0	505·6	—
1	452·1	0·0564	1	437·6	0·0625
2	376·3	0·0680	2	352·9	0·0781
3	301·6	0·0774	3	260·1	0·0962
4	242·9	0·0817	4	199·1	0·1012
5	178·4	0·0922			
7	87·6	0·1099			

The continuous stimulation of the surface in each of the above experiments was not due to any permanent oxidation of the gauze, since the ratio H_2/O_2 for the residual gas at the end of Experiment V. was exactly 2·0. Nor could it be ascribed to a mere reduction in pressure, as the following experiment (VI.) proves.

Before this experiment the apparatus had been continuously exhausted for three days, the combustion tube being maintained at 220° all the time, so as to extract as far as possible any gas condensed or occluded by the metal. A charge of normal electrolytic gas was then admitted, and the rate of combination during the next hour determined. At the end of the hour more gas was admitted until the original pressure was restored, and the rate again determined during the next hour. This procedure was repeated several times. The results showed that whereas the three days' continuous exhaustion at 220° had greatly diminished the catalysing power of the surface, it was subsequently very rapidly restored as the combination of the gases proceeded. The conditions under which this experiment was performed leave no room for doubt but that this rapid stimulation of the surface was due to the progressive condensation of one or other of the reacting gases.

EXPERIMENT VI.

June 18, 1905.
Normal electrolytic gas.

Interval.	Pressure fall.	k_1.
hours.	millims.	
0 to 1	From 510·1 to 497·1	0·0122
1 ,, 2	,, 510·1 ,, 475·1	0·0309
2 ,, 3	,, 509·3 ,, 443·0	0·0614
3 ,, 4	,, 510·0 ,, 421·0	0·0832

The two following experiments (Nos. VII. and VIII.) were made with an original mixture corresponding very nearly to $3H_2+O_2$. In each case, the activity of the surface was greatly stimulated by the increasing excess of hydrogen as the experiment proceeded.

EXPERIMENT VII.

June 9, 1905.
$3H_2+O_2$.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	373·7	124·6	—	—
1	322·4	98·9	0·0640	0·1003
2	259·4	67·4	0·0758	0·1334
3	180·2	27·8	0·1055	0·2172
4	135·6	5·6	0·1100	0·3391

EXPERIMENT VIII.

June 15, 1905.
$3H_2+O_2$.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	383·0	127·6	—	—
1	292·8	83·5	0·1137	0·1842
2	203·9	38·1	0·1367	0·2620
$2\frac{1}{2}$	169·1	20·7	0·1420	0·3156
3	144·4	8·4	0·1412	0·3904

At the conclusion of VIII., the residual gas was as rapidly as possible pumped out of the apparatus, and the rate for normal electrolytic gas immediately afterwards determined (Experiment IX.). The "hydrogenised" surface was now much more than normally active, and the values for "k_1" remained nearly constant throughout. This shows that after a certain degree of "hydrogenation" of the surface, the rate of combination is practically proportional to the pressure of the dry gas.

Experiment IX.*

June 15, 1905.
Normal electrolytic gas over "hydrogenised" surface.

t	0	1	2	3	4	5 hours.
P . . .	505·6	363·7	257·6	179·3	122·1	78·2 millims.
k_1 . . .	—	0·1430	0·1464	0·1501	0·1543	0·1621

In the final experiment of the series, a mixture corresponding to H_2+3O_2 was employed. The excess of oxygen, however, almost prevented any combination, the pressure in the apparatus only falling from 504·8 to 503·0 millims. during the first hour ($k_{H_2} = 0·0042$). This result, taken in conjunction with the results of the three preceding experiments, proves that the catalytic process depends in no way upon occluded oxygen, or superficial oxidation of the metal, but rather upon an association of the surface with hydrogen. A microscopic examination of the gauze at the conclusion of the above series of experiments revealed nothing indicative of any chemical action on the metal (*e.g.*, hydride formation). There had been no pitting of the surface, as in the case of silver, nor were the mechanical properties of the metal at all impaired.

