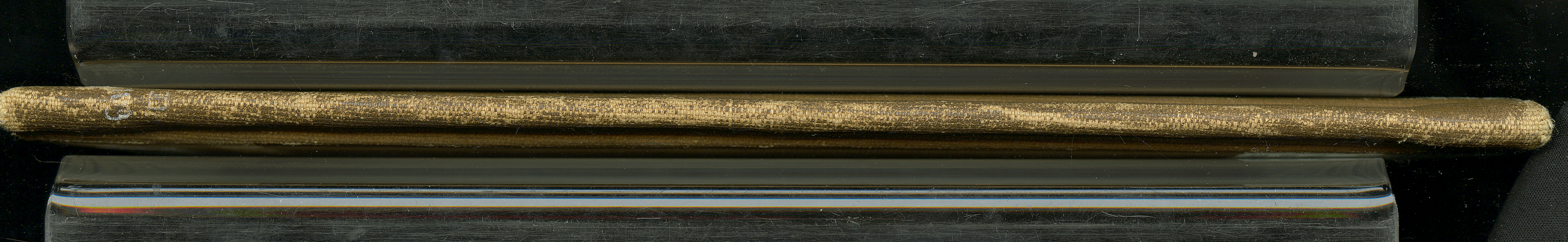


CARBON MONOXIDE AS A POISON IN THE ETHYLENE - HYDROGEN COMBINATION IN THE PRESENCE OF METALLIC COPPER

BY

LELAND STEWART

CARBON MONOXIDE AS A POISON
IN THE ETHYLENE-HYDROGEN COMBINATION
IN THE PRESENCE OF METALLIC COPPER

By

Leland Stewart

1924

CARBON MONOXIDE AS A POISON
IN THE ETHYLENE-HYDROGEN COMBINATION
IN THE PRESENCE OF METALLIC COPPER

A Thesis

Presented to the Academic Faculty
of the
University of Virginia
In Candidacy for the Degree of
Master of Science

ACKNOWLEDGMENT

I wish to express my gratitude to Dr. R.N.Pease who initiated and directed this research.

CARBON MONOXIDE AS A POISON IN THE ETHYLENE-HYDROGEN COMBINATION IN THE PRESENCE OF METALLIC COPPER

Introduction.

According to the adsorption theory of contact catalysis, any substance which is condensed on the surface of the catalyst in preference to the reactants, which the surface activates, should decrease the activity of the catalyst, or, as it is said at present, should act as a poison. The poison or inhibitant may be some foreign non-volatile substance such as grease or it may be some compound which forms on the surface, for example a sulphur or arsenic compound, which remains permanently located on the surface, thereby covering or "masking" it. The above cases are known as permanent poisoning. Again, the poison may be some substance which is reversibly adsorbed, but adsorbed in preference to the substance to be activated. This substance may be one of the reactants or products, or it may be some foreign substance present as an impurity, which is preferentially adsorbed. Thus in the contact process for the manufacture of sulphuric acid, SO_3 has been shown by Fink to be strongly adsorbed and in this way acts as a poison. An example of a reactant acting as a poison is the

ethylene-hydrogen combination, metallic copper being used as a catalyst. The ethylene is preferentially adsorbed as was shown by adsorption measurements and also by certain internal evidence. The above cases are known as temporary poisoning.

Taylor and Burns have shown that carbon monoxide is strongly adsorbed on nickel and copper. Recently much work has been done by Pease (J.A.C.S. 45, 1196, 1923; 45, 2235, 1923; and 45, 2296, 1923) on the adsorption of gases on metallic copper and on the reaction velocities of the ethylene-hydrogen combination to give ethane, using metallic copper as a catalyst. Among other things, he found that carbon monoxide is much more strongly adsorbed at low pressures than either ethylene or hydrogen, and should, therefore, according to the theory of poisoning, act as a poison in the ethylene_ hydrogen combination. Accordingly since no quantitative data exist relating strong adsorption and tempprary poisoning, work was begun under his direction to clear up this problem. This thesis is a preliminary report on the work that has been carried out so far.

The writer chose the same catalyst and the same reaction that Pease used in his work on adsorptions and reaction velocities for the following reasons; (1) a large amount of data has been accumulated on the adsorption of these gases (namely CO, C_2H_4, H_2 and C_2H_6); (2) the reactants and product are gaseous and reasonably stable, (3) the reaction goes practically to completion, (4) there is no possibility of

interaction of catalyst or of side reactions,(5) the reaction takes place at normal temperatures,(6) its course is easily followed,since it occurs with a decrease of pressure at constant volume. CO was chosen for the following reasons: (1) it is a well known poison,(2) data are already possessed regarding its adsorption,(3) it is very strongly adsorbed and should therefore be a good poison,(4) it is easily prepared and purified,(5)it is a gas and does not react with reactants, products,or catalyst,and (6) it is not a permanent poison, the catalytic powers of the catalyst being regenerated on heating and pumping out.

