THE DECOMPOSITION OF ETHYLENE GLYCOL IN

THE PRESENCE OF CATALYSTS

BY

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Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

1933.

UMI Number: DP71116

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ACKNOWLEDGMENT

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INTRODUCTION

The increasing commercial demand for ethylene
glycol requires more efficient and less expensive methods
for its preparation. If its formation could be effected
from carbon monoxide and hydrogen, an important step
would have been taken to fulfill these requirements.

The present research was initiated in order to
determine the effect of various catalysts on the
decomposition of ethylene glycol into carbon monoxide
and hydrogen, the ideal reaction desired being,

$$2CO + 3H_2 = CH_2OH \ CH_2OH$$
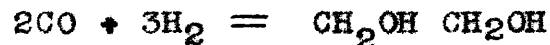
The kinetic view of equilibrium in a chemical reaction
shows that a catalyst which accelerates the rate of a
reaction in one direction must also accelerate the rate
of the reverse reaction. In more appropriate terms, a
catalyst which decomposes glycol into carbon monoxide
and hydrogen, may, under thermodynamically suitable
conditions, form glycol from these gases. The following
experiments, thus, have a practical interest in that
they represent a simple method for testing catalysts for
the formation of glycol from carbon monoxide and hydrogen,
without resorting to the use of costly and cumbersome high
pressure apparatus.

If the decomposition of glycol could be induced to

occur in accordance with the above equation, the
synthesis would be greatly facilitated by operating
under high pressure.

According to Parks and Huffman[1] the free energy
of formation of liquid glycol from its elements is,

$$F_{298} = -80,200 \text{ cal.}$$

and for gaseous carbon monoxide,

$$F_{298} = -32,700 \text{ cal.}$$

Consequently, for the reaction

$$2CO(g) + 3H_2(g) = CH_2OH\ CH_2OH(l)$$
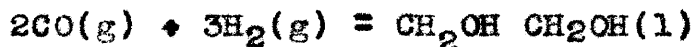
$$F_{298} = -14,800 \text{ cal.}$$

From a consideration of these thermodynamic data
the synthesis of glycol from carbon monoxide and hydrogen
becomes the problem of choosing the proper temperature,
pressure, and catalyst for carrying out this reaction.

This thermodynamic possibility may not be realized
in a practical way because of the many side reactions
which are possible in a system as complex as the one
under consideration. There is, nevertheless, nothing
thermodynamically unsound in attempting to devise a
method of carrying out the reaction.

REVIEW OF LITERATURE

Ethylene glycol is at present prepared on a commercial scale in most cases by reacting chlorine or hypochlorous acid and ethylene, and subsequently hydrolyzing the ethylene dichloride, or hydrogen by means of an aqueous solution of a chlorine acceptor at elevated temperatures, the main reaction resulting in the formation of glycol[2,3,4,5,6] In contrast there has been very little reported work on the catalytic synthesis of this glycol. The first method approaching a catalytic process is recorded in a patent granted to Hough[7]. In this method ethylene is reacted with chlorine and the Cl group of the ethylene dichloride thus formed, are substituted by OH groups under the influence of an iron oxide catalyst. Youtz[8] reports the electrolytic oxidation under high pressure of olefines to the corresponding glycols using caustic soda as the electrolyte. Recently Skarblom[9] has effected its formation by reacting ethylene, and oxygen with water in the presence of iodine, or a substance capable of readily liberating iodine and then combining with it again. Among the latter he mentions, hydrogen iodide, ethylene diiodide, potassium triiodide, and ferric iodide. The reaction is allowed to take place in a closed vessel at

a temperature below 50°C, and a pressure above atmospheric. The presence of a carrier, or an oxidation catalyst, for example, an iron or manganese salt, prevents the formation of by-products due to the generation of hydrogen iodide.

In the catalytic decomposition of ethylene glycol there has, also, been very little work reported. Sabatier[10], states that glycol heated at 400°C. with alumina yields chiefly acetaldehyde which partially condenses to paraldehyde. Trillat[11] passed glycol over a platinum spiral, and obtained formaldehyde, glycollic aldehyde, and glyoxal as decomposition products. Previous work by Drake and Smith[12] has showed that glycol vapor when passed over vanadium pentoxide at temperatures ranging from 250°C to 400°C, yields principally acetaldehyde and ethylene, together with small amounts of carbon monoxide, carbon dioxide, acetic acid, and methane.

There is no reported work on the catalytic action of metallic copper, zinc oxide, or chromic oxide, or their mixtures, on ethylene glycol. They have, however, been used very extensively in other catalytic processes. Sabatier[10] has stated that in the decomposition of methanol, metallic copper and zinc oxide are principally dehydrogenating in their catalytic action, while chromium oxide is dehydrating in character. However, Lazier and

Adkins[13] have shown that zinc exhibits dehydrating as well as dehydrogenating properties in its effect on alcohols, the predominance of ether reaction depending upon the method of preparing the catalyst. Others, as for example, Ghosh[14], Ghosh and Baksi[15], Hara[16], and Mannich and Geilman[17] have studied the catalytic effect of copper on the decomposition of methanol, while Palmer[18], Rideal[19], and Constable[20] have investigated the decomposition of ethanol by the same catalyst. Patart[21] in studying the decomposition and synthesis, and Fischer[22] the synthesis, and Frolich[23] the decomposition of methanol, found that zinc oxide alone was a good catalyst. Patart and Frolich, however, obtained better results with mixed catalysts. For example, Patart's experiments showed that a catalyst composed of 90% metallic copper and 10% zinc oxide was more effective than one consisting of pure zinc oxide. Similarly Frolich has shown that a catalyst containing 98.6 mol percent zinc oxide and 1.4 mol percent copper oxide decomposes 41% the methanol, whereas pure zinc oxide decomposes 33% under parallel conditions. Fenske and Frolich[24], and Dreyfus[25] state that zinc oxide possesses moderate activity in the synthesis and decomposition of methanol. Smith and Hawk[26], Woodruff and Bloomfield[27] in studying the formation and Cryder and Frolich[28], Smith and Hawk[29], Huffman and Dodge[30],

Platnikov and Ivanov[31], and Storch[32] the decomposition
and synthesis of methanol, have shown that mixtures of
zinc oxide and chromium oxide show a greater activity
than does pure zinc oxide. Lormand[33], Frolich and
collaborators[34], and Frolich and Lewis[35] state that
mixtures of copper and zinc oxide are superior to pure
zinc oxide in the synthesis of this same alcohol.

A large number of patents relating to the
synthesis of methanol and similar oxygenated organic
compounds mention copper[36], zinc oxide[37] and mixtures
and alloys of zinc oxide and copper[38] as catalysts.
One patent,[39] furthermore, states that zinc oxide,
ordinarily considered a non-reducible oxide, is reduced
in the presence of copper. Rogers[40] verifies this
statement. His experiments indicate that in a mixture
consisting of 91.51% cuprous oxide, 7.68% zinc oxide and
.36% ferric oxide, the zinc oxide is completely reduced
by hydrogen at 300°C.

Fenske and Frolich[24], Platnikov, Ivanov and
Pospekhov[41] studied the activity of ternary mixtures
of copper, zinc oxide and chromium oxide on the methanol
synthesis and found that such catalysts were more
effective than either the pure materials, or their binary
mixtures. The latter investigators have also shown that
the optimum proportions for this ternary mixture are at

zinc oxide: chromium oxide equals 11:1, and highest
activity was obtained when these oxides constituted
30% of the catalyst. These same investigators[42]
report that a catalyst composed of 90% copper oxide,
8% zinc oxide, and 2% chromium oxide is effective in
the decomposition of methanol. Likewise, they later[43]
studied the synthesis of this alcohol from carbon
monoxide and hydrogen at pressure up to 162 atmospheres,
with a high space velocity of the reacting gases and
temperatures up to 320°C. in the presence of various
catalysts. Copper proved to be a weak catalyst, while
zinc oxide possessed high activity. Chromium oxide
promoted the reaction,

$$2CO + 2H_2 = CH_4 + CO_2$$

The addition of zinc oxide to copper produced no
appreciable effect. At this high space velocity zinc
and chromium oxides promoted the formation of hydrocarbons
instead of methanol. Woodruff and Bloomfield[44] received
a patent for the formation of methanol by using catalysts
composed of zinc oxide, chromium oxide, ferric oxide and
zinc chloride. Tropsch and Koehlen[45] passed formaldehyde
vapor over zinc oxide at 400°C. and obtained carbon
monoxide and hydrogen from dry formaldehyde and carbon
dioxide and hydrogen from moist formaldehyde. With

chromic oxide they obtained in addition to the above products, an 8% yield of methane. According to Sandonnine and Bezzi[46] cetyl alcohol when passed over chromic oxide, or zinc oxide yields 61% and 93% hydrogen respectively. Lazier[47] found that chromic oxide possesses the unique property of hydrogenating the double bond. He obtained good yields of ethane by hydrogenating ethylene in the presence of this oxide. Sabatier[10] states that zinc oxide and copper decompose formic acid exclusively into carbon dioxide and hydrogen. When organic acids are passed over Zn oxide the corresponding ketones are produced[10]. In the field of aromatic chemistry Ullmann[48] found that copper greatly facilitates the action of ammonia under reduced pressure at $170^{\circ}C$. on chloronitrobenzene to form amino nitro benzene.

Many additional references may be cited. It should be noted that zinc oxide, copper, and chromic oxide have been used in a great variety of organic catalytic processes, and when used separately have, in most cases, shown less activity than when binary, or ternary mixtures have been employed. Copper can be classed as a purely dehydrogenation catalyst. Zinc oxide and chromic oxide show both dehydrogenation and dehydration effects. In view of the extensive application of these materials in the field of catalytic chemistry the present investigation of their catalytic effect on ethylene glycol was initiated.

