in acid solution. The method is accurate to within 0.1% if care is taken to eliminate the oxygen-iodide error and if the loss of hydrazoic acid by volatilization is prevented. Hydrazoic acid cannot be determined in the presence of hydrazine, but the two can be readily separated. Ammonium ion has no effect on the method.

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[CONTRIBUTION NO. 36 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

THE ADSORPTION OF HYDROGEN AND ETHYLENE ON A COPPER CATALYST POISONED WITH CARBON MONOXIDE

BY CARROLL W. GRIFFIN

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Some years ago Taylor and Burns[1] in studying the adsorption of gases on metallic catalysts found that catalytically active copper adsorbed ethylene strongly at low temperatures and hydrogen less strongly. Later Pease[2] took up the study of the hydrogenation of ethylene using copper as the catalyst. He pointed out the apparent correlation of catalytic activity and strong or low-pressure adsorption of reactants in view of the fact that either mercury poisoning or heat treatment of the copper caused a simultaneous and marked decrease of both of these properties. This was followed by a study by Pease and Stewart[3] of the effect of carbon monoxide as a poison to the reaction. They showed that less than 0.05 cc. of carbon monoxide reduced by 88% the activity (towards an ethylene-hydrogen mixture) of a copper catalyst which adsorbed at less than one mm. pressure approximately 1 cc. of hydrogen, 2 cc. of ethylene or 5 cc. of carbon monoxide. Their conclusion was that the copper surface owed 88% of its catalytic activity to less than 1% of the centers active in adsorption, thus emphasizing the existence on the copper surface of centers of different degrees of activity. The adsorption of the reactants on the catalyst poisoned with carbon monoxide had not been measured and it was suggested to the writer by Dr. R. N. Pease that such measurements be made.

Procedure

The apparatus, the method of preparation of the catalyst, of the hydrogen and of the ethylene, as well as the taking of measurements and the limit of accuracy, were as Pease[4] has previously described. Pure carbon monoxide was obtained by the decomposition of formic acid and passage of the gas over phosphorus pentoxide and soda lime. The 63.42 grams

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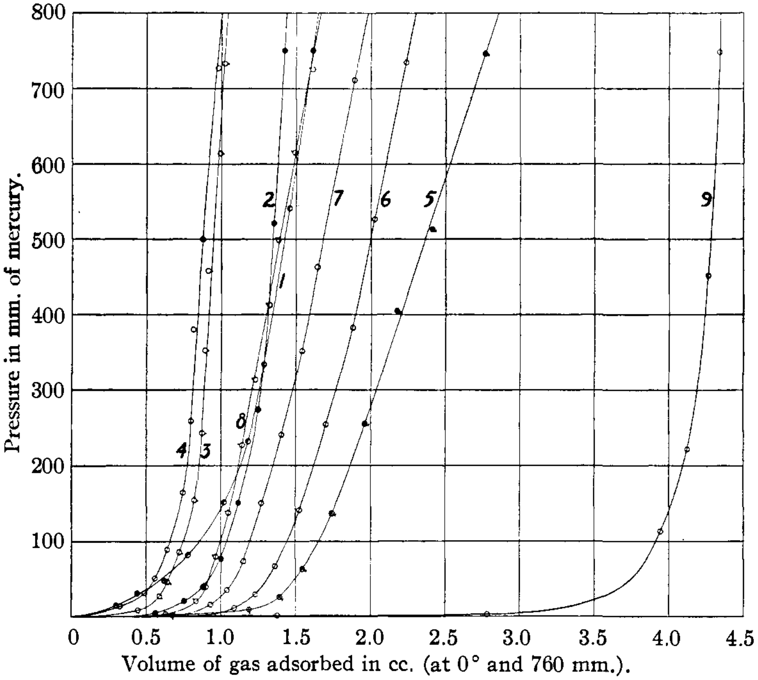
[1] Taylor and Burns, THIS JOURNAL, **43**, 1273 (1921).