Because of the known variability among samples of catalytically active material both as regards catalytic activity and adsorptive capacity,it was considered vital to obtain measurements of the relative adsorptions and the reaction velocities on the same sample of catalyst,and,if possible,to establish a relation between the two. This was done. The measurements of the velocity without poison have usually been alternated with those with poison so as to take account of any change in activity of the catalyst. The adsorption measuremts were also made at the beginning of the investigation and at the end so as to catch any change in the adsorptive capacities.

- Apparatus and Procedure -

The apparatus used is pictured in Fig. I.

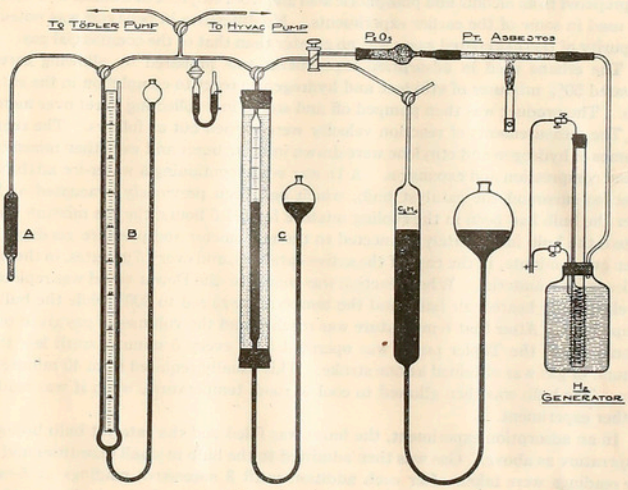


Fig. 1.—Apparatus.

Its essential parts are:-

A. Catalyst Bulb.

B. Mercury Manometer.

C. Gas Buret.

The apparatus is similar to the one used by Pease (J.A.C.S. 45, 1197, 1923) in his work and for detailed description of the apparatus see the above table. The catalyst, ethylene, etc., were prepared and the procedures carried out as therein described. Where differences occur they will be given in this paper.

The catalyst was prepared from C.P. Kahlbaum copper oxide as described above.

The CO was prepared by dropping formic acid into warm conc. sulphuric acid. It was purified by passing through a tower containing a solution of KOH, glass beads being used to break up the bubles, and then through a tube immersed in a mixture of solid carbon dioxide and alcohol to remove condensible impurities. It was then stored in a gasometer (not shown in diagram but similar to the ethylene gasometer) and was used as needed.

The measurements of reaction velocity were carried out as described by Pease with some few changes. For simple reaction velocity measurements i.e. where no CO was used, the ethylene and hydrogen were always mixed in as nearly equal volumes as it was possible to mix them. Usually, however, there was slightly more ethylene than hydrogen, the total volume of gases being about 65 cc. Where CO was used as a poison two different procedures were used. The first differed from the regular procedure in that the CO was run into the catalyst bulb with the ethylene and hydrogen, it being run into the buret second, the hydrogen being run in first, the ethylene last. The gases were then mixed and run into the catalyst bulb as in the regular procedure. The other procedure used was as follows: the CO was run into the catalyst bulb before the ethylene-hydrogen mixture. Varying amounts of CO could be let into the bulb by evacuating the manometer (B on diagram) and running the CO into it first and then from the manometer into the catalyst bulb. For measuring the 0.03 cc of CO, just the hole in the stopcock on the manometer B was filled at atmospheric pressure with CO and just this volume run into the

catalyst bulb. The hole in the stopcock was afterwards calibrated with mercury and its volume found to be about 0.03 cc. After the CO was run over, the regular ethylene-hydrogen mixture was made up in the buret and run into the bulb. About 30-45 minutes usually elapsed between the time that the CO was run in and the time the ethylene-hydrogen mixture was run in, thus giving the CO plenty of time to be adsorbed.

All of the experiments carried out were run at 0°C and the catalyst bulb was always evacuated at 250°C after a run was made.

