I. THE REDUCTION OF NICKELOUS AND FERRIC OXIDES BY HYDROGEN.

II. THE CATALYTIC SYNTHESIS OF WATER VAPOR IN THE PRESENCE OF METALLIC NICKEL.

Thesis

by

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THE REDUCTION OF NICKELOUS AND FERRIC OXIDES BY HYDROGEN

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Introduction

The assumption that the "active mass" of a solid in heterogeneous reactions is represented by its surface area, has been shown by Langmuir[2] to lead to conclusions in conflict with the requirements of the phase rule in the large class of reactions in which a solid substance appears on each side of the reaction equation, *provided that the two solids form separate phases of constant composition.* It was shown that in all probability such reactions take place only, or mainly, at the interface between the two solid phases. Since the interface area will ordinarily increase during the early stages of the reaction, it is evident that the occurrence of auto-catalysis in such cases should be the general rule. If, on the other hand, the two solid phases are *miscible*, Langmuir argued that the reaction must be of the "non-interfacial" type, in which the rate depends upon the surface area of the reacting solid rather than upon the area of the interface. Hence, in reactions in which the two solids form solid solutions, the rate should be a maximum at the start and decrease continuously thereafter.

A study of the dissociation pressures of ferric oxide led Sosman and Hostetter[3] to the conclusion that at temperatures above 1100°, ferric oxide and ferro-ferric oxide form a nearly complete series of solid solutions. If solutions, rather than pure phases, constitute the stable arrangement at lower temperatures also, the reduction of ferric oxide to ferro-ferric oxide should be a non-interfacial reaction. In the case of nickelous oxide, on the other hand, the measurements of Wöhler and Balz[4] on the equilibrium in the reduction of this oxide by hydrogen at 450° show that solid solutions are not formed under these circumstances. This reaction should therefore exhibit the characteristics of auto-catalysis.

Accordingly, we have considered these two reactions suitable for testing the idea that the phase relations at equilibrium may be used to predict qualitatively the course of heterogeneous reactions. We have chosen the case of nickel oxide also as a necessary preliminary to an investigation of the behavior of nickel as a catalyst in the synthesis of water vapor.

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[1] National Research Fellow in Chemistry during the period covered by this investigation.

[2] Langmuir, THIS JOURNAL, **38**, 2263 (1916).

[3] Sosman and Hostetter, *ibid.*, **38**, 807 (1916).

[4] Wöhler and Balz, *Z. Elektrochem.*, **27**, 413 (1921).

Both of these reactions have been the subjects of previous investigations, by Wright and Rennie[5] in the case of ferric oxide and by Sabatier and Espil[6] and by Berger[7] in the case of nickel oxide. However, in neither reaction have results been obtained which lend themselves readily to a solution of the problems under consideration.

Experimental Method

Apparatus and Procedure.—The method of carrying out the experiments was similar to that employed by Pease and Taylor[8] in a recent study of the reduction of cupric oxide.

Electrolytic hydrogen from a tank, purified by successive passage through absorbent cotton, solid potassium hydroxide and heated palladized asbestos, was metered in a resistance-tube flow-meter, dried over phosphorus pentoxide and passed into the reduction furnace. Here the preheated gas passed down through the oxide sample and finally out to the atmosphere through a calcium chloride weighing tube. Condensation of water was avoided by electrically heating the exit tube of the furnace. The hydrogen flow was maintained constant at 50 cc. per minute (0°, 760 mm.) throughout the experiments. Rates of reaction are expressed as milligrams of water absorbed in the calcium chloride tube during five minutes' passage of the exit gases.

In the experiments hydrogen was passed through the cold furnace until all air was displaced, and the temperature was then quickly raised by the application of two or three times the amount of current needed to maintain the desired temperature. After a little practise, it proved to be a matter of no great difficulty to bring the contents of the furnace to the required temperature within 10 or 12 minutes after first applying the current, and to maintain it constant thereafter within the limits of ±1°. The instant at which the temperature first reached a point within 1° of the desired temperature has been considered as zero time. Great care was taken that the bulb of the calibrated thermometer should extend well into the oxide sample.

Oxygen was mixed with the hydrogen, when desired, by electrolyzing saturated barium hydroxide solution between chromel electrodes and passing the resulting electrolytic gas over phosphorus pentoxide and into the hydrogen line at a point close to the furnace. Mixtures of hydrogen with water vapor were obtained in the same way, except that the hydrogen-oxygen mixture was by-passed to the furnace by means of a 3-way cock, through a tube containing heated palladized asbestos and heated electrically to avoid condensation of the water formed. The desired concentration of oxygen or water vapor was obtained by holding the electrolyzing current constant at 360 milliamperes. The oxygen so added is sufficient to furnish, on complete conversion, 10.1 mg. of water per 5-minute interval. The volume concentrations are 2.45% in the case of oxygen and 4.77% in the case of water vapor.

The samples were supported in the inner furnace tube by a plug of glass wool, and were always approximately 2.5 cm. in height. Since the diameter of the tube was 2.1 cm., the apparent volume of oxide employed was 8.7 cc. In the case of nickel oxide, this volume weighed between 4.6 and 5.0 g., averaging about 4.8; the same volume of ferric oxide (prepared from nitrate) weighed on the average about 5.4 g.

The reduction furnace used in a number of preliminary experiments was similar to

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[5] Wright and Rennie, *J. Chem. Soc.*, **37**, 757 (1880).

[6] Sabatier and Espil, *Compt. rend.*, **158**, 668 (1914); **159**, 137 (1914).

[7] Berger, *ibid.*, **158**, 1798 (1914); **174**, 1341 (1922).

[8] Pease and Taylor, THIS JOURNAL, **43**, 2179 (1921).

the one described by Pease and Taylor.[8] It early became apparent, however, that at the higher temperatures here required, certain modifications were essential in order to avoid the poisoning action of vapors from rubber connections in the heated zone. This was accomplished by extending the upper and lower parts of the furnace for some distance beyond the heating element and by replacing the rubber stopper with a ground-glass joint. As a result of these changes the few unavoidable rubber connections remained at room temperature, but as a further precaution the rubber tubing was boiled with sodium hydroxide solution.

Preparation of the Oxides. (*a*) NICKELOUS OXIDE.—The nickel oxide was made by calcination of C. P. hydrated nickel nitrate. The latter was dehydrated in an open dish over a sand-bath at a low temperature and then transferred to the electric furnace, where the decomposition was effected in a current of air or nitrogen at temperatures raised progressively from room temperature to the maximum given below. Each "charge" thus prepared was sufficiently large to furnish a number of "samples" for the separate experiments.

Charges X and XI were prepared by heating in a current of air for about 100 hours to a maximum temperature of approximately 400°.

Charge XIII was heated in a current of purified atmospheric nitrogen for 115 hours, to 360°, and cooled out of contact with air.

Charge XIV was heated in a current of air for 230 hours, to 360°.

The charges were preserved in glass-stoppered bottles. Immediately before reduction each sample was dried by heating for a short time in a current of air (or nitrogen in the case of samples from Charge XIII) at a temperature not exceeding that employed in preparation.

Analyses of two portions of Charge XI by determining the water formed on complete reduction in hydrogen gave 21.55% and 21.60% of oxygen, respectively. Since pure nickelous oxide contains 21.43% of oxygen, these analyses point to the presence of a trace of higher oxide.

