[Contribution from the Chemical Laboratory of Harvard University]

THE EFFECT OF WATER AND OF CARBON DIOXIDE ON THE CATALYTIC OXIDATION OF CARBON MONOXIDE AND HYDROGEN BY OXYGEN

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Received October 27, 1924 Published January 8, 1925

The accelerating effect of minute traces of water or, conversely, the retarding effect of extreme dryness, on many gaseous as well as liquid reactions is a well recognized phenomenon.[1] Yet occasionally small amounts of water—amounts, however, usually greater than the minute traces just mentioned—exert the reverse effect; that is, they retard rather than accelerate reactions. Instances of this kind occur in the synthesis of ammonia in the presence of iron and other catalysts;[2] in the reduction of copper oxide by hydrogen, where moisture appears to prolong the so-called induction period;[3] and in the combination of hydrogen and oxygen in the presence of platinum.[4] Another and particularly interesting instance of this sort is observed in the catalytic oxidation of sulfur trioxide by gaseous oxygen in the presence of various oxide catalysts.[5] Here both effects are exhibited; when moderate amounts of water are present the catalysts are quite inactive; with better drying, such as can be secured with concd. sulfuric acid, a maximum activity is attained, while with rigorous drying, by the use of phosphorus pentoxide, the catalysts become decidedly less active. A final instance, especially pronounced, is the retarding effect of water on the oxidation of carbon monoxide and hydrogen by oxygen gas in the presence of the catalytic mixture of manganese dioxide and cupric oxide known as Hopcalite.[6] Here, amounts of water vapor as small as 0.1% in the gas mixture produce a noticeable retardation and, indeed, an efficient dryer has to be provided for mine, fire and similar rescue masks containing Hopcalite and it is the exhaustion of this dryer rather than of the catalyst which sets a limit to the life of the mask.

In all of these instances the reactions are catalytic in nature and the retarding effect can evidently be explained by assuming that in some way the water has lessened the activity of the catalyst. This reduction of

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[1] *J. Chem. Soc.*, **65**, 611 (1894); **81**, 1272 (1902).

[2] Larson and Tour, *Chem. Met. Eng.*, **26**, 650 (1922).

[3] Pease and Taylor, This Journal, **43**, 2179 (1921); **44**, 1637 (1922).

[4] Bodenstein, *Z. physik. Chem.*, **46**, 725 (1903).

[5] Lunge and Pollett, *Z. angew. Chem.*, **15**, 1105 (1902). Küster, *Z. anorg. Chem.*, **42**, 460 (1904).

[6] (a) Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920). (b) Rogers, Piggot, Bahlke and Jennings, This Journal, **43**, 1973 (1921). (c) Merrill and Scalione, *ibid.*, **43**, 1982 (1921). (d) Lamb, Scalione and Edgar, *ibid.*, **44**, 738 (1922). (e) Almquist and Bray, *ibid.*, **45**, 2305 (1923). (f) Whitesell and Frazer, *ibid.*, **45**, 2841 (1923).

activity could take place in a number of ways: (1) the water might be adsorbed as such on the catalyst and thus hinder the access of the reactants to, or the escape of the products from, the catalyst surface; (2) the water might react stoichiometrically with all or a part of the surface layer of the catalyst to form a layer of inactive material which would behave similarly to the layer of adsorbed water; (3) the water vapor might absorb the active radiation or the electrons emitted from the catalyst, or it might react with the activated molecules, ions or atoms of the gases near the catalyst surface and so diminish the number of reacting particles; (4) more than one of these effects might be simultaneously operative.

The first requisite in the elucidation of this phenomenon is accurate data as to its magnitude and the effect of various factors upon it. We have, therefore, secured such data for the effect of water on the oxidation of carbon monoxide by oxygen gas in contact with Hopcalite. Such data have a practical value as well, in view of the above-mentioned effect of moisture in many of the industrial uses of this catalyst. We have at the same time secured similar data for the oxidation of hydrogen by oxygen in the presence of Hopcalite.

Specifically, our first task was to measure accurately the retardation produced by water over as wide ranges of temperature and of water content of the gas as was feasible; our second was to correlate retardation of catalytic activity with the surface water content of the catalyst.

Variation of the Catalytic Activity with the Temperature and with the Water Content of the Gas

Some measurements of the retarding effect of water vapor on the catalytic oxidation of carbon monoxide and hydrogen have already been made.[7] In these measurements a dilute mixture of the combustible gas with air containing various amounts of water vapor was passed over the catalyst, and the fraction of the gas oxidized was ascertained. We have followed much the same procedure with various added refinements over the temperature range of 25–100° for carbon monoxide, and 55–140° for hydrogen, and over the range of partial vapor pressures of water from 0 to 50 mm. of mercury. Our standard gas mixture, containing 0.25% of either carbon monoxide or hydrogen, obtained by means of suitable flowmeters, was charged with the desired amount of water vapor and was drawn by suction through a carefully thermostated reaction tube containing the catalyst. The partially oxidized gases were then drawn through a calorimetric analyzer and the residual content of carbon monoxide or hydrogen was thus ascertained. The more important details of the apparatus, at least in so far as they differ from those previously described, are given below. The general arrangement of the apparatus is shown in Fig. 1.

[7] Ref. 6 c. Ref. 6 d. Ref. 6 e, p. 2317.

Preparation of the Carbon Monoxide and Hydrogen.—The carbon monoxide was prepared by dropping formic acid into concd. sulfuric acid at 100°. The evolved gas was passed through a tower containing beads wet with a 10% solution of sodium hydroxide and then stored over water in a large carboy. From this stock supply sufficient gas was removed from time to time to afford about 100 liters of a 5% mixture with air, which was stored in a large copper-lined, water-sealed gasometer. In use, this gas mixture was drawn through a tower containing glass beads moistened with concd. sulfuric acid, then through a flowmeter, and finally into a diluting stream of similarly dried air. The dilute gas then passed through a second flowmeter, so that its approximate composition was known from the composition of the gas in the gasometer and the