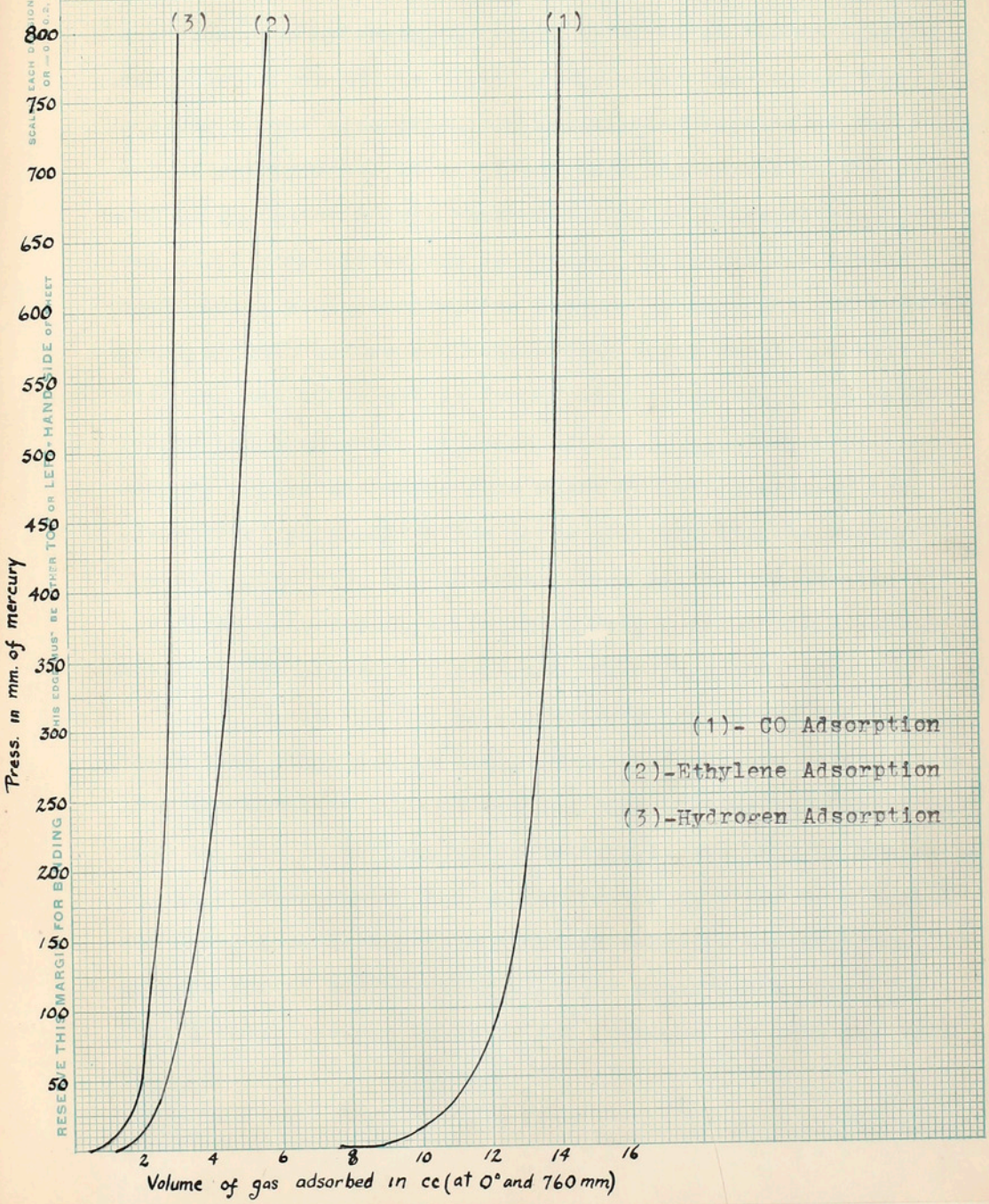
-Adsorption Measurements and Discussion-

As has been pointed out the object of this research was to correlate strong adsorption with poisoning, this being done through the change in reaction velocity produced through the addition of varying amounts of CO.

It has been shown by Taylor and Burns (J.A.C.S. 43, 1273, 1921) and others that both the activity and adsorptive ability of a catalyst depends on the method of preparation, heat treatment, and other factors. Due to these many variable factors that play a part as to the activity and absorptive ability of the catalyst, the catalyst used in this investigation does not give exactly the same results as those obtained by Pease. The curves showing the relation between the absorptive ability of the catalyst used for the three gases are given in Fig. II.

