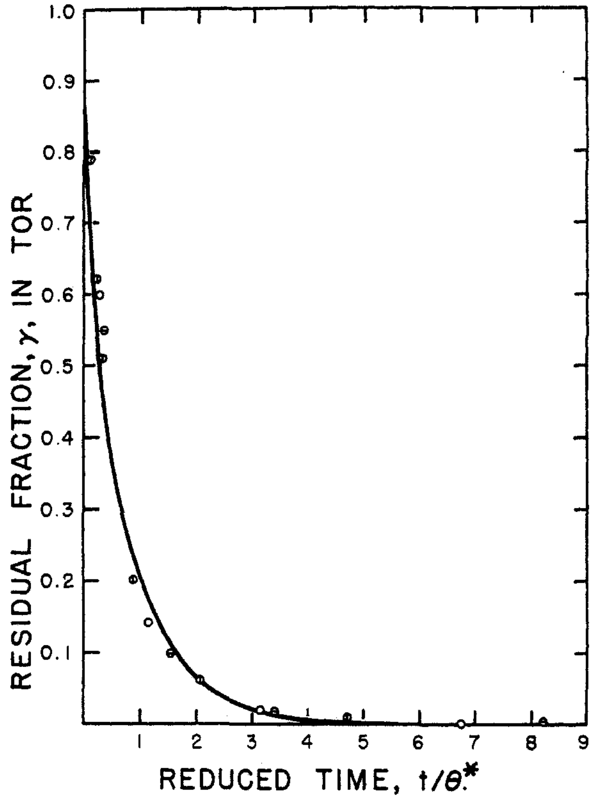

Fig. 1.—Transport of serum albumin by electrophoresis-convection: ⦶, run 18; ○, run 19; ⊖, run 20.

value is near 0.5. The ratio depends upon the specific protein under investigation as well as upon electrophoretic mobility and diffusion constant. It decreases in general with increasing values of $\mu Ea/D$, which were carried far beyond the range in which the theory is expected to be quantitatively valid. The curve of Fig. 1 compares the theoretical relation for the fraction of protein, γ, residual in the top reservoir as a function of t/θ^* with the results of three serum albumin runs under practical conditions.

A number of simplifying assumptions underlying the derivation of Eq. (1) are not exactly realized in practice and would be expected to contribute to quantitative disagreement with experiment even when the parameter $\mu Ea/D$ is small relative to unity. Perfect mixing in the reservoirs is assumed but undoubtedly not completely attained. Imperfect mixing would retard transport. The actual electric field in the channel is certainly lower than the measured nominal field in the external buffer due to chemical potential gradients of the ion constituents in the channel and due to field jumps at the membranes where the protein ion constituent disappears. Also retarding the transport is the flow of solvent across the channel opposing the motion of the protein. This flow arises from an osmotic influx of solvent at the membrane at which the protein molecules accumulate and an efflux at the opposite depleted side.

Examination of the data of Table III shows that while the characteristic times of transport in the exploratory experiments vary by a factor of 1000, the ratio E^*/E varies only by a factor of about 5. The practical utility of the theory for the prediction of times of transport and for the planning of separations by electrophoresis-convection is thus clearly demonstrated. A single experiment allows the determination of the ratio E^*/E under the given conditions, and this ratio may be employed to predict transport as a function of time. In the absence of a pilot experiment, assignment of a value of 0.25 to the ratio E^*/E permits the determination of an upper bound to the time required for the transport of a given fraction of protein from the top reservoir of the apparatus.