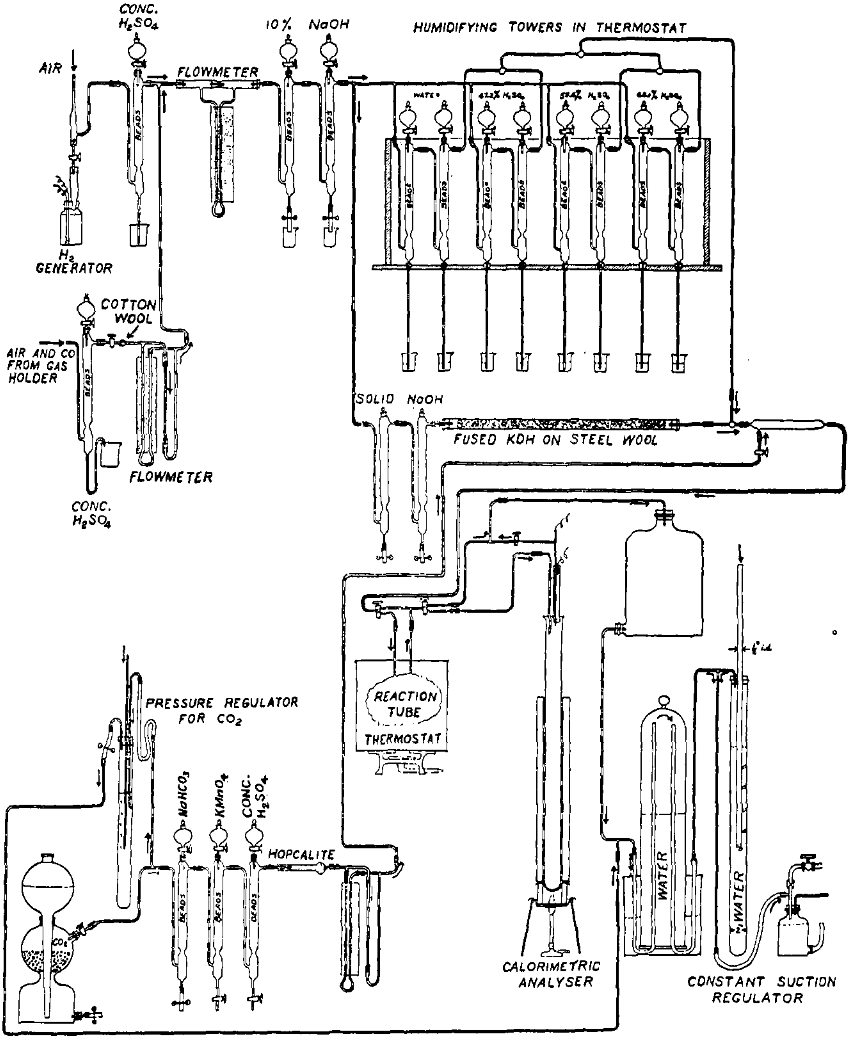

Fig. 1.

readings of the flowmeter, which had been calibrated with dry air under the conditions of use by the method of water displacement. The composition was checked by analyses of 500cc. samples by the iodine pentoxide method, the liberated iodine being titrated with 0.002 *N* sodium thiosulfate solution.

The hydrogen when required was added to the air stream by means of an electrolytic generator (Fig. 1) which discharged into the line just ahead of the first drying tower. The electrolyte was 10% chloride-free sodium hydroxide solution. The electrodes were of platinum, and the current was furnished by a large storage battery, and was controlled by means of a rheostat and a shunted millivoltmeter. There was very little gas space in the generator. The 10 × 1.5-cm. exit tube was filled with moistened beads, in order to catch the spray of electrolyte which otherwise was carried along with the gas stream. This exit tube was connected with the air line through a capillary stopcock which prevented any entry of air into the generator and any considerable lag in the response of the calorimetric analyzer to variations in the electrolyzing current. The whole generator, up to the capillary tube, was kept immersed in a large jar of water. The readings of the millivoltmeter were checked by means of a silver coulometer.

Purification and Humidification of the Gas Mixture.—After the diluted gas mixture had been drawn through the main flowmeter, it passed through two Emmerling towers whose beads were moistened with a 10% solution of sodium hydroxide supplied from dropping funnels at the top. From here the gas mixture on its way to the catalyst could be passed either through a rigorous drying system, or through a humidifying system. The drying system consisted of two towers in series packed with sticks of sodium hydroxide, followed by a Pyrex glass tube 60 × 2.5 cm. packed with wads of steel wool which had been dipped in molten potassium hydroxide. The humidifying system consisted of a manifold leading to four series-pairs of Emmerling towers, filled with beads and completely submerged in a large water thermostat. The towers were provided with dropping funnels from which the humidifying liquid was fed at 10-minute intervals, and with trapped outlets extending through the bottom of the thermostat from which the liquid could escape. The first tower in each pair was thoroughly flushed before every new run. A second manifold, almost wholly submerged in the thermostat, connected the exits of the towers with the catalyst tube. At high humidities its emergent part was kept hot enough to prevent any condensation.

By a proper manipulation of the stopcocks in this system the gas mixture could be passed through any one of the four pairs of towers. The solutions used were 22.74%, 47.10%, 58.55% and 68.04% sulfuric acid, and sometimes distilled water, and the vapor pressures of water from them at various temperatures were read from the convenient curves of R. E. Wilson.[8]

The Catalyst Reaction Tube.—The dry or suitably humidified gas mixture passed to the catalyst reaction tube. This was of a special design,[9] since previous measurements indicated that because of the considerable heat evolved, and the low thermal conductivity of Hopcalite, a temperature rise of as much as 3.0° would occur with 0.25% carbon monoxide at space velocities of 7500 per hour in a copper tube of 10mm. bore. It was not feasible to attempt a bore of less than 5 mm., because of possible channeling along the walls and difficulties in filling. Resort was, therefore, taken to a tube of annular cross section made of two concentric thin-walled copper tubes, Fig. 2. The diameter of the inner tube was 7.5 mm., of the

[8] Wilson, *J. Ind. Eng. Chem.*, 13, 326 (1921).

[9] Ref. 6 d, p. 754.

outer 16 mm., the width of the annular space was about 4.25 mm., and its cross sectional area, therefore, 1.56 sq. cm. The layer of catalyst was 4.0 cm. deep, and its volume, therefore, 6.25 cc. Three fine copper—Advance thermojunctions projected halfway through the catalyst at heights of 5, 20 and 35 mm. from its lower surface, and their leads issued through small side tubes soldered to the catalyst tube. All of this tube to above the level of the catalyst was submerged in a thermostat bath whose temperature could be adjusted over the range of 25–140°, and which kept constant to within a few hundredths of a degree. A small centrifugal pump, integral with the stirrer of the thermostat, pumped liquid from the thermostat bath upward through the axial cavity of the catalyst tube. The gas mixture was brought accurately to the temperature of the thermostat by passing through 2.1 meters of small copper tubing spirally arranged and submerged in the bath of the thermostat, and entered the catalyst tube just below a perforated copper disk on which the catalyst rested.