Summarising the results obtained with the four metals examined, we find a substantial agreement in respect of four important particulars, namely, (1) that the catalytic action is in each case primarily due 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; (2) that with normal electrolytic gas the rate of combination is proportional to the pressure of the gas; (3) that whereas the activity of a surface may always be stimulated by previous exposure to hydrogen at moderately high temperatures, oxygen *per se* has no such accelerating influence, but rather, owing to its "dehydrogenising" action, the reverse; (4) that when an excess of either gas is present, the rate of combination is nearly proportional to the

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* It was at the conclusion of this experiment that the apparatus was continuously exhausted at 220° for three days in order to as far as possible "dehydrogenise" the gauze in preparation for Experiment VI. (June 18, 1905). The result of this operation was to greatly reduce the activity of the surface (*vide* Experiment VI.), where $k_1 = 0·0122$ for the first hour.

partial pressure of the hydrogen (in the case of silver, however, this only holds good up to a point of "maximum hydrogenation" of the surface).

The evidence in favour of the "occlusion" theory is particularly strong in the case of nickel, where the "normal" condition of activity can be reduced to almost 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.

Part VII.—Experiments with Easily Reducible Metallic Oxides.

It remained now to examine the action of easily reducible oxides, and for this purpose calcined spathic iron ore, copper oxide, and nickel oxide were selected. A necessary condition for the complete success of the experiments was the finding, in each case, of some temperature at which the catalytic combination of the gases would proceed with fair velocity without the surface itself undergoing any permanent change. This condition was fulfilled at 200° in the cases of calcined spathic iron ore and copper oxide, and at 160° in the case of nickel oxide.

A. *Experiment with Calcined Spathic Iron Ore.*

The catalysing material was prepared by calcining fragments of spathic iron ore at dull red heat in a current of air. It contained 79·0 per cent. of ferric oxide and 14·5 per cent. of manganous oxide.

1st *Group.*

The very powerful catalysing action of these oxides at 200° may be judged from the following experiment with normal electrolytic gas. Readings were made every 10 minutes during the first hour, but, for purposes of comparison with later experiments, the values of "k_1" are calculated on the basis of an hour as the unit of time.

Experiment I.

November 28, 1904.
Normal electrolytic gas. T = 200°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.	*t.*	P.	k_1.
minutes.	millims.		minutes.	millims.	
0	373·5	—	50	219·0	0·2783
10	336·5	0·2724	60	197·5	0·2767
20	302·5	0·2748	80	163·5	0·2691
30	272·5	0·2738	140	86·7	0·2718
40	243·5	0·2787			

The ratio H_2/O_2 in the residual gas was exactly 2·0, a sufficient proof that there had been no permanent oxidation or reduction of the catalysing material. The remarkably constant values of "k_1" show that the rate of combination was proportional to the pressure of the dry gas throughout the experiment.

In two of the three following experiments (II. and IV.), the original mixture corresponded very nearly to H_2+2O_2; in the third experiment, normal electrolytic gas was employed. The rate of circulation (1 in 60 minutes) was the same for all three.

EXPERIMENT II.

November 29, 1904.
Original mixture = H_2+2O_2 nearly. T = 200°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	124·8	273·1	—	—
½	88·8	255·0	0·2956	0·0598
1	63·8	242·5	0·2914	0·0517
1½	44·8	233·1	0·2966	0·0459
2	32·0	226·6	0·2955	0·0405

EXPERIMENT III.

December 4, 1904.
Normal electrolytic gas. T = 200°.
Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	380·4	—
½	276·3	0·2778
1	200·0	0·2793
1½	140·0	0·2895
2	96·0	0·2990
3	43·0	0·3156

EXPERIMENT IV.

December 6, 1905.
Original mixture = H_2+2O_2 nearly. T = 200°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	126·4	244·1	—	—
½	90·8	226·3	0·2874	0·0656
1	66·2	214·0	0·2809	0·0572
1½	49·6	205·7	0·2708	0·0495
2	39·0	200·5	0·2553	0·0427
2½	30·8	196·4	0·2453	0·0378
3	24·4	193·1	0·2381	0·0339

These results, which were confirmed by those of similar experiments, prove that in any given experiment the rate of combination is mainly determined by the partial pressure of the hydrogen.[*] If the catalytic process really involves a series of rapidly

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[*] It may also be observed that, in the four experiments under discussion, the rate at which the hydrogen disappeared was practically the same, viz., about 28 to 30 per cent. during the first hour in each case. This clearly proves that excess of oxygen *per se* has no effect, accelerating or otherwise, on the rate of combination.

alternating reductions and oxidations of the material composing the surface, it follows from the facts brought to light in the above experiments (1) that the rate of reduction of the surface by hydrogen at 200° must be excessively small compared with its rate of re-oxidation by oxygen, and (2) that the rate of combination with electrolytic gas must be comparable with the rate of reduction of the surface by hydrogen. That these conditions were not fulfilled will be seen from the following group of experiments :—

2nd Group.