Two sets of absorption measurements were run. One set, the first one run, came about the middle of the investigation;

Figure II.



the other set came at the end of the investigation. On calculating the results of the first set of measurements it was found that the amount of hydrogen and ethylene adsorbed was practically the same, the ethylene being adsorbed slightly more than the hydrogen. As would be expected the CO adsorption curve comes far to the right of the other two curves, thus showing strong adsorption. On calculating results of the second set of measurements, it was found that the curves gotten approach in character nearer those obtained by Pease, although there was still some difference in degree. Unfortunately, during these later measurements, some mercury by accident got into the catalyst bulb before a CO adsorption measurement had been made, and the curve gotten for CO adsorption was of no value; for, as has been shown by Pease (J.A.C.S. 45, 2300, 1923), mercury shifts the curve from right to left (decreases the adsorption) parallel to the curve obtained with no mercury in the catalyst bulb. The CO curve given is the one obtained in the first measurement, while the hydrogen and ethylene curves are those obtained in the second set of measurements.

Since the two sets of adsorption curves did not check each other due to small amounts of mercury getting over into the catalyst bulb at various times during the investigation and due to various other factors, it was thought advisable to check these curves, and an indirect method had been worked out using data gotten from reaction velocity measurements. If we take one of our reaction velocity experiments where very little CO is present (0.03 cc for instance), we know the total

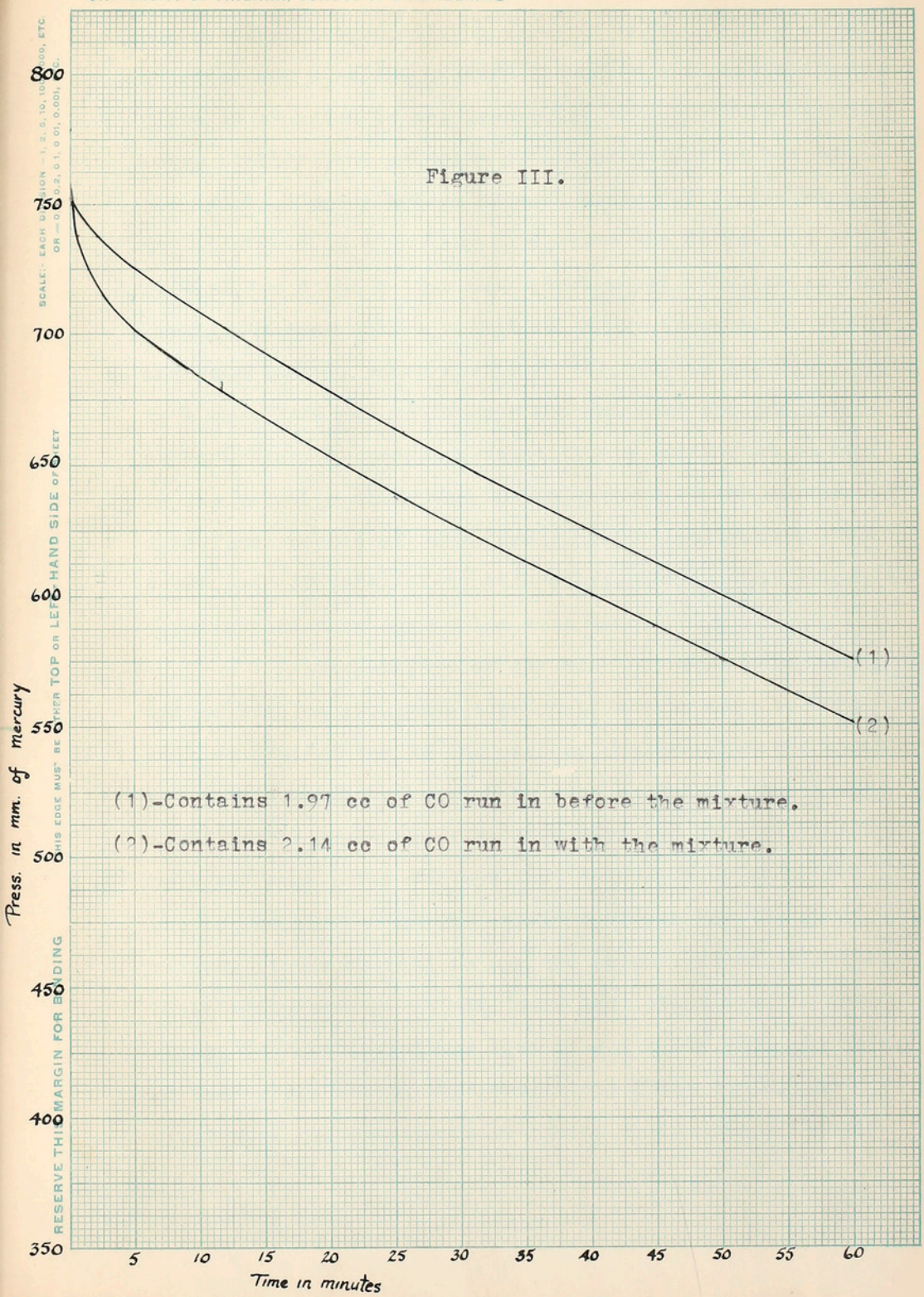
volume in bulb and we have the initial pressure. If we subtract the helium value, corresponding to the same initial pressure, from this total volume run in, we get the number of cc adsorbed and we assume that this all hydrogen and ethylene, the amount of CO being small enough to neglect. Now using the reaction velocity experiment in which 9.14 cc of CO was used, we find the total volume of the gases run in and the initial pressure and subtract the corresponding helium value from it. This gives us the number of cc of gas adsorbed. Thus we found one half an atmosphere of ethylene plus one half an atmosphere of hydrogen gives an adsorption value of 5.30 cc, while one half an atmosphere of ethylene plus one half an atmosphere of hydrogen plus 9.14 cc of CO gives a value of 7.80 cc adsorbed. If the latter is all adsorption of CO, this adsorption is 7.80 cc, the partial pressure of CO being 30 mm. if the latter is adsorption of CO plus adsorption of ethylene and hydrogen (this being same as normally i.e. 5.30 cc) then the adsorption of the CO is 2.50 cc, the partial pressure of CO being 95mm.