PASADENA, CALIFORNIA RECEIVED MARCH 5, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

A Technique for the Study of Solid-Gas Surface Reactions; The Decomposition of Nitrous Oxide on Iron Oxide–Zinc Oxide Catalysts[1,2,3]

BY LAMAR P. BUPP[4] AND ALLEN B. SCOTT

A method for the measurement of surface area, magnetic susceptibility and catalytic efficiency for solid catalysts is described. The decomposition of N_2O at 500° and 1 atm. pressure over α-Fe_2O_3 and several ZnO–Fe_2O_3 catalysts has been studied by this method. The pure α-Fe_2O_3 is the most efficient of the catalysts studied. The efficiency for equal molar mixtures of ZnO and α-Fe_2O_3 pretreated at a series of temperatures shows a regular decrease in activity with pretreatment temperature. There is no evidence of a catalytically active phase intermediate between the mixture and zinc ferrite. The surface area also decreases regularly with pretreatment temperature, and the loss of catalytic activity may be due to this effect, though other possibilities are discussed. No correlation is observed between magnetic susceptibility and catalytic activity.

A combined interest in surface chemistry and magnetochemistry led to the investigation described in this paper. Studies of the influence of magnetism on catalytic processes occurring at a solid–gas interface have been investigated many times and are reviewed by Selwood.[5] Irregularities and strains in the crystal lattice of solid materials may often impart heterogeneous adsorptive properties to the surface.[6] In addition to the effects of magnetism and surface condition, the absolute magni-

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[1] From a thesis submitted by Lamar P. Bupp in partial fulfillment of the requirements for the Ph.D. degree at Oregon State College; published with the approval of the Oregon State College Monographs Committee, Research Paper No. 181, Department of Chemistry, School of Science.

[2] The principal portion of the work described in this paper was carried out with the aid of a Postgraduate Fellowship in Chemistry granted by the E. I. du Pont de Nemours and Co.

[3] Presented in part before the Pacific Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June 10, 1950, and in part before the 119th meeting of the A. C. S., Cleveland, Ohio, April, 9, 1951.

[4] General Electric Co., Hanford Works, Washington.

[5] Selwood, *Chem. Revs.*, **38**, 41 (1946).

[6] Taylor and Liang, THIS JOURNAL, **69**, 1306, 2989 (1947).

tude of the surface area may be expected to affect the catalytic efficiency of a solid.

The objectives of this work were twofold; first, to integrate improved experimental techniques into an apparatus for the study of contact catalysis and, second, to explore a reaction which may be influenced both by the magnetic state and the surface area of the catalytic material.

The apparatus described below is one in which consecutive measurements of surface area, magnetic susceptibility and catalytic efficiency may be obtained from the same catalyst sample *in situ*. In this manner variables which alter the character of the surface forces from sample to sample of the same catalyst material are eliminated and likewise any changes in the measured variables which are due to conditions imposed during the experiment are detected by consecutive determinations.

The decomposition of nitrous oxide was selected for study because it is well understood and has the added advantages that it is safe, easy to control, has no side reactions and lends itself well to some of the restrictions imposed by the experimental system chosen. The function of this reaction was that of serving as an index of the efficiency of the various catalysts employed for its decomposition.

Other investigations have been made on the decomposition of nitrous oxide on iron oxide–zinc oxide mixtures and the zinc ferrite spinel by Hüttig.[7] Some of the results of this work will be compared with those of Hüttig.

Experimental

Apparatus.—The principal unit of the experimental system is shown in Fig. 1. The catalyst sample, consisting of about five grams of uniform powder, was contained in a sample tube. This tube, surrounded by an electrical heater section, was freely suspended from a glass fiber, which in turn, was hung from a fine copper–beryllium spring. This suspension is similar to one used by Josefowitz and Othmer,[8] except that the spring used was larger. The spring had a coefficient of 17.3 mg./mm. with a total load of ten grams. Readings of elongation were made with a traveling microscope graduated to 0.01 mm. When the thermal environment of the spring was held to ±0.02°, weight changes of the order of 0.1 mg. could easily be detected. The same spring was used throughout the investigation and no fatigue effects were noted.