Normal electrolytic gas was circulated at 200° over the material (which for some weeks previously had not been in use) until a constant rate of combination was attained. The two following determinations of the rate for normal electrolytic gas were then made :—

EXPERIMENT V. January 31, 1905. Normal electrolytic gas. T = 200°.			EXPERIMENT VI. February 1, 1905. Normal electrolytic gas. T = 200°.		
t.	P.	k_1.	*t.*	P.	k_1.
hours.	millims.		hours.	millims.	
0	367·3	—	0	380·4	—
1	293·4	0·0976	1	306·2	0·0943
2	215·1	0·1162	2	235·7	0·1040
3	163·5	0·1160	3	170·4	0·1163
4	126·2	0·1160	4	130·9	0·1158
5	96·4	0·1162	5	100·0	0·1160

The fall in pressure during the first hour in each of these experiments corresponded with the disappearance of as nearly as possible 20 per cent. of the original gas.

Pure hydrogen was next circulated over the surface at 200°, but the pressure fell from 301·7 to 288·5 millims., or by 4·4 per cent. only, during the first hour, a rate of reduction which is many times slower than the rate of combination with electrolytic gas at the same temperature. On raising the temperature of the combustion tube to 300°, the reduction of the surface proceeded with fair velocity, the fall in pressure being about 100 millims. per hour. The reduction was continued until $2\frac{1}{4}$ litres of hydrogen had been used, an amount exceeding the quantity of hydrogen in four full charges of electrolytic gas.

The apparatus was then thoroughly exhausted during 36 hours, and the temperature of the combustion tube lowered to 200° again. A charge of oxygen was thereupon admitted, and the rate of re-oxidation of the reduced surface determined; the fall in pressure observed during the first hour was, however, only 29·7 out of 406·1 millims., or about 7 per cent., and during the next four hours there was a total further fall of

11 millims. only. These results were fully confirmed in the 3rd group of experiments at 200° in which a new surface of the freshly calcined material was used.

3rd Group.

The rate of combination for normal electrolytic gas over the new surface at 200° corresponded to the disappearance of 27·4 per cent. of the original gas during the first hour ($k_1 = 0·140$). The ratio H_2/O_2 for the residual gas at the end of three hours was 2·0 exactly.

On circulating pure hydrogen over the surface at 200° the pressure fell from 449·5 to 420·4 millims., or by 6·5 per cent. only, during the first hour. After the surface had been reduced at 300° by several successive full charges of hydrogen, oxygen was finally circulated over it at 200°. The pressure now fell from 486·9 to 460·5 millims., or by 5·4 per cent. only, during the first hour.

B. *Experiments with Nickel Oxide.*

For these experiments, the combustion tube of the apparatus was packed with porous lumps of grey oxide of nickel containing 99 per cent. of NiO. After some preliminary trials a temperature of 160° was selected as fulfilling the condition that the gases would combine with fair velocity without the surface itself undergoing any permanent reduction or oxidation. In all the five experiments of this series the rate of circulation was 1 in 35 minutes.

Experiment I., with normal electrolytic gas, gives the "normal" value of "k_1" for the series, and also proves that the rate of combination was proportional to the pressure of the dry gas. In Experiment II., an original mixture H_2+2O_2 was employed; from the values "k_{H_2}" it will be seen that the surface was no more than "normally" active, and that the rate of combination was determined by the partial pressure of the hydrogen throughout. Experiment III., which gives the rate for normal electrolytic gas after the residual oxygen from II. had been circulated over the surface at 200° for 48 hours, proves that its catalysing power had remained unaltered.

Proof that the catalytic process had not involved any permanent reduction or oxidation of the surface was afforded by the analysis of samples of the gas shut off at regular intervals during the course of Experiments I. and II. The ratios H_2/O_2 for the samples in I. varied between 2·05 and 2·10 only, whilst for the samples obtained in III. they were all 2·00 exactly. The falls in pressure obtained during the first hour in these two experiments corresponded with the disappearance of 20·4 and 20·7 per cent. respectively of the original gas. Moreover, the values of "k_{H_2}" in Experiment II. show that the excess of oxygen had no accelerating effect on the rate of disappearance of the hydrogen (exactly 20 per cent. of it disappeared during the first hour).