(b) FERRIC OXIDE.—Two charges of ferric oxide were used. One was obtained by ignition of pure ferric nitrate in a current of air for 135 hours, to a maximum temperature of 525°. The other was prepared by precipitation with ammonia from a hot, dilute solution of ferric ammonium sulfate, washing by decantation until tests for impurities were negative and finally drying in a current of air for 45 hours, up to a maximum temperature of 350°.

Results with Nickelous Oxide

The results of a number of representative experiments on the reduction of nickel oxide with pure hydrogen are collected in Fig. 1, in which the ordinates signify the rate of reaction, expressed in milligrams of water formed per 5-minute interval, and the abscissas represent the time in hours. Neglecting Curve E for the moment, it is seen that the rate of reaction is small at first, but increases rapidly up to a maximum and finally falls off gradually to the end. This is the behavior characteristic of auto-catalysis.

The curves of Fig. 1 illustrate a number of points of secondary interest. Thus Curves A and B show that, when exactly similar samples are reduced at different temperatures, the reaction rate is greater at the higher temperature, and the maximum is reached in a shorter time and at an earlier stage of the reduction. The samples used in obtaining Curves D and E were reduced at still higher temperatures, but the former was prepared by heating the nitrate to 525° and the latter was a commercial C. P. nickelous oxide which had evidently been heated to a high temperature. It appears, therefore, that the higher the temperature to which the oxide had been heated, the more difficult it was to reduce. When reduced at 280°, the commercial oxide gave little evidence of any accelerating period. After complete reduction and subsequent re-oxidation to constant weight in air at 400°, this oxide yielded a reduction curve at 188° very similar to those obtained for samples prepared from nitrate at 400°, shown in A and C, Fig. 1.

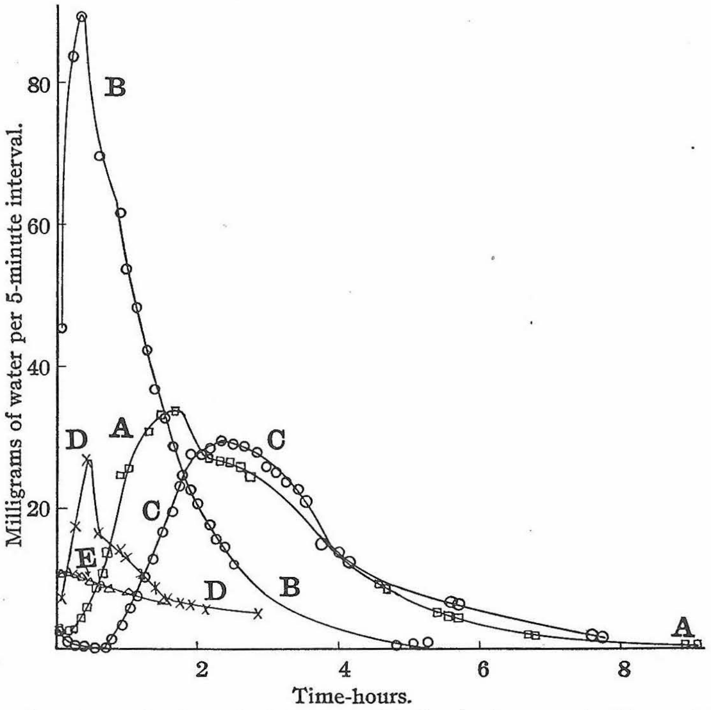

Fig. 1.—Reduction of nickelous oxide by hydrogen. A. Charge X at 188°. B. Charge X at 206°. C. Charge XIII at 188°. D. Reduction at 250° of oxide prepared at 525°. E. Reduction at 280° of commercial oxide.

In a number of experiments, as will be noticed from the curves, small quantities of water were produced at the start in a manner suggestive of the presence of higher oxide. This was especially pronounced in the case of samples from Charge XIV, which had been prepared from the nitrate by heating for many hours in a current of air at 360°. Here the initial descending branch of the curves represented more than 30 mg. of water. Since the conditions of the experiments precluded the possibility of adsorbed water being present in more than traces at the start, it seems reasonable to attribute this initial water to the presence of higher oxide. If so, the oxide of Charge XIV contained 0.68% of oxygen in excess of the 21.43% required to form the monoxide and accordingly had the average composition of $NiO_{1.032}$. All the other charges gave evidence of only traces of higher oxide. In order to discover whether the elimination of these traces would exert any influence on the course of the reduction of the monoxide, Charge XIII was prepared in a current of nitrogen instead of air. The results with this charge (Curve C, Fig. 1) showed that, aside from an increase in the length of the incubation period, there was no essential difference between the curves obtained for the samples prepared in nitrogen and in air.

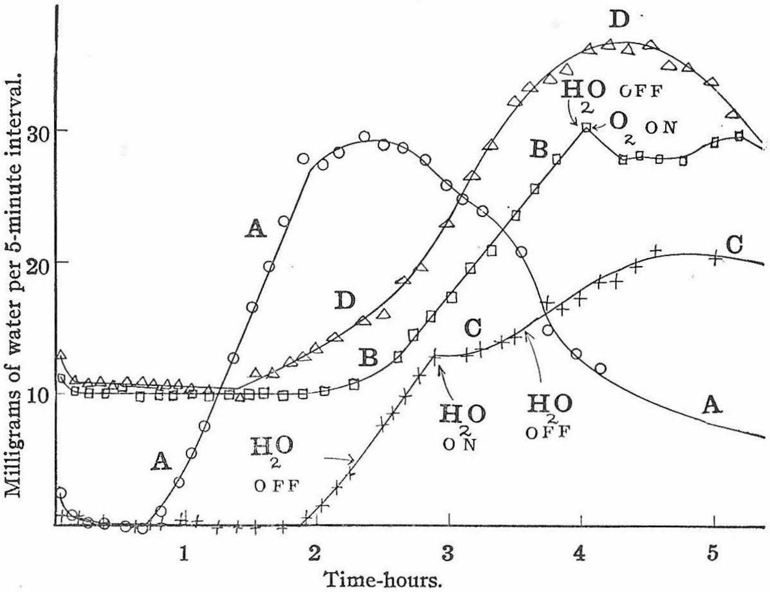

Fig. 2.—Effect of water and oxygen on reduction of nickelous oxide by hydrogen at 188°. A. Normal reduction (Charge XIII). B. Effect of 10 mg. of water per 5-minute interval (Charge XIII). C. Effect of 10 mg. of water per 5-minute interval (Charge XI). D. Effect of oxygen equivalent to 10 mg. of water per 5-minute interval (Charge XIII).

Effect of Water Vapor.—The auto-catalytic nature of the reduction suggests that water does not greatly inhibit the reaction after it has started. To determine its effect in the early stages, reduction was carried out with hydrogen to which was added in the manner already described 10 mg. of water vapor per 5-minute interval. The results are shown in Curve B, Fig. 2. On comparison with Curve A for the reduction with pure hydrogen, it is evident that the water vapor greatly increased the length of the incubation period. After about two hours, however, the reaction began and accelerated only a little less rapidly than in the absence of the added water. Curve C shows the results of a similar experiment on another sample. (For convenience we have subtracted from the ordinates the 10 mg. of water introduced along with the hydrogen, before plotting Curve C.) Here again the principal effect of the added water was to delay the start of the reduction, though at later stages of the reaction also a slight but definite retardation was produced. From these results it is clear that the water formed in the reduction is not the autocatalyst.