The sample tube was made from special thin-walled Pyrex tubing having a diameter of about 12 mm. o.d. The length of the tube was about 12 cm. The top of the container was formed and carefully ground to fit into the $^{12}/_{30}$ standard taper joint which extended downward from the suspension section and was positioned directly over the hanging sample tube. The base of the sample tube was sealed to a medium-grade fritted glass disc. The catalyst sample was supported by the sample tube in the sample section where the temperature could be controlled and any changes of mass noted by the elongation of the spring suspension. By seating the sample tube in the joint above it, gas passing into the sample section was forced to pass through the catalyst bed *via* the porous glass base.

A chromel–alumel thermocouple was positioned directly beneath the suspended sample by means of a thermocouple well. The vertical walls of the sample section were covered with asbestos paper, wrapped uniformly with resistance wire and lagged with asbestos cord and alundum cement. This assembly could be immersed in liquid nitrogen during the surface area determinations; or the pole pieces of a permanent magnet could be positioned transverse to the suspended sample in a manner shown by the dotted circle in Fig. 1. Thermocouples were calibrated and the temperature gradient in the furnace was determined at several temperatures. Temperatures reported are accurate within 5°.

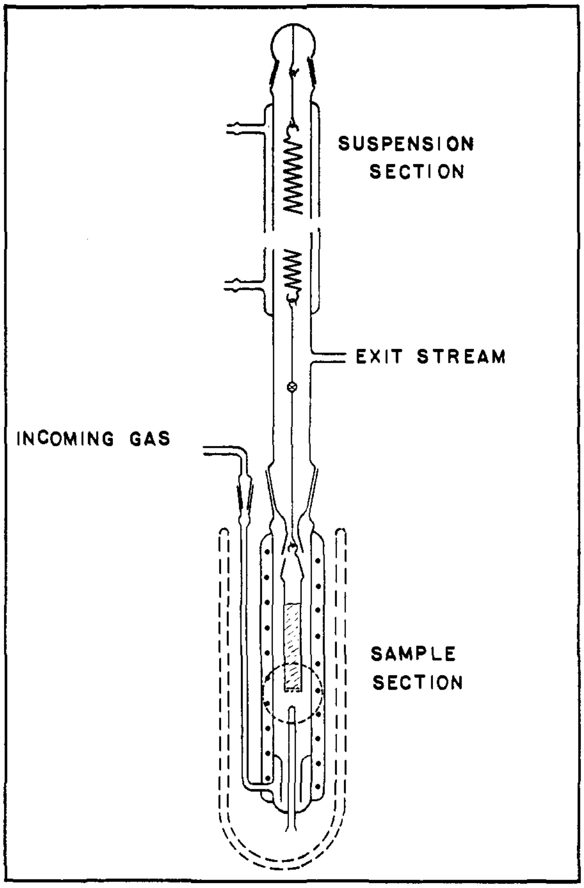

Fig. 1.—Experimental apparatus; suspension and sample section.

The efficiency of catalyst samples was measured by the increase in flow rate of N_2O after passing through the sample section, using flowmeters of the type described by Yudowitch[9] and maintaining the total pressure at 1.00 atm. by means of a Cartesian manostat.

Reagents.—The nitrous oxide was obtained from the Ohio Chemical Co. and was indicated to be 99% pure with the remainder being nitrogen and a trace of oxygen.

The nitrogen for the surface area determinations was obtained from standard commercial tank stock. Prior to being used in the apparatus, the gas was passed consecutively through copper turnings held at 400°, a 10% solution of alkaline pyrogallic acid, a calcium chloride drying tower and a liquid nitrogen trap.

The α-Fe_2O_3 used in the catalyst mixtures was obtained from C.P. stock and further purified by a method used at the Bureau of Standards.[10] Spectrographic analysis of this material made by the Bureau of Mines, Albany, Oregon, indicated a 99.94+% purity with the principal impurities being molybdenum and manganese.

The ZnO was made by adding reagent-grade zinc metal in excess to a dilute solution of sulfuric acid. After standing 24 hours, the excess zinc was filtered off and the zinc sulfate solution poured slowly into a boiling solution of sodium carbonate. The basic zinc carbonate formed was filtered, washed four times with water and calcined in an electric oven at 500° for 12 hours. A spectrographic analysis of this material indicated a purity of 99.8+% with the principal impurities being aluminum, calcium, magnesium and silicon.