[2] (a) Pease, *ibid.*, **45**, 1196 (1923); (b) **45**, 2296 (1923).

[3] Pease and Stewart, *ibid.*, **47**, 1235 (1925).

[4] Pease, Refs. 2 and 3.

of copper used was the second catalyst employed by Pease and Griffin[5] and thus already established as permanently active to a high degree. The poison, carbon monoxide, was always introduced into the catalyst bulb approximately a half hour before a run was started. At the end of the run pumping out at 200° completely removed the hydrogen or ethylene and also the poison. Measurements were made at 20 and at 0°. Helium, assumed unadsorbed, was used as a reference gas.



Curve 1, H_2 with no CO; 2, H_2 with 0.038 cc. CO; 3, H_2 with 0.26 cc. CO; 4, H_2 with 0.74 cc. CO; 5, C_2H_4 with no CO; 6, C_2H_4 with 0.038 cc. CO; 7, C_2H_4 with 0.24 cc. CO; 8, C_2H_4 with 0.73 cc. CO; 9, pure CO.

Fig. 1.—Adsorptions of hydrogen and ethylene on copper poisoned with carbon monoxide at 0°. Weight of copper catalyst: 63.42 g. Volume of dead space: 22.35 cc.

Adsorptions of the three gases on the pure catalyst were made first. Then hydrogen adsorption was alternated with ethylene on the catalyst poisoned first with 0.038 cc. of carbon monoxide and then with about 0.75 cc. and finally with about 0.25 cc. A run at 20° was always followed by the corresponding run at 0°.

Constancy of Activity.—Reaction velocity runs with 1:1 mixtures of ethylene and hydrogen were used as checks on the activity of the catalyst.

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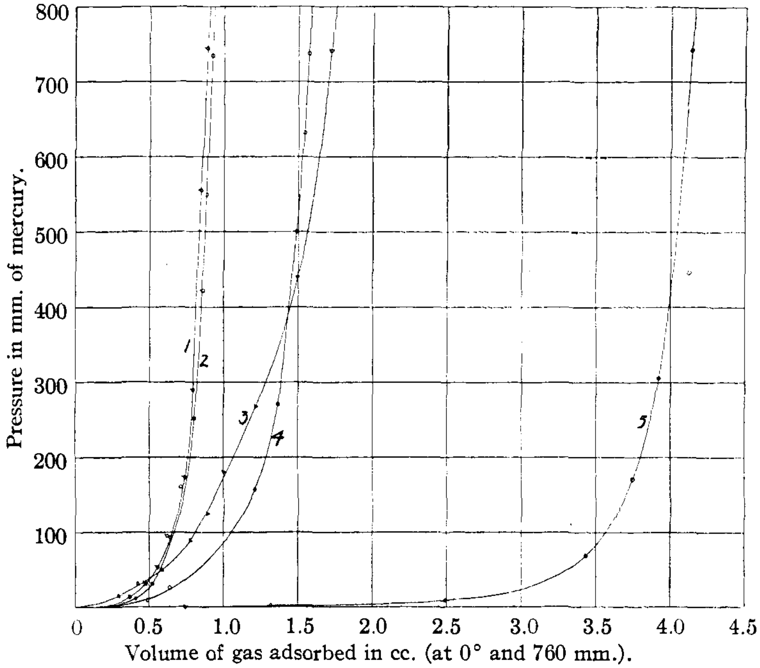
[5] Pease and Griffin, This Journal, **49**, 25 (1927).

The first was made at the beginning of the investigation, another midway, and a third at the end of the research. Taking the activity of the first as 100%, the second proved to be 104% (based on the time required for the pressure to drop from 700 mm. to 600 mm.) and the third 106%. Due to the fact that the reaction velocity was very rapid (being practically completed in 7 minutes) these are considered as very satisfactory checks.