Effect of Oxygen.—In Fig. 2, Curve D, are shown the results of an experiment in which the hydrogen was mixed with sufficient oxygen (2.45%) to yield, if completely converted, 10 mg. of water per 5-minute interval. The curve is very similar to that obtained when water instead of oxygen was introduced with the hydrogen. It is evident that all the oxygen was converted to water, although for 80 minutes no reduction occurred. When the reaction did start, it accelerated more slowly at first, but afterwards more rapidly, than in the presence of added water. These minor differences are doubtless to be accounted for on the supposition that the oxygen is not completely converted to water until it has passed through a considerable portion of the sample. For this reason it is perhaps justifiable to conclude that small quantities of oxygen actually exert an inhibitory influence in the early stages of the reduction. The results shown in Curve B, Fig. 2, point in the same direction, since here, when an equivalent amount of oxygen was substituted for the water in the entering gas, the yield fell off, although it is improbable that any oxygen passed through the sample unchanged. It may therefore be supposed that, if the oxygen were not converted to water, it would exert a powerful inhibitive effect in the early part of the reduction.

Mechanism of Reduction.—Since the reduction of nickel oxide by hydrogen is auto-catalytic and is not accelerated by water, the cause of the increasing rate must be sought either in the nickel produced in the reaction, or in some progressive change in the oxide itself, such as the gradual disintegration of its crystals. The latter hypothesis is rendered very improbable by the results of several experiments in which it was found that samples which had been completely reduced and then reoxidized in air at the same temperature as in the original preparation from the nitrate gave reduction curves practically identical with those obtained in the first reduction. With some samples re-oxidations were carried out at lower temperatures and the alternate reduction and reoxidation repeated three or four times, with no diminution in the autocatalytic acceleration of the reduction. There can be little doubt, therefore, that the nickel formed in the reaction is the auto-catalyst. Nevertheless, negative results were obtained in attempts which were made to shorten the incubation period by starting with a layer of reduced nickel in contact with the oxide. The nickel employed for this purpose had been reduced at 400° in an effort to diminish its pyrophoric properties and considerable care was taken to prevent the access of air, but it is conceivable that sufficient oxygen entered to cause superficial oxidation. In any case it is not to be expected that nickel prepared at this relatively high temperature and merely in loose contact with the oxide, would be so active a catalyst as that formed in the progress of the regular reductions.

In view of all the facts, the conclusion appears inevitable that the reduction of nickelous oxide by hydrogen takes place, under a wide variety of experimental conditions, most rapidly at the interface between the two solid phases. This behavior can hardly be due to a local rise of temperature at the interface because the heat effect of the reaction is very small.[9] Consequently, either the oxygen atoms at the interface are more reactive than the rest, or the hydrogen is activated by contact with the nickel. In discussing the reduction of cupric oxide by hydrogen, a reaction which also exhibits interfacial characteristics,[8] Langmuir,[10] and later Palmer[11] have taken the view that the auto-catalytic acceleration is due to the ability of the metallic copper to adsorb and activate the hydrogen. This idea could be employed with even greater force in the case of nickel, which adsorbs relatively large quantities of hydrogen. On the other hand, an entirely different explanation would be needed for the acceleration observed in the thermal decomposition of silver oxide.[12] For this reason it seems to us preferable for the present to suppose that in all these cases the oxygen atoms of the oxide are rendered more active by contact with the free metal.

A simple interpretation of the differences in shape of the curves obtained is found in the hypothesis that the rate of reduction is proportional to the interface area and that the interface area present at any time depends not only on the extent to which the reaction has proceeded, but also on the manner in which it began. If reaction starts at only one or two points, it is to be expected that considerable reduction will take place before the maximum rate is reached; but if the process begins at many centers, each will spread and soon overlap neighboring centers,

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[9] There is a discrepancy of 6400 cal. between the values given for the heat of formation of nickelous oxide by Berthelot and by Mixter. The calculated value of the heat evolved in the reduction reaction is —200 cal. in the former case and +6200 in the latter. Many of our experiments have indicated that the negative value is more nearly correct, as it was usually necessary to increase the heating current slightly as reduction accelerated, in order to hold the temperature constant.

[10] Langmuir, *Trans. Faraday Soc.*, **17**, 620 (1922).

[11] Palmer, *Proc. Roy. Soc.* (London) **103A**, 444 (1923).

[12] Lewis, *Z. physik. Chem.*, **52**, 310 (1905).

with the result that the maximum rate should occur at an earlier stage of the reduction. Thus it is probable that an increased temperature of reduction causes reaction to start in more points, since the percentage of the oxide which had been reduced when the maximum rate was reached, was less at the higher temperatures (compare Fig. 1). Other comparisons of this sort are difficult to make because different charges did not give uniform results, although duplicate runs with samples from the same charge showed remarkable agreement. Such factors as the location of the starting point and the character of the contacts between particles doubtless enter here. It would be interesting to study the effect of varying the shape of the sample.

Hydrogen-Oxygen Catalysis over Nickel Oxide.—The experiments already described, in which oxygen was added to the hydrogen, permit certain conclusions to be drawn concerning the mechanism of the catalytic combination of hydrogen and oxygen in presence of nickelous oxide. Curve D, Fig. 2, shows that the rate of water formation remained approximately equivalent to the added oxygen for considerably more than an hour. The shape of the curve itself suggests that reduction did not commence during this time and the same conclusion is reached by comparison with the other curves of Fig. 2. Evidently the initial, horizontal part of curve D represents complete conversion of the added oxygen, unaccompanied by any reduction of the oxide. For this reason the hydrogen-oxygen catalysis over nickelous oxide cannot be attributed to reduction to metallic nickel and subsequent re-oxidation. This point is illustrated even more strikingly by a similar experiment on Charge XIV, in which the rate of water formation remained just equivalent to the added oxygen for the six hours' duration of the run. The same facts argue against the view that the catalysis depends on adsorption and consequent activation of the hydrogen, since it is to be expected that the water, which for a long period protects the oxide from reduction by the hydrogen, would also prevent the adsorption of hydrogen. Two hopeful possibilities remain: activation of the oxygen molecules by adsorption, and oscillating oxidation and reduction between nickelous oxide and a higher oxide. If this hypothetical oxidation is merely superficial, the two cases become indistinguishable. Indirect evidence for the view that it is the oxygen which is activated, is found in the observation of Bone and Wheeler[13] that the rate of this catalytic reaction in presence of nickel oxide is independent of the pressure of the oxygen. This could hardly be the case if the reaction occurred mainly as a result of impacts between gaseous oxygen and adsorbed hydrogen; on the other hand, the

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[13] Bone and Wheeler, *Phil. Trans.*, **206A**, 1 (1906). It should be noted that our interpretation of the reaction kinetics observed by Bone and Wheeler is the exact opposite of the one proposed by them.

mechanism preferred above leads at once to this relation if the quantity of oxygen adsorbed is independent of the pressure.

Results with Ferric Oxide

The results of reduction experiments on two different samples of ferric oxide are given in Fig. 3. Curve A refers to the precipitated oxide dried at 350° and Curve B to the oxide prepared from nitrate at 525°. In both cases the observed rate of reduction is greatest at the start and decreases continuously up to and somewhat beyond a point corresponding to the composition Fe_3O_4. The effects produced by adding water or oxygen to the hydrogen were also investigated, as with nickel oxide, but the only definite influence in either case was a slight retardation of the initial rate.

It will be noted that the oxide prepared from nitrate reduced much less readily at 300° than the precipitated oxide at 285°. This difference in reactivity largely disappears when the magnetic oxide stage is reached, as indicated by the relative position of the two curves in the latter part of the reduction. No special study was made of the reduction kinetics of the magnetic oxide, but the curves of Fig. 3 suggest at least the possibility that it is autocatalytic.

