3. The rate of production of vitamin D is directly proportional to the number of light quanta *absorbed* by ergosterol and independent of the wave length of the light used.

4. Vitamin D absorbs in the same wave length region as ergosterol and is destroyed by light of the same wave length as that which forms it.

5. The highest concentration of vitamin D which can be produced by direct irradiation of ergosterol is 35%. This is an absolute maximum and the probable value is lower.

6. The quantum efficiency is 0.3 molecules of vitamin D per quantum of light absorbed.

SCHENECTADY, NEW YORK

[CONTRIBUTION NO. 31 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

REDUCTION OF METAL OXIDES BY HYDROGEN

BY GUY B. TAYLOR AND HOWARD W. STARKWEATHER

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A common method for the preparation of metal catalysts consists in first preparing a finely divided oxide and then reducing the oxide with hydrogen. Usually the lower the temperature of reduction the greater the catalytic activity. Low temperature means a slow process of reduction. The present article is concerned with a new method for studying the rate of reduction. Nearly all prior work in this field has been done by passing hydrogen over the heated oxide and collecting and weighing the water formed at definite time intervals. The present method involves following the rate of reduction by measuring the volume of hydrogen consumed.

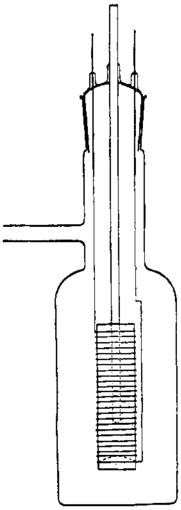

Fig. 1.

Method.—The essential feature of the apparatus is shown in Fig. 1. Platinum wire was wound on a mica cylinder to make a small electric heater, 2 by 6 cm. This heater was suspended on stout nickel wires in a pyrex vessel. The nickel wires were brazed to tungsten wires for sealing through the ground stopper of the vessel. These stout wires served both as supports and electrical leads. A small glass tube sealed to the stopper extended to the middle of the heater and served as a well for a fine-wire chromel–alumel thermocouple. The bottom of the mica cylinder was closed with a piece of platinum gauze wedged on the inside.

The rest of the apparatus consisted of a compensated gas buret, electrolytic hydrogen generator, and Hyvac pump. Electrolytic hydrogen was generated from sodium hydroxide with nickel electrodes, passed over a glowing platinum wire to free it from traces of oxygen, and dried by Dehydrite. Suitable stopcocks were provided so that the buret could be refilled rapidly and repeatedly during the course of a run.

The heater was charged by putting a layer of porcelain chips in the bottom, then the oxide, usually three cubic centimeters, and more chips on top. This insured a bed of reacting material in the middle of the heater surrounding the thermocouple hot-junction. The oxide was then heated in air and finally in a vacuum before admitting hydrogen to the vessel in order to drive out moisture and adsorbed gases. During a run the vessel was immersed in a bath at constant temperature, usually running tap water. The temperature of the bath definitely fixed the partial pressure of water vapor during a run just as soon as any of the water formed by the reduction condensed on the walls. Runs in an atmosphere of dry hydrogen were made by surrounding the vessel with a bath of solid carbon dioxide in methanol or by putting phosphorus pentoxide directly in the vessel.

The heat capacity of the charge and heater was only a few calories, so that it was possible to raise the temperature to 450° in three or four minutes with the current required to hold that temperature during a run. The heating current was drawn from a storage battery, and by merely keeping an ammeter at a definite mark, constant temperature was easily maintained.

In starting a run the gas buret was only partly filled with hydrogen, to allow for expansion on heating the charge. Correction for the expansion was obtained by a preliminary calibration with porcelain chips in the heater. Table I shows the complete data of a typical run. In this case the correction for expansion on heating the sample from 25 to 400° was 35 cc.; from 400 to 450° the correction was 3.5 cc.