About a week after all the runs were completed a small crack occurred in the catalyst bulb, which allowed a very slight oxidation of the copper to take place. The crack was sealed and a new helium run was made. A subsequent reaction velocity run showed a less active catalyst, 64%, and an ethylene adsorption run at 20° following this showed an adsorption practically unchanged up to one-half atmosphere and only 7.8% less at one atmosphere. This confirmed the belief that reaction velocity is a more sensitive test of surface condition than adsorption, and that during the course of the investigation the catalyst remained substantially constant in both its catalytic and adsorptive activity.

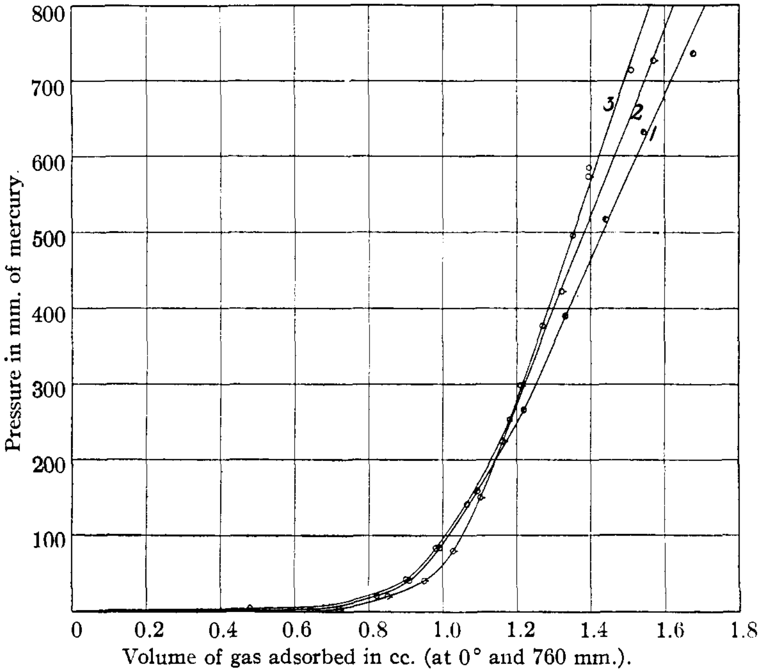


Curve 1, H_2 with 0.76 cc. CO; 2, H_2 with 0.27 cc. CO; 3, H_2 with no CO; 4, H_2 with 0.038 cc. CO; 5, pure CO.

Fig. 2.—Adsorption of hydrogen on copper poisoned with carbon monoxide at 20°. Weight of copper catalyst: 63.42 g. Volume of dead space: 22.35 cc.

Following experiments with this sample of copper, another sample was used with which five runs were made. The first and last were ethylene runs on the pure sample, poisoned runs intervening. The adsorption activity was identical in the first and fifth runs.

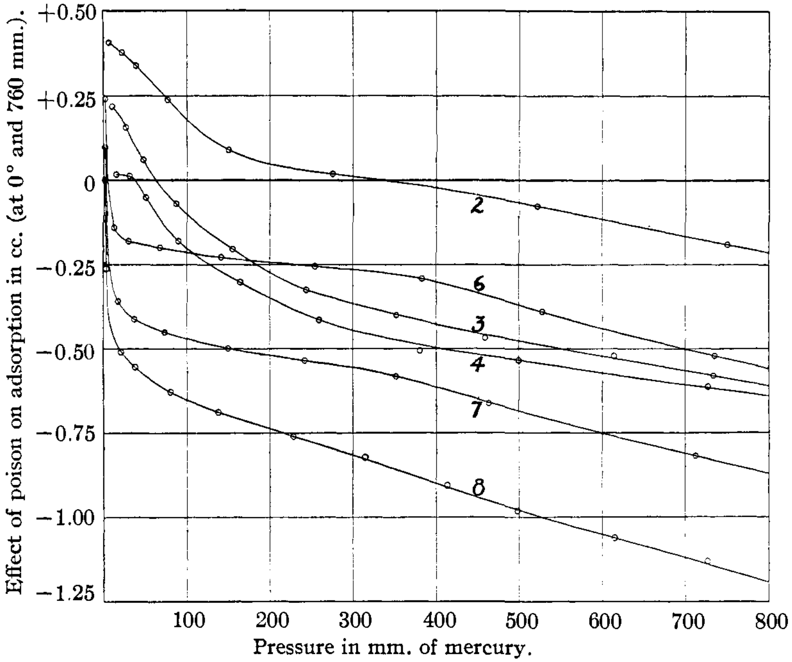
It is noteworthy that throughout the first several runs, in addition to measurements made as gas was admitted to the catalyst bulb, portions of gas were withdrawn and readings taken. The points so secured fall on the curves with the same accuracy as those obtained when the gas was admitted, thus showing the absence of hysteresis.