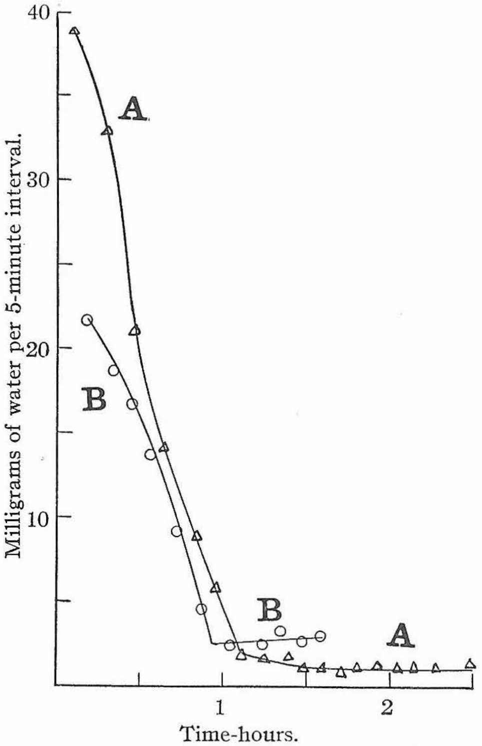

Fig. 3.—Reduction of ferric oxide by hydrogen. A. Reduction of precipitated oxide at 285°. B. Reduction at 300° of oxide prepared from nitrate.

These experiments indicate that, if the reduction of ferric to ferro-ferric oxide is catalyzed by the products of reaction, the initial acceleration is so great that the rate has passed through its maximum in less than six to ten minutes after the reaction temperature is reached. This is presumably what would happen in case the reaction spread auto-catalytically from a very large number of centers distributed over the whole surface of the sample. The principal objections to this view are that no evidence has been obtained in support of it and that nickel oxide samples prepared from nitrate always gave unmistakable maxima.

There is a further objection in the case of the precipitated oxide, for we have found that the interfacial characteristics of the reduction of cupric oxide are marked even with samples prepared by this method. Accordingly, the conclusion appears justified that the reduction of ferric oxide to the magnetic oxide by hydrogen is a "non-interfacial" reaction.

In conclusion, we wish to record our indebtedness to the Carnegie Institution of Washington for financial aid in the prosecution of this investigation, made in the form of a grant to Professor A. A. Noyes.

Summary

An investigation has been made of the kinetics of reduction by hydrogen of nickelous and ferric oxides, prepared by various methods.

The nickel oxide reduction is auto-catalytic, proceeding mainly at the interface between the solid phases. In the reduction of ferric to ferroferric oxide no auto-catalysis was observed, the reaction rate being greatest at the start and decreasing continuously. The characteristics of these reactions are in agreement with Langmuir's theory that heterogeneous reactions involving a solid substance on each side of the reaction equation should be "interfacial" when the two solids form separate phases of constant composition (nickel oxide) and "non-interfacial" when solid solutions occur (ferric oxide).

In the case of nickel oxide the following observations were made: (1) reduction takes place less readily, the higher the temperature of preparation of the sample; (2) at higher reduction temperatures the maximum rate is higher and occurs at an earlier stage of the reduction; (3) water vapor retards the reaction, especially at the start; (4) oxygen in the hydrogen produced effects similar to those of water vapor, being completely converted to the latter even before any reduction of the oxide could be detected.

The most satisfactory mechanism for the hydrogen-oxygen catalysis over nickelous oxide appears to be that of activation of the oxygen by adsorption or by superficial conversion to a higher oxide of nickel.

PASADENA, CALIFORNIA

THE CATALYTIC SYNTHESIS OF WATER VAPOR IN PRESENCE OF METALLIC NICKEL.

By Arthur F. Benton[1] and Paul H. Emmett.

Introduction

When the oxidation of a metal and the reduction of the resulting oxide take place at temperatures not far removed from that at which the metal begins to promote the union of hydrogen and oxygen, it is natural to suppose that the catalysis proceeds by a mechanism of successive oxidation and reduction. Pease and Taylor[2] have shown that this hypothesis furnishes a satisfactory explanation for all their results on the hydrogen-oxygen catalysis by metallic copper. With nickel, however, the claim is made that this mechanism is incapable of accounting for the observed facts, because nickel induces the combination of hydrogen and oxygen at temperatures considerably below that at which the reduction of nickel oxide begins. There are, however, several reasons for believing that the oxide formed during catalysis is more readily reduced than ordinary nickel oxide. In the first place, we have shown[3] that the reduction of nickel oxide by hydrogen is an interfacial reaction, that is, a reaction whose rate depends upon the area of contact between the two solid phases Ni and NiO. Starting with pure nickel oxide the initial rate is zero, and only after a certain lapse of time, which is longer at lower temperatures, does measurable reduction occur. Hence only when the process is started by metallic nickel making its appearance can the reduction rate attain a considerable value. In the second place,

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[1] National Research Fellow in Chemistry.

[2] Pease and Taylor, Jour. Amer. Chem. Soc., 44, 1637 (1922).

[3] Benton and Emmett, Jour. Amer. Chem. Soc., 46, 2728 (1924).

our results in the reduction of pure nickel oxide at low temperatures suggest that the reaction begins at only one or two points and spreads more or less spherically from these as centers. Under these conditions the area of contact between the two solid phases will always be very small in comparison with the area that would be present if the reaction began at many points distributed over the whole surface of the sample. If, however, we suppose that the condition of the surface during the progress of the hydrogen-oxygen catalysis is such as to present a large number of nickel nuclei, the oxide formed in the catalytic process would reduce at a faster rate than pure nickel oxide at the same temperature. Finally, our reduction experiments on nickel oxide again illustrated the well-known fact that oxides reduce less readily the higher the temperature to which they have been previously heated. For this reason also the oxide formed during catalysis at low temperatures would reduce more readily than ordinary nickel oxide.

These considerations lead to the conclusion that the mechanism of successive oxidation and reduction is by no means an impossibility in the case of the combination of hydrogen and oxygen in contact with metallic nickel. Nevertheless there are two observations to be considered, which might be thought in conflict with this view of the mechanism. In the first place, our previous work showed that the hydrogen-oxygen catalysis over nickel oxide at low temperatures could not be explained by the hypothesis of reduction to metallic nickel and subsequent reoxidation. The considerations advanced in the previous paragraph show, however, that this conclusion is not a real objection to the oxidation-reduction mechanism in the case of the catalysis with metallic nickel. Only in case the surface of the nickel became <u>completely</u> oxidized could this view of the process be excluded. The other apparent objection is the observation of Bone and Wheeler[4] that the rate of combination of hydrogen and oxygen in contact with metallic nickel is nearly proportional to the partial pressure of the hydrogen and independent of the partial pressure of the oxygen. This was explained on the assumption that the mechanism of the catalysis consisted in the adsorption and consequent activation of the hydrogen by the nickel. Subsequent work by various authors[5] has shown, however, that the adsorption of hydrogen by nickel is independent of the pressure of the hydrogen over a wide range. Consequently, if the water formation really were due to impacts between oxygen molecules and adsorbed hydrogen, the reaction rate should be proportional to the partial pressure of the oxygen and independent of the hydrogen pressure. The relations observed by Bone and Wheeler seem to us, therefore, very strong evidence against the view that activation of the hydrogen by adsorption is the dominant factor in this catalytic reaction.[6]

The present investigation of the combination of hydrogen and oxygen over metallic nickel was undertaken in the hope that definite evidence might be obtained, either for or against the oxidation-reduction mechanism. In particular we wished to find whether oxide is actually formed under the conditions of the catalysis, and if so, whether hydrogen would reduce this oxide at the same temperature.

