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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<sup>2</sup> 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<sup>3</sup> 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<sup>4</sup> 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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<sup>2</sup> Langmuir, *THIS JOURNAL*, **38**, 2263 (1916).

<sup>3</sup> Sosman and Hostetter, *ibid.*, **38**, 807 (1916).

<sup>4</sup> Wöhler and Balz, *Z. Elektrochem.*, **27**, 413 (1921).

Both of these reactions have been the subjects of previous investigations, by Wright and Rennie<sup>5</sup> in the case of ferric oxide and by Sabatier and Espil<sup>6</sup> and by Berger<sup>7</sup> 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<sup>8</sup> 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  $\pm 1^\circ$ . The instant at which the temperature first reached a point within  $1^\circ$  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

<sup>5</sup> Wright and Rennie, *J. Chem. Soc.*, **37**, 757 (1880).

<sup>6</sup> Sabatier and Espil, *Compt. rend.*, **158**, 668 (1914); **159**, 137 (1914).

<sup>7</sup> Berger, *ibid.*, **158**, 1798 (1914); **174**, 1341 (1922).

<sup>8</sup> Pease and Taylor, *THIS JOURNAL*, **43**, 2179 (1921).

the one described by Pease and Taylor.<sup>8</sup> 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  $525^{\circ}$  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  $280^{\circ}$ , the commercial oxide gave little evidence of any accelerating period. After complete reduction and subsequent re-oxidation to constant weight in air at  $400^{\circ}$ , this oxide yielded a reduction curve at  $188^{\circ}$  very similar

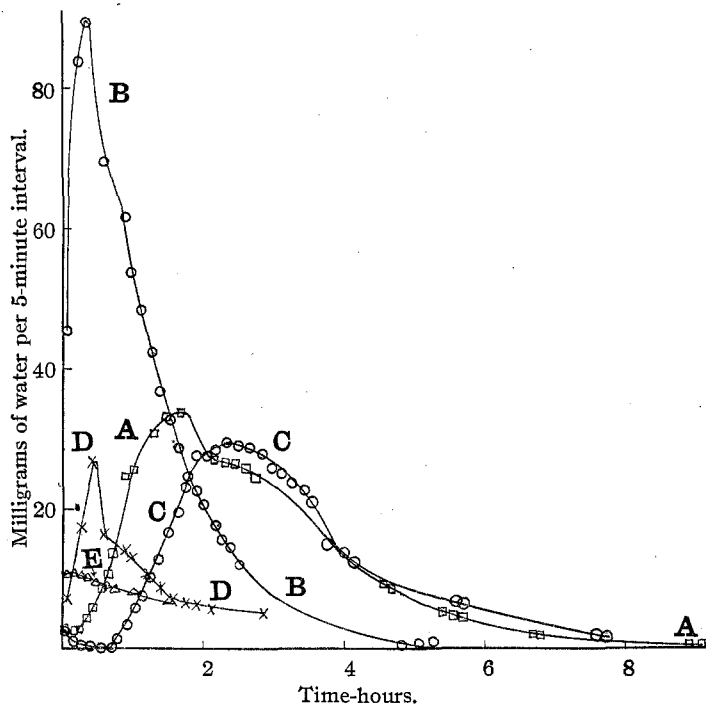


Fig. 1.—Reduction of nickelous oxide by hydrogen. A. Charge X at  $188^{\circ}$ . B. Charge X at  $206^{\circ}$ . C. Charge XIII at  $188^{\circ}$ . D. Reduction at  $250^{\circ}$  of oxide prepared at  $525^{\circ}$ . E. Reduction at  $280^{\circ}$  of commercial oxide.

to those obtained for samples prepared from nitrate at  $400^{\circ}$ , shown in A and C, Fig. 1.

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  $360^{\circ}$ . 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 ad-

sorbed 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  $\text{NiO}_{1.032}$ . 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.