Curve 1, C_2H_4 with no CO; 2, C_2H_4 with 0.24 cc. CO; 3, C_2H_4 with 0.72 cc. CO.

Fig. 3.—Adsorption of ethylene on copper poisoned with carbon monoxide at 20°. Weight of copper catalyst: 63.42 g. Volume of dead space: 22.35 cc.

Results.—Adsorption isotherms at 0° are shown in Fig. 1. On the unpoisoned catalyst these are essentially the same as obtained by Pease. Curves 2, 3 and 4 for hydrogen and 6, 7 and 8 for ethylene show the effect of poisoning with progressively greater amounts of carbon monoxide. Considering for the moment higher pressures, it is noticed that both in the case of ethylene and hydrogen the effect of the poison is a progressive decrease of adsorption with increase of carbon monoxide. In the isotherms at 20° (shown for hydrogen in Fig. 2 and for ethylene in Fig. 3) at pressures of about a half to one atmosphere the same result is found. In Figs. 2 and 3 it is seen that at lower pressures there is an *increase* of adsorption where poison was used. This increase diminishes as the pressure increases, the curve crossing the isotherm of the gas on the unpoisoned copper and representing thereafter a *decrease* in adsorption for the higher pressures. This increase of adsorption persists, in general, to higher pressures for hydrogen than for ethylene, and for either gas the smallest amount of poison causes the greatest increase of adsorption at low pressures and the least decrease of adsorption at high pressures.

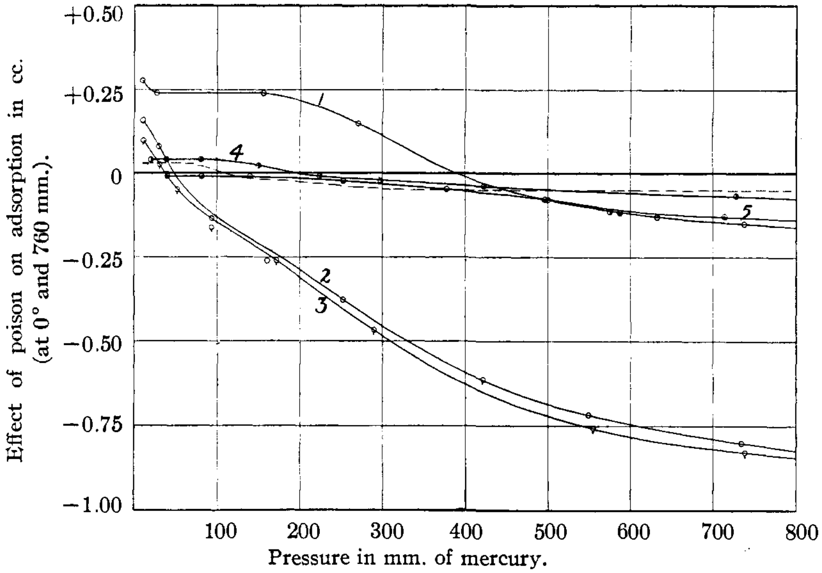


Curve 2, H_2 with 0.038 cc. CO; 3, H_2 with 0.26 cc. CO; 4, H_2 with 0.74 cc. CO; 6, C_2H_4 with 0.038 cc. CO; 7, C_2H_4 with 0.24 cc. CO; 8, C_2H_4 with 0.73 cc. CO.