PREPARATION OF CATALYSTS

Chromium Oxide

This catalyst was prepared by adding aqueous ammonia (sp. gr. .958) containing 10.47% NH_3 to a solution consisting of 250 grams of a basic chromic nitrate (28.42% chromium) dissolved in 3 liters of distilled water. The solution was maintained at a constant temperature of 90°C, and thoroughly agitated by means of a motor driven stirrer. The ammonia was added at a constant rate of 20 cc. per minute until the end point was reached.

The chromic hydroxide was washed in the following manner: When precipitation was complete, the agitator was stopped, and the suspension allowed to cool. The hydroxide was permitted to settle for several hours, or preferably overnight, and the supernatant liquid siphoned off. The remaining gelatinous mass was filtered by suction. The filter cake was treated with 4 liters of boiling distilled water and the resulting suspension agitated for 1 hour at 90°C. This washing process was carried out 3 times. After each filtration the precipitate was pressed firmly onto the filter and sucked dry in order to remove as much of the mother liquor as possible.

The chromic hydroxide now in the form of a cake

of about the consistency of dry putty was pressed into cylindrical worms 2 mm. in diameter by means of a clean sodium press, and dried for 2 hours in an electric oven at 110°C. The material thus obtained was dried in a muffle furnace at 400°C. for 2 hours, and finally screened with a 40 mesh sieve to remove the fine particles. The yield of catalyst was about 50 grams.

Zinc Oxide

Precipitation of zinc hydroxide from a solution consisting of 1 mol C.P. $Zn(NO_3)_2 \cdot 6H_2O$ in 3 liters of distilled water was effected by the same method which was used in case of the chromium catalyst. The procedure for washing the crude hydroxide was, however, somewhat different.

Referring to preparation of zinc catalyst, the suspension resulting from the precipitation was allowed to cool until the zinc hydroxide had settled. The supernatant liquid was siphoned off, the hydroxide treated with 4 liters of boiling distilled water, and resulting suspension agitated for 1 hour at 90°C. Filtration by suction was not employed as the zinc hydroxide settled much more completely than did the chromic hydroxide. This washing process was carried out 3 times. Subsequent to the final washing the procedure was identical to that used in the case of the chromium

catalyst.

Zinc-Oxide - Copper Oxide Catalysts

These catalysts were prepared by adding ammonia
to one-half mol of a mixture of chemically pure zinc
and copper nitrates dissolved in 3 liters of distilled
water. The solution was heated to 60°C. and maintained
at this temperature during the precipitation, which was
carried out in a 5 liter 3 necked flask equipped with an
efficient mechanical stirrer, a small separatory funnel,
and a thermometer. Ammonia (sp. gr. .958) containing
10.47% NH_3 was added from the funnel at a constant rate
of 13 cc. per minute until the end point was reached,
the hydroxides of copper and zinc being precipitated
together.

The precipitates were washed 3 times according to
the procedure given above for pure zinc hydroxide with
the exception that the wash water was heated to 60°C.
and the system maintained at this temperature during
the interval of stirring. Following the third washing,
however, the mixed hydroxides, then in the form of a
dried cake on the filter, were washed with 2 liters of
distilled water at 60°C., the hydroxides on the filter
being stirred as much as possible. They were finally

dried by suction[*], pressed into cylindrical worms 2 mm. in diameter, and dried for 24 hours in an electric oven at 110°C. The material thus obtained was heated for 2 hours at 400°C., the hydroxides being converted to the oxides and any adhering ammonium salts volatilized and carried off by a constant stream of air passing through the heating chamber.

Zinc Oxide - Chromium Oxide Catalysts

These catalysts were prepared by exactly the same proceudre used in the above preparation for zinc oxide - copper oxide catalysts.

The chromium nitrate used was shown by analysis to contain 28.42% chromium. This value is in fair agreement with that for mono basic chromic nitrate which contains 26.94% chromium. Consequently, in calculating

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[*] In the case of catalysts high in copper content considerable difficulty was encountered in transforming the hydroxides into the forms of cylindrical worms. They possessed a marked tendency to absorb water and passed through the circular opening of the sodium press not in the solid form but rather in a semi-solid form. This difficulty was successfully overcome by allowing the hydroxide cake to remain on a clay plate at room temperature for at least twelve hours before putting it through the press.

the weights for one-half mol of a mixture of zinc and chromium nitrates, the molecular formula for the chromium salt was assumed to be $Cr(OH)(NO_3)_2$.

Glycol Employed

This was obtained by distilling commercial ethylene glycol, Prestone, under reduced pressure and collecting the fraction boiling at $101^{\circ}C$. at 17 mm.

To R²

Thermocouple

To Line

Thermocouple

D

To Line

To R²

B

To Line To R²

To Line
To lamp bank

K

To Gas Analyzer

To R¹

To Line

To R¹

Thermocouple

To Line

To N₂ Tank

A

C

E

F

To Atmosphere

To receiver

G

H

To Atmosphere

J

Desk Line

I To Receiver

Scale 1cm = 8cm.
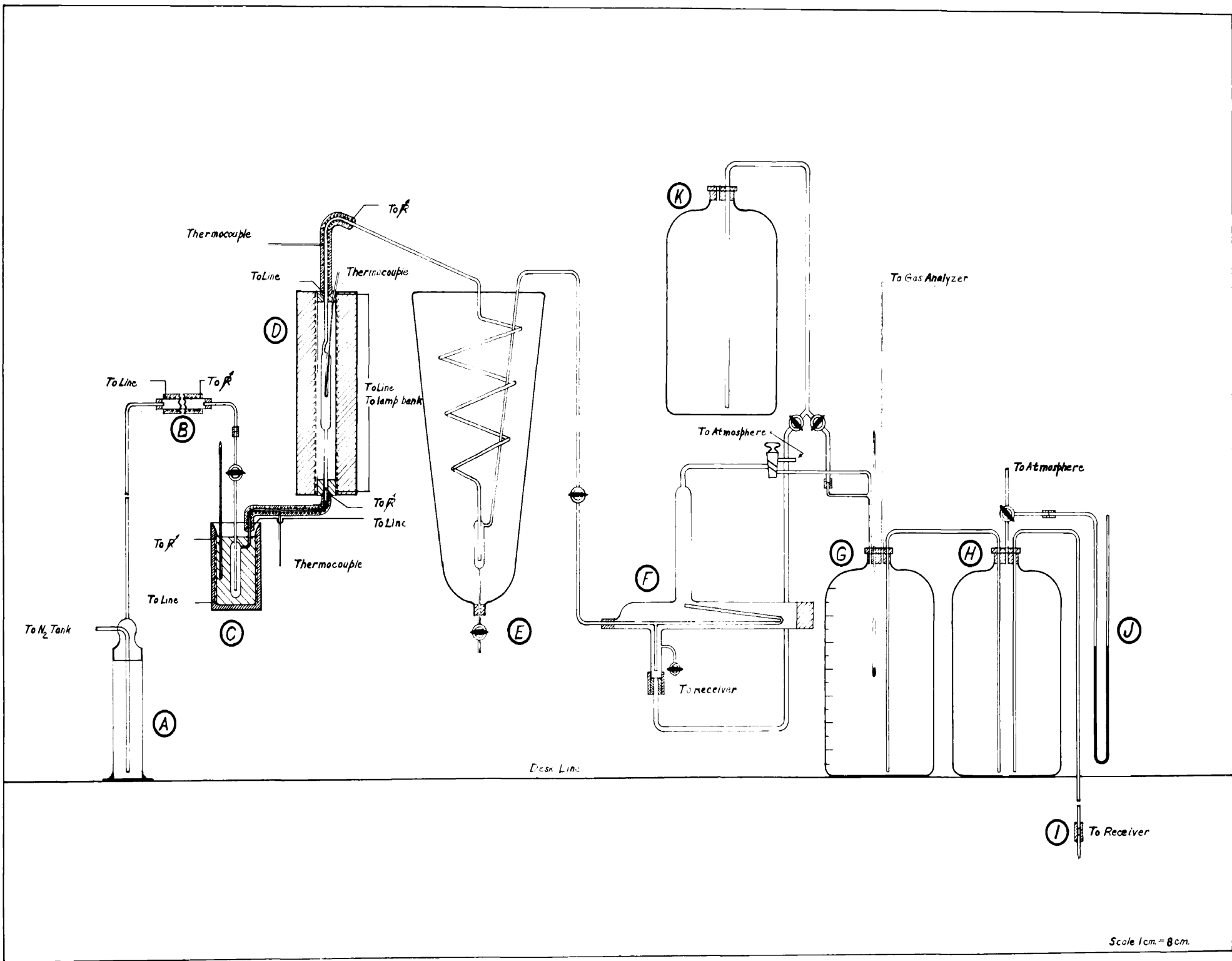
APPARATUS

The apparatus used is shown in the figure.
It was similar to that used by Drake and Smith (loc.cit.).
There are, however, some very important changes.