Experimental Procedure.—The catalyst samples used in this work were pure α-Fe_2O_3, pure ZnO and equal molar mix-

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[7] Hüttig and his school have published a great number of papers on this system. The best review of his work appears in J. Hedvall, "Reaktionsfähigkeit fester Stoffe," J. A. Barth, 1938, pp. 151–160.

[8] Josefowitz and Othmer, *Ind. Eng. Chem.*, **40**, 739 (1948).

[9] Yudowitch, *Anal. Chem.*, **20**, 86 (1948).

[10] Cleaves and Thompson, *J. Research Natl. Bur. Standards*, **18**, 595 (1937).

tures of these two components which had previously received various heat treatments. After each catalyst had been prepared, it was uniformly mixed and ground in a porcelain container and then placed in the sample tube. The tube was tapped sharply about one hundred times to pack the fine powder and the height of the packing noted at the beginning and the end of the experiment to detect any loosening of the column due to the pressure drop across the tube during the catalytic efficiency determinations. The full sample tube was next suspended and outgassed by heating at 400° in a vacuum.

After cooling to room temperature, the sample section was immersed in liquid nitrogen. Nitrogen gas was admitted into the system and maintained at constant pressure in the range 50–300 mm. by means of a manostat. With the system at constant pressure and the sample at liquid nitrogen temperaure, the weight of the nitrogen which was adsorbed on the catalyst powder was obtained by following the elongation of the spring until an equilibrium maximum reading was obtained on the traveling microscope. Such a series of pressure–weight relationships yielded an adsorption isotherm and the surface area was calculated using the relationships derived by Brunauer, Emmett and Teller.[11] Corrections were made in this determination for the buoyant effect of the sample and spring and also for the apparent surface area of the assembly other than the catalyst sample. Surfaces as low as one square meter per gram were measured by the above method.

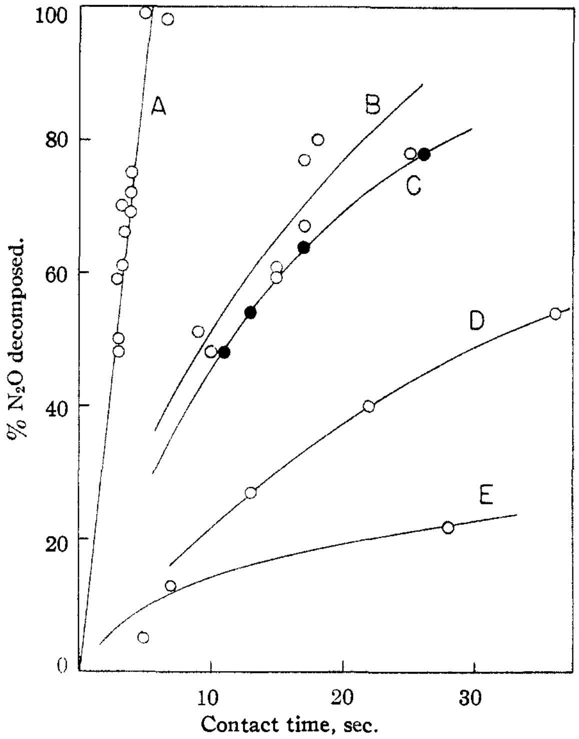

Fig. 2.—Efficiency of Fe_2O_3 and Fe_2O_3–ZnO catalysts: (A) pure α-Fe_2O_3; (B) mixture, no heat treatment; (C) mixture, after 6 hours at 530° (solid circles); (D) same, 670°; (E) same, 830°.