Table I

Rate of Reduction of NiO, Supported (0.6 Gram Nickel)

Run No. 15. Bath temperature, 21.5°

Time	°C.	Heating current, amp.	Buret readings		Consumption of H_2,	
			Cc.	Refill, cc.	Minutes	cc. H_2, 25°C., 1 atm.
9:51	25	5.30	7.0			
9:53	300	5.30	23.1			
9:55	390	5.30	7.6		4	34.4
9:56	400	5.30	0	50.2		
9:58	400	5.30	34.2		7	58.0
10:01	400	5.30	23.1		10	69.1
10:04	400	5.30	13.8		13	78.4
10:09	400	5.25	4.1	50.0	18	88.1
10:19	400	5.25	35.6		28	102.5
10:29	400	5.25	26.9		38	111.2
10:39	400	5.25	21.0		48	117.1
10:49	400	5.25	16.7		58	121.4
11:00	400	5.25	13.4		69	124.7
11:17	400	5.22	8.5		86	129.6
11:32	400	5.22	5.3		101	132.8
11:47	395	5.22	2.5		116	135.6
11:57	395	5.22	1.4	49.2	126	136.7
12:50	395	5.22	41.9		179	144.0
1:30	395	5.70	38.5		219	147.4
1:33	450	5.70	42.0			
1:40	450	5.65	36.2		229	153.2
1:45	450	5.65	32.0		234	157.4
1:55	450	5.65	26.3		244	163.1
2:06	450	5.65	21.7		255	167.7
2:26	450	5.65	15.7		275	173.7

In most cases the samples were prepared as granules 8- to 14-mesh. Unless otherwise stated all reductions were carried out in hydrogen saturated with moisture at 10 to 25°, *i. e.*, the reaction vessel was kept in running tap water. The volume of hydrogen measured for any reduction experiment includes that adsorbed by the sample above room temperature or desorbed on heating. In most cases such effects are negligible.

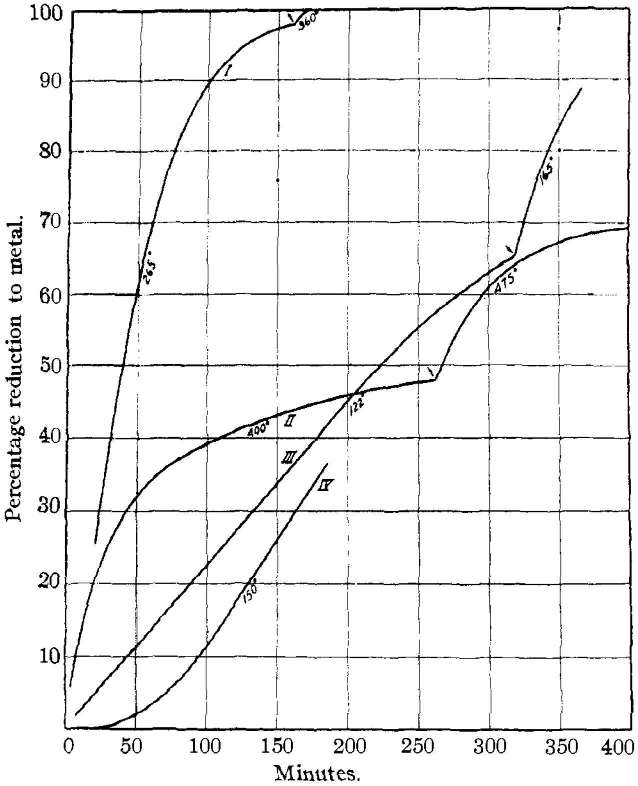

Fig. 2.—Curve I, NiO by ignition of the oxalate at 400°; II, NiO on kieselguhr; III, CuO by ignition of the oxalate; IV, CuO, wire form; ↓, temperature change.

Reduction of Single Oxides.—In Fig. 2 are shown some representative results with nickel and copper oxides in hydrogen saturated with water vapor at about 20°. Nickel oxide on a kieselguhr support proved much more difficult to reduce than a sample of unsupported material.[1] Whether the curve for copper oxide is autocatalytic in character depends largely on the individual sample. The work of Wright, Luff and Rennie[2] and of Pease and Taylor[3] shows that the reduction occurs at the metal–metal oxide

[1] Rideal and Taylor, "Catalysis in Theory and Practice," The Macmillan Co., London, **1926**, p. 242.