A, a washing tower containing a little concentrated
sulfuric acid, was connected through a piece of small
pyrex tubing and a rubber stopper to B, a 15 mm. combustion
tube. The latter was filled with reduced wire form copper
oxide and electrically heated to 250°C. to remove traces
of oxygen from the nitrogen which was supplied from a
nitrogen cylinder. The vaporizer C, a pyrex tube of 10
cc. capacity, and containing glycol, was heated to the
desired temperature by means of an electrically heated
Crisco bath. Glycol was introduced by removing the
rubber connection and introducing a small glass capillary
through the stopcock attached to the pyrex bulb. A
small hole was blown into the inner tube of the vaporizer
at a point 3 cm. below the ring seal. This device
permitted flushing the system with nitrogen after intro-
ducing the glycol without bubbling the gas through the
glycol. Connecting the vaporizer with the furnace D,
was a 1 mm. capillary pyrex tube, electrically heated to
210°C. Glycol vapor generated in C passed through this
capillary at a constant rate into the catalyst tube. The

latter consisted of a 11 cc. pyrex bulb 140 mm. x 10 mm., into which was sealed a piece of 70 x 5 mm. tubing. This smaller tube acted as a receptor for the thermocouple. A small piece of glass wool placed in the base of the catalyst tube prevented the catalyst from falling down into the lower arm of the tube. The furnace, D, was made from a pyrex tube 34 mm. x 26 cm. This was first wrapped with thin asbestos paper and then wound with chromel ribbon followed by a layer of thicker asbestos paper. Further insulation was secured by use of asbestos magnesia pipe covering with walls 2.5 cm. thick and a length of 30 cm. Fitting snuggly against the ends of the tube were asbestos plugs 2 cm. thick sealed to the inner walls of the asbestos pipe covering by means of glycerin litharge cement. In the plugs were holes sufficiently large to permit the introduction of the catalyst tube. The temperature of the catalyst was regulated by means of a lamp bank in series with the furnace. The upper bent arm of the catalyst tube was electrically heated to $250^{\circ}C$. The catalyst tube was removed from the heating chamber by raising the furnace and cutting the arms just above and below the asbestos wrapping. E consists of a coil condenser fitted into a bell jar by means of a closely fitting rubber stopper.

The coil, cooled in an ice bath during the experiments, was provided with a condenser trap carrying a stopcock for removing the condensate. The low head scrubber, F, filled with 500 cc. of 4 N magnesium sulfate, connected the coil to the gasometer, G. The latter was provided with a tenth degree thermometer, a connection to the gas analyzer, and a siphon tube. It had a volume of 8 liters and was calibrated to 500 cc. divisions. The siphon tube connected the gasometer to H, a smaller bottle equipped with a second siphon tube, I, and a 3 way stopcock which could be opened either to the atmosphere, or the mercury manometer, J. The primary purpose of this bottle was to provide automatic adjustment of the gas mixture in the gasometer to variations in the atmospheric temperature and pressure. G, H, and the scrubber, F, were filled with 4 N magnesium sulfate by means of the aspirator, K.

The catalyst was removed as described above. After each experiment the catalyst tube was cleaned with concentrated sulfuric acid containing a few cubic centimeters of nitric acid. The products of decomposition together with undecomposed glycol passed into the condenser, where the glycol, water, small amounts of resin, acetic acid, and the major portion of the acetaldehyde were condensed and removed from the trap through the stopcock. The remainder of the acetaldehyde was absorbed in the

scrubber. The internal pressure of the system was regulated by means of a pinch clamp on the lower end of the siphon, I, and the mercury manometer, J.

At the conclusion of each experiment the scrubber liquid was withdrawn through the stopcock. The acetaldehyde was recovered by distillation from a 500 cc. distilling flask into a small coil condenser. The end of the condenser extended a few cm. below ice water contained in a 125 cc. Erlenmeyer flask.

METHOD OF PROCEDURE

The procedure used with pure zinc oxide, or
zinc oxide - chromic oxide mixture as contact material
was as follows: The catalyst was introduced into the
catalyst tube and the latter sealed into the apparatus
as shown in the diagram. The thermocouple was then
put in place. In order to completely close the heating
chamber from the air asbestos fibre was pressed firmly
around the arms of the catalyst tube at the top and
bottom of the furnace. .0613 mol of glycol was run
into the vaporizer C, and the reduced copper in the
furnace B heated to 250°C. The switch to the lamp bank
was closed and the catalyst furnace heated to the desired
temperature. The stopcock in the scrubber exit tube
was opened to the air and the system flushed out with
nitrogen for 3 hours. Meanwhile, the scrubber, gasometer,
and H were filled with 4 N magnesium sulfate and the
stopcock in H opened to the manometer. At the conclusion
of the 3 hour flushing period the above mentioned scrubber
stopcock was turned so that the reaction gases could pass
into the gasometer G. With the system thus in readiness
to collect the decomposition products, the temperature of
the Crisco bath C was raised to $205^{\circ} - 210^{\circ}$C. and maintained
at this temperature until the glycol was completely vaporized.

The extent of the vaporization could be followed through a small opening in the asbestos paper covering the beaker containing the Crisco. Throughout the experiment the pinch cock on the siphon tube leading from H was so adjusted that a few mm. pressure was maintained within the system.

The temperature of the Crisco bath was so regulated that 40 minutes were required for complete vaporization of the glycol. At the end of this time a slow stream of nitrogen was passed through the system in order to carry the residual gases into the gasometer. When approximately 500 cc. of nitrogen had entered, the stopcock on the exit tube of the scrubber and that of H were opened to the air, the scrubber liquid removed, and the catalyst cooled in an atmosphere of nitrogen.

Chromic Oxide as Contact Material

The method of procedure for this material as catalyst was the same as the preceding one, except for the following differences: 6.5 cc. (equivalent to 6.5 grams) of chromic oxide were used in each experiment and the temperature of the Crisco bath was so adjusted that the complete vaporization of the glycol required 2 hours.

Pure Copper and Copper-Zinc Oxide Catalysts

The procedure here was the same as the first mentioned with the following exception: Previous to the experimental run, oxides were reduced by hydrogen at $506°C$. Hydrogen from a cylinder was washed with an aqueous solution of potassium permanganate and passed through the catalyst. This method of reduction was used because experiments showed that catalysts obtained by reduction with glycol vapor were inferior in activity to those obtained by reduction with hydrogen.

ANALYTICAL METHODS

Decomposition Products

The analytical methods were essentially the same as those used in previous work[12]. The decomposition gases were analyzed in a Fisher Universal Gas Analyzer; carbon monoxide, oxygen, unsaturates, carbon dioxide, hydrogen, and methane were determined in the order mentioned. Carbon dioxide was absorbed by 33% aqueous potassium hydroxide; oxygen by sodium anthraquinone beta sulfonate solution[49]; ethylene by 24% fuming sulfuric acid; and carbon monoxide by ammoniacal cuprous chloride solution[50]. Hydrogen was burned in a copper oxide tube at $310^{\circ}C$ and methane in a slow burning pipette.

At the conclusion of each experiment the condensate from E of the diagram was drawn off into a 125 cc. Erlenmeyer flask. Distilled water was then drawn up into coil and the washings collected in the Erlenmeyer flask. Acetaldehyde was determined by adding 1 gram of hydroxylamine hydrochloride[51] to a 25 cc. portion of the aqueous condensate, allowing the resulting solution to stand for at least 30 minutes and titrating the hydrochloric acid liberated with N/4 sodium hydroxide using tetrabrom phenol blue as indicator.[52]

The acetic acid was determined by titrating
another 25 cc. portion with N/4 alkali using phenol-
phthalein as indicator.

The acetaldehyde contained in the scrubber
liquid was driven off by distillation and collected
directly in a 125 cc. Erlenmeyer flask containing
a cold aqueous solution of hydroxylamine hydrochloride
and titrated as above.

ANALYSIS OF CATALYST MIXTURES

Copper Oxide - Zinc Oxide

The copper was determined by dissolving a sample containing approximately .1 gram of copper in 6 N sulfuric acid. The resulting clear solution was made alkaline with concentrated ammonia and cooled. 50% acetic acid was added in slight excess.

The solution, now about 30 cc. in volume, was treated with 3 grams of potassium iodide. After five minutes the liberated iodine was titrated with N/10 sodium thiosulfate using starch as indicator. The per cent zinc was determined by difference. The analyses were made after the oxides had been heated for 2 hours at 400°C. as described under the preparation of the catalysts.

The following table represents the results obtained from the copper oxide - zinc oxide catalysts using the above method of analysis.

Cat. No.	% Cu	% CuO	% ZnO	Mol % Cu	Mol % ZnO
1	0	0	100	0	100
2	1.29	1.61	98.39	1.63	98.37
3	5.76	7.20	92.80	7.32	92.68
4	13.32	16.65	83.35	16.95	83.05
5	18.47	23.09	76.91	23.49	76.51
6	24.13	30.16	69.84	30.64	69.36
7	34.39	42.99	57.01	43.55	56.45
8	52.12	65.15	34.85	65.65	34.35
9	67.04	83.80	16.20	84.11	15.89
10	78.94	98.70	0	?	0

The values for copper were determined by analysis,
and those of zinc oxide by difference. The last two columns
represent the values of metallic copper and zinc oxide after
reduction of the mixtures at 506°C., assuming that only
the copper oxide was reduced. The error involved in making
this assumption[40] is realized but for a qualitative
representation of the catalytic effects the above values
will suffice. This point will be discussed more at length
in the subsequent pages.

In plotting these values in the following graphs
the last value of column 5 is taken as 100 mol % copper.
In reality it is probably not more than 99 mol %. This

discrepancy can be explained on the basis of incomplete dehydration of the copper hydroxide at 400°C.

Chromic Oxide - Zinc Oxide Catalysts

.1 - .5 gram of catalyst, depending upon the chromium content, was dissolved by prolonged heating in 10 to 15 cc. of nitric acid (2 cc. conc. HNO_3 to 1 cc. water). The resulting clear solution was cooled and made strongly alkaline with concentrated sodium hydroxide solution. 10 - 15 grams of sodium peroxide were added. When effervescence had subsided, the solution was boiled for a few minutes. Oxidation was completed by continued boiling after the addition of a drop of liquid bromine. After cooling ammonium carbonate was added to neutralize the greater portion of the sodium hydroxide, whereupon the solution was filtered from a trace of iron. 6 N sulfuric acid was added until a permanent brown color appeared, 20 cc. of 30% potassium acid sulfate added, and the solution boiled to expel the last traces of oxidizing agent. After cooling, the solution was acidified with 6 N sulfuric acid. 5 cc. of acid per 100 cc. of solution were added in excess. The resulting cold solution was treated with 4 grams potassium iodide and after 5 minutes the liberated iodine titrated with $\frac{N}{4}$ sodium thiosulfate solution.