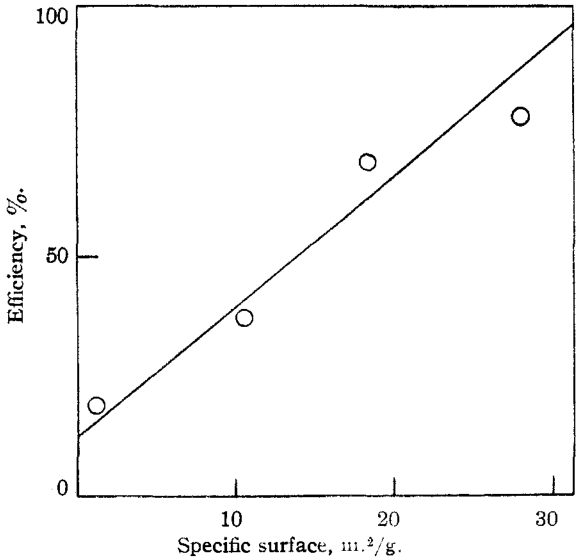

Fig. 3.—Effect of surface area of Fe_2O_3–ZnO catalysts upon catalytic efficiency, at 20 seconds contact time.

Following the surface determination, the system was again evacuated and outgassed. Nitrous oxide was admitted to atmospheric pressure. The sample tube was seated in a socket directly above it by shortening the top support rod of the spring suspension. The sample section heater was energized and a temperature of 500° maintained during the determination. Flowmeter recordings were made for a series of different flow rates. The principal error in this determination was the one due to the leakage of gas around the glass-to-glass joint at the top of the sample tube. At the end of this work a sample tube was sealed off and ballasted with sand. This control sample was inserted into the joint in a manner similar to an efficiency run and the amount of gas leaking through as a function of pressure drop was obtained directly. This leakage was found to be a linear function of pressure but the average deviation from the mean for three determinations was 6%. This feature imposes a limitation on the accuracy of any kinetic information taken for this work, but on the other hand the spread in efficiencies from one catalyst to the next was so great as to make this leakage error less significant. All gas calculations were based on standard conditions and the assumption that the nitrogen and nitrous oxide obeyed the ideal gas laws under the condition of the tests. The quantity of gas that leaked around the sample tube was subtracted from the total quantity flowing as judged by the flowmeter indications and the catalytic efficiency, E, the per cent. of nitrous oxide decomposed, was calculated from the equation

$$E = \frac{2(R - R_0) \times 100}{R_0}$$

where R and R_0 represent the ratio of outlet to inlet flow rates for the conditions of the test and for a blank run, respectively. Knowing the flow rate and the total volume and packing density of the catalyst sample, the time of contact of the nitrous oxide with the sample was calculated. Allowance was made for thermal expansion on passing through the heated catalyst and for the progressive increase in flow rate during the time of contact due to decomposition.

At any time during the previously described determinations the magnetic susceptibility of the catalyst could be ascertained by a conventional Gouy method, previously described.[12] The magnet used had a field strength of 1800 oersteds and with the other variables considered, the magnetic susceptibility could be determined within 0.2×10^{-6} c.g.s. units.

It should be noted here that the order in which measurements of surface area, catalytic efficiency, and magnetic susceptibility were taken on any one sample is arbitrary. Although such determinations were usually taken in the order mentioned, there were cases where this order was not followed and also cases where several consecutive measurements were made on the same sample.

Experimental Results.—Equal molar mixtures of α-Fe_2O_3 and zinc oxide were thoroughly mixed and portions heated for six hours at 530, 670 and 830° in alundum boats in an electric furnace. The results of tests made on these catalysts are shown graphically in Figs. 2 and 3.

It may be noted that pure α-Fe_2O_3 was the most efficient of the catalysts tested. During the course of efficiency measurements the magnetic susceptibility, measured at 25°, decreased from 20.4 to 18.1 $\times 10^{-6}$ c.g.s. units, and the specific surface decreased from 25 to 18 m.²/g. but no appreciable change in activity was observed. This is illustrated by curve A, Fig. 2, for which the points are represen-

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[11] Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

[12] Hrostowski and Scott, *J. Chem. Phys.*, **18**, 105 (1950).

tative of varying specific surfaces within the above range, but all lie fairly nearly along a straight line passing through the origin. It may be concluded that the decomposition is approximately of zero-order at one atmosphere total pressure and for surfaces in the neighborhood of 20 m.^{2}/g., with a decomposition rate of 18% per second. For this catalyst the initial surface was 43 m.^{2}/g. but dropped to 25 during the first catalytic measurement, so that the effect of a higher specific surface is uncertain.