Direct experiments showed that the adsorption of ethylene alone at 100 mm. pressure was 2.72 cc while the adsorption of hydrogen was 1.78 cc at 100 mm. pressure. At the very least, therefore, almost as much CO is adsorbed at 90-30 mm. pressure as ethylene (and more than hydrogen) at about 100 mm. pressure; and as a maximum the CO adsorption may amount to three times the ethylene adsorption although at only one third the pressure of the ethylene. No doubt

the truth lies somewhere in between these values. As has been pointed out the adsorption curves obtained by direct measurements probably vary from the true curves to some extent, yet they are not very far wrong, as is shown by comparing them with the above calculated values. Although these curves do not express the true adsorptive capacities of the catalyst during the entire investigation, we know that they are sufficiently near to the truth to use them, since the main object of running these adsorption measurements was to show that the CO was adsorbed considerably more than ethylene, and that ethylene in turn was more adsorbed than hydrogen. This has been shown. It might be noted also that these curves approach those obtained by Pease in shape and relation to one another, differing only in degree.

-Reaction Velocity Measurements and Discussion-

As has been mentioned, reaction velocities have been run, where the method of introducing the CO was varied in two ways. One way, the first tried, was to mix the CO in with the hydrogen and ethylene and run them into catalyst bulb together. The other way was to run in the CO first, and then the hydrogen and ethylene were mixed and run into the bulb. The two methods gave two types of curves as shown in Fig. III. They differ in character only during the first six or seven minutes. There was practically the same amount of CO in the