From the titration values the per cent of
chromium was calculated. The per cent of zinc was
found by difference. The following table represents
the values obtained for the various chromic oxide -
zinc oxide catalysts.

Cat. No.	% Cr	% Cr_2O_3	% ZnO	Mol % Cr_2O_3
1	-	-	100.00	-
2	1.68	2.45	97.55	1.32
3	3.05	4.45	95.55	2.43
4	7.70	11.25	88.75	6.35
5	14.19	20.74	79.26	12.25
6	21.51	31.44	68.56	19.73
7	36.30	53.05	46.95	37.73
8	49.23	71.95	28.05	57.82
9	57.36	88.83	11.17	81.54
10	65.82	96.19	00.00	?

As in the case of the copper oxide - zinc oxide
catalysts dehydration of the hydroxides was not complete
at 400°C. There is no information in the literature as
to the lowest temperature for complete dehydration of
chromic hydroxide. Treadwell and Hall state that the

correct procedure is to ignite the hydroxide. Here also for purposes of a qualitative comparison of catalytic effects, the last value of column 5 was taken as 100 mol per cent.

Model Calculations

The carbon balance from which the total decomposition was figured was obtained in the following way:

Catalyst = 11 cc. of 100 mol per cent ZnO.

Temperature = $506^{\circ}C$.

Entering glycol = .0613 mols.

Mols reaction gases plus nitrogen = .1330.

Gas Analysis

	Per Cent	Liquid Compounds	Mols
Carbon dioxide	20.83	Acetaldehyde	.0111
Ethylene	6.66	Acetic Acid	.0000
Carbon Monoxide	4.95		
Hydrogen	44.30		
Methane	0.74		

Carbon Balance

	Mol	C
Carbon dioxide	.0277	.0277
Ethylene	.0089	.0177
Carbon monoxide	.0066	.0066
Hydrogen	.0594	-
Methane	.0010	.0010
Acetaldehyde	.0111	.0222
Acetic acid	.0000	.0000
	.1167	.0752

Since no attempt was made to determine the
quantity of water formed from the decomposition reactions,
the percentage decomposition was figured on the basis
of carbon. Thus,

$$\frac{.0752 \times 100}{.0613 \times 2} = 61.3 \text{ per cent}$$

The individual decomposition products listed
above were expressed as per cent of the total glycol used.

$$\text{Carbon dioxide} = \frac{.0277 \times 100}{.0613 \times 2} = 22.6 \text{ per cent.}$$

$$\text{Ethylene} = \frac{.0089 \times 2 \times 100}{.0613 \times 2} = 14.52 \text{ per cent.}$$

PYROLYSIS OF ETHYLENE GLYCOL

Pyrolysis of glycol was determined by passing the vapors through the empty catalyst tube heated to 506°C, this temperature being the highest at which experiments were made. The following table gives the results of such a determination.

Temperature = 506°C.

Entering glycol = .0613 mols.

Per cent decomposition = 5.1.

TABLE I

| Substance	Mols	Mol Percent of Decomposition Products
Carbon dioxide	.0003	5.88
Ethylene	.0001	1.99
Carbon monoxide	.0003	5.88
Hydrogen	.0016	31.37
Methane	.0002	3.98
Acetaldehyde	.0026	50.98
Acetic acid	.0000	00.00

The above data indicates that glycol is very stable even at 506°C., an observation confirmed by Hurd[53]. He states that ethylene glycol starts to decompose at 500° to 520°C. and that the decomposition is appreciable at

550°C. At this latter temperature he recovered
14.4 grams from an original charge of 40 grams of
glycol. The decomposition products consisted of
acetaldehyde (7 cc.), water (5 cc.), some croton-
aldehyde (traces), and 4.5 liters of gas, the latter
being composed of 50% carbon monoxide, 11.5% hydrogen,
and 38.5% methane. No unsaturated compounds were
formed which is in close agreement with the above
experiment.

Referring to Table I it is evident that the
primary reaction of the pyrolysis is the decomposition
of glycol into acetaldehyde and water, according to the
following equation:

$$CH_2OHCH_2OH = CH_3CHO + H_2O.$$

The formation of hydrogen, methane and the oxides
of carbon may be accounted for by the equations,

$$CH_2OHCH_2OH = 2CO + 3H_2$$

$$CH_3CHO = CH_4 + CO$$

and

$$CO + H_2O = CO_2 + H_2$$
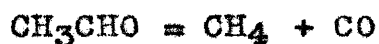
Since the pyrolysis was very slight (only 5.1%)
it is not considered necessary to give further discussion
on these equations at the present stage of the thesis.
It should be noted, however, that no traces of acetic acid

could be detected in the decomposition products. This interesting observation will be considered later in the light of the data obtained from the catalysis experiments.
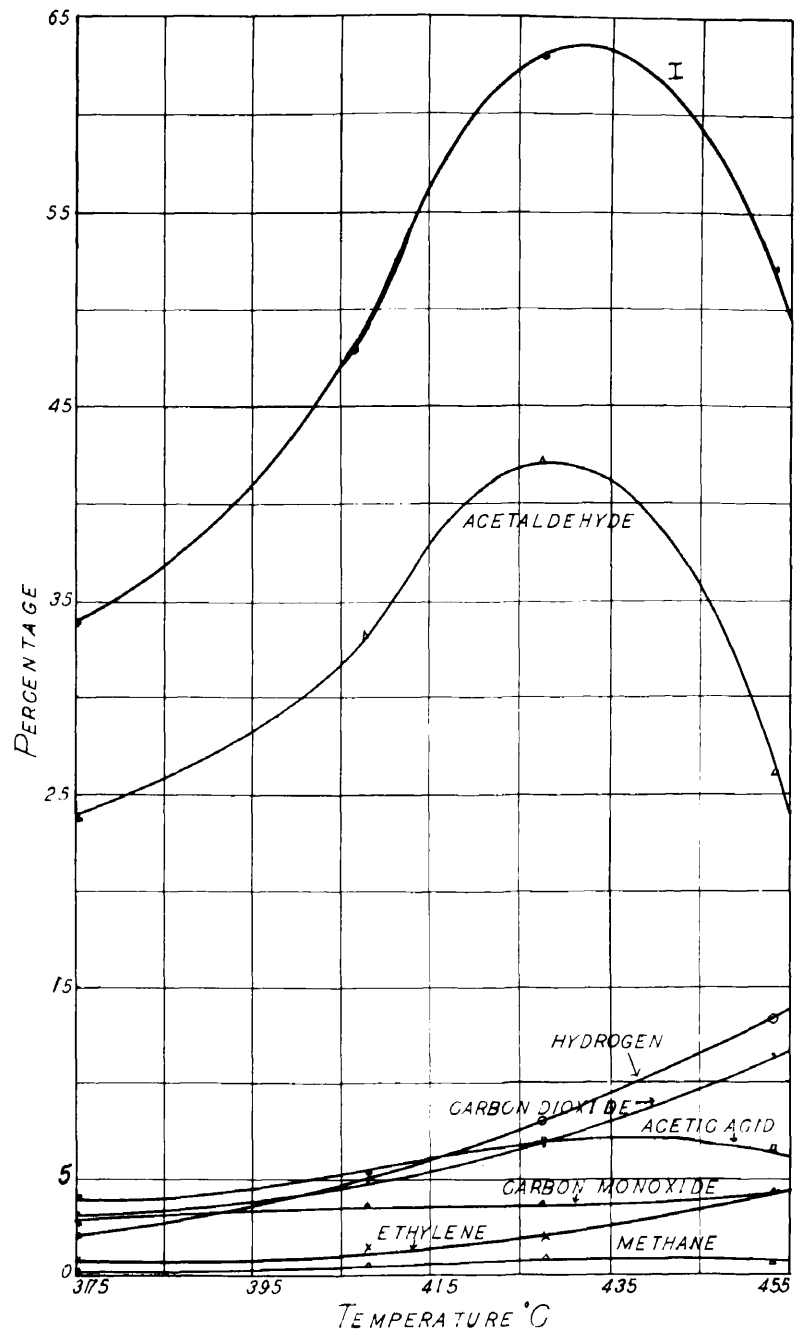
FIG. 1—TOTAL DECOMPOSITION AND PERCENTAGE
OF TOTAL GLYCOL USED DECOMPOSED INTO ACET-
ALDEHYDE, ETHYLENE, CARBON-MONOXIDE, CARBON-
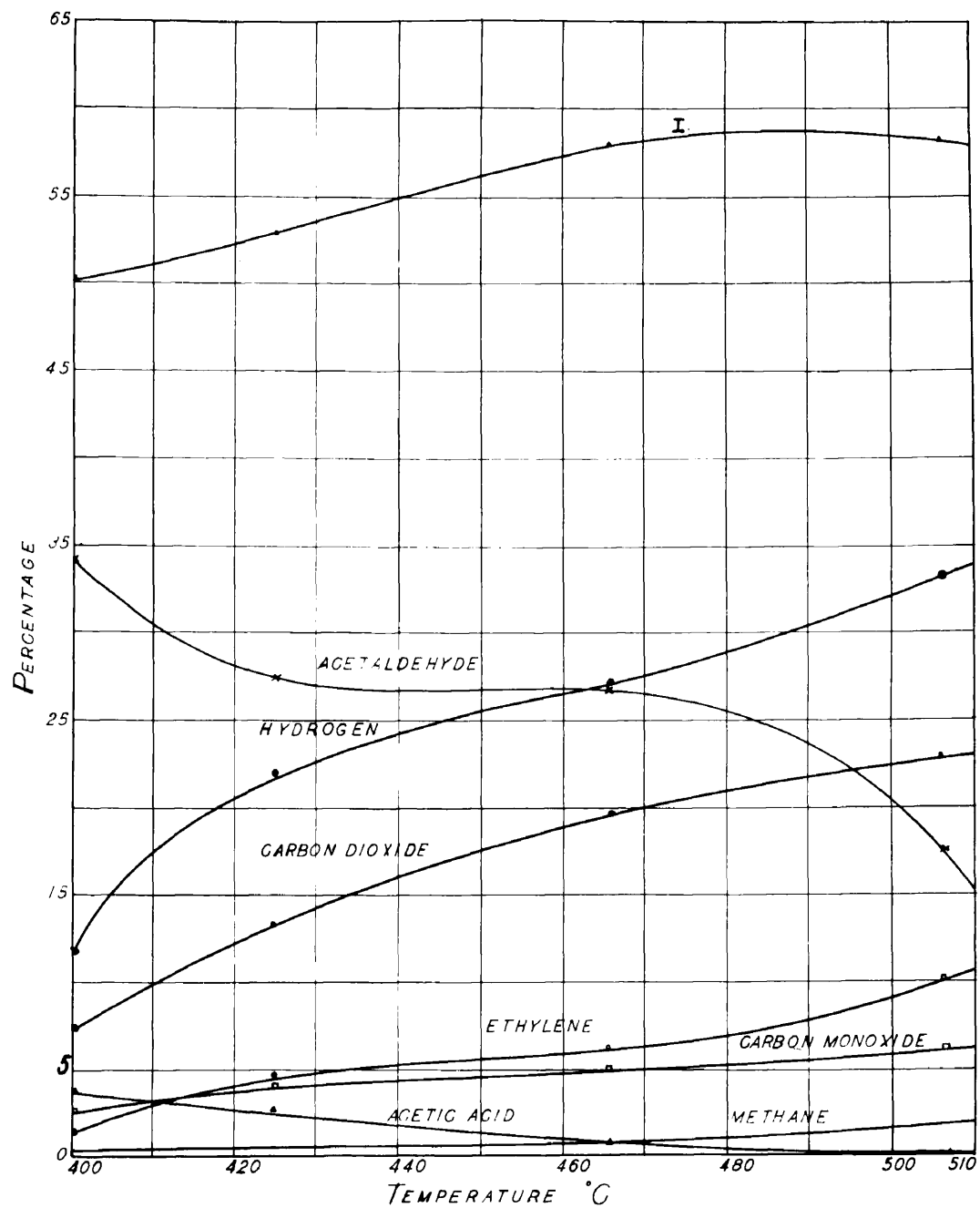DIOXIDE, METHANE, AND ACETIC-ACID. Cr_2O_3-CAT.