A sample of α-Fe_2O_3, heated at 710° for 21 hours, had a specific surface of less than 1 m.^{2}/g. and the efficiency was only 6% for 6 seconds contact, suggesting a strong dependence of catalytic activity upon specific surface with decreasing surface.

The decomposition on pure zinc oxide, having a specific surface of 5 m.^{2}/g. was negligible even after a contact time of 54 seconds.

There was a general decrease in efficiency of the ZnO–Fe_2O_3 mixtures with increasing pretreatment temperatures, as shown by the remaining curves of Fig. 2. The efficiency of the sample of mixture given no prior heat treatment, curve B, was somewhat greater than that of material pretreated for six hours at 530°. Due to the fact that the efficiency determinations were made at 500°, and considerable change in surface and susceptibility was always observed to occur during the measurements, the results given by curve B cannot be strictly construed as representing the behavior of an unheated sample, and in fact the curve is nearly coincident with that of the sample pretreated at 530°, but much more erratic.

The specific surfaces of the mixtures also decreased with increasing pretreatment temperature, suggesting the likelihood that the catalytic efficiency for the mixtures is closely related to the surface. An approximately linear relationship is shown in Fig. 3, in which the efficiency at 20 seconds contact time, from Fig. 2, is plotted against the specific surface of the ZnO–Fe_2O_3 catalysts.

The magneto-chemical investigations of these oxide mixtures proved to be interesting. The magneto-thermal curves for each sample showed in general an increase in susceptibility with increasing temperature. These data showed no possible correlation with the Curie or Curie–Weiss equations. This is not surprising in view of the irregular temperature dependence of the α-Fe_2O_3 phase present in the mixture.[13] Kittel and Hüttig[14] have shown that similar oxide mixtures do not display field strength dependency of susceptibility until pre-treatment temperatures are in excess of 650°. In Table I the results of this study and those of Kittel and Hüttig are compared.

TABLE I

MAGNETIC SUSCEPTIBILITIES FOR THE ZINC OXIDE FERRIC OXIDE MIXTURES AT 25°

Sample	Pretreatment temperature, °C.	Kittel × 10^6	Observed × 10^6
Fe_2O_3	None	37.6	20.4
Fe_2O_3 and ZnO mix	20	19.33	13.9
	400	21.39	..
	500	21.77	16.7
	530	...	18.7
	600	21.74	..
	650	47.76	..
	670	...	47.0

It appears that the observed susceptibilities follow the same general change with respect to heat treatment as those of Kittel and Hüttig when account is taken of the fact that the susceptibility of the alpha ferric oxide is considerably different than that obtained by these authors. Selwood[5] in reviewing the most probable values of the mass susceptibilities of many pure components quotes a value of 22 × 10^{-6} for pure α-Fe_2O_3 at 25°.

While taking susceptibility data on the ZnO–Fe_2O_3 mixture which had been pretreated at a temperature of 670°, it was observed that the magnetic susceptibility taken at 500° increased with time. Over a period of 65 minutes the values rose from 34.2 to 36.7 × 10^{-6} c.g.s. units with a corresponding increase in the values of 25°. This trend seemed to continue at a constant rate. It is believed that this observation indicates the transition of the mixture toward the homogeneous zinc ferrite phase. Kittel and Hüttig[14] have observed a value of about 140 × 10^{-6} for the magnetic susceptibility of zinc ferrite at 25°. If Wiedemann's law is followed, then we would expect the mixture to approach this value as the reaction proceeded. With samples heat treated in excess of 750°, the magnetic susceptibility measured at 25° was in excess of 100 × 10^{-6}, however, these materials are in the region of ferromagnetism and it is difficult to interpret the data without knowledge of the variation of the observed susceptibilities with magnetic field strength.