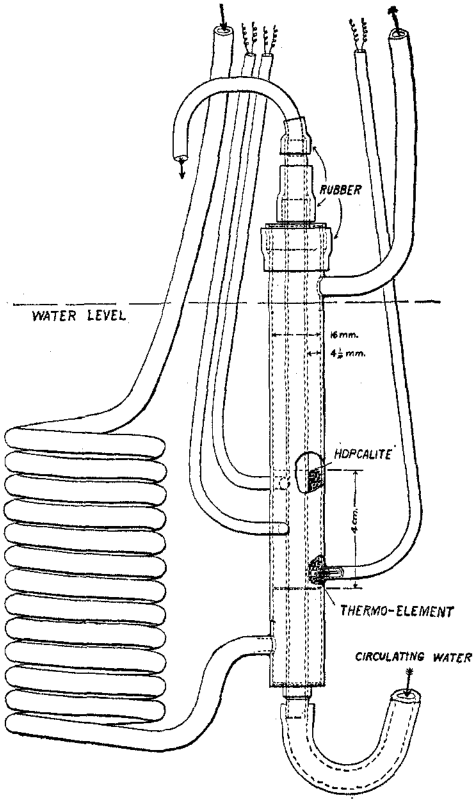

Fig. 2.—Reaction tube.

The indications of the thermojunctions under typical conditions with 0.20% carbon monoxide at a space velocity of 4800 are shown in Fig. 3. A dry gas mixture was used during the first two hours. As can be seen from the curves, the efficiency of combustion was practically 100% during this interval, and practically all of the combustion occurred near the point of entry and the bottom thermojunction, with a maximum temperature rise at this point of 0.8°. When 1.6 mm. of moisture was introduced after two hours, a momentary further rise of 0.2° occurred at the lowest thermojunction, evidently as a result of the heat of adsorption of the water, followed by a sharp drop in temperature due to the upward movement of the zone of combustion. The middle and top thermojunctions also show the upward movement of the hot zone and the final, nearly constant temperature throughout the catalyst, a result both of the wider distribution of the reaction zone and the lessened efficiency of the catalyst.

These curves show that in this reaction tube under these conditions, the temperature of the catalyst is not in any case more than 1° above the prevailing temperature in the thermostat bath.

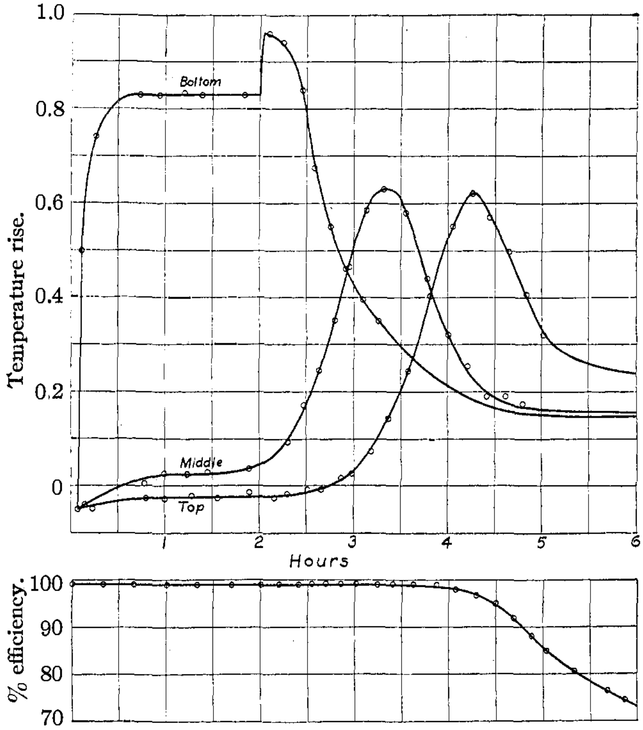

Fig. 3.—The upper curves show the temperature rise at different levels in the mass of catalyst when 0.2% carbon monoxide is passed at 40°. After 2 hours, moisture equivalent to an aqueous tension of 1.6 mm. was added to the hitherto dry gas. The lower curves shows the corresponding catalytic efficiencies.

The Calorimetric Analyzer.—The gases issuing from the reaction tube could, by an appropriate setting of the stopcocks, be passed to the pressure-regulating devices, either directly, or first through a calorimetric analyzer (Fig. 1) for an analysis of the content of combustible gas. This analyzer was that of Lamb and Larson,[10] with slight modifications similar to those introduced by Larson and White.[11] In addition, we found it advantageous to place the catalyst in a short reverse bend of the inner tube so that the combustible gas enters the catalyst at the top rather than at the bottom,

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[10] Lamb and Larson, This Journal, 41, 1909 (1919).

[11] Larson and White, *ibid.*, **44**, 20 (1922).

and thus escapes any premature combustion on the fine platinum dust which falls from the catalyst, with consequent loss of heat. We also found it advantageous to maintain the asbestos jacket of the outer tube at a temperature about 50° below the boiling point of the diphenylamine by means of electrically-heated resistance wire, to avoid the necessity of a too intensive heating of the liquid diphenylamine. Even then, if a precision of one part in 500 was to be maintained, we found it necessary to renew the diphenylamine frequently.

The galvanometer had a sensitivity such that with 300–400 ohms in series 0.25% of carbon monoxide gave a deflection of 40 cm. on the scale, which could be read to a third of a millimeter. The full deflection under these conditions was attained in less than a half minute.

The analyzer was calibrated for various contents of carbon monoxide and hydrogen at various rates of flow. At a constant rate of flow the readings were found to be proportional to the content of carbon monoxide within the accuracy of the flowmeter settings (one part in 500). With constant composition but varying rate of flow the deflections were nearly proportional to the absolute amounts of carbon monoxide reaching the catalyst per unit of time. In agreement with this, it was found that when the amount of carbon monoxide entering the air stream per minute was kept constant, the rate of flow of the gas mixture could be varied from 490 cc. to 510 cc. per minute, that is, by 4%, without producing a noticeable variation in the galvanometer deflection.[12]

The Pressure Regulator.—The gases issuing from the calorimetric analyzer entered an 8-liter bottle which served as a buffer or ballast, and from it entered the top of a combination air and water cushion (Fig. 1) of about 300 sq. cm. cross section, similar to that described by Bohart and Adams.[13] From here they went directly to the water aspirator pump, and were discharged through a water-sealed exhaust into a pipe opening out-of-doors. Connected in parallel to the suction line of the pump was a water seal with an inlet tube of 12 mm. bore which could be moved up and down, and a precise regulation of the suction thereby obtained. The water cushion and buffer smoothed out the effects of the bubbling in this regulator so completely that no oscillation of the manometers in the flowmeters could be detected.

Analysis of the Hopcalite.—The Hopcalite was a sample of a commercial product kindly furnished us by the Mine Safety Appliances Company of Pittsburgh, Pennsylvania.

(a) The copper was determined iodimetrically in a solution of the Hopcalite in hydrochloric acid. (b) The manganese dioxide was determined by triturating the Hopcalite with a solution of 3 g. of potassium iodide and 10 g. of sodium acetate in 10 cc. of 10% acetic acid. The concentration of iodine was kept low by the gradual addition

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[12] A similar situation is revealed by an examination of the calibration data of this analyzer by Larson and White (Ref. 11) using small quantities of oxygen in hydrogen. These data, recalculated to a fixed rate of flow of oxygen per second and plotted, show a change of only one part in 350 for a change of 490 cc. to 500 cc. per minute total flow.