FIG. 2—TOTAL DECOMPOSITION AND PERCENTAGE OF TOTAL
GLYCOL USED DECOMPOSED INTO ACETALDEHYDE, ETHYLENE, CARBON-
MONOXIDE, CARBON-DIOXIDE, METHANE, AND ACETIC-ACID. ZnO-CAT.

DISCUSSION OF RESULTS

Chromic Oxide as Catalyst

The experimental results obtained from
chromic oxide as catalyst are presented graphically
in Figure I. Curve 1 represents the decomposition of
glycol plotted as a function of temperature. The
remaining curves represent the percentage of entering
glycol decomposed into the various products which were
identified. The following table gives the data
included in Figure I.

Temp.	% Decomp.	% of glycol used decomposed into:						
		CO_2	C_2H_4	CO	H_2	CH_4	CH_3CHO	CH_3COOH
375	34	3.1	0.7	3.0	2.0	0.1	23.7	4.0
408	49	4.9	1.5	3.8	5.0	0.4	33.2	5.3
428	63	6.8	2.1	3.9	8.4	0.7	42.3	7.2
453	52	11.3	4.5	4.5	13.3	0.5	26.2	6.1

Volume of catalyst = 6.5 cc.

Time of each experiment = 2 hours.

In considering this data it must be remembered that
the decomposition can be a true measure of catalytic
activity only when the space velocity and concentrations

are the same in each experiment. At each temperature
the rate of flow of gaseous glycol into the reaction
chamber was .0532 mol per hour. This rate of flow
over 6.5 cc. of catalyst would give at the several
temperatures the following space velocities, the
latter being given in the usual units of cubic
centimeters of gas per hour per cubic centimeter of
catalyst.

Temp. ^{o}C.	S. V.
375	433
408	456
428	469
453	486

Furthermore, the decomposition products are
constantly diluting the reacting constituents, and
since the process in question proceeds with an increase
in the number of mols the time of contact is constantly
decreasing along the length of the catalyst layer.

The net affect of these two factors, namely, the
increase in temperature and the dilution by the decompo-
sition products, is a flatening out of the curves at the
higher temperatures.

Referring to Curve 1, Figure I, it will be noted
that the slope becomes zero in the vicinity of 435°C.,

and assumes a negative value thereafter. An inspection
of the aldehyde curve indicates that this same condition
prevails in this case. On the other hand, the curves for
hydrogen, carbon dioxide, and ethylene show a decided
increase in these substances between these temperatures.
In more appropriate terms, the desired reaction, namely,
the dehydrogenation of glycol, was favored, while the
dehydration was diminished. At this point, however, it
should be stated that at 453°C. a considerable quantity
of an unknown oily product was obtained in the condensate.
It is probable that this substance was produced by the
condensation of acetaldehyde. This explanation would
account for the rapid decline in both the aldehyde curve
and Curve 1, since acetaldehyde is the dominant product
of the decomposition. This conclusion will be obvious
when it is remembered that the total decomposition was
obtained by means of a carbon balance based on the
determinable products of the reaction. It is believed,
therefore, that nothing would be gained by operating at
a temperature above 435°C., a conclusion which is in close
agreement with the observations of Reitz[54]. He states that
the optimum temperature is 410°C.

Referring again to Figure I, it will be seen that
the decomposition is by no means a simple process, as
evidenced by the complexity of the products. Methane,

ethylene, and acetic acid were formed in addition to acetaldehyde, carbon monoxide, carbon dioxide and hydrogen. The most important gaseous products were carbon monoxide, carbon dioxide, and hydrogen. The dominant reaction was the one resulting in the formation of acetaldehyde. For example, at 375°C. the per cent total decomposition and percentage of entering glycol decomposed into acetaldehyde were respectively, 34 and 24. Consequently, approximately 71% of the total glycol decomposed occurred as acetaldehyde.

Drake[12] has suggested two mechanisms for the production of acetaldehyde from gaseous glycol with vanadium pentoxide as catalyst.

$$CH_2OHCH_2OH = CH_2 = CHOH + H_2O$$
$$CH_2 = CHOH = CH_3CHO$$
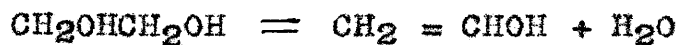
"Ipatiev[55] has studied the behavior of oxides on heating both in the presence and absence of catalysts. Ethylene oxide passed through a glass tube was found to begin to decompose at 500°C. In the presence of aluminum oxide, however, rearrangement of the oxide into acetaldehyde took place readily between 200° and 300°C. The work of Nef[56] confirms in a general way that of Ipatiev. Nef observed a slow rearrangement of ethylene oxide into acetaldehyde in glass tubes at 400 - 420°C. No evolution

of gas took place within this temperature interval.

The behavior of many substituted ethylene oxides on heating has been studied by Tiffeneau and Levy[57], and Levy and Sfiras[58]. Many of the oxides investigated undergo a rearrangement like that of ethylene oxide into acetaldehyde. This rearrangement, therefore, is common to alpha oxides, and it is possible, consequently, that ethylene oxide was the intermediate from which both acetaldehyde and ethylene were formed. The following reaction would account for the ethylene

$$CH_2 - CH_2 = CH_2 = CH_2 + \tfrac{1}{2}O_2 \text{ "}$$
$$\diagdown O \diagup$$

The complete reactions for the formation of acetaldehyde and ethylene from glycol would be

$$CH_2OHCH_2OH = CH_3CHO + H_2O \qquad (2)$$
$$CH_2OHCH_2OH = CH_2 = CH_2 + H_2O + \tfrac{1}{2}O_2 \qquad (3)$$

These dehydration reactions would be expected from the usual catalytic effects of chromic oxide. Sabatier[10] states that chromic oxide is dehydrating in its effect on alcohols. Cryder and Frolich[28] state that Cr_2O_3 when added in excess to ZnO causes an increase in the dehydration of methanol.

Acetic acid was undoubtedly produced by the oxidation of acetaldehyde. The amount of acid formed

was conditioned by two factors, (a) the concentration of the aldehyde in the reaction products, and (b) the amount of available oxygen. The latter in turn depended upon the reducibility of the catalyst and the extent to which reaction (3) proceeded. Although the catalyst did show a physical change (evidenced from a change of color from the original deep green to an olive green) it is believed that the greater part of the available oxygen came from reaction (5). From Figure I it is seen that the contour of the acetic acid curve follows roughly the means of the contours of the aldehyde and ethylene curves.