[2] Wright, Luff and Rennie, *J. Chem. Soc.*, **33**, 1 (1878); **35**, 475 (1879).

[3] Pease and Taylor, This Journal, **43**, 2179 (1921).

interface. If, at the beginning of the reduction, relatively few interfaces are developed, a curve showing an induction period followed by autoacceleration is obtained as with the wire-form sample. The result with the other sample of copper oxide, prepared from the oxalate, may be explained on the assumption of the initial formation of a large number of interfaces. One of the samples checks the observations of Pease and Taylor and the other those of Larson and Smith.[4] The mechanism of nickel oxide reduction is probably the same as that for copper oxide.[5]

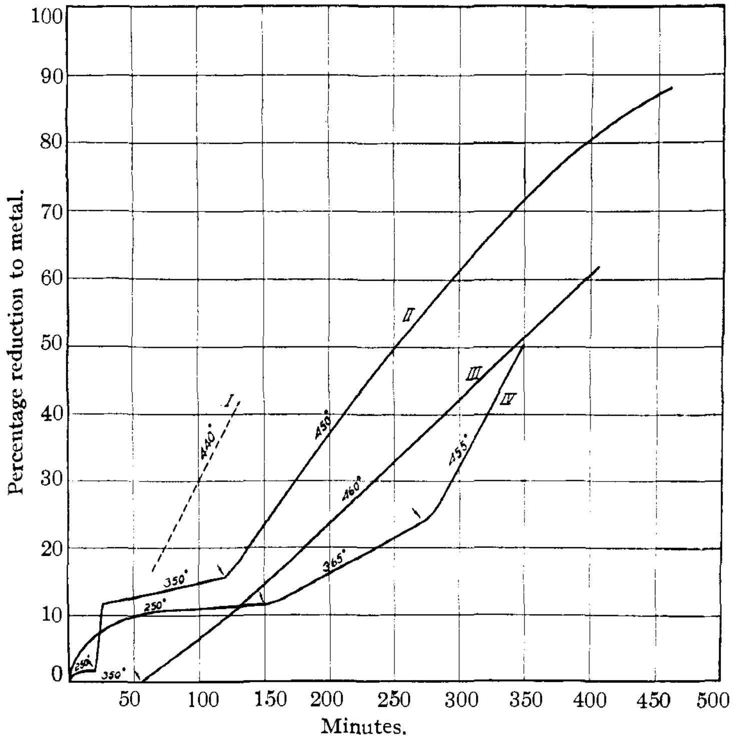

Fig. 3.—Ferric oxides. Curve I, Sample XII in dry hydrogen; II, Sample XII in wet hydrogen; III, Sample XII ignited at 900°; IV, Sample XXVII; ↓, temperature change.

Figure 3 shows some representative results on the rate of reduction of ferric oxide. Sample XII was prepared by precipitating a solution of ferric nitrate (10 g. of $Fe(NO_3)_3 \cdot 9H_2O$ per 100 g. of H_2O) with 7% ammonium hydroxide solution, washing free from nitrate, and drying at 150°. Sample XXVII was prepared from the same salt and alkali four times as

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[4] Larson and Smith, *ibid.*, **47**, 346 (1925).

[5] Benton and Emmett, THIS JOURNAL, **46**, 2728 (1924); Pease and Taylor, *ibid.*, **44**, 2179 (1922).

concentrated. Curve II is typical of many preparations of iron oxide gel. There is a slight reduction at 250°. On raising the temperature to 350° the reduction rises sharply to 11%, which corresponds to reduction of Fe_2O_3 to Fe_3O_4. The rate then slows down. On raising the temperature to 450° the reaction proceeds steadily until all the oxide is reduced to metal. Sample XXVII, precipitated from the more concentrated solutions, reduced to Fe_3O_4 at as low as 250°.

Curve I of Fig. 3 merely shows the slope of the reduction curve at 440° when the reaction vessel was kept at $-78°$ and consequently the vapor pressure of water is less than 0.001 mm. The rate is somewhat faster than when the vessel was kept in running water (Curve II). The rate of reduction at 250 and 350° in dry hydrogen was substantially the same as in wet hydrogen and is not shown in the figure.