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

[5] Taylor and Burns, Jour. Amer. Chem. Soc., 43, 1273 (1921); Gauger and Taylor, ibid., 45, 920 (1923).

[6] Similar considerations may be advanced in opposition to the conclusions of Bone and Wheeler in the case of all the catalysts studied by them in the

(Continued on page 4).

Experimental Method

The apparatus and experimental procedure were the same as those employed in the previous work on the reduction of nickel and iron oxides.[3] The method, which is essentially the same as that used by Pease and Taylor[2] in their study of the hydrogen-oxygen catalysis by metallic copper, was briefly as follows. A constant current of pure dry hydrogen was passed through the catalyst, which was supported in the inner tube of a double-walled electric furnace. Oxygen was added to the hydrogen in any desired proportion by electrolysing barium hydroxide solution at a suitable rate, and admitting into the hydrogen line the electrolytic gas thus produced. The rate of reaction was determined at frequent intervals by absorbing and weighing in a calcium chloride tube the water formed during (usually) 5 minutes passage of the exit gases from the furnace. Particular care was taken to prevent condensation of the water before reaching the calcium chloride tube. To insure reliable results it was found necessary to have the bulb of the thermometer used in measuring the reaction temperature extend well into the catalyst mass, and also to avoid the use of rubber connections in the heated zone.

The hydrogen current was maintained constant throughout each experiment at 50 cc. per minute (0°, 760 mm.). Since the hydrogen was always in excess, it is convenient to express the oxygen concentrations in terms of the number of milligrams of water which would be formed if all the oxygen passing through the catalyst during a 5-minute period were converted to water.

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research already referred to. Even when, as in many cases, the adsorption isotherms are unknown, the fact that the reaction rate is independent of the oxygen pressure is alone sufficient to show that their views must be modified.

For this purpose we will employ the expression, "Oxygen equivalent to X milligrams of water (per 5-minute interval)". The corresponding volume concentrations are 2.45% when X equals 10, and 4.77% when X equals 20. The rate of the reaction is expressed as the number of milligrams of water actually obtained per 5-minute interval..

The same sample of catalyst was used in all the experiments. It was obtained by reduction with hydrogen at 400° of a sample of strongly ignited nickel oxide. The sample was supported on a plug of glass wool, and reduction carried out in situ. The loose catalyst mass thus formed was cylindrical in shape, 2.1 cm. in diameter and approximately 2.5 cm. high, and weighed about 15 grams.

Experimental Results

A number of preliminary runs were made at different temperatures with a concentration of oxygen equivalent to 10 mg. of water per 5-minute interval. At 100° and at higher temperatures the oxygen was converted quantitatively into water, with little or no permanent oxidation of the surface. At 35° the conversion to water was nearly zero, although large quantities of oxide were formed. The results obtained at two intermediate temperatures, 65° and 82°, are shown in curves 5 and 6, Fig. 1.

At 65° the rate of water formation rose gradually from practically zero at the start to about 50% conversion at the end of 80 minutes, and then quickly decreased to about 5% conversion. Here the oxygen was cut off and hydrogen alone passed over the catalyst at the same temperature, with the result that the water yield at once decreased to an immeasurably small value. After some time oxygen equivalent to 10 mg. of water per 5-minute interval was again introduced with the hydrogen. As curve 5 shows, the rate of water formation rose temporarily nearly to 20% conversion, but soon fell off to a small value. At this point the oxygen was again cut off, the temperature was raised to 108°, and hydrogen alone passed over the catalyst. In 4 hours 83 mg. of water were obtained; at the end of this time reduction was still taking place, but at a very slow rate. Since this 83 mg. of water must have been produced by reduction of oxide, it is evident that in this run nickel oxide was actually formed during the progress of the catalysis. It is natural to infer, then, that the sudden decrease in the rate of catalysis which occurred 80 minutes after the start of the run was due to complete oxidation of the surface of the nickel. That the conversion decreased only to 5% rather than to zero, would indicate that nickel oxide itself possesses considerable catalytic activity in the hydrogen-oxygen reaction, a fact which we had previously observed.[3] When the oxygen was cut off with the surface in the completely oxidized condition, hardly a trace of reduction occurred, doubtless because the surface did not contain the nickel nuclei which are necessary for the progress of this auto-catalytic reduction. That a very slight reduction did finally occur, however, is shown by the fact that on subsequently readmitting the oxygen-hydrogen mixture, water was produced for a short time at a rate 3 or 4 times as great as that obtained with the completely oxidized surface.

The run at 82° (curve 6, Fig. 1) followed the one at 65°, just described, after the oxide formed in the latter had been reduced at 108° for a long time, but not to completion. At 82° the conversion increased rapidly almost to 100% and then slowly declined to a roughly constant value of approximately 70%. Evidently at this temperature the surface did not become completely oxidized, although the run was continued for nearly 2½ hours.

The reduction curve obtained after shutting off the oxygen indicates, however, that some oxide was present on the surface and that it was reduced at this temperature, at least partially.

After these preliminary experiments the catalyst was alternately oxidized and reduced several times, the last reduction being at 250°. As would be expected, the catalytic activity of the nickel was considerably increased by this treatment; at 65°, 100% conversion of the oxygen (equivalent to 10 mg. of water per 5-minute interval) was now obtained. To avoid the use of inconveniently low temperatures, we then decreased the activity of the catalyst slightly by heating it in a current of hydrogen for 5 hours at 350°. After this treatment it still showed a high order of activity, giving complete conversion of "10 mg." of oxygen at 85°. The experiments with this catalyst are described below in the order in which they were run. All were made with an oxygen concentration equivalent to 20 mg. of water per 5-minute interval.

The first experiment (run 10) was begun at 85°. (No curve is given for this run, as its essential features are similar to those shown in curve 14, Fig. 3.) The rate of water formation increased rapidly at first and then more gradually to about 74% conversion at the end of 90 minutes. At this point the rate decreased very suddenly, finally reaching a roughly constant value corresponding to about 3% conversion. On raising the temperature to 100° the rate more than doubled, but the surface apparently remained completely oxidized. On cutting off the oxygen the water yield at first decreased as the small amount of adsorbed water was removed, but soon the reduction of the nickel oxide began, and proceeded in the characteristic auto-catalytic manner. While reduction was still taking place, the oxygen was again turned on, with the result that the water yield temporarily rose to at least 25.5 mg. (per 5-minute interval) and possibly higher. Of this yield not less than 5.5 mg. must have come from reduction of oxide, in spite of the fact that the final reduction rate before turning on the oxygen was only 2.3 mg.

The next run (curve 11, Fig. 2) was started at the same temperature (85°) as that used in the first part of the previous run. As the curve shows, the nickel was somewhat more active than before, the minimum conversion now being 87%. After about four and a half hours the temperature was lowered to 75°, with the result that the rate of catalysis somewhat decreased for a time, and then dropped off sharply to a very low value. Here the oxygen was cut off, and hydrogen alone passed over the catalyst at 75°. After 3 or 4 mg. of water had been obtained by reduction the oxygen was again turned on. The conversion rapidly rose to more than 30%, but quickly decreased to a small value almost immediately, indicating that the oxidation of the surface had again become complete. The oxygen was then cut off once more and the temperature raised to 154°. After 2 hours the reduction was practically complete; 167 mg. of water were obtained during this time.