Carbon dioxide may have been produced according to either or both of the following equations. The reaction

$$CO + H_2O = CO_2 + H_2 \quad (4)$$

is advanced on the basis of the use of chromic oxide as a promoter in the catalytic process for the production of hydrogen from water gas[60]. Plotnikov, Ivanov and Pospekhov[43] in their studies on the synthesis of methanol from carbon monoxide and hydrogen found that Cr_2O_3 promotes the reaction

$$2CO + 2H_2 = CH_4 + CO_2 \quad (5)$$

This reaction not only accounts for the presence of carbon dioxide, but it also predicts the simultaneous formation of an equivalent amount of methane. These

reactions were favored by increasing the temperature. It is seen from Figure I that the carbon dioxide curve shows a decided increase at the higher temperatures, while the methane curve is nearly a straight line. It is evident that the greater part of the carbon dioxide is produced by reaction (4).

For the production of carbon monoxide two mechanisms are proposed. It is known that Cr_2O_3 acts as a dehydrogenation catalyst. Lazier[47] states that Cr_2O_3 gives 50% each of dehydration and dehydrogenation of alcohols. The same investigator has also shown that chromic oxide is effective in the hydrogenation of ethylene to ethane. The reactions

$$CH_2OHCH_2OH = CHOCHO + 2H_2 \quad (6)$$

$$CHOCHO = 2CO + H_2O \quad (7)$$

readily account for the presence of carbon monoxide and hydrogen.

Hinshelwood and Hutchinson[59] in their studies on the thermal decomposition of acetaldehyde have shown that this substance decomposes smoothly at $500^\circ C$. according to the following equation,

$$CH_3CHO = CO + CH_4 \quad (8)$$

A consideration of equations (4), (5), (6), and (7) indicates that the sum of the hydrogen and methane values in Figure I should be roughly equal to the sum of the carbon monoxide value and one and two-thirds the carbon dioxide value, since the latter is produced from carbon monoxide with the liberation of an equivalent amount of hydrogen. This conclusion is roughly substantiated by Figure I. There is, however, a shortage of hydrogen especially at the lower temperatures. It is believed that this discrepancy can be explained on the basis of two side reactions, namely, the production of carbon dioxide by oxidation of carbon monoxide, and by the removal of hydrogen through the formation of water.

Pure Zinc Oxide as Catalyst

The graphic presentation of the experimental results using this oxide as catalyst is identical with that used in the case of chromic oxide. Table II gives the data plotted in Figure 2.

TABLE II

Temp.	% Decomp.	% total glycol used decomposed into:						
		CO_2	C_2H_4	CO	H_2	CH_4	CH_3CHO	CH_3COOH
400	50	7.3	1.5	2.5	11.8	0.3	34.2	3.9
425	53	13.3	4.8	4.0	20.2	0.5	27.3	2.9
466	58	19.7	6.2	5.0	27.1	0.7	26.5	0.7
506	58	22.8	10.1	6.1	33.7	1.7	17.5	0.0

Volume catalyst = 7.1 cc.

Time of each experiment = 40 minutes.

Glycol used = .0613 mols.

By the previous method of calculation the following space velocities are obtained for the experiments using this contact material.

Temp.	S.V.
400	713
425	740
466	783
506	826

Curve 1 of Figure 2 represents the percent total decomposition as a function of temperature. An inspection of this curve shows that the decomposition increased steadily from 400 to 466°C, and remained nearly constant

thereafter. On the other hand, there was a very
marked variation in the quantities of the reaction
products. It is interesting and significant to note
that at the lower temperatures the chief product was
acetaldehyde. At the higher temperatures, however,
the picture is quite different. The amounts of the
desired products, namely, carbon dioxide, carbon
monoxide, and hydrogen increased at the expense of
the aldehyde. For example, at $400^{o}C$. the per cent
of the total glycol used decomposed into acetaldehyde
was 34.2%, while at $506^{o}C$. it had fallen to 17.5%.
In comparison, at these same temperatures the correspond-
ing values for the sum of the remaining carbon compounds,
were respectively, 15.5 and 39.7. It would seem, therefore,
that the optimum temperature in this case would be in the
vicinity of $510^{o}C$. It will be recalled that considerable
pyrolysis occurs at $520-550^{o}C$. This reaction would not
permit of operation at temperatures much above $510^{o}C$.

A comparison of Figures 1 and 2 will emphasize
the relative dehydration and dehydrogenation characters
of chromic and zinc oxides. This comparison is diminished
in its significance by the fact that the data for the two
catalysts were not obtained under identical conditions.
It will suffice to say that there is a decided difference
in the dehydration and dehydrogenation effects of the two

catalysts, the zinc oxide being far superior to chromic oxide in its dehydrogenation effect on the decomposition of glycol.

Furthermore, with zinc oxide the oily resin formation was very slight even at the higher temperatures. With chromic oxide there was considerable resin formation even at the lower temperatures.

Referring to Figure 2, it will be seen that the decomposition of glycol results in the formation of the same products as in the case of chromic oxide, the chief difference being the relative proportions of these various products. Zinc oxide shows a decided catalytic effect on reactions 1, 2 and 4.

$$CH_2OH\ CH_2OH = 2CO + 3H_2 \quad (1)$$
$$CO + H_2O = CO_2 + H_2 \quad (4)$$
$$CH_2OHCH_2OH = CH_3CHO + H_2O \quad (2)$$
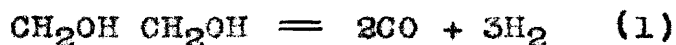
The presence of methane and acetic acid is explained in a manner identical to that used in the case of chromic oxide. It is significant to note that the contour of the acetic acid curve follows very closely that of the acetaldehyde, and is directly opposite that of the ethylene curve. This fact lends strong support to the hypothesis that the acetic acid is formed by the

oxidation of acetaldehyde, the oxygen coming from the catalyst and not from reaction 3. Furthermore, the catalyst showed a decided color change from snow white to steel gray.

That the ZnO was at least partially reduced is supported by evidence presented in several published articles. Lemarchands[61] states that zinc oxide is reduced by carbon monoxide at temperatures as low as $350 - 400^{\circ}C$. Platnikov and Ivanov[31] found that the oxide shows signs of reduction by hydrogen at temperatures as low as $325^{\circ}C$. St.John[62] passed dry hydrogen over ZnO and noticed appreciable reduction at $310^{\circ}C$.

The presence of ethylene is explained by reaction 3.

$$CH_2OH \; CH_2OH \; \rightleftharpoons \; CH_2 = CH_2 + H_2O + \tfrac{1}{2}O_2$$

From Figure 2 it is seen that the curves for hydrogen, carbon monoxide, and carbon dioxide are nearly parallel assuming that reaction 1 was the source of the hydrogen, and further that carbon dioxide was produced by the oxidation of carbon monoxide, then the area under the hydrogen curve should be equal to the sum of the areas under the curves of the other two. If, however, carbon dioxide were produced by reaction 4, the above equality would no longer exist, the hydrogen area being larger by an amount equivalent to two-thirds of the carbon

dioxide area.

Figure 2 shows that the percentage of entering glycol decomposed into hydrogen is from 3 to 5% higher than the sum of the percentages of glycol which occurred as carbon monoxide and carbon dioxide. It would seem, therefore, that the carbon dioxide was produced by both of the following reactions,

$$CO + H_2O = CO_2 + H_2$$
$$CO + \tfrac{1}{2}O_2 = CO_2 \quad (9)$$
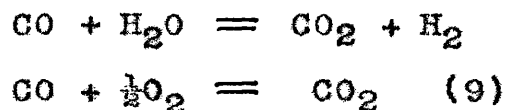
It would be very interesting to study the reduction of zinc oxide by a mixture of carbon monoxide and hydrogen over the temperature of 400 - 500°C. Such a study would undoubtedly throw some light upon the question at hand.

Finally, it may be stated that zinc oxide possessed good activity in the decomposition of ethylene glycol into carbon monoxide and hydrogen. It also gave considerable dehydration into acetaldehyde. As the temperature of operation was increased the formation of aldehyde was suppressed. In contrast with this the dehydrogenation according to the desired reaction

$$CH_2OH \; CH_2OH = 2CO + 3H_2$$
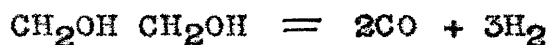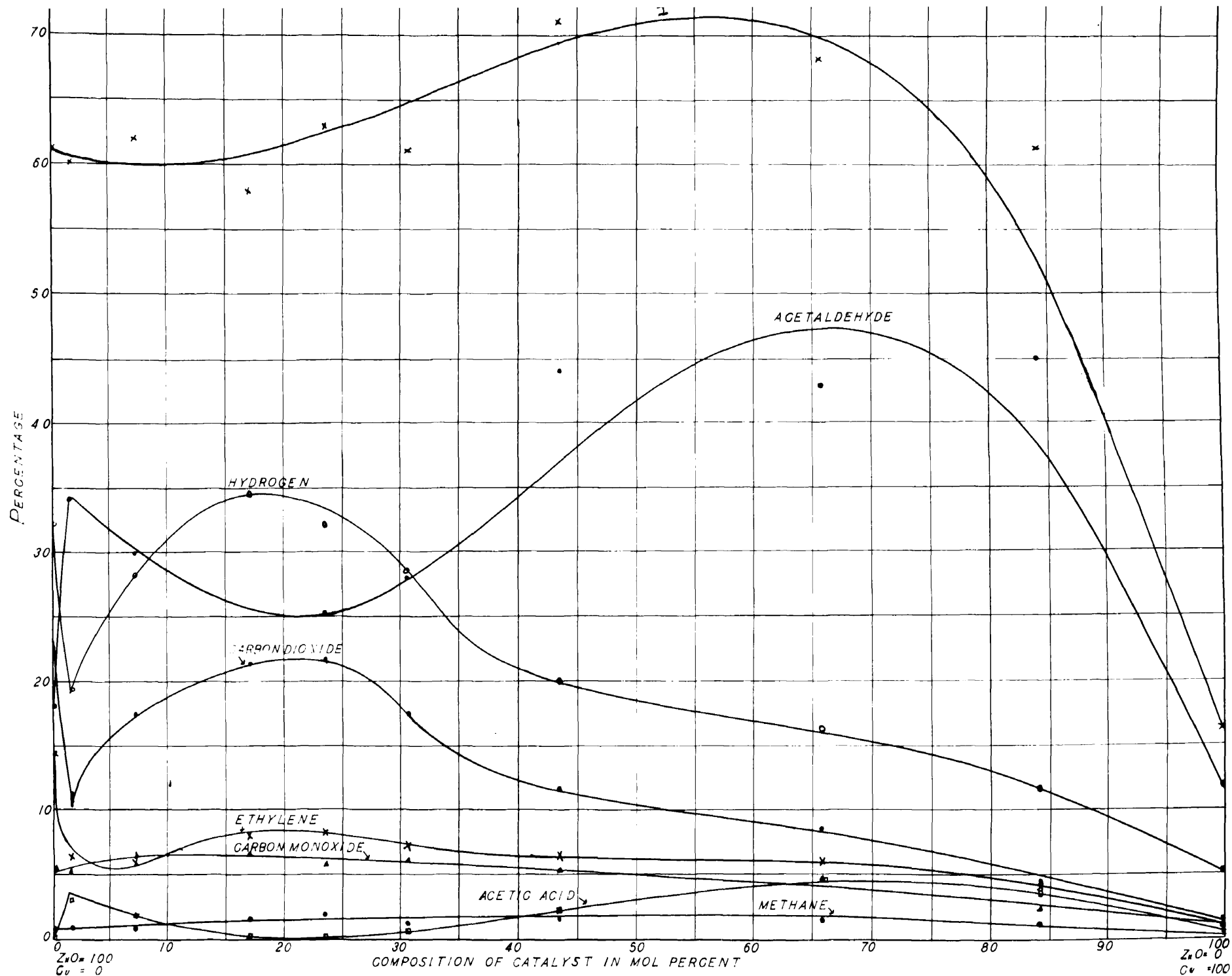
was increased with increasing temperature.