EXPERIMENT I. May 7, 1905. Normal electrolytic gas. T = 160°. Rate of circulation = 1 in 35 minutes.			EXPERIMENT II. May 8, 1905. Original mixture = H_2+2O_2. T = 160°. Rate of circulation = 1 in 35 minutes.					EXPERIMENT III. May 11, 1905. Normal electrolytic gas after O_2. T = 160°. Rate of circulation = 1 in 35 minutes.		
t.	P.	k_1.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k_1.
hours.	millims.		hours.	millims.	millims.			hours.	millims.	
0	468·5	—	0	150·7	301·4	—	—	0	453·1	—
½	415·0	0·1056	1	120·7	268·4	0·0965	0·0222	½	430·6	0·1070
1	373·0	0·0991	2	100·1	276·1	0·0888	0·0190	1	359·3	0·1007
2	289·5	0·1047	3	80·9	266·4	0·0901	0·0179	2	286·3	0·0997
4	196·1	0·0951	4	64·1	257·8	0·0928	0·0170	3	227·9	0·0995
5	155·2	0·0960	5	51·4	251·3	0·0934	0·0158	4	181·7	0·0992

The rate of reduction of the surface by hydrogen at 160° was next determined, and in order to make the experimental conditions as nearly as possible the same as those in I. and III., a mixture of hydrogen and nitrogen corresponding to $2H_2+N_2$ was employed. The results showed, however, that only 8 per cent. of the original hydrogen disappeared during the first hour as compared with over 20 per cent. in the two experiments with electrolytic gas.

EXPERIMENT IV.

May 12, 1905.
Reduction of surface by $2H_2+N_2$ at 160°.

t	0	½	1	1½	2 hours.
P	460·3	444·3	436·3	431·3	427·8 millims.
P_{H_2}	299·3	283·5	275·5	270·5	267·0 ,,
k_{H_2}	—	0·0464	0·0354	0·0286	0·0243

Finally, after the surface had been reduced by circulating several successive full charges of hydrogen over it (the temperature being raised to 300° in order to accelerate the process), the rate of re-oxidation of the reduced material with oxygen at 160° was determined as follows:—

EXPERIMENT V.

May 17, 1905.
Re-oxidation of reduced surface at 160°.

t	0	1	2	3	5 hours.
P_{O_2} . . .	448·2	415·6	396·3	387·5	376·3 millims.
k_{1O_2} . . .	—	0·0300	0·0253	0·0201	0·0146

The catalytic action of nickel oxide, therefore, resembles that of the reducible oxides contained in calcined spathic iron ore. In both cases it has been proved (1) that the gases will combine quite rapidly without producing any permanent change in the catalysing surface; (2) that the rate of combination with normal electrolytic gas is always proportional to the pressure of the dry gas, and far exceeds either the rate of reduction of the catalysing surface by hydrogen, or its rate of re-oxidation by oxygen; and (3) that when the gases are not present in combining proportions, the rate of combination is solely determined by the partial pressure of the hydrogen.

C. *Experiments with Copper Oxide.*

It had been our intention at the outset of the research to study the catalytic action of copper, as well as that of its oxide, on electrolytic gas. All attempts to obtain reliable velocity measurements in the case of the metal were, however, frustrated by the fact that at even the lowest temperature, where there was any marked action on the gases, the formation of steam was always accompanied by an *independent* oxidation of the surface, at least during the initial stages of an experiment. Nevertheless, it will be necessary to refer to one experiment with copper gauze, since the same gauze, thoroughly oxidised, was employed in the two following series of experiments. The experiment with the reduced gauze is, for purposes of comparison, included in the first series.

1*st Series.*

100 grammes of fine copper gauze, made into a long cylindrical roll, were first of all reduced in hydrogen at dull red heat, and subsequently heated for several hours, and finally allowed to cool *in vacuo*, in order to effect the decomposition of any superficial layer of hydride.

Electrolytic gas was afterwards circulated over the reduced gauze at 214°, when rapid combination took place, as the following pressure records indicate:—

Experiment I.