The effect of sintering is strikingly shown by Curve III. Sample XII was heated in an electric muffle at 900° for twenty hours and then reduced. There was no reaction at 350°. At 450° the reduction apparently goes to metal since there is no break in the curve at the Fe_3O_4 stage.

Several samples of precipitated oxide were prepared by varying the concentration, the nature of the ferric salt, or that of the alkali. All gave results similar either to Curve II or IV of Fig. 3. The use of potassium instead of ammonium hydroxide did not alter rates of reduction, and this alkali was used for coprecipitating iron and other metals. It will be noted that iron oxide is not reduced autocatalytically. Benton and Emmett[5] have already pointed this out.

Glow Phenomenon.—Nearly all our samples of ferric oxide showed the gel-glow phenomenon[6] when heated in hydrogen. Figure 4 shows the most conspicuous example. The bottom curve shows the reaction rate, the middle one the current supplied the heater, and the top the temperature registered by the thermocouple, all plotted against time. The temperature rise during the first few minutes is extremely rapid, so rapid that the actual temperature reached by the oxide is no doubt higher than that registered by the thermocouple. This effect does not occur when the material is heated in air or in vacuum. Some reduction must occur before the glow can take place. On the other hand, it is possible to reduce the sample by heating it slowly without the glow being evident. While the reaction between hydrogen and ferric oxide to give ferroso-ferric oxide is strongly exothermic, the data given in the figure show conclusively that this reaction is too slow to account for the sudden temperature rise.

Reduction of Mixed Oxides.—Mixed oxides of nickel, copper and silver with iron were prepared by coprecipitation of solutions of sulfate or nitrate

[6] L. Wohler, *Kolloid-Z.*, 11, 241 (1913). For a discussion of the glow phenomenon; see H. B. Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926, pp. 78–81.

by potassium hydroxide. The precipitates were washed and then electrodialyzed until free of the negative ion. They were dried at 102° before placing in the reduction apparatus. The metals were present in about equal-atom proportions.

Figure 5 shows the effect of added nickel. It is of course impossible to tell which oxide is being reduced the faster, but the slopes of the curves at 450° indicate that the nickel accelerates the final reduction of the iron, since nickel oxide is probably completely reduced before this temperature is reached. Silver and copper gave results of similar character, hence it may be concluded that the presence of a foreign metal interface speeds iron oxide reduction. In the test with silver, silver oxide was dissociated by heating in vacuum before reduction was started.

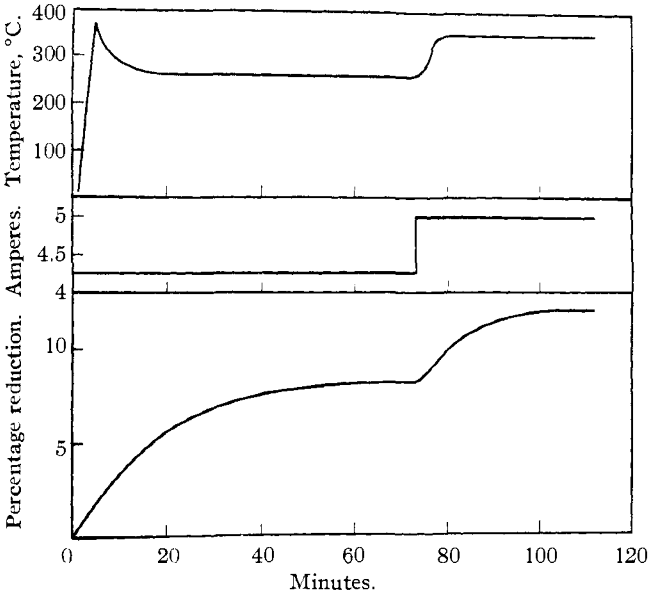

Fig. 4.—Reduction of Fe_2O_3 showing glow phenomenon.