The next experiment, at 75°, (curve 12, Fig. 2) was practically a repetition of the previous one, except that the oxygen was cut off before the surface was completely oxidized, and the subsequent reduction was carried considerably further than before. In the latter part of the run, with more than half the surface probably still covered with oxide, the rate of catalysis was much greater than in the first part, and a further quantity of the oxide already present was reduced in addition.

Another experiment was then made at 75° (curve 13, Fig. 3). The catalytic conversion in this run was always close to 100%, and accordingly there was no opportunity for any considerable permanent oxidation of the surface to occur. This conclusion is verified by the shape of the curve obtained after cutting off the oxygen.

The final run (curve 14, Fig. 3) was begun at 67°. After about 3 hours the surface had evidently become completely oxidized. Increasing the temperature to 100° increased the conversion 4 or 5 times. After cutting off the oxygen the surface was partly reduced and the oxygen again admitted. Not only were the 20 mg. of water equivalent to the added oxygen completely recovered, but the rate of reduction of the oxide previously present increased from 4.5 mg. of water per 5-minute interval to at least 6.8 mg. On turning off the oxygen after most of the oxide had been reduced, the rate of reduction appears to have decreased considerably, indicating that under these conditions also reduction is more rapid in the presence of oxygen. At the end of this run the temperature was raised to 150° to complete the reduction of the oxide; approximately 40 mg. of water were thus obtained.

In these experiments it will be noted that when the oxygen is introduced the water yield starts at zero and increases very rapidly during the first few minutes. This behavior is doubtless due in part to the fact that the oxygen-hydrogen mixture does not immediately displace all the hydrogen previously present in the furnace[7]. The principle reason, however, is probably the retention by the catalyst of much of the water formed at the start. Both of these factors also enter in the descending branches of the curves, after the oxygen is cut off. During the main part of the catalysis the rate of water

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[7] It should be mentioned that after the preliminary experiments the apparatus was modified in such a way as to reduce this factor to a minimum.

formation increases with time in some of the curves, and decreases in others. These differences are undoubtedly due in the main to the fact that varying quantities of oxide were present on the surface at the start of different runs. When oxide was known to be almost entirely absent at the start, as in runs 5 and 12, the curves rose continuously until the surface was nearly completely oxidized. In the other runs it is impossible to estimate accurately the amount of oxide initially present, because, on standing over night in an atmosphere of hydrogen, the catalyst apparently became oxidized to a slight extent by air diffusing into the furnace through the rubber connections. For this reason no exact calculations can be made of the amount of oxygen which passed unchanged through the catalyst in the different runs. Nevertheless, it seems improbable that any large quantity escaped in this way, even at the lowest temperature, until the oxidation of the surface was nearly complete.

In some of the experiments the amount of oxygen necessary to "poison" the surface completely can be estimated from the subsequent reductions. In run 5 it is thus found that oxide equivalent to about 83 mg. of water was sufficient to produce complete poisoning; in run 11, 167 mg. were required; in run 14, 190-200 mg. These results show that as the catalyst became more active in successive runs, more oxygen was needed to form a complete layer of oxide. Although it is probable that the increase in activity is accompanied by an increase in surface area, it is not thought that these large quantities of oxide represent a monomolecular layer.

As mentioned above, the shape of the descending branches of the curves obtained after cutting off the oxygen during a run is affected by the desorption of water from the catalyst and by the unavoidable delay in sweeping the oxygen out of the furnace. When so much oxide has been formed that the reduction rate increases autocatalytically, these factors are easily distinguishable from the actual reduction. On the other hand, when only a small amount of oxide is present, the course of the subsequent reduction is masked to a large extent. To overcome this uncertainty in cases of the latter kind, the expedient was tried of first substituting nitrogen for the oxygen-hydrogen mixture, in order to drive out the adsorbed water before beginning the reduction. These experiments proved to be of little value, however, because of adsorption of the water formed in the reduction itself.

Conclusions

These experiments as a whole leave no doubt that when the catalyst is functioning at less than 100% efficiency, oxide is actually formed during the process. At low temperatures the surface eventually becomes completely oxidized and the rate of catalysis drops off sharply to a small value. The reduction of such a completely oxidized surface is very slow at first, but accelerates as the area of contact between the oxide and the nickel grows. The highest rate of reduction observed at 75° (curve 12, Fig. 2) was 1.3 mg. of water per 5-minute interval; at 100° the maximum rate was 3.0 mg. in run 10, and 4.5 mg. in run 14 (in which the catalyst was considerably more active than in run 10). Even with the relatively inactive catalyst of run 5 some reduction occurred at 65°, and the rate would doubtless have considerably increased had the run been continued. These results show that even at the lowest temperatures used in the catalysis, reduction takes place at an appreciable rate as long as the surface is not completely covered with oxide. But they also show that unless the rate of reduction *in the catalytic process* is much greater than the rates here observed, successive oxidation and reduction can not be a significant part of the catalytic mechanism.

There are two reasons for believing that the rate of reduction in the catalytic process is actually greater than the rates observed in these experiments with hydrogen alone. In the first place, addition of oxygen to the hydrogen produces a pronounced increase in the reduction rate[g].

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[g] Since the temperature was ordinarily constant within ± 0.5° and the thermometer bulb was imbedded in the catalyst, there seems to be no possibility that these increases are due to a general rise of temperature throughout the catalyst. A purely *local* temperature rise resulting from the combination of hydrogen and oxygen is, however, not improbable.

In run 10 the rate increased from 2.3 mg. per 5-minute interval to at least 5.5 mg., and in run 14 from 4.5 mg. to 6.8 mg. Striking as these increases are, they are nevertheless far from sufficient to make the rate of reduction comparable with that of the catalysis.

The other and more important factor tending to increase the reduction rate in the catalysis is the increased area of contact between the nickel oxide and the nickel. As already mentioned, the reduction of a completely oxidized surface by hydrogen at these low temperatures probably begins at only a few points. Spreading from these the reaction accelerates, but at any instant only a relatively small number of oxygen atoms lie at the interface. If, on the other hand, the surface is only partially oxidised, leaving free nickel atoms distributed throughout, each of these can serve as a nucleus for reduction of adjacent oxide. Under these conditions the rate of reduction would be comparatively very great. This raises the question whether the oxidation of the nickel actually occurs in such a way as to produce a relatively large area of contact between the two solid phases. Evidently the first oxygen molecules which strike the metal surface and form oxide must be in a very active state, since they are surrounded on all sides by free nickel atoms. Nevertheless, if the oxidation of a completely reduced surface, like the reduction of a completely oxidized one, spread auto-catalytically from only one or two centers, there would be no reason to believe that the area of the interface would be greater in the catalytic process than in the reduction of the completely oxidized surface with hydrogen alone. Since all available data shows[9], however, that oxidation begins practically simultaneously over

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[9] Although there are strong theoretical reasons for believing that the oxidation of a metal must take place more readily at the interface between the solid phase if the reduction (or dissociation) of the oxide is interfacial, the experiments of Tammann and Koster (Z. anorg. Chem., 123, 196 (1922)) and others show that

(Continued on page 14.)

the whole surface, the conclusion follows that the interface area, and consequently the rate of reduction, must be very much greater in the catalysis than is indicated by the results of our reduction experiments. An 5- or 10-fold increase is all that is necessary to make the reduction rate comparable with the observed rates of catalysis.