September 20, 1904.
Normal electrolytic gas over reduced copper gauze. T = 214°. Rate of circulation = 1 in 40 minutes.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{4}$	$1\frac{1}{2}$ hours.
P	384·3	291·8	230·0	176·0	148·5	117·7	87·0 millims.
k_1	—	0·4780	0·4460	0·4520	0·4128	0·4180	0·4360

The values "k_1," calculated in each case on the assumption that the whole fall in pressure was due to steam formation, have really no precise significance, since there was a slight permanent oxidation of the metal (20·7 millims. of oxygen disappeared in this way during the experiment), and the ratio H_2/O_2 for the residual 87 millims. of gas was 4·7. The hydrogen which disappeared as steam was, however, 184·4 out of the 256·2 millims. originally present, or about 76 per cent., in $1\frac{1}{2}$ hours. Inasmuch as a number of other experiments showed that the slight oxidation of the surface was independent of, and had but little influence on, the catalytic process proper, the reaction constant for the latter, $k_1 = 0·3683$, deduced from the partial pressures of the hydrogen at the beginning and end of the experiment, may serve as a fair index of the velocity for comparison with the results obtained in subsequent experiments with the oxidised gauze.

At the conclusion of the above experiment, oxygen was circulated over the gauze at 450°, for about 20 hours, until no further absorption of the gas occurred; its surface was now completely covered with a thick layer of cupric oxide. The temperature of the combustion tube was then lowered to 214° again, and the rate of combination for normal electrolytic gas over the "oxidised" surface determined as follows:—

Experiment II.

September 23, 1904.
Normal electrolytic gas over "oxidised" gauze. T = 214°.
Rate of circulation = 1 in 40 minutes.

t.	P.	k_1.	k_1 after 1st hour.	t.	P.	k_1.	k_1 after 1st hour.
hours.	millims.			hours.	millims.		
0	437·3	—	—	5	222·4	0·0587	0·0634
1	399·3	0·0395	—	6	187·5	0·0612	0·0656
2	345·4	0·0511	0·0627	7	155·6	0·0641	0·0682
3	299·6	0·0547	0·0622	8	125·4	0·0678	0·0718
4	259·6	0·0566	0·0622				

The ratio H_2/O_2 for the 125·4 millims. of residual gas was 2·11, a circumstance indicative of a slight absorption of oxygen rather than of any permanent reduction of the oxide during the experiment. The values "k_1" for the whole duration of the experiment (third column) indicate, at first sight, a steadily accelerated velocity. Reckoning from the end of the first hour, however, the values given in the fourth column are obtained. The two series of values, therefore, indicate an accelerated velocity during the first hour, after which it varied directly with the pressure of the dry gas.

The most striking feature about the experiment is the extremely slow rate of steam formation as compared with that observed in the previous experiment with the reduced gauze; to put the matter briefly, no less than 8 hours were required with the oxidised gauze to effect the same percentage of change as was observed in $1\frac{1}{2}$ hours with the reduced surface in Experiment I.

The two following experiments at 214° were next made with mixtures originally containing excess of oxygen (H_2+2O_2 nearly), which proved the rate of change to be nearly proportional to the partial pressure of the oxygen.

EXPERIMENT III. September 26, 1904. "Oxidised" gauze at 214°. Original mixture = H_2+2O_2 nearly. Rate of circulation = 1 in 40 minutes.					EXPERIMENT IV. September 27, 1904. "Oxidised" gauze at 214°. Original mixture = H_2+2O_2 nearly. Rate of circulation = 1 in 40 minutes.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	144·1	273·6	—	—	0	124·5	259·8	—	—
1	133·5	268·3	0·0332	0·0085	1	112·7	253·9	0·0433	0·0101
2	124·2	263·7	0·0323	0·0080	2	100·1	247·6	0·0473	0·0104
3	110·0	256·6	0·0391	0·0093	3	87·0	241·0	0·0519	0·0109
5	80·9	242·1	0·0501	0·0106	5	62·1	228·7	0·0604	0·0110
7	55·7	229·3	0·0589	0·0109	7	39·5	217·5	0·0698	0·0110
9	34·7	219·0	0·0687	0·0107	9	19·9	207·7	0·0885	0·0108
11	18·9	211·1	0·0802	0·0103	11	3·9	199·6	0·1388	0·0104
13	10·3	206·7	0·0881	0·0094					

Finally, in Experiment V., the rate of reduction of the "oxidised" gauze by hydrogen at 214° was measured; this proved to be something like ten times as fast as the rate of steam formation observed when electrolytic gas was circulated over the "oxidised" gauze at the same temperature in Experiment II. So fast indeed was the reduction process that a charge of 700 cub. centims. of hydrogen introduced into the apparatus almost entirely disappeared within an hour, as the following pressure records for two successive charges indicate :—

EXPERIMENT V.