Figure 6 shows the effects of oxides that cannot be reduced by hydrogen to metal. Mixed oxides of iron and chromium and of iron and aluminum, equimolar, were prepared by precipitation. These oxides materially lowered the rate of reduction of the iron oxide at 450°, but if the chromium oxide was mixed mechanically by grinding with ferric oxide, no such effect occurred. Emmett and Love[7] also found that even as small amounts of coprecipitated Al_2O_3 as 1.5% reduced the rate of reduction of Fe_3O_4 to metallic iron.

The curves in Fig. 6 show that the amount of hydrogen consumed at

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[7] Emmett and Love, *J. Phys. Chem.*, **34**, 56 (1930).

360° was greater than that required to reduce the Fe_2O_3 to Fe_3O_4. The Cr_2O_3 in the material reduced according to Curve II was prepared from an hydroxide gel made from the sulfate and ignited to 450° in air. It was then of a dark green color, but when reduced by hydrogen it became bright green. This bright green material was used in preparing the mechanical mixture for Curve II.

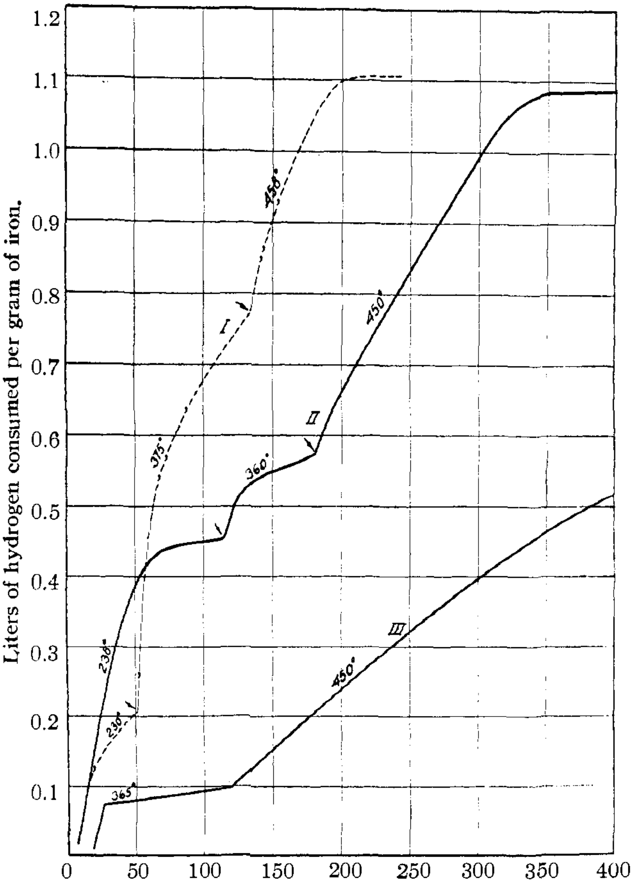

Fig. 5.—Reduction of mixed nickel and ferric oxides. Curve I, $NiO-Fe_2O_3$ precipitated together; II, NiO and Fe_2O_3 mixed dry; III, Fe_2O_3 alone, Sample XII; ↓ , temperature change.

A 3-g. sample of the coprecipitated Fe_2O_3-Cr_2O_3 used in obtaining Curve I was placed in the apparatus, heated to 250° in vacuum, and cooled to room temperature. Oxygen was then admitted and the sample heated, eventually to 380°; 40 cc. of oxygen was consumed, indicating oxidation of Cr_2O_3. The apparatus was then cooled to room temperature and the oxygen replaced by hydrogen. This oxidized sample was then reduced as usual, giving results similar to those shown in Curve I, save that 80 cc. additional hydrogen equivalent to the above quantity of oxygen was consumed at 238°.

It was further found that pure Cr_2O_3, after being heated in the air, liberated iodine from acidified potassium iodide solution.

Coprecipitated zinc and ferric oxides from nitrate solutions yielded a product difficult to purify. Electrodialysis could not be used to purify this material. The precipitate was washed on a filter and dried at 102° and analyzed 25% iron. The sample in the reduction apparatus was heated for ninety minutes at 250° and fifteen minutes at 350° to decompose traces of nitrates. Thereafter a reduction experiment gave a curve much like Curve II, Fig. 6. In this case the non-reducible oxide did not slow down reduction of the iron oxide at 450°.