[13] Bohart and Adams, THIS JOURNAL, **42**, 523 (1920).

of a standard solution of thiosulfate. Finally, 5 cc. of diluted sulfuric acid was added and the titration completed. Deductions were made for the amounts of copper and ferric iron present. (c) The total manganese was determined by dissolving the Hopcalite in hydrochloric acid, evaporating with sulfuric acid, nearly neutralizing with sodium hydroxide, adding finally an excess of zinc oxide, and titrating an aliquot portion of the supernatant liquid with permanganate after the addition of more zinc sulfate. (d) Iron was determined by the basic acetate method. (e) The combined calcium and magnesium were determined, after removal of the heavy metals, by precipitation with an aqueous alcoholic ammoniacal solution of ammonium carbonate and ignition. (f) Carbon dioxide was determined by boiling with dil. sulfuric acid and passing the dried gas through potassium hydroxide with a current of air. (g) The alkalies were determined as sulfates and computed to potassium oxide. (h) Chlorine was absent. (i) Water was determined by ignition to a dull-red heat, and collecting the water in a U-tube containing sulfuric acid. The collected results are given in Table I.

TABLE I

ANALYSIS OF HOPCALITE

	MnO_2	MnO	CuO	Fe_2O_3	CaO + MgO	K_2O	CO_2	SO_3	H_2O	Total
%..................	60.1	3.0	22.4	0.6	1.2	1.6	0.5	0.5	10.3	100.2
Rel. no. of molecules..	1.0	0.06	0.43	0.006	...	0.024	0.015	.009	0.80	2.4

It is evident that this is a nearly 3:1 mixture of partially hydrated manganese dioxide and copper oxide with some alkali and alkaline earth sulfates, carbonates and oxides presumably present as impurities originating in the manufacture of the material and adsorbed on the manganese and copper oxides. The potassium oxide is evidently substantially equivalent to the carbon dioxide and the sulfur trioxide.

Execution of the Measurements.—The calorimetric analyzer and the thermostat were first adjusted to the desired temperature. Dry air was then passed to the former at the rate of 500 cc. per minute and the reading of the galvanometer taken. The small deflection was found to remain constant for several hours, but it was usually taken again at the end of the run. The supply of 0.25% carbon monoxide was then passed to the analyzer at the same rate of flow, and the constant deflection of the galvanometer again observed. This gas mixture was then passed through the catalyst tube and thence to the analyzer and readings were taken at five-minute intervals. These readings, in conjunction with the initial reading and the calibration curve of the analyzer, gave at once the fraction or percentage of gas oxidized in passing through the catalyst, that is, the efficiency of the catalyst under these conditions. In general, however, except when the efficiency was below 5% or above 95%, we considered it more certain, after having taken the galvanometer reading on the gas mixture which had passed through the catalyst, to pass the original gas mixture directly to the analyzer, that is, to shunt it around the catalyst tube and then to adjust the supply of carbon monoxide so that substantially the *same deflection* was obtained as with the gas mixture which had passed through the catalyst. From this reading and that of the carbon monoxide flowmeter the percentage oxidation could be accurately obtained.

Similar measurements were then made with the admixture of various amounts of water vapor. A longer time was required to reach a constant reading with moist than with dry mixtures. This time varied from several hours with low humidities and temperatures down to half an hour or less with the higher humidities and temperatures.

The results could, in general, be duplicated to within 1%. Prolonged exposure to high humidities tended to decrease the efficiency of the catalyst when tested again at lower humidities, but prolonged operation on the dryer gas brought about recovery. Water evidently penetrates the more deep seated parts of the catalyst granules and diffusing slowly to the surface lowers the activity of the catalyst at the lower humidities until it has all been eliminated.

TABLE II

TYPICAL RESULTS

Temperature = 40°. Humidity = 10 mm. Hg. Flow = 500 cc. per min. 4-cm. deep layer of Hopcalite.

Time	Galvanometer reading			
			Corrected	
	Direct	Shunted	Shunt	Zero
10 A.M.	No CO. CO FLOWMETER = 0			
1:16 P.M.	−2.27	−2.42	0.15	...
19	−2.27	−2.37	.10	...
22	−2.25	−2.35	.10	...
1:25	0.25 CO THROUGH CATALYST. CO FLOWMETER = 11.00			
1:45	14.10	−2.07	16.17	16.07
2:00	14.80	−2.20	17.00	16.90
2:15	15.17	−2.02	17.20	17.10
2:30	15.30	−2.00	17.30	17.20
2:45	15.85	−1.77	17.62	17.52
3:00	16.42	−1.45	17.87	17.77
3:15	16.50	−1.32	17.82	17.72
3:25	16.55	−1.32	17.87	17.77
3:35	16.45	−1.45	17.90	17.80
3:50	16.30	−1.60	17.90	17.80
	CO-AIR DIRECT TO ANALYZER. CO FLOWMETER = 7.48			
4:00	15.30	−1.62	16.92	16.82
4:05	15.32	−1.62	17.15	17.05
4:10	15.57	−1.60	17.17	17.07
4:15	15.57	−1.55	17.12	17.02

The corrected deflection reached as a steady state (17.80) divided by the corrected deflection of the gas when flowing directly to the analyzer (17.05) and multiplied by the ratio of the flowmeter readings $\left(\frac{7.48}{11.00}\right)$ and by 100 gives the percentage of unoxidized carbon monoxide, or 71.1% and therefore an efficiency of 28.9%.

The Results.—Typical results obtained with one sample of catalyst with carbon monoxide at 40° and at a vapor pressure of water equivalent to 10 mm. of mercury are presented in full in Table II as illustrative. They show the concordance of the measurements, the time of adjustment, and illustrate the method of calculation. The results, as a whole, are presented graphically in Figs. 4 and 5. They bring out clearly the marked effect of temperature and of the partial vapor pressure of water on the activity of the catalyst. They also show the decidedly greater activity of the catalyst toward carbon monoxide than toward hydrogen, thus indicating that by means of Hopcalite a quantitative separation of a little carbon monoxide from air containing an equal amount of hydrogen can be obtained, with little or no action on the hydrogen at all temperatures between 25° and 100° by a suitable admixture of water vapor. This supplements the similar method previously worked out for the quantitative separation of a little carbon monoxide from hydrogen containing a little oxygen.[6d]