Discussion

It is interesting to note that although there are a great number of studies on the decomposition of nitrous oxide over mixed oxide catalysts reported in the literature, there were none found that reported quantitatively the decomposition over pure iron oxide in spite of the fact that this material was used as a component in a number of the mixed catalysts employed. The results of this study indicate that α-Fe_2O_3 *as prepared for the experiments mentioned previously* is a very active catalyst, however, further thermal annealing decreased this activity considerably. The surface area of the material was reduced by a factor of about fifty during this thermal treatment, but we are not in a position to state whether the resultant decrease in activity was due to this change or some other such as localized conditions of strain in the ferric oxide lattice. The data indicate that the reaction rate is independent of surface area in the range of from twenty to forty-three square meters per gram but it must be conceded from the nature of the reaction that there is a lower limit of surface below which the extent of the solid interface is one of the rate controlling factors.

The results of the investigation with equal molar mixtures of ZnO and α-Fe_2O_3 as catalysts for the decomposition of nitrous oxide do not agree with the results published by Hüttig and his co-workers.[7]

These workers have studied the variation of several properties with the pretreatment temperature of mixtures of α-Fe_2O_3 and ZnO. Hüttig indicates that the catalytic efficiency shows maximum activity after six hours pre-treatment at about 410° and also 650° with a distinct minimum activity at 500°. The magnetic susceptibilities and surface areas show corresponding irregularities. The maximum catalytic activity at 650° was attributed to an active phase intermediate between the mixture and the compound zinc ferrite.

Surface determinations made by Hüttig were conducted by measuring the adsorption of high molecular weight dyes. It is questionable whether this procedure yields a surface area which is representative of that surface available to a small molecule like nitrous oxide.

Hüttig included results obtained from mixed oxide catalysts with pre-treatment temperatures as low as 300°, however, these materials were heated an additional two hours at 500° prior to taking any data during the catalytic efficiency determination.[15] The magnetic susceptibility measurements were made on a portion of the mixture without this additional two hours at 500°.

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[13] Herroun and Wilson, *Proc. Phys. Soc.* (*London*), **33**, 196 (1921).

[14] Kittel and Hüttig, *Z. anorg. allgem. Chem.*, **210**, 26 (1933).

[15] Hüttig, Tachakert and Kittel, *Z. anorg. Chem.*, **223**, 241 (1935).

Catalytic efficiencies were obtained in this study as soon as temperature equilibrium was reached and it has been shown that magnetic changes occurred during this short interval of time even for the mixed catalyst with a pre-treatment of 6 hours at 670°. On this basis it does not seem reasonable to attach any significance to Hüttig's results for α-Fe_2O_3–ZnO catalysts which were pretreated below 500° and it is not surprising to find that our results do not agree with his above 500°; in particular, no indication of an active intermediate phase can be found in the present experimental results as the maximum in catalytic activity for a pretreatment temperature of 650° was not observed.

If we assume, as Hüttig did, that upon the formation of zinc ferrite from the two solid oxide components, the mobility of the ferric oxide is greater than that of the zinc oxide, then the ferrite structure would be formed by the diffusion of the ferric oxide into the zinc oxide lattice, the diffusional rate increasing in a regular manner with temperature. Similarly, the decrease in surface of the finely divided components should follow from the diffusion of ferric oxide into zinc oxide and be augmented by the simultaneous coagulation of associated particles. The rate of this phenomenon should likewise be a regular function of temperature. It is not possible at present to attribute the catalytic efficiency of these mixtures to the extent of total surface area exposed, to the extent of α-Fe_2O_3 oxide remaining as such in the mixture or to the decrease in structural strains which the increasing temperature treatments would cause, but any of the three effects offer a logical explanation of the regular decrease in catalytic efficiency with pretreatment temperature.