Fig. 4.—Effect of poison on adsorption at 0°.

With one exception the same kind of behavior is found in the 0° curves, but in some cases the points at which the poison curves cross the unpoisoned isotherms are at such low pressures as probably not to be at once evident in Fig. 1. To bring out these considerations more distinctly, Figs. 4 and 5 are drawn in which pressure is plotted against $V_1 - V_2$, where V_1 is the volume of the gas adsorbed by the poisoned catalyst and V_2 is the volume of the gas adsorbed by the pure catalyst. The exception referred to above is the case of ethylene at 20° with 0.72 cc. of carbon monoxide as poison. Here at the lowest pressure measured there is already a decrease in adsorption due to the poison. By extrapolation, however, it is evident that here also at very low pressure there is an increase over normal adsorption.

It will be noted that no curve is given for ethylene at 20° with 0.038 cc. of poison. Such a run was made; however, it was found to show a decrease in adsorption considerably greater than the run in which even 0.72 cc. of carbon monoxide had been used. Since such a result is not compatible with the research as a whole, it is believed that some unknown source of error entered this run. As calculations were not made until practically all the runs had been completed, this incongruity was not noticed until after the catalyst was no longer available. A new sample of copper oxide was later reduced and five runs made on the copper (125 g.) including a run of ethylene on the pure copper followed by a carbon monoxide run and then ethylene on the catalyst poisoned first with 0.038 cc. of carbon monoxide and then with 0.24 cc. The 0.038 cc. poison run showed a low-pressure increase of adsorption and a high-pressure decrease; the decrease, however, as had been expected, was less than that caused by 0.24 cc. of poison on the same catalyst. In Fig. 5 the effect of the 0.038 cc. of carbon monoxide on this new catalyst is shown by the broken curve. (This broken curve is the only one from the new catalyst. All other curves refer to the original catalyst.)



Curve 1, H_2 with 0.038 cc. CO; 2, H_2 with 0.27 cc. CO; 3, H_2 with 0.76 cc. CO; 4, C_2H_4 with 0.24 cc. CO; 5, C_2H_4 with 0.72 cc. CO; broken line, C_2H_4 with 0.038 cc. CO (new catalyst).

Fig. 5.—Effect of poison on adsorption at 20°.

A reaction velocity measurement with a 1:1 mixture of ethylene and hydrogen on the catalyst poisoned with 0.038 cc. carbon monoxide showed a decrease in catalytic activity of 80%, a fair check with the result of 88% obtained by Pease and Stewart[3] with their catalyst.

Discussion of Results

The fact that the results of this work show as an effect of carbon monoxide poisoning an increase of low-pressure adsorption of hydrogen and ethylene is precisely the opposite of what was expected in view of the results of previous workers. Rather, it had been believed that isotherms similar to those found where mercury had been used as a poison or where the copper had been treated with heat would be obtained. It was even as great a surprise to find, whatever the effect, that it should be reversed at higher pressure.

Doubtless there are more ways than one of viewing these results. The low-pressure increase of adsorption due to the poison is quite definite, and even in those cases where the increase is only very slight and possibly within the magnitude of the experimental error, it is believed that they are nevertheless real and significant in view of the fact that without exception every run exhibited the low-pressure increase.

It is conceivable that the carbon monoxide simply caused a redistribution of adsorptive power among the active centers, altering the adsorption at various pressures without changing the number of centers and thus without changing appreciably the total, eventual adsorption at an indefinitely higher pressure. It hardly seems, however, that such reasoning could explain the results obtained, for it would then be difficult at least to explain a decrease of adsorption greater than the amount of poison added.

Inasmuch as the critical temperature of hydrogen is very low, namely, —234.5°, and qualitatively hydrogen and ethylene behave alike in their adsorption on the poisoned catalyst, it is evident that capillary condensation does not take place and thus any peculiar effect of the poison on that process is presumably out of the question.