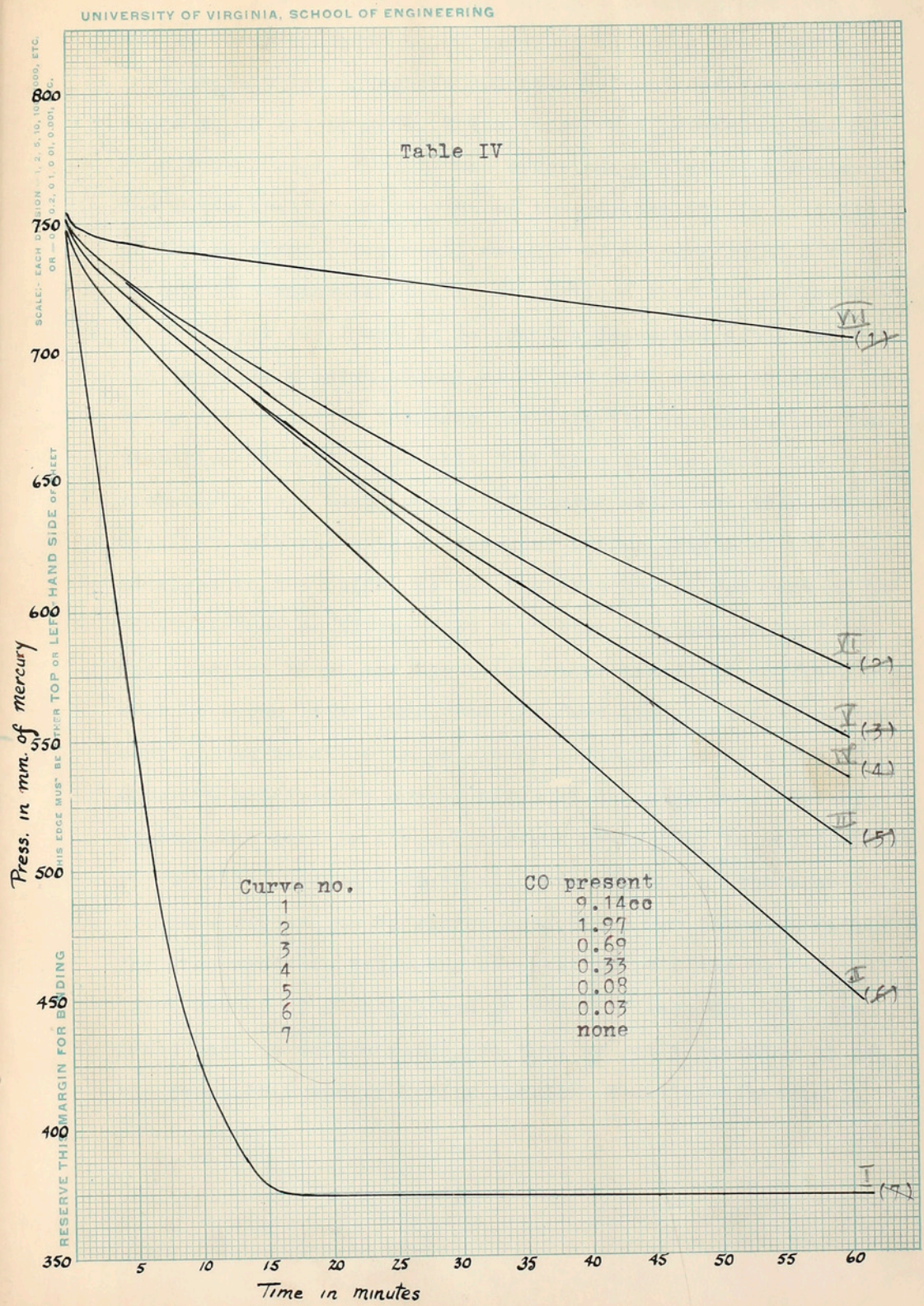
bulb during both reactions. Where the CO was run in first the catalyst's surface is covered up with CO and when the hydrogen and ethylene mixture is run in, the reaction takes place at practically the same speed throughout the entire range studied, the velocity depending mainly on how fast the hydrogen and ethylene molecules can get to the surface of the catalyst. On the other hand, where the CO was run with the mixture, for a short time the hydrogen and ethylene had practically the same chance to get to the surface and be adsorbed, and consequently react, as the CO did. During the time that it took the CO to get to the surface and shut off the hydrogen and ethylene the reaction velocity was quite fast as compared to the velocity after the CO has covered up the surface. After this first period of relatively high velocity, note that the curves go off parallel to each other, showing that after this first period they are of the same type.

A greater part of the work was done using the first method, but the results gotten could not be made to check as well as desired due to the various factors that the reaction velocity depended upon, such as ; the extent the gases were mixed in the buret, how fast they were run into the catalyst bulb, and such other factors that determine which of the gases got to the surface of the catalyst first. For the above reasons, it was decided to try the second method of running these measurements. It was found that check results could be gotten by this method and also it was known from the nature of the curves gotten what was taking place during the first minutes of the reaction, since there was not such a rapid

drop in the pressure for the first few minutes as was the case in the first method used and this was important for explaining the mechanism of the reaction. Accordingly a set of measurements were made by this method, the amount of CO being varied over a wide range. These measurements are summarized in Table I and the curves are given in Fig. IV.

Table I.

Expt. no.	dp in mm. per. minute	CO present (cc)	% inhib.
23	41.15	none	
24	3.38	0.69	7.8%
25	3.63	0.33	8.3
26	4.02	0.08	9.2
27	45.66	none	
28	4.95	0.03	10.9
29	0.57	9.14	1.3
30	2.72	1.97	5±
31	64.10	none	
32	57.47	none	
		H_2 run in before mixture	
33	99.03	8.81	
		C_2H_4 run in before mixture	
34	55.55	9.80	
35	49.03	none	