FIG.3. TOTAL DECOMPOSITION AND PERCENTAGE OF GLYCOL USED DECOMPOSED INTO ACETALDEHYDE, ETHYLENE, CARBON-DIOXIDE, CARBON-MONOXIDE, HYDROGEN, METHANE, AND ACETIC-ACID AS A FUNCTION OF CATALYST COMPOSITION.

Copper - Zinc Oxide as Catalyst

Figure 3 presents graphically the decomposition of ethylene glycol plotted as a function of catalyst composition. The experiments with these catalysts were carried out at a constant temperature of $506^{\circ}C$. This temperature of operation was chosen subsequent to an examination of the results obtained from pure zinc oxide. Table III contains the data from which Figure 3 was obtained.

TABLE III

Mol % Cu	% Decomp.	% glycol used decomposed into:						
		CO_2	C_2H_4	CO	H_2	CH_4	CH_3CHO	CH_3COOH
0	61	22.6	14.5	5.4	32.3	0.8	18.1	0.0
1.63	60	11.3	6.4	5.2	19.4	1.1	34.2	3.3
7.32	62	17.4	6.0	6.3	28.1	0.9	30.0	1.8
16.95	58	21.4	8.0	6.4	34.6	1.5	20.0	0.2
23.49	63	21.6	8.3	5.7	32.0	2.0	25.1	0.0
30.64	61	17.5	7.2	6.0	28.5	1.3	28.0	0.8
43.55	71	11.4	6.5	5.3	20.0	1.6	43.9	2.2
65.65	68	8.5	6.0	4.8	16.2	1.5	42.7	4.5
84.11	61	4.5	4.1	2.4	11.5	1.1	45.0	3.6
100.00	16	1.4	1.1	1.2	5.0	0.25	11.7	0.5

Volume catalyst = 11 cc.

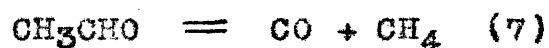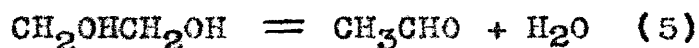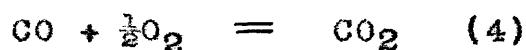Time of each experiment = 40 minutes.
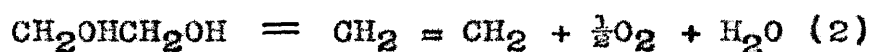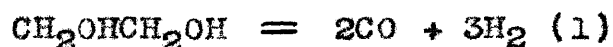
Temperature = 506°C.

Glycol used = .0613 mols.

Under these conditions the space velocity based on the entering glycol was 534.

Referring to Curve 1, Figure 3 it is seen that the addition of zinc oxide to copper increased the decomposition very rapidly until 40 to 45 mol percent zinc oxide was present. At this composition the

decomposition had increased almost five fold over that for pure copper. In contrast, the presence of a small amount of copper with zinc oxide slightly depressed the decomposition. Over the range 5 to 20 mol percent copper the decomposition remained nearly constant. With further addition of copper to the point where copper was present in preponderating quantities there was, however, a small but noticeable increase in the decomposition.

An inspection of the remaining curves of Figure 3 shows that the decomposition over mixed catalysts of copper and zinc oxide was complex and cannot be represented by a single reaction. Here as in the cases of the simple catalysts the chief products were acetaldehyde, hydrogen, carbon monoxide, carbon dioxide and ethylene, together with small amounts of methane and acetic acid. The decomposition may be represented by the reactions already given, namely,

$$CH_2OHCH_2OH = 2CO + 3H_2 \quad (1)$$
$$CH_2OHCH_2OH = CH_2 = CH_2 + \tfrac{1}{2}O_2 + H_2O \quad (2)$$
$$CO + H_2O = CO_2 + H_2 \quad (3)$$
$$CO + \tfrac{1}{2}O_2 = CO_2 \quad (4)$$
$$CH_2OHCH_2OH = CH_3CHO + H_2O \quad (5)$$
$$CH_3CHO + \tfrac{1}{2}O_2 = CH_3COOH \quad (6)$$
$$CH_3CHO = CO + CH_4 \quad (7)$$

Referring to these reactions it is seen
from Figure 3 that the extent to which any of these
reactions proceeded was dependent upon the copper -
zinc oxide ratio. The addition of a small amount
of copper to zinc oxide favors reactions (5) and (6).
At the copper - zinc oxide ratio of 1.6 to 98.4 mol
per cent this promoter action had reached a maximum.
The presence of more copper favored the reactions
(1), (2), (3) and (4) and suppressed the formation of
aldehyde. At 20 mol per cent copper the extent to
which reactions (1), (3) and (4) proceeded had reached
the maximum for the entire range of catalyst composition.
In contrast the curves for aldehyde and acetic acid
show minima at this same per cent copper. From the
point where copper was in excess the major portion of
the glycol decomposed occurred as acetaldehyde.
Consequently, for the decomposition of glycol into
hydrogen and carbon oxides the optimum catalyst
composition was 20 mol per cent copper and 80 mol per
cent zinc oxide.

It is significant to note that the hydrogen,
carbon monoxide and carbon dioxide curves have the same
general shape. This condition should prevail if reaction
(1) accounts for the production of hydrogen and carbon
monoxide. It is understood that the formation of carbon

dioxide was a secondary reaction, the extent of which was determined, mainly by the extent to which reaction (1) proceeded. Here, as in the case of the simple catalysts, the hydrogen values are a few per cent greater than the sum of the corresponding carbon monoxide and carbon dioxide values. From a consideration of the data at hand it is believed that the carbon dioxide was produced by the reactions (3) and (4).

From Figure 3 it is seen that the contours of the acetic acid and acetaldehyde curves are almost identical, indicating that the amount of acetic acid formed was dependent upon the concentrations of aldehyde.

Methane was probably formed according to reaction (7) with an equivalent amount of carbon monoxide.