Reduction of "oxidised" gauze by hydrogen at 214°.

1st charge.			2nd charge.		
t.	P.	k_1.*	t.	P.	k_1.*
minutes.	millims.		minutes.	millims.	
0	374·3	—	0	334·3	—
10	208·3	1·5288	10	176·3	1·6692
20	108·3	1·6188	20	103·3	1·5600
30	50·3	1·6272	30	53·3	1·5960
40	22·3	1·7472	40	25·3	1·6896
50	8·3	1·9116	45	16·3	1·7592
60	2·3	2·1600			

2nd Series.

In order to confirm the results of the previous experiments as regards the striking difference between the rate of steam formation with electrolytic gas and copper oxide, and the rate of reduction of the oxide by hydrogen, the gauze was thoroughly re-oxidised at 450°, and subsequently comparative experiments with (1) normal electrolytic gas, and (2) a mixture of hydrogen and nitrogen corresponding very nearly to $2H_2+N_2$, were made at 214°, as follows:—

EXPERIMENT VI.

October 18, 1904.
Normal electrolytic gas over "oxidised" gauze. T = 214°.

t.	P.	k_1.
hours.	millims.	
0	364·5	—
1	316·1	0·0619
2	257·0	0·0759
3	195·4	0·0912
4	151·4	0·0964
5	111·6	0·1028

EXPERIMENT VII.

October 19, 1904.
Mixture $2H_2+N_2$ over "oxidised" gauze. T = 214°.

t.	P.	P_{H_2}.	k_{H_2}.†
minutes.	millims.	millims.	
0	395·7	263·8	—
10	313·2	181·3	0·9774
20	248·2	116·3	1·0671
30	207·6	75·7	1·0844
40	183·1	51·2	1·0680
50	166·8	34·9	1·0542
60	162·8	30·9	0·9313
90	141·4	9·5	0·9624

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* In order to make these values comparable with those given in other experiments, they have been calculated on the basis of an hour as the unit of time.

† Calculated on the basis of an hour as the unit of time.

The remarkable difference between the results of these two experiments is shown by the two curves for the partial pressures of the hydrogen reproduced in Diagram VI. By substituting inert nitrogen for the oxygen of electrolytic gas the rate of disappearance of hydrogen was increased something like seven-fold, a fact which at once disproves the theory that the catalytic process involves a rapidly alternating series of reductions and re-oxidations of the surface.