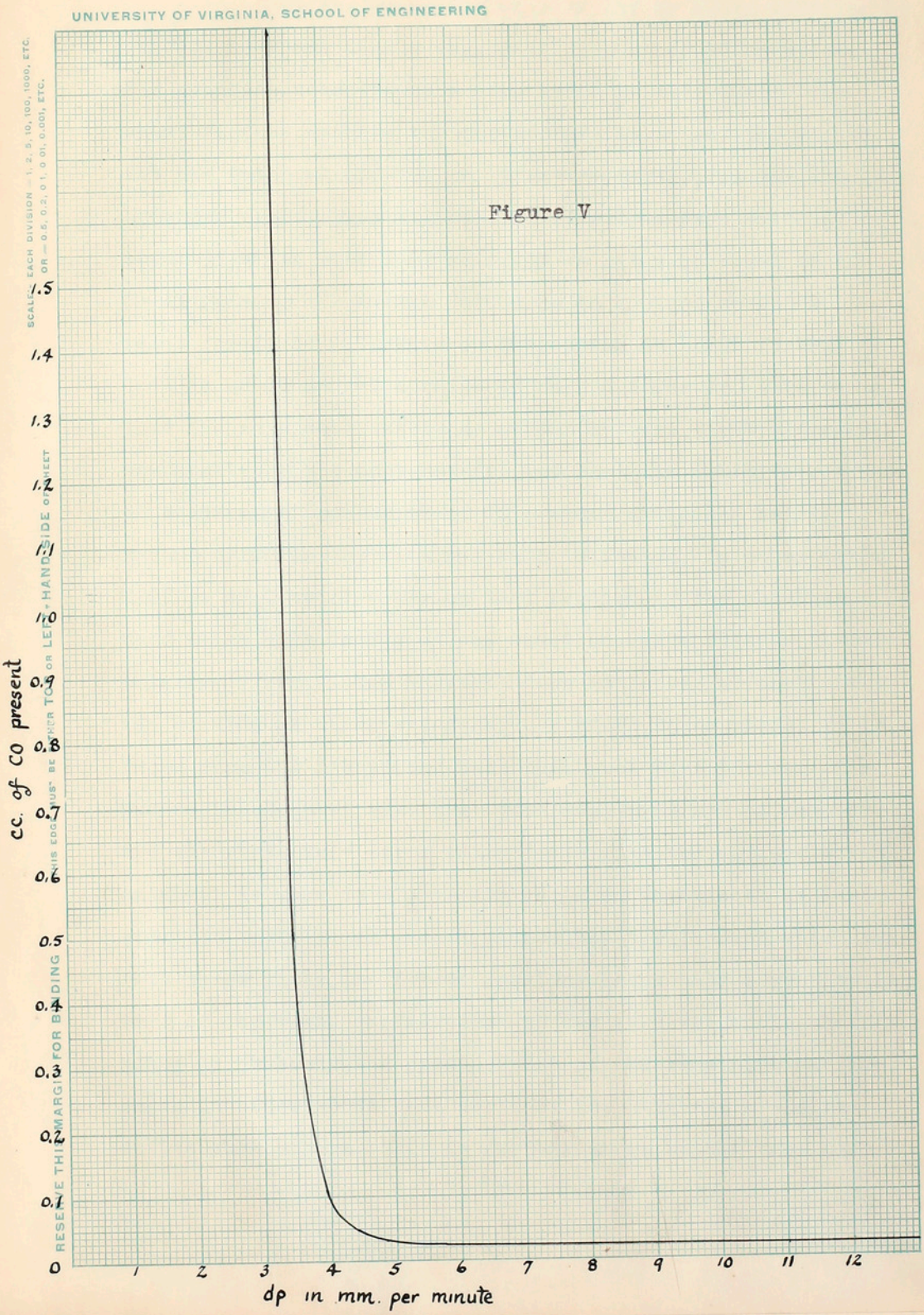

UNIVERSITY OF VIRGINIA, SCHOOL OF ENGINEERING
Table IV
Press. in mm. of mercury
Time in minutes
800
750
700
650
600
550
500
450
400
350
5
10
15
20
25
30
35
40
45
50
55
60
VII (1)
VI (2)
V (3)
IV (4)
III (5)
II (6)
I (7)
Curve no.
1
2
3
4
5
6
7
CO present
9.14cc
1.97
0.69
0.33
0.08
0.03
none