Further consideration of Figure 3 shows that little is to be gained by the addition of copper to zinc oxide. For example, with pure zinc oxide as catalyst the total percentage of glycol decomposed into carbon oxides was 28, whereas with the optimum mixture of 20 mol per cent Cu and 80 mol per cent zinc oxide this value was 27.5. The corresponding values for acetaldehyde were 18.1 and 25. If, however, the production of acetaldehyde were the primary purpose of the investigation, a catalyst composed of 65 mol per cent copper and 35 mol per cent zinc oxide would be effective. At this composition
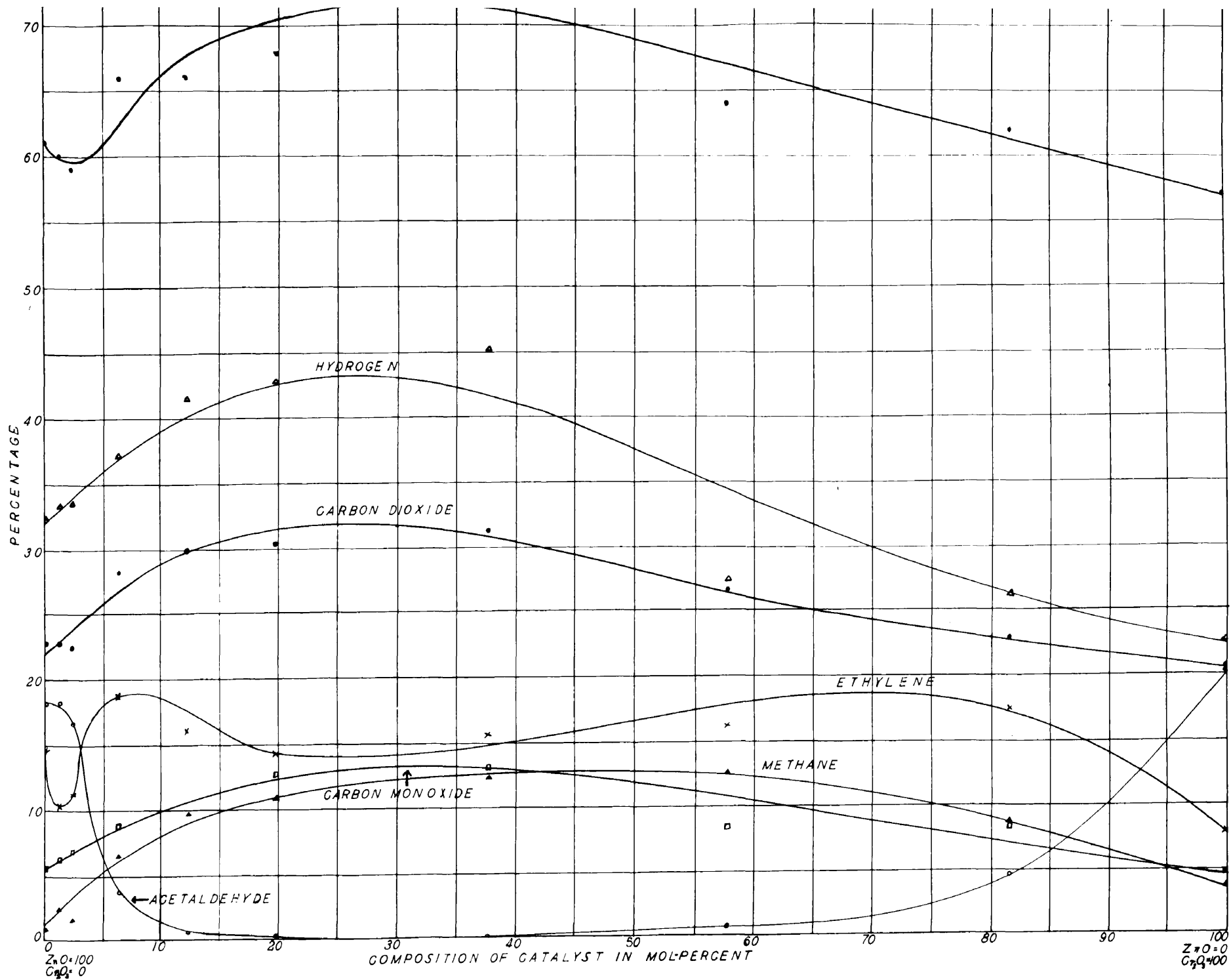
FIG.4.—TOTAL DECOMPOSITION AND PERCENTAGE OF GLYCOL USED DECOMPOSED INTO ACETALDEHYDE, ETHYLENE, CARBON-DIOXIDE, CARBON MONOXIDE, HYDROGEN, METHANE, AND ACETIC ACID AS A FUNCTION OF CATALYST COMPOSITION

approximately 47% of the total glycol used was
decomposed into acetaldehyde.

Chromic Oxide - Zinc Oxide Catalysts

The literature contains many references on the
use of mixed catalysts composed of zinc oxide and chromic
oxide. Smith and Hawk[63] investigated the catalytic
activity of thirty-six different catalysts on the
decomposition of methanol. They report that a catalyst
composed of these oxides in a ratio of four of zinc
oxide to one of chromic oxide was found to be among the
best of the catalysts studied. They also state that
chromic oxide when mixed with zinc oxide does not show
its specific character.

Cryder and Frolich[28] have shown that ZnO - Cr_2O_3
catalysts are very effective both in the synthesis and
decomposition of methanol. Smith and Hirst[29], and
Huffman and Dodge[30] have studied the use of this mixture
in the synthesis and decomposition of methanol. The
latter investigators state that the addition of Cr_2O_3
to ZnO lowers the decomposition. This decrease is followed
by a sharp increase with a maximum at about twenty-five
atomic per cent chromium.

With this information and the data obtained in

this investigation on zinc oxide alone it was decided
to study the catalytic effect of intimate mixtures of
zinc oxide and chromic oxide in the decomposition of
glycol.

Figure 4 presents the results obtained with
this catalytic material. The percentage decomposition
is plotted as a function of catalyst composition.
Table IV contains the data from which Figure 4 was
obtained.

TABLE IV

Mol % Cr_2O_3	% Decomp.	% of glycol used decomposed into:					
		CO_2	C_2H_4	CO	H_2	CH_4	CH_3CHO
0	61	22.6	14.5	5.4	32.3	0.8	18.1
1.32	60	22.6	10.3	6.4	33.4	2.5	18.1
2.43	59	22.2	11.2	6.9	33.6	1.6	16.6
6.35	66	28.1	18.8	8.8	37.2	6.9	3.6
12.25	66	29.8	16.0	9.5	41.6	9.8	0.5
19.73	68	30.2	14.2	12.6	42.8	10.9	0.2
37.73	72	31.3	15.6	13.0	45.3	12.3	trace
57.82	64	26.5	16.3	8.3	27.2	12.6	0.7
81.54	62	22.8	17.5	8.5	26.08	8.7	4.7
100.00	57	20.5	7.8	4.8	22.7	3.3	20.2

Volume catalyst = 11 cc.
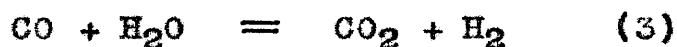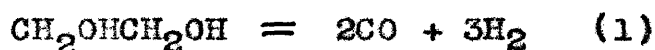
Time of experiment = 40 minutes

Temperature = 506°C.

Glycol used = .0613 mols.

Space velocity = 534

Curve 1, Figure 4 gives the total decomposition plotted as a function catalyst composition. It is seen that the addition of a small amount of chrmoic oxide to zinc oxide slightly decreased the decomposition. This observation is in accord with the work of Huffman and Dodge[30] on the decomposition of methanol. Between 3 and 25 mol per cent Cr_2O_3 the decomposition increased rapidly. From the point where chromic oxide preponderates there was a constant decrease until at the point 100% chromic oxide where the decomposition was nearly the same as that for pure zinc oxide.

The remaining curves of Figure 4 represent the extent to which the following reactions proceeded.

$$CH_2OHCH_2OH = 2CO + 3H_2 \quad (1)$$

$$CH_2OHCH_2OH = CH_2 = CH_2 = CH_2 + \tfrac{1}{2}O_2 + H_2O \quad (2)$$

$$CO + H_2O = CO_2 + H_2 \quad (3)$$

$$CO + \tfrac{1}{2}O_2 = CO + \tfrac{1}{2}O_2 \quad (4)$$

$$CH_2OHCH_2OH = CH_3CHO + H_2O \quad (5)$$

$$CH_3CHO + \tfrac{1}{2}O_2 = CH_3COOH \quad (6)$$

$$CH_3CHO = CH_4 + CO \quad (7)$$

As in the case of the Cu - ZnO catalysts
the extent to which these reactions proceeded was a
function of the Cr_2O_3 - ZnO ratio. It is of special
interest to note that the production of aldehyde was very
rapidly decreased by the addition of a small amount of
chromic oxide to zinc oxide. The same was true for the
addition of zinc oxide to chromic oxide. Between 10
and 70 mol per cent of Cr_2O_3 there was practically
no evidence of aldehyde formation. With pure zinc
oxide as well as with pure chromic oxide a small quantity
of acetic acid was formed. With the catalytic mixture
it could not be detected in the reaction products.

It is seen from Figure 4 that reactions (2)
and (7) proceeded to a considerable extent. The
result is in striking contrast with the results of
the preceding catalysts. The formation of methane may
possibly have accounted for the disappearance of the
aldehyde. It is possible, however, that at least a
portion of the methane was produced by the reduction
of carbon monoxide.

The hydrogen values are roughly equal to the
sum of the corresponding carbon monoxide, and carbon
dioxide values. This condition is in accord with
equation (1). It is encouraging that the maximum
production of hydrogen, carbon monoxide and carbon dioxide

occurred with a Cr_2O_3 - ZnO ratio of approximately
1:3, this also being the ratio for maximum decomposition.
Consequently for the decomposition of glycol into carbon
monoxide and hydrogen the optimum mol per cent of Cr_2O_3 -
ZnO is 1:3.

From a consideration of this data it is evident
that catalysts composed of zinc oxide and chromic oxide
are effective for the decomposition of ethylene glycol
into carbon monoxide and hydrogen. Furthermore, it
does not appear presumptuous to state that a catalyst
composed of zinc and chromic oxides in the ratio of
3:1 would be effective in the synthesis of glycol from
carbon monoxide and hydrogen. It is seen that the
decomposition is a very complex process. Likewise it
is probable that in the synthesis side reactions would
be a determining factor in the conversion of carbon
monoxide and hydrogen into glycol.

SUMMARY

A study has been made of the catalytic effects of various catalysts on the decomposition of ethylene glycol. The catalysts used were: ZnO, Cr_2O_3, $Cu - ZnO$, and $ZnO - Cr_2O_3$. Of these the latter showed the greatest catalytic effect.

The reaction products consisted of acetaldehyde, carbon dioxide, carbon monoxide, hydrogen, and ethylene, together with small amounts of methane and acetic acid. Mechanisms have been proposed to account for the formation of these products.

Cr_2O_3 was principally dehydrating in character while ZnO gave about 50% each of dehydration and dehydrogenation. The addition of a small amount of copper to the zinc oxide, for example 2 mol per cent, produced a decided increase in the dehydration reaction, and a corresponding decrease in the dehydrogenation reaction. Further addition of copper favored dehydrogenation. At the point where copper preponderated principally dehydration occurred. In the case of the $Cr_2O_3 - ZnO$ catalysts the principle reaction was that of dehydrogenation. In this mixture Cr_2O_3 did not show its specific character. The dominate products were hydrogen and the oxides of carbon.

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