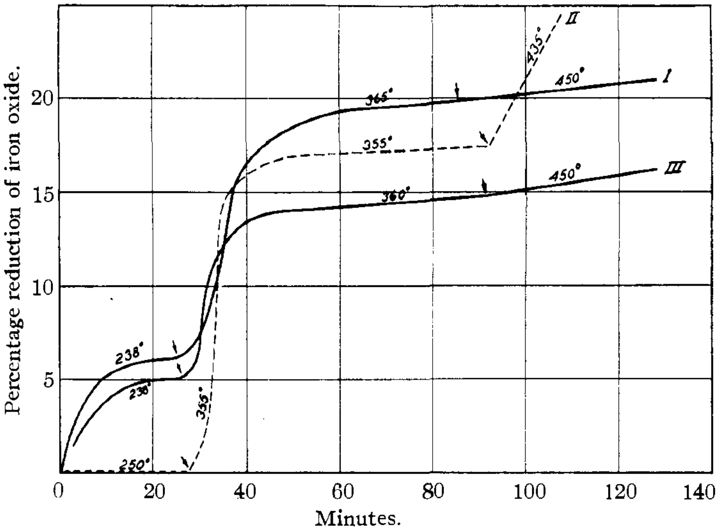

Fig. 6.—Curve I, Fe_2O_3–Cr_2O_3 coprecipitated; II, Fe_2O_3–Cr_2O_3, mechanical mixture; III, Fe_2O_3–Al_2O_3 coprecipitated; ↓, temperature change.

Figure 7 shows the rate of reduction of ferrous oxide. The oxide was prepared by decomposing ferrous oxalate in a vacuum in the reduction apparatus by slow heating to 400°. It did not come in contact with air before reduction. After reduction the iron powder was brilliantly pyrophoric, giving a shower of sparks as it was poured from the heater.

There have been several instances mentioned in the recent literature indicating the reduction of zinc oxide at low temperatures. Rogers[8]

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[8] Rogers, This Journal, 49, 1432 (1927).

completely reduced a fused mixture of cuprous oxide and zinc oxide with hydrogen at 300°. Frolich, Davidson and Fenske[9] found evidence for the reduction of zinc oxide in the presence of copper oxide by methanol vapor at 220°. St. John[10] claims to have detected reduction of pure zinc oxide by hydrogen at as low a temperature as 310°. Taylor and Kistiakowsky[11] in their work on adsorption of hydrogen by pure zinc oxide noted gray spots formed on the oxide in a hydrogen atmosphere.

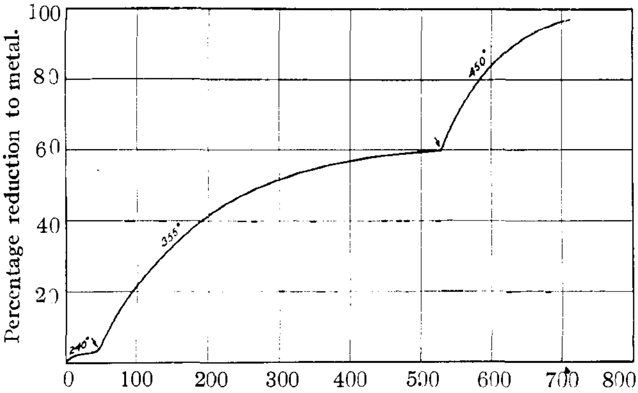

Fig. 7.—Reduction of FeO.

In view of these observations and the fact that zinc oxide is generally considered as non-reducible below the melting point of zinc, calculations were made to determine the conditions under which crystallized zinc oxide might be expected to be reduced by hydrogen.

The free energy of the reaction

$$ZnO(s) + H_2(g) = Zn(s) + H_2O(g) \qquad (1)$$

may be used to calculate the partial pressure of water vapor which must not be exceeded, if the zinc oxide is to be reduced, by the relation

$$\Delta F^\circ = -RT \ln K$$

where $K = [H_2O]/[H_2]$.