The activity of the catalyst remained constant during these experiments, as is shown by curve no. 7, which represents three different reaction velocity experiments where no CO was present. These three runs bracketted the CO runs shown. Great trouble was experienced elsewhere during the investigation on account of the variability in activity of the catalyst. Very small amounts of mercury getting to it change it permanently, and it was noticed that the activity of the catalyst was found to be greatly increased after each CO run in which a large amount of CO was used, seven or eight cc being sufficient to increase the activity considerably. The probable explanation of this fact lies in the fact that probably a very small amount of oxygen would get into the catalyst bulb and oxidize the most active points of the catalyst to the oxide. We say the most active portions of the catalyst because of the fact that when ethylene or hydrogen are adsorbed these are the points that are first covered (this will be shown later) and from the fact that on these points most of the reaction takes place. Consequently if a few of them are oxidized to copper oxide by the very small amount of oxygen that gets in through various means, then we would expect the ethylene-hydrogen combination (a measure of the constancy of the activity) to be slowed down, since CuO is not a catalyst for the reaction. After the catalyst is oxidized to CuO, the large amount of CO being run in reduces these now inactive parts back to active parts, and thus we get a speeding up of the reaction velocity during the next run. This invariably

happened after the addition of a large amount of CO. This probably was the cause of the difference between results gotten in the two sets of ethylene and hydrogen adsorption measurements; for the first set was made after the CO measurement of adsorption, while in the second case the CO adsorption measurements were made after those of hydrogen and ethylene.

We see that the curves in Fig. IV fall in the order that is to be expected from the theory advanced, namely that the velocity should be decreased more in the case where more CO is present. However it might be said for the curves gotten by the first method of measurement, that in spite of the variability of the activity they usually fall in the order that they should, that is, those that were carried out with a large amount of CO were slower than those where a smaller amount was used.

Taking the data from the curves in Fig. IV and plotting the cc of CO used against dp, the change in pressure per minute, for the interval 600mm. pressure to 700 mm. pressure, we get the curve shown in Fig. V. The most important part of this curve is that part down at very low concentrations of CO, and to bring this part out it was necessary to leave out two points at higher concentrations. However, these lie on an extension of the curve shown, as was shown by plotting on larger coordinate paper using a smaller scale. The curve should also touch the dp axis at some value about 50, but this too could not be shown on account of the scale used.



From the curves in Fig. IV, and as shown differently in Fig. V, we see that a very small amount of CO cuts down the reaction velocity to a very large extent. Giving the exact figures we have for the average dp in mm. per minute for the interval 600-700 mm. pressure of Hg., for the ethylene-hydrogen combination without CO being present, a value of about 50, while with 0.03 cc of CO we get a dp equal to 5. On increasing the amount of CO up to 1.97 cc we get a value for dp of 2.7, while on increasing it still furthur to 9.14 cc of CO we get a value of only 0.6 for dp. This shows that the very smallest trace of CO that was first added was comparatively the most harmful, and that the inhibitive effect of successive increments of CO present decreases as the amount of CO in the catalyst bulb increases. In other words 0.03 cc of CO will cover up that portion of the catalyst upon which nine tenths of the reaction takes place, while a relatively very large increase does not cover up completely the portion on which the other one tenth takes place. It is known from the adsorption data that much more CO than this 0.03cc is adsorbed, also that much more hydrogen or ethylene are adsorbed. This seems to indicate that the surface of the catalyst is made up of certain parts on which most of the reaction takes place and certain other portions on which the rest takes place, the former portions being only a very small part of the total surface area of the catalyst, while the latter makes up, probably, the greater part of the remaining surface area. In other words some parts of the catalyst are more active than others. This is furthur shown by the fact that

over one cc of any of the gases can be added before an appreciable pressure can be gotten, while more is adsorbed at higher pressures. This, however, does not mean that all of this gas that is adsorbed is a measure of the active portions, but that it is adsorbed by the most active and some of those next in activity, in other words it is a measure of those relatively high in activity.

In connection with these experiments it seemed that furthur light could be thrown on the mechanism of the reaction by running in part of the ethylene or hydrogen first, just as the CO was run in first. Accordingly such experiments were carried out, the sum of the reactant that was run into bulb first together with that in the mixture being enough to give a regular one-to-one mixture. It was found that if about ten cc (one third of the total hydrogen volume) was run over first that the reaction velocity was about twice that ordinarily gotten, that is, dp was about 100. However the value gotten where ethylene was run over first was about the same as that gotten for the ordinary run. The absence of any difference in velocity, whether the ethylene was run over first or not, may mean, either that it is normally present in full concentration on the surface, or that it is unnecessary that it be activated, and that the reaction depends primarily on the activation of the hydrogen only.

SUMMARY

1. It has been shown that CO does poison the catalytic combination of ethylene and hydrogen, copper being used as a catalyst. Reaction velocities and adsorption measurements have been made at 0°C .

2. It was found that very small quantities (0.03 cc) of CO were enough to decrease the reaction velocity to about nine tenths the value gotten where no CO was present.

3. These results appear to indicate that of the surface active in adsorption only about 1 % is responsible for 90% of the catalytic activity at 0°C .