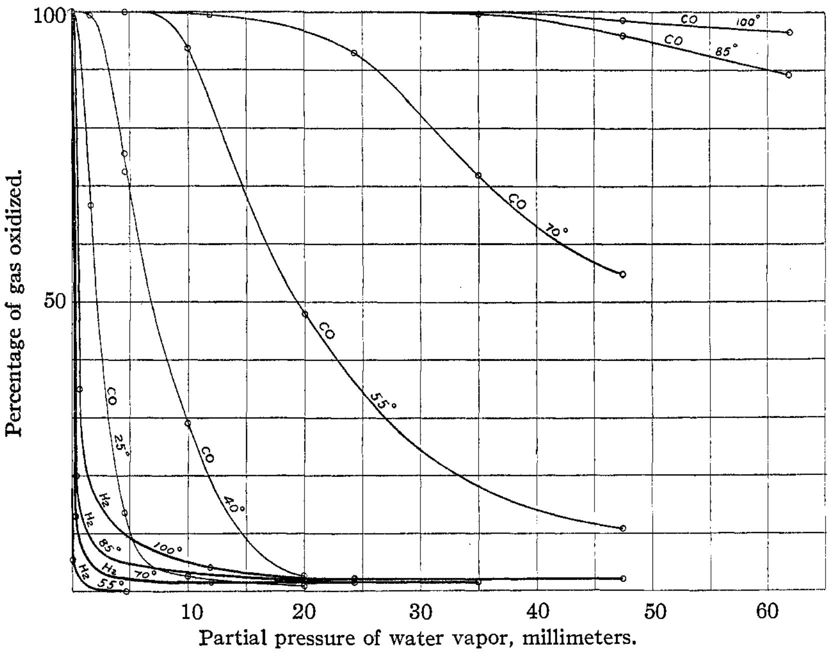

Fig. 4.—Effect of moisture on oxidation of 0.25% CO and 0.25% H_2 when passed through 6.25 cc. of Hopcalite at a space velocity of 4800.

Correlation of Catalytic Activity and Water Content of Catalyst

The above measurements suffice to show the effect of water in the vapor phase on the catalytic activity. Information regarding the amount of water on the surface of the catalyst at various temperatures and activities was equally desirable. We could devise no direct method of securing this information, and so resorted to the indirect method of equilibrating the catalyst with currents of air containing the same amounts of water vapor that were used in the above experiments but no carbon monoxide, and determining the water content of the catalyst as a whole from its increase in weight. By this prolonged treatment the same moisture equilibrium which is rapidly established on the surface must be set up throughout the catalyst. The percentage water content of the whole must, therefore, be similar with such a highly porous substance as Hopcalite to that of the surface layers. This method of attack was found more feasible than to attempt a *simultaneous* determination of water content and catalytic activity, partly because of the experimental difficulties which the combined method would have involved, and partly because the adjustment of the moisture equilibria is very slow as compared with that of the catalytic equilibria—two or three days sometimes being required.

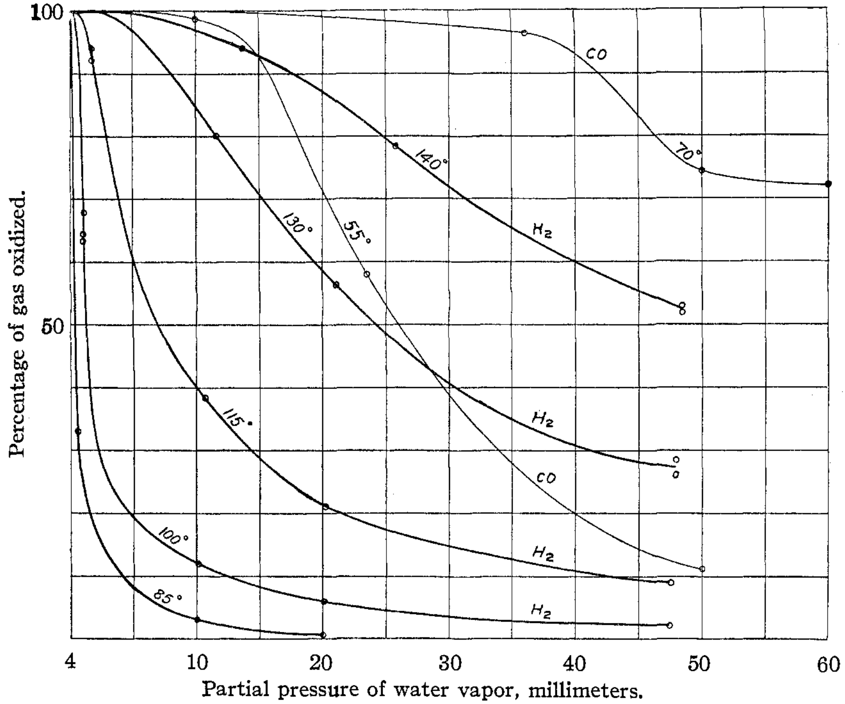

Fig. 5.—Effect of moisture on oxidation of 0.25% of CO and 0.25% of H_2 when passed through 8.3 cc. of Hopcalite at a space velocity of 3620.

The procedure was as follows. About 5 g. of the catalyst of known water content was placed in a glass tube A enclosed in the brass box B shown in

Fig. 6. The conditioned air entered this box after passing through a 4.5-meter coil of copper tubing submerged in the thermostat bath, flowed downward through the catalyst, and out through an exit tube fixed in the top of the brass box. The catalyst rested on a perforated porcelain disk covered with a matt of asbestos. This prevented the loss of any dust from the catalyst. The glass tube could be conveniently removed and weighed from time to time until a constant weight had been attained. The water content of a reference sample was determined by heating at 300° in a current of dry air in the right hand tube of Fig. 6, and collecting the water to constant weight.

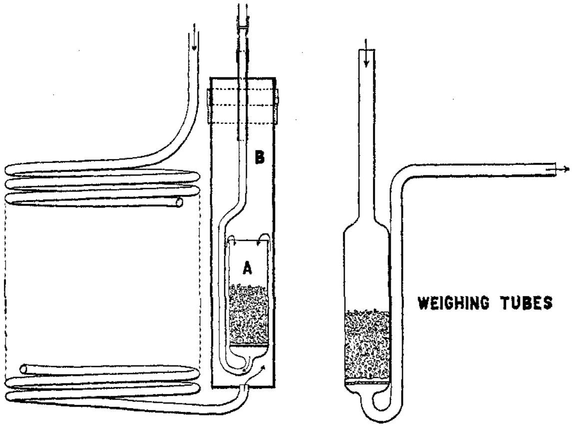

Fig. 6.

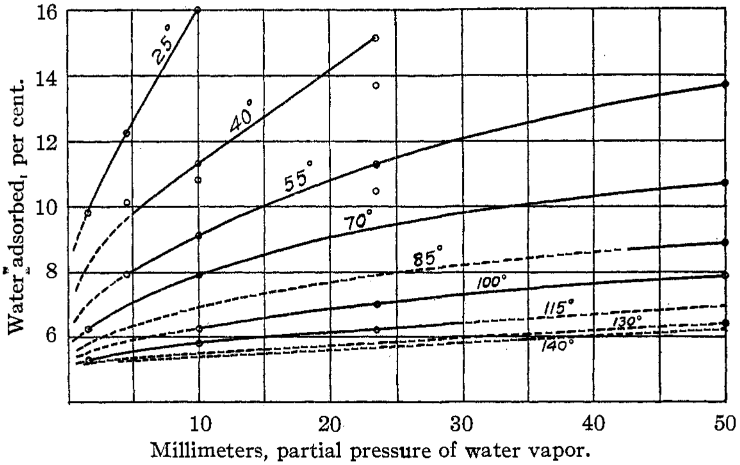

Fig. 7.—Adsorption of water from moist air by Hopcalite.