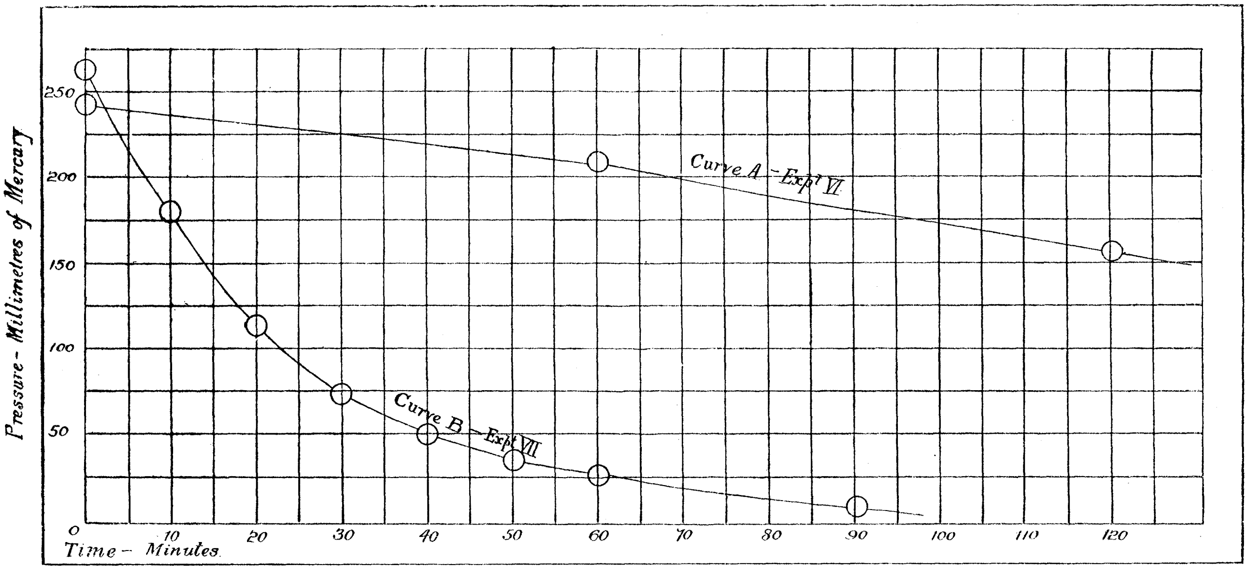

Diagram VI. Experiments with copper oxide. Partial pressures of hydrogen. Curve A, for $2H_2+O_2$; Curve B, for $2H_2+N_2$.

In a final experiment (VIII.) the quantity of "oxidised" gauze employed was only 27·8 grammes, instead of the 100 grammes used in previous experiments, in order to extend the combination over a longer period of time. The ratio H_2/O_2 found for samples of the gas shut off in the "bye-pass" tubes during the experiment indicated hardly any perceptible permanent change in the catalysing surface during the first 24 hours, although towards the end of the experiment, when the pressure in the apparatus had fallen considerably, some slight permanent reduction apparently did take place. The rate of circulation was 1 in 40 minutes.

Experiment VIII.

November 4, 1904.
Normal electrolytic gas over "oxidised" gauze. T = 214°.

t.	P.	k_1.	Ratio, H_2/O_2.	t.	P.	k_1.	Ratio, H_2/O_2.
hours.	millims.			hours.	millims.		
0	319·9	—	—	12	240·0	0·0104	—
1	312·1	0·0107	—	24	170·0	0·0114	1·96
3	299·0	0·0100	2·0	48	76·1	0·0130	—
6	277·4	0·0103	—	70	29·2	0·0148	1·72
9	258·2	0·0103	1·97				

The fall in pressure during the first hour in the above experiment corresponded to the disappearance of only 5·2 out of the original 213·3 millims. of hydrogen, or less than 2·5 per cent. On subsequently circulating pure hydrogen over the gauze at the same temperature (214°), the pressure fell from 331 to 100 millims. in an hour, representing the disappearance of no less than 70 per cent. of the gas.

3rd Series.

A final series of experiments was made in which the combustion tube was packed with granular copper oxide such as is used in the analysis of organic compounds. The material had previously been heated to dull redness in a current of air for 6 hours, and afterwards in a stream of oxygen for 12 hours longer. The following two experiments were then made at 200° : (1) with normal electrolytic gas (IX.), and (2) with a mixture of hydrogen and nitrogen corresponding very nearly to $2H_2+N_2$ (X.). The rate of circulation was 1 in 45 minutes in each case. It will be observed that whereas only 9·7 per cent. of the original hydrogen disappeared during the first hour in Experiment IX., no less than 50 per cent. of the gas disappeared when nitrogen was substituted for the oxygen of the electrolytic gas.

EXPERIMENT IX. Original mixture = $2H_2+O_2$. Rate of circulation = 1 in 45 minutes.				EXPERIMENT X. Original mixture = $2H_2+N_2$. Rate of circulation = 1 in 45 minutes.			
	t.	P.	k_1.	*t.*	P.	P_{H_2}.	k_{H_2}.
	hours.	millims.		hours.	millims.	millims.	
No permanent reduction of the copper oxide. H_2/O_2 = 2·0.	0	488·8	—	0	333·5	210·7	—
	1	441·7	0·0440	1	226·0	103·2	0·3100
	2	399·1	0·0440	2	162·3	38·5	0·3690
	3	360·0	0·0443	3	131·9	8·1	0·4720
H_2/O_2 = 1·82.	4	319·0	0·0465				
	5	284·5	0·0470				
	6	242·0	0·0509				
H_2/O_2 = 1·47.	8	169·5	0·0575				
	10	120·3	0·0608				
	11	97·8	0·0635				

It is a significant fact that during the first three hours in Experiment IX., when the pressure in the apparatus was fairly high, there was no permanent reduction of the surface; at the end of the sixth hour the ratio H_2/O_2 for the gases was 1·823, indicating incipient reduction, and for the residual gas at the end of the experiment the ratio was 1·469. In this connection it may be pointed out that, so long as there was no appreciable permanent reduction of the surface (say up to about the end of the fourth or fifth hour), the values "k_1" remained nearly constant, whereas at lower pressures, when reduction did set in, they rapidly increased. The same remark applies also to Experiment VIII. with the "oxidised" gauze.