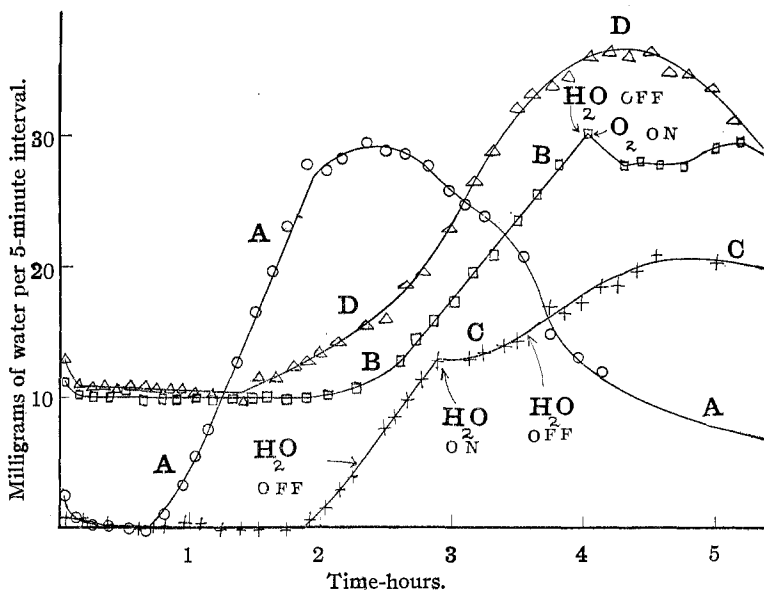


Fig. 2.—Effect of water and oxygen on reduction of nickelous oxide by hydrogen at 188°. A. Normal reduction (Charge XIII). B. Effect of 10 mg. of water per 5-minute interval (Charge XIII). C. Effect of 10 mg. of water per 5-minute interval (Charge XI). D. Effect of oxygen equivalent to 10 mg. of water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

**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 re-oxidized 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 re-oxidation repeated three or four times, with no diminution in the auto-catalytic acceleration of the reduction. There can be little doubt, therefore, that the nickel formed in the reaction is the auto-catalyst. Never-

theless, 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.<sup>9</sup> 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,<sup>8</sup> Langmuir,<sup>10</sup> and later Palmer<sup>11</sup> 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.<sup>12</sup> 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,

<sup>9</sup> There is a discrepancy of 6400 cal. between the values given for the heat of formation of nickelous oxide by Berthelot and by Mixer. 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.

<sup>10</sup> Langmuir, *Trans. Faraday Soc.*, **17**, 620 (1922).

<sup>11</sup> Palmer, *Proc. Roy. Soc. (London)* **103A**, 444 (1923).

<sup>12</sup> 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<sup>13</sup> 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

<sup>13</sup> 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  $\text{Fe}_3\text{O}_4$ . 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.

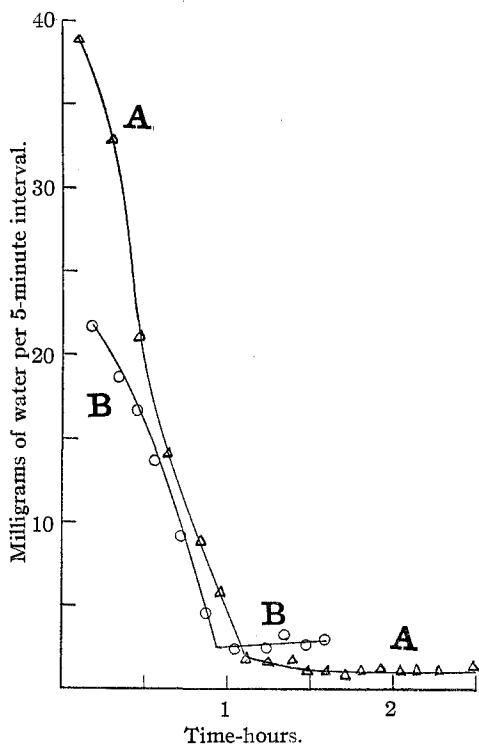


Fig. 3.—Reduction of ferric oxide by hydrogen. A. Reduction of precipitated oxide at 285°. B. Reduction at 300° of oxide prepared from nitrate.

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.

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 auto-catalytic.

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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 ferro-ferric 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.

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