The results obtained, that is, percentages of water based on dry Hop-

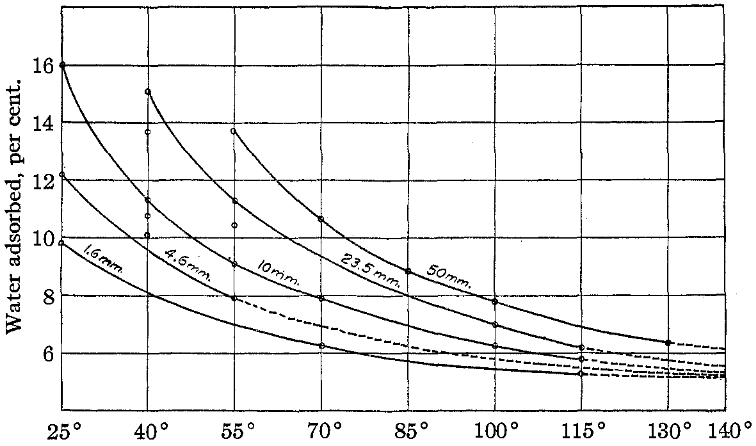

Fig. 8.—Adsorption of water from moist air by Hopcalite.

calite in equilibrium with various partial vapor pressures of water are shown in Figs. 7 and 8. Some of the equilibria were approached from above,

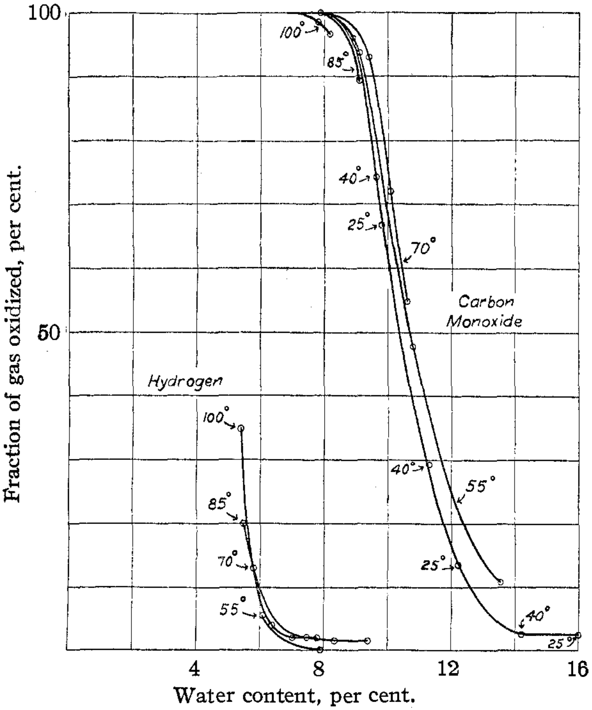

Fig. 9.—Catalytic efficiency of 6.25 cc. of Hopcalite. Space velocity = 4800.

some from below and some from both sides. The rate of adjustment was very slow, particularly at the lower humidities and temperatures. Moreover, exposure to the higher humidities and temperatures produced a decrease in the hygroscopicity of the catalyst at lower temperatures which apparently was not recovered on prolonged running. As a consequence, these data can hardly be considered reproducible to within less than ±1%, although their relative accuracy is probably somewhat greater.

To connect the water content of catalyst and the activity, we have read from Fig. 7 the water content and from Figs. 4 and 5 the catalytic activity corresponding to the same partial pressures of water vapor at various temperatures. In the case of hydrogen, allowance was made for the water produced in the catalytic oxidation. The resulting isotherms are shown in Figs. 9 and 10.

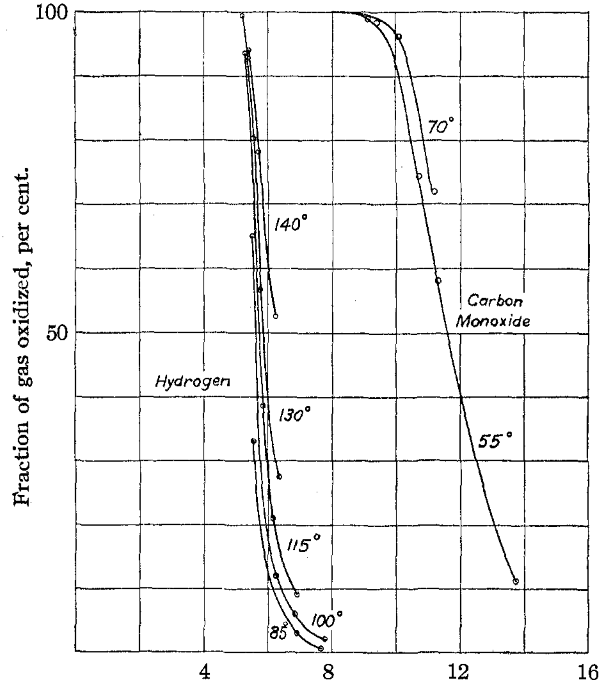

Fig. 10.—Catalytic efficiency of 8.3 cc. of Hopcalite, at a space velocity of 3620.

These isotherms are illuminating. Except at their lower ends they are almost coincident at all temperatures! This means that the activity of the catalyst is primarily governed by its water content and is only slightly dependent on the temperature. Stated in another way, a given amount of water-free catalyst produces a definite catalytic action which is only slightly increased by a rise in temperature.

To compare this slight effect of temperature with the effect of temperature on the activity of *dry* Hopcalite, we have dried a sample of Hopcalite very thoroughly, and have measured its activity at very high space velocities over the temperature range of 25–70°.

We used for this purpose a layer of Hopcalite 9 mm. deep in a copper tube of 6mm. bore, submerged together with its 4-meter preheating coil in the thermostat bath; 100 to 500 cc. of a dry 0.20% mixture of carbon monoxide and air was sent through the catalyst per minute, corresponding to a space velocity 5 to 25 times greater than we employed in our previously mentioned experiments.