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 catalysing oxide from the attacks of the hydrogen, which would otherwise energetically reduce it. 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 on to 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 re-oxidised, does not harmonise with the purely chemical theory. It is difficult to resist the conclusion that in these cases also the catalytic action is primarily due to a physical condensation of one or other of the reacting gases at the surface. And since in all experiments where the gases were not present in combining ratios the rate of combination was always proportional to the partial pressure of the hydrogen, it would appear to be the hydrogen which is condensed and so rendered active.

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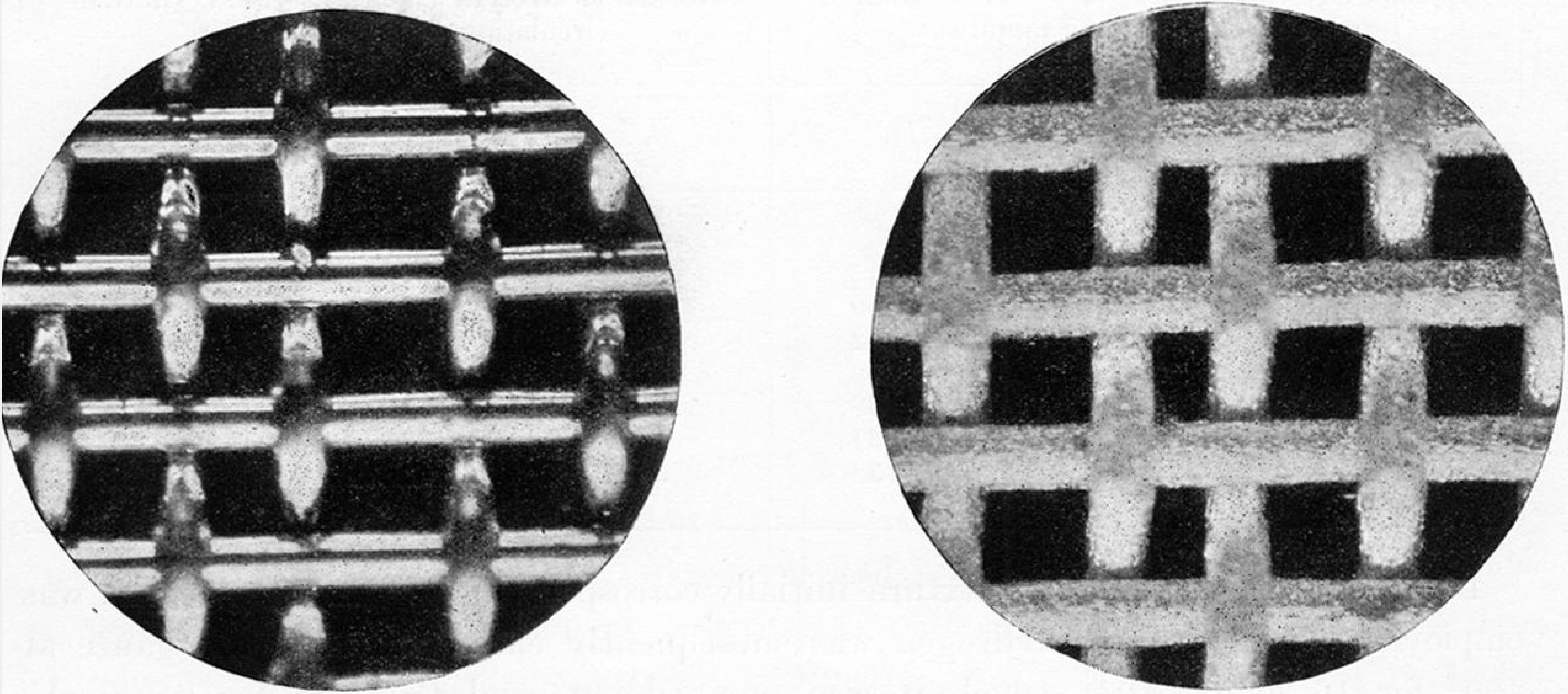

A. In its original condition.

B. After first series of experiments at 400° and subsequent heating (*vide* p. 36).

Photomicrographs of the silver gauze.