It is evident, therefore, that some and possibly all of the catalytic water formation is due to successive oxidation and reduction of the catalyst. It is by no means inconceivable, however, that some of the water might be formed as a result of impacts between gaseous oxygen and adsorbed hydrogen, since at these temperatures considerable quantities of hydrogen are adsorbed and presumably activated by metallic nickel[5]. If the latter mechanism were the predominating one, the observed rate of catalysis should decrease progressively during a run, because the amount of metallic nickel available for hydrogen adsorption must decrease as the amount of oxide increases. Our results show, however, that when oxide was known to be absent at the start (runs 5 and 12), the rate of catalysis *increased* as the quantity of oxide increased, and finally dropped off *suddenly* when the surface oxidation had become complete. From these facts and from the reaction kinetics reported by Bone and Wheeler (discussed in the introduction of this paper), it seems justifiable to conclude that impacts between gaseous oxygen and adsorbed hydrogen do not play an important part in the catalytic process.

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the initial formation of oxide nuclei occurs at such a large number of centers that auto-catalysis is not ordinarily observed in these cases.

Summary

A study has been made by a flow method of the combination of hydrogen and oxygen in contact with reduced nickel, using oxygen concentrations up to 5%.

1. At all temperatures at which any water formation could be detected it was found that superficial oxidation of the nickel readily took place. At the lower temperatures this oxidation eventually covered the whole surface, with the result that the rate of catalysis suddenly decreased to a small value.

2. When hydrogen was passed over a catalyst superficially oxidized in this way, the rate of reduction accelerated auto-catalytically, in conformity with the previous observation that the reduction of ordinary nickel oxide is an interfacial reaction, that is, a reaction whose rate depends on the area of contact between the two solid phases. However, the maximum rates of reduction so obtained were always very small in comparison with the rates of the hydrogen-oxygen catalysis at the same temperature.

3. It was found that under certain conditions the rate of reduction was considerably increased by the presence of oxygen in the hydrogen.

4. Arguments are presented to show that the area of contact between the nickel oxide and the nickel, and therefore also the rate of reduction, are very much greater in the catalytic process than in the reduction of a completely oxidized surface by hydrogen alone.

5. The conclusion is reached that the catalytic water formation can be largely and perhaps entirely accounted for on the theory of successive oxidation and reduction of the catalyst.

In conclusion we wish to record our indebtedness to the Carnegie Institution of Washington for financial aid in this investigation from a grant made to Prof. A. A. Noyes.

Pasadena, California.

SUB-TITLES TO ACCOMPANY FIGURES

Fig. 1. - Oxygen concentration equivalent to 10 mg. of water per 5-minute interval. Curve 5: run 5 at 65°; curve 6: run 6 at 82°.

Fig. 2. - Oxygen concentration equivalent to 20 mg. of water per 5-minute interval. Curve 11: 85° at start, later lowered to 75°; curve 12: 75°.

Fig. 3. - Oxygen concentration equivalent to 20 mg. of water per 5-minute interval. Curve 13: 75°; curve 14: 67° at start, later increased to 100°.

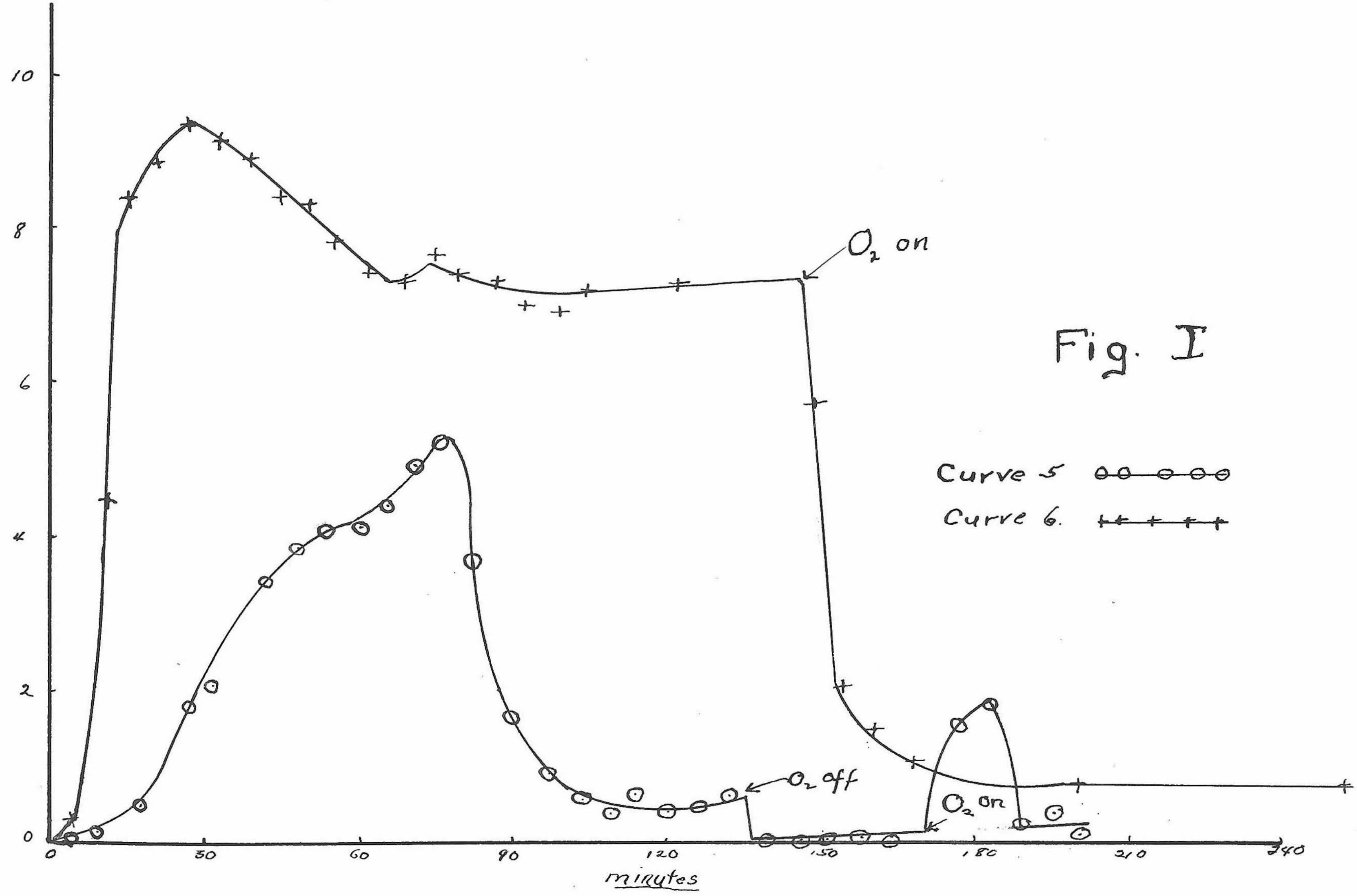

Fig. I

10
8
6
4
2
0
0
30
60
90
120
150
180
210
240
minutes
O2 on
O2 off
O2 on
Curve 5
Curve 6.