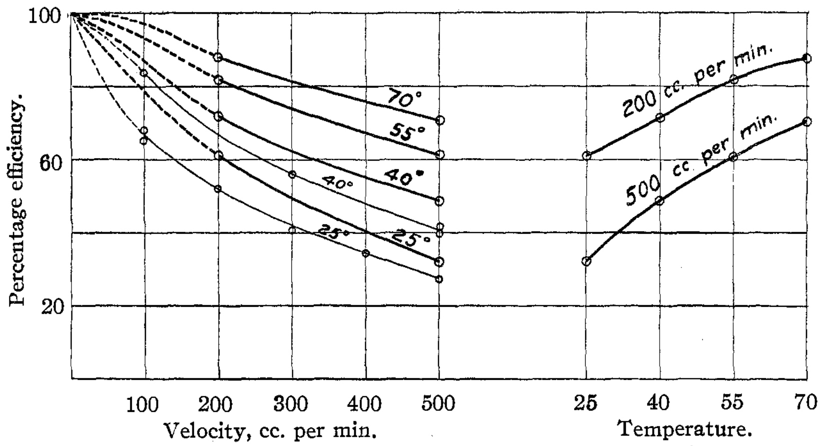

Fig. 11.—Influence of temperature and velocity of gas on efficiency of dry Hopcalite toward 0.25% carbon monoxide in dry air. The curves drawn lightly are for a different sample of catalyst.

The results for carbon monoxide are shown in Fig. 11. It can be seen from these curves that temperature has only a moderate effect on the activity of the catalyst; efficiencies in the neighborhood of 50% were increased by about 10% per 10° rise in temperature. The effect is, therefore, similar in magnitude to that shown by the curves in Figs. 9 and 10.

We may conclude, therefore, that the activity of the catalyst is primarily determined by its water content and only increases with rising temperature by an amount comparable with that characteristic of dry Hopcalite under similar conditions.

Our results can be expressed in a different way. It is evident from Figs. 9 and 10 that oxidation of the hydrogen and carbon monoxide is complete at about 5% and 8% of water, respectively, and then falls off rapidly, and practically ceases at 7% and 14%, respectively. This would mean that with hydrogen, for instance, so long as less than 5% of water is contained in the catalyst, oxidation is very rapid; enough unhydrated active molecules are present so that all of the hydrogen is oxidized. With further adsorption of water the remaining active molecules are soon eliminated and at 7% water content this elimination is complete. It is of interest to inquire as to the molecular ratios of these amounts of water to the various constituents of the Hopcalite. Seven per cent. corresponds to 1.25 and 0.5 molecules of water, respectively, per molecule of copper oxide and manganese dioxide; 14% to 2.5 and 1, respectively. On this basis, then, one could infer that hydrogen ceases to be oxidized as soon as all of the manganese dioxide is converted into $MnO_2.0.5H_2O$, while carbon monoxide ceases to be oxidized when all of the manganese dioxide is converted into $MnO_2.H_2O$.

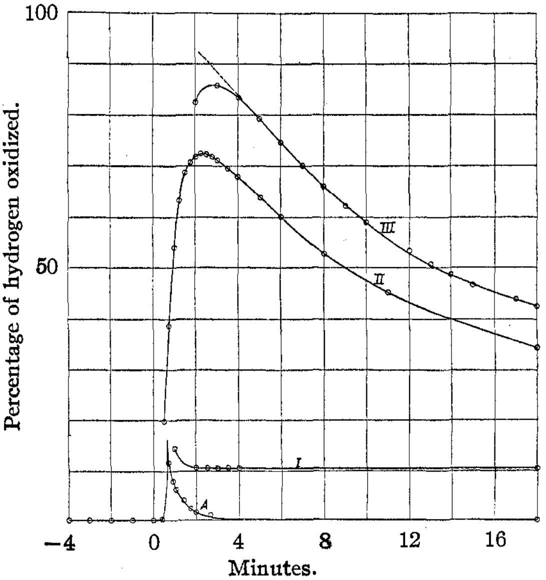

Fig. 12.—The activity of extra dry Hopcalite toward hydrogen at 27°.

It must be realized, however, that other than this probably fortuitous nearly integral relationship, there is no evidence for a definite chemical compound, as distinguished from an adsorbed layer of water.

Behavior of Very Dry Hopcalite

We were not able to obtain similar data for the effect of temperature upon the activity of dry Hopcalite toward dry mixtures of hydrogen and air, because the water formed vitiates the results. In the course of unsuccessful attempts to overcome this difficulty by rapid measurement and extrapolation to zero time, we discovered that thoroughly dry Hopcalite has an initial activity toward a dry mixture of hydrogen and air far greater than has been hitherto suspected. This is shown clearly by the data represented graphically in Fig. 12, which were obtained using 10.5 cc. of Hopcalite in a layer 6.75 cm. deep in the large reaction tube shown in Fig. 2, and a 0.24% mixture of hydrogen in air flowing at the rate of 500 cc. per minute (space velocity of 2860), at 27°. The instant when the hydrogen-air mixture was switched through the catalyst tube is taken as zero time. Curve A shows the results obtained with the reaction tube empty; Curves I, II and III, those obtained with samples of progressively greater dryness. No. I had been dried for three hours at 200°, No. II for five hours at 300°, No. III for 130 hours at 200°, in a current of dry air free from carbon dioxide.

Curve A shows a slight amount of combustion immediately after the switch has taken place, but this of course is only apparent and is due to the dilution of the hydrogen by the hydrogen-free air in the catalyst line. Sample I shows a slight initial activity of its catalyst beyond what could be explained by the dilution effect. This activity quickly dropped to about 10% and remained constant. Sample II shows a marked initial activity which, however, rapidly diminishes and evidently approaches that of Sample I, as the water produced in the reaction accumulates in the catalyst. Sample III shows a still greater activity; indeed, if account is taken of the depressing effect which the water formed must have exerted, even during the first two minutes, the initial activity of this sample must have been well over 90%.

Very dry Hopcalite is then decidedly active toward hydrogen even at 27°, so that the very great disparity which has been thought to exist between its activity toward hydrogen and that toward carbon monoxide has been exaggerated.

A similar high initial efficiency was then looked for in the case of the oxidation of carbon monoxide. This gas at a concentration of 0.20% at 25° and at ordinary space velocities is almost completely oxidized by Hopcalite, so that a space velocity of 114,000 per hour was adopted, the gas mixture being carefully dried and freed from carbon dioxide.

The results are shown in Fig. 13. Curve I was obtained at 25° with a sample of Hopcalite which had been dried for three hours at 200°; Curve II was obtained with the same sample at 40° on the following day; Curve III was obtained with the same sample after it had been further dried *in situ* for three hours at 200° in a current of dry air.

In every case a high initial efficiency is exhibited which gradually drops to a constant and much lower value. Carbon dioxide evidently is being adsorbed progressively by the catalyst, just as the water was in the case of hydrogen. The change is, however, much less rapid than with hydrogen, presumably because of the much less rapid and complete adsorption of the latter portions of the carbon dioxide as compared with the corresponding portions of the water vapor. The recovery of the Hopcalite on standing overnight, as shown in Curve II, is presumably due to the loss of carbon dioxide from the surface of the catalyst both by evaporation and by diffusion into the deeper portions of the catalyst granules.