Therefore, it seems necessary to assume that an adsorbed carbon monoxide molecule is capable of linking several hydrogen or ethylene molecules, perhaps to itself, perhaps by increasing the activity of neighboring centers, or possibly both. If this is true then the results may be looked upon as follows. The carbon monoxide must be adsorbed on the very active centers in view of the marked decrease in catalytic activity caused by an extremely small amount of poison. The carbon monoxide thereafter takes up hydrogen or ethylene molecules to such an extent that the total adsorption at a given low pressure is greater than on the unpoisoned catalyst where each very active point presumably holds only one molecule. This could explain that part of the curve showing an increase of adsorption.

It is difficult to say why an increase of adsorption should at higher pressure give way to a decrease. The accumulation of more and more data on the subject of adsorption seems to indicate that the process probably is complex, involving not simply one kind of action but nearly always several agencies, all included under the term sorption. It may be true that in the case of ethylene and hydrogen on copper, the measurements made have not been a record of adsorption, pure and simple. In the case in hand, possibly in addition to adsorption of the gases on the surface, actual solution of the gases is involved. If solution actually did take place it might indicate the presence of more or less amorphous copper. Rideal[6] assumes the presence of the amorphous form in such samples as have been employed by Pease; he even supposes the strongest catalytically active centers of copper to be amorphous "patches."

It is true that Sieverts'[7] studies do not indicate solution of hydrogen in copper at the temperatures of 20 and 0°. However, Sieverts used electrolytic copper wire, whereas that employed in this research was obtained by slow reduction of copper oxide at 150°.

Assuming a secondary action in addition to that of straight adsorption, Curve X of Fig. 6 could represent that due strictly to adsorption. Curve Z would represent the sorption actually observed on the pure catalyst and due to surface adsorption plus the secondary action. If the secondary action were that of solution it would be negligible at low pressure and thus practically coincident with Curve X in that region. One would expect the increase of surface adsorption due to the poison to continue at all pressures. If, in addition, the poison prevents the solution process, the sorption on the poisoned catalyst would be represented by Curve Y. Curves Z and Y represent what actually are found on the pure and on the poisoned catalyst, respectively, while Curves X and Y represent what might be found were the secondary action absent.

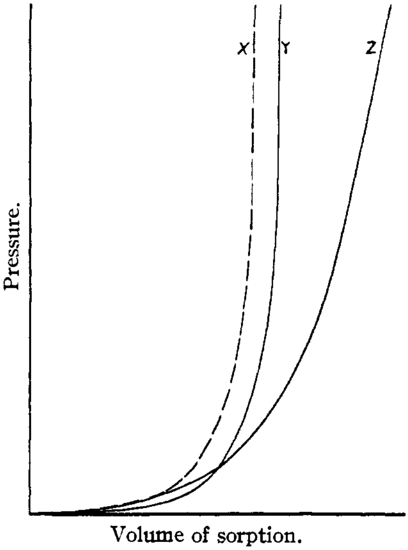


Fig. 6.

Suppose the secondary factor to be solution. If the carbon monoxide attaches little or no more hydrogen at higher pressures than at zero pressure, and were the amount dissolved unaffected, then the curves of Figs.

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[6] Rideal, "Surface Chemistry," Cambridge University Press, **1926**, p. 163.

[7] Sieverts, *Z. physik. Chem.*, **60**, 145 (1907).

4 and 5 would be horizontal lines. The vertical distances between such a line and the actual curve at a given pressure would represent the difference in the amount of gas dissolved in the pure copper and in the poisoned copper. By extrapolating the three hydrogen curves of Fig. 4 to zero pressure and arithmetically adding to these values the corresponding decrease at 700 mm. pressure, the result is roughly 0.60 cc. for the smallest amount of poison and 0.85 cc. for each of the two larger amounts. Such a relation indicates that 0.038 cc. of the poison was almost enough and 0.26 cc. or 0.74 cc. entirely sufficient to prevent solution. At 20° (Fig. 5) the hydrogen curve for 0.038 cc. of poison exhibits a relatively slight difference of solution compared to that of the unpoisoned copper, and the curves for the two larger amounts of poison show diminutions practically identical in themselves but much greater than that for the smallest quantity of poison. Comparison of hydrogen curves at 0 and 20° in Figs. 4 and 5 shows that the solubility is slightly greater at 20 than at 0°, as would be expected. With the larger amounts of poison the solubility difference between pure and poisoned copper is about 0.98 cc. at 20° as compared with 0.85 cc. at 0°. The approximately parabolic form of these curves indicates that the solubility is proportional to the square root of the pressure as Sieverts and Krumbhaar[8] found to be the case for hydrogen in copper at higher temperatures.