The physical dilution of the α-Fe_2O_3 with inactive ZnO, prior to any heat treatment, should reduce the time for which the gases were in actual contact with the α-Fe_2O_3, though a calculation of the decrease in efficiency to be expected would hardly be justified in view of uncertainties in the way the two materials would pack together, and in the extent of change in the mixture during the efficiency measurement at 500°. Actually, Fig. 2 shows that to obtain a given efficiency the contact time for the mixture was about four times that for the pure α-Fe_2O_3.

It has been pointed out that the magnetic susceptibility of the catalyst mixtures changed appreciably during some of the tests conducted. This observation points to the danger of correlating the catalytic efficiency of such mixtures with magnetic susceptibility measured at room temperature on a separate portion of the same mixture. Unless such correlations can be assigned to significant changes in the magnetic susceptibility measured simultaneously or consecutively they are not felt to be justifiable. No such correlation of catalytic efficiency to magnetic changes in the catalyst was found in this study. However, the value of the magnetic susceptibility measurements to indicate physical or chemical changes in the solid catalyst phase is readily apparent.

CORVALLIS, OREGON RECEIVED JANUARY 29, 1951

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

II. The Efficiency of the Primary Photochemical Process for Halogens in Water. The Photochemical Reaction of Mn(II) and Br_2

BY AARON C. RUTENBERG AND HENRY TAUBE

The quantum yields of the photoreaction of Br_2, Br_3^- and Br_2Cl^- with Mn(II) in the presence of pyrophosphate under a variety of conditions have been measured. The kinetic behavior of the system indicates that the quantum yields are the values of the primary efficiency for the absorbing substances. The primary efficiencies for the three substances at 19° and λ = 4360 Å. are 0.043, 0.122 and 0.142, respectively. The primary efficiency increases with temperature, the energy per quantum, and for Br_3^-, with increase in concentration of Br^-. The activation energies for Br_2 and Br_3^- are very nearly the same, about 7 kcal. An interpretation is given of the effect of bromide ion on the primary efficiency, and of the effect of changing temperature, wave length and ionic strength. Data for other halogens in water are also discussed.

The chemical method described in an earlier paper[1] for measuring the efficiency of the primary photoreaction for chlorine in water has been applied to bromine in water solution. The reducing agent Mn(II) in the presence of pyrophosphate serves as an efficient reactant for the primarily produced species also in the bromine system.[2] The results of experiments performed with light of wave lengths 4360 Å. and 3650 Å. with bromine (and derivatives) as absorbing species are presented and discussed. Some discussion is also made of observations recorded for chlorine and I_3^- as absorbing species.

Experimental

The general procedure described in the earlier paper[1] was followed in the present study. The extent of reaction was measured by iodimetric determination of the amount of manganic ion formed, after bromine was extracted with carbon tetrachloride.

The Br_2–Mn(II) system is much more manageable than is the Cl_2–Mn(II) system previously described. Thermal reactions were found to make negligible contributions to the over-all change under the experimental conditions, and no corrections were necessary for hydrolysis of the halogen. In addition, the absorption by bromine species was so high relative to that of manganipyrophosphate that the correction due to the inner filter effect of this product was always slight, amounting to only 3% in the most extreme case. Duplicate experiments agreed to better than 2%. The absolute values of quantum yield are considered to be accurate to 5%.

The decadic extinction coefficients for Br_2 at the wave lengths 4360 Å. and 3650 Å. were found to be 127 and 145, respectively; for Br_3^- at the same wave lengths, 183 and 974, respectively. Some measurements of the extinction coefficients of Br_2 in 3 *M* NaCl and 0.1 *M* $HClO_4$ at λ = 4360 Å. were also made. The results were

$(Br_2) \times 10^3$	2.32	3.51	5.32	7.25
$\alpha_{\Sigma Br_2}$	93	99	107	112

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[1] Rutenberg and Taube, THIS JOURNAL, **72**, 5561 (1950).

[2] Taube, *ibid.*, **70**, 3931 (1948).