It is clear from these results that in each case the product of the reaction markedly depresses the rate of the reaction, presumably because of its progressive adsorption. To see whether the reaction product as such has a special, specific depressing effect upon the velocity of the reaction that produces it, we have compared the effects of fresh additions of water, carbon dioxide and nitrogen on the activity of Hopcalite toward mixtures of hydrogen and air and of carbon monoxide and air after the catalysts have reached substantial equilibrium with the reaction products. For this purpose, we employed the reaction tube previously used for studying the change in the activity of dry Hopcalite with the temperature, and a layer of catalyst 17 mm. deep. This, with a flow of 500 cc. per minute, gave a space velocity of about 60,000 per hour. The carbon dioxide or nitrogen, each after suitable purification and drying, or the water vapor was introduced into the system just in advance of the catalyst tube. The temperature was 25° in the tests with carbon monoxide and 130° in those with hydrogen. This space velocity and these temperatures were chosen so that an efficiency of about 50% might be secured, at which efficiency any change in the activity of the catalyst should produce a maximum effect on the reading.

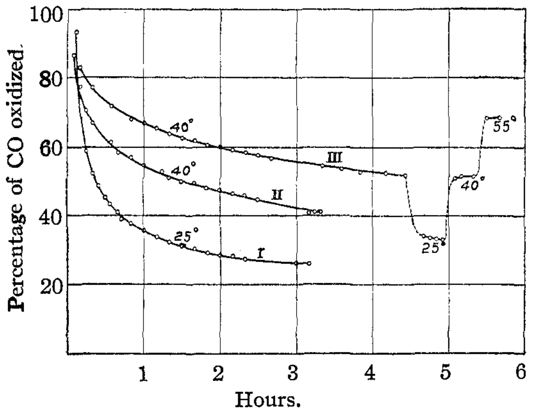

Fig. 13.

The results for both carbon monoxide and hydrogen are shown in Fig. 14. It is evident that the effect of three different admixtures is substantially the same with both gases. There is then no specific effect of the product of the reaction on the velocity of the reaction itself, at least under these conditions. The effect of nitrogen is negligible, that of carbon dioxide slight, and that of water pronounced. This is, of course, in agreement with the order of the boiling points and the degree of adsorbability of the three gases on various solids.

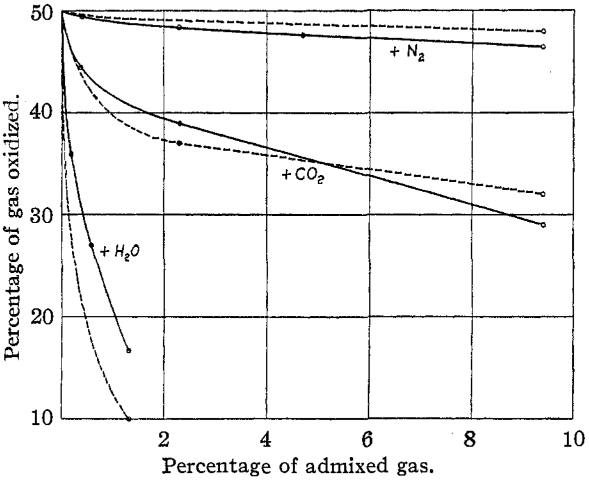

Fig. 14.—Full lines, 0.25% of CO at 25°; broken lines, 0.25% of H_2 at 130°.

Summary

1. The slackening effect of water vapor on the catalytic oxidation of carbon monoxide and hydrogen by the oxygen of the air in contact with Hopcalite has been carefully measured over a considerable range of temperatures and partial vapor pressures of water.

2. The water content of Hopcalite in equilibrium with moist air has been measured over this same range of temperatures and partial vapor pressures of water.

3. It has been found by combining the data obtained under (1) and (2) that, for a given equilibrium water content of the catalyst and hence presumably for a given water content of the catalyst surface, the activity is nearly independent of the temperature. The slightly greater activity at higher temperatures is no more than would be expected from the observed increase in activity of dry Hopcalite with increasing temperature.

4. It has been found that very dry Hopcalite has a considerable initial catalytic activity toward mixtures of hydrogen and air at room temperatures, an activity many times greater than has previously been observed. This activity drops in a few minutes because of the water produced by the reaction, to the usual very slight activity. A similar enhanced initial efficiency of Hopcalite toward a mixture of carbon monoxide and air and a

rapid decay of this activity were also observed. However, larger amounts of water vapor, of carbon dioxide and of nitrogen affected equally the activity of Hopcalite toward mixtures of hydrogen and air and of carbon monoxide and air, and to about the extent to be expected from the relative adsorbabilities of the three gases.

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NOTE

A New Reagent for Aluminum.—The dye aurin tricarboxylic acid[1] forms with aluminum salts a bright red lake which may be used as a test for aluminum ion. The difficulty with the attractive idea of using the property of lake formation as a test for aluminum has been that other metallic ions, particularly chromium, possess the same property. In this case interference by chromium is prevented by an unusual property of the aluminum lake, which when once formed in an acetic acid acetate buffer is not decomposed in any reasonable time when the solution is made alkaline with ammonium hydroxide, although it does not form in alkaline solution. The chromium lake, which resembles the aluminum compound in appearance, forms in an acetate solution, but is decolorized upon the addition of amonium hydroxide.

The test may be made on a supposed precipitate of aluminum hydroxide as follows. The precipitate is dissolved in 5 cc. of N hydrochloric acid, and 5 cc. of 3 N ammonium acetate and 5 cc. of a 0.1% solution of the ammonium salt of aurin tricarboxylic acid are added. After mixing to allow the lake formation to take place, the solution is made alkaline with ammonium hydroxide containing ammonium carbonate. A bright red precipitate persisting in the alkaline solution indicates the presence of aluminum.

Silicic acid and salts of bismuth, lead, antimony, stannic tin, mercuric mercury and titanium give white precipitates. Salts of cadmium, zinc, nickel, cobalt and manganese give no precipitate. Large amounts of alkaline earths give red precipitates, which are decolorized by carbonate ion. Ferric salts give a deep violet precipitate in the acetic acid solution, which is converted to a reddish-brown by ammonium hydroxide; but the separation of iron from aluminum by sodium hydroxide or peroxide is sufficiently complete and iron should not interfere. It is well to abandon the usual method of using porcelain for alkaline solutions, for while hot strong alkalies may dissolve more total substance from glass than from porcelain, they dissolve less aluminum. Phosphate in large excess prevents

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[1] No. 557, Schultz, "Farbstofftabellen," Berlin, 1923. The dye may be prepared easily by the second method of Ger. pat., 49,970 (1889), Friedländer II, 50. Extraction of the crude dye acid with hot water, solution in an excess of ammonium hydroxide and evaporation to dryness gives an ammonium salt of sufficient purity.