That a very small quantity of poison is sufficient to prevent solution in the copper may be attributed to its ability to incapacitate the very active centers on the copper surface, thereby depriving the molecular hydrogen of its dissociating agency. The nature of the ethylene curves differs from that of hydrogen chiefly in that at 0° they bend more abruptly in approaching zero pressure. Without further hypothesizing it is, therefore, difficult to draw similar conclusions for ethylene.

It appears that a different attack on the problem presented by this investigation may be pursued, since a supported catalyst should largely do away with all except surface adsorption, and it seems that much might be learned by poisoning such a catalyst. It is planned to investigate this possibility.

Finally, it should be mentioned that it appears now more certainly than ever that adsorptions even at very low pressures do not serve as a measure of catalytic activity. Furthermore, it should be recorded that those molecules of hydrogen or ethylene which give the low-pressure increase of adsorption—that is, those molecules which owe their linkage to the poison itself, either directly or indirectly—are *not* activated. That this is definitely a fact is evidenced by the catalytic inactivity of the poisoned copper, for although in the low-pressure region the adsorption of both gases is actually increased by the poison, nevertheless the copper is practically inert as a catalyst.

[8] Sieverts and Krumbhaar, *Z. physik. Chem.*, **74**, 277 (1910).

The writer wishes to express his heartiest thanks to Dr. A. F. Benton, whose frequent advice was of great value.

Summary

1. Adsorption measurements have been made for ethylene and hydrogen on a copper catalyst poisoned with carbon monoxide.

2. It has been found that the poison causes a low-pressure increase and a high-pressure decrease of adsorption as compared to measurements made on the unpoisoned catalyst. The poison decreases the catalytic activity very markedly.

3. A possible, general interpretation of the results has been outlined, assuming the process of sorption to comprise a secondary factor such as solution in addition to surface adsorption.

4. It has been shown that carbon monoxide in causing extra, low-pressure sorption of the gases does not leave the hydrogen or ethylene in an activated state.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PHOTOCHEMICAL REARRANGEMENT OF ACETYLCHLORO-AMINOBENZENE

BY C. W. PORTER AND PAUL WILBUR

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The photochemical rearrangement of acetylchloro-aminobenzene to *p*-chloro-acetanilide has been the subject of many investigations, but heretofore the absorption coefficients in the region of effective radiation have not been determined A study of factors governing the rearrangement in the solid phase has not been made, although Slosson[1] long ago reported the observation that heat alone causes the change. The rearrangement in the presence of various solvents has received careful attention.[2]

We have undertaken to measure the energy required to convert one molecule of the chloro-amine into the isomeric form. As a preliminary step we determined the absorption coefficients of acetylchloro-aminobenzene and of the *p*-chloro-acetanilide over the range between 2200 and 3400 Ångström units. These results, with some observations relating to the rearrangement in the solid phase, are presented in this paper. The energy measurements which have been made on the absorption of certain narrow bands in the spectrum will be published after we have made further attempts to obtain results with pure monochromatic light.

The absorption coefficients were determined as follows. The spectrum

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[1] Slosson, *Am. Chem. J.*, **29**, 289 (1903).

[2] (a) Acree and Johnson, *Am. Chem. J.*, **37**, 258 (1907); (b) Rivett, *Z. physik. Chem.*, **82**, 201 (1913); (c) Mathews and Williamson, THIS JOURNAL, **45**, 2574 (1923).