The free energy of Reaction 1 was calculated by combining the two reactions

$$ZnO(s) = Zn(s) + {}^1/_2O_2(g) \qquad (2)$$

$$H_2(g) + {}^1/_2(O_2)(g) = H_2O(g) \qquad (3)$$

For Reaction 2,[12]

$$\Delta F^\circ = 83{,}285 + 1.61T \ln T - 0.26 \times 10^{-3}T^2 - 0.645 \times 10^{-7}T^3 - 34.23\,T$$

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[9] Frolich, Davidson and Fenske, *Ind. Eng. Chem.*, **21**, 109 (1929).

[10] St. John, *J. Phys. Chem.*, **33**, 1438 (1929).

[11] Taylor and Kistiakowsky, THIS JOURNAL, **49**, 2468 (1927).

[12] Maier and Ralston, THIS JOURNAL, **48**, 371 (1926).

and for Reaction 3,[13]

$$\Delta F^\circ = -57{,}410 + 0.94T \ln T + 1.65 \times 10^{-3}T^2 - 3.7 \times 10^{-7}T^3 + 3.92T$$

Adding these equations to get for Reaction 1

$$\Delta F^\circ = 25{,}875 + 2.55\,T \ln T + 1.39 \times 10^{-3}T^2 - 4.345 \times 10^{-7}T^3 - 30.31T$$

then for 300°, $\Delta F^\circ = 18{,}100$ and for 419°, the melting point of zinc, $\Delta F^\circ = 16{,}950$ calories.

In the presence of copper the compound Cu_2Zn_3, a constituent of brass can be formed. The heat capacity of brass is substantially the sum of the heat capacities of copper and zinc entering into its formation, so that ΔH may be taken equal to ΔF°, assuming the heat capacity of brass remains additive all the way to 0°K. The heat of formation of Cu_2Zn_3 is 16,000 calories,[14] so that for each gram-atom of zinc $\Delta F^\circ = -5300$.

The following table gives the calculated partial pressures of water vapor that will prevent the reduction of zinc oxide when the hydrogen pressure is one atmosphere.

EQUILIBRIUM CALCULATIONS

	°C.	ΔF°	K	Water vapor press., mm. Hg
Pure ZnO	300	18100	1.3×10^{-7}	0.0001
Pure ZnO	419	16950	4.4×10^{-6}	0.0033
ZnO + Cu	300	12800	1.3×10^{-5}	0.01
ZnO + Cu	419	11650	2×10^{-4}	0.15

An experiment was carried out to see if zinc oxide alone could be appreciably reduced under the most favorable conditions possible with our apparatus. Three grams of an especially pure form of zinc oxide was heated in hydrogen at 516° for one hour while the walls of the vessel were cooled to −78° by solid carbon dioxide in methanol. The measured hydrogen consumption was less than 2 cc., which is within the experimental error under the extreme conditions of the test. After the experiment the oxide showed gray spots like those described by Taylor and Kistiakowsky.

Three samples of mixed oxides of copper and zinc were prepared as follows. No. XXIX.—A solution of copper and zinc nitrates was added to potassium hydroxide solution in calculated equivalents to insure complete precipitation. The precipitate was washed on the filter and dried at 102°; analysis: 35.46% Cu, 26.14% Zn. Before reduction it was heated in the apparatus in vacuum to decompose traces of nitrate before hydrogen was admitted.

No. XXXI.—Pure zinc and copper oxides were ground together to pass a 100-mesh sieve and made into pellets in a pill machine; analysis: 40.57% Cu, 39.12% Zn.

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[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 485.

[14] Biltz, *Z. anorg. allgem. Chem.*, **134**, 25 (1924).

No. XXXII.—Sample was prepared the same as No. XXXI, then heated in a muffle at 900° overnight and blasted for half an hour in an oxygen–gas flame; analysis: 41.81% Cu, 38.57% Zn.