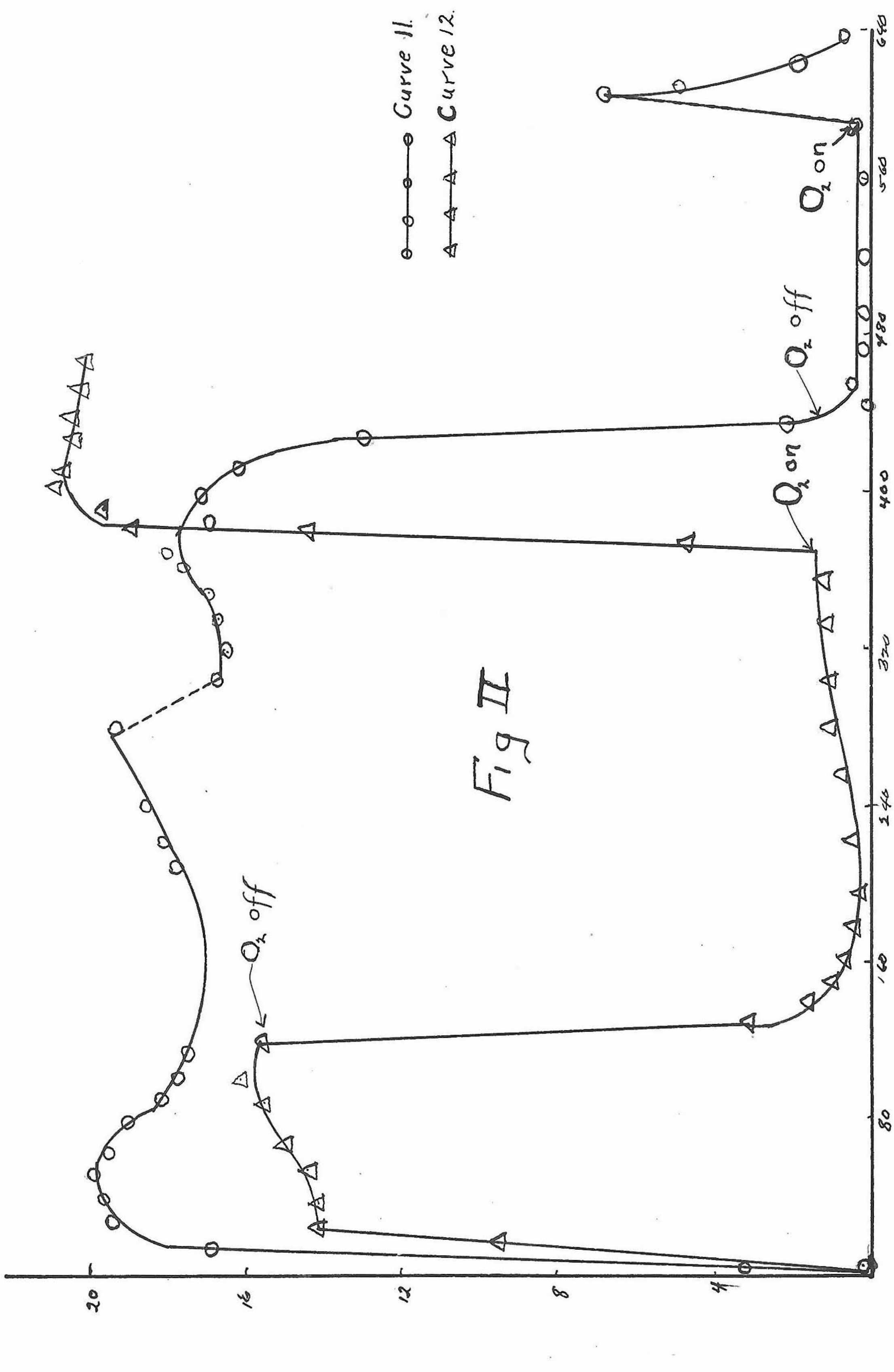
Curve 11.
Curve 12.
O_2 off
O_2 on
O_2 off
O_2 on
20
16
12
8
4
80
160
240
320
400
480
560
640

Fig II

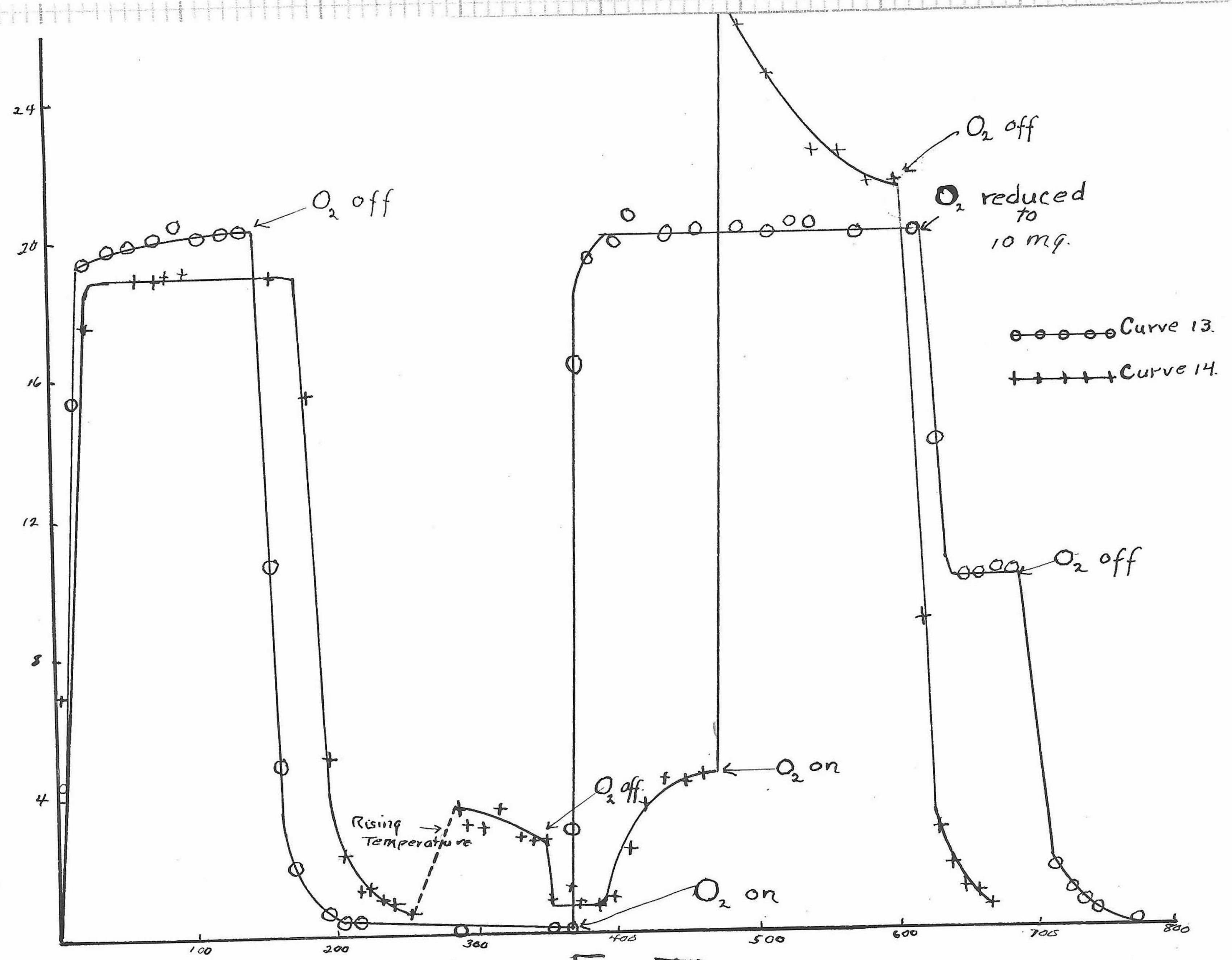
24
20
16
12
8
4
100
200
300
400
500
600
700
800
O₂ off
O₂ off
O₂ reduced to 10 mg.
Curve 13.
Curve 14.
O₂ off
O₂ on
O₂ off
O₂ on
Rising Temperature

Fig III.