Sample No. XXIX was heated in wet hydrogen (reaction vessel in water) for 145 minutes, raising the temperature stepwise to 360°. Hydrogen equivalent to CuO in the sample was consumed at 238° and there was no further reduction at 360°. On raising the temperature to 440°, there was a small consumption of hydrogen and then no reaction in thirty minutes. The vessel was then surrounded by the cold bath at −78° and reduction proceeded steadily at 460° at a uniform rate for an hour until the experiment was discontinued. Tests with Sample XXXI under nearly the same conditions were quite similar. With phosphoric oxide in the vessel there was a slow but measurable reduction of the zinc oxide at 365°. After reducing the copper oxide in sample XXXII, condensed water was removed and phosphoric oxide put into the vessel. The reduction of the zinc oxide was then allowed to proceed for eight hours at 350°.

After the three samples were reduced, they were washed with dilute hydrochloric acid to dissolve zinc oxide and examined by x-rays. A chemical analysis of one of the samples was also made. Below are summarized the data of the examination of the reduced samples which prove that alpha brass was formed in all cases.

Composition of Reduced Samples

Sample no.	X-ray examination Cube edge, Å.	 % Zn in brass[a]	Calcd. % Zn in brass from reduction data	Chemical analysis
XXIX	3.636	10	12	13% Zn, 84.5% Cu
XXXI	3.643	15	15	......
XXXII	3.625	8	9	......

[a] Calculated by comparison with data for alpha brasses given in "International Critical Tables," McGraw-Hill Book Co., New York, 1926, p. 350, Vol. 1.

There thus appears to be nothing mysterious about the reduction of zinc oxide in the presence of copper. It is simply a case of carrying out the reduction in a sufficiently dry atmosphere, to be on the right side of the equilibrium position. A sufficiently dry atmosphere of hydrogen in the case of zinc oxide alone, at temperatures at which it can be reduced in the presence of copper, is difficult if not impossible to realize experimentally.

The authors wish to thank Dr. A. W. Kenney of this Laboratory for making the x-ray examinations, and Dr. H. G. Tanner, also of this Laboratory, for assistance in the free-energy calculations.

Summary

1. A new method for studying the rate of reduction of metal oxides at temperatures below 500° has been described. In this method the volume of hydrogen consumed is measured.

2. Results with this method for nickel, copper, iron and zinc oxides have been presented.

3. Ferric oxide gel is reduced to ferroso-ferric oxide at 350° and to metallic iron at 450°. Ignited ferric oxide is not reduced at an appreciable rate at 350° and goes to metal at 450°.

4. Foreign metal interfaces with iron oxide accelerate the reduction to iron.

5. Alumina and chromium oxide greatly retard reduction of ferroso-ferric oxide.

6. Ferric oxide gels show the glow phenomenon in hydrogen at fairly low temperatures, but not in air or in vacuum.

7. The thermodynamics of zinc oxide reduction in the presence of copper have been worked out, giving an explanation in the formation of alpha brass.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 58]

ADSORPTION OF HYDROGEN BY NICKEL AT LOW TEMPERATURES[1]

BY ARTHUR F. BENTON AND T. A. WHITE

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Introduction

Although it is now recognized that the occurrence of catalytic reactions at solid surfaces is intimately connected with the nature and extent of the adsorptions of the reacting species and products, nevertheless, attempts to obtain a quantitative treatment of the relations involved have met with little success. The main difficulty appears to be the lack of an adequate general theory of adsorption at catalytically active surfaces.

Numerous adsorption measurements,[2] especially by Taylor and his co-workers, have shown that adsorption of gases may be accompanied by more or less "activation" of the adsorbed molecules, and that this activation is a prerequisite to any marked catalytic action of the solid. It is known that this activation is conditioned by the chemical rather than the physical properties of the substances involved, but its occurrence is unpredictable theoretically. Experimentally, however, the two limiting types of adsorption, the "secondary" type involving little or no activation and the "primary" type in which relatively great activation occurs, can be

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29–May 3, 1929.

[2] Critical summaries of the extensive work in this field may be found in the following papers: Taylor, *J. Phys. Chem.*, **28**, 897 (1924); **30**, 145 (1926); *Proc. Roy. Soc.* (London), **A113**, 77 (1926); Taylor and Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927); Langmuir, THIS JOURNAL, **38**, 2221 (1916); **40**, 1361 (1918).