

Less extensive studies of the effect of hydrogen and iodide ion concentrations on the action of other interfering substances indicate that conditions satisfactory in the presence of manganese dioxide would suffice for nitrite or iron. Some organic chloramines or chlorine derivatives of low bactericidal potency, if present, will be partially measured as chlorine under any conditions

suitable for thiosulfate titration. Any values of  $pH$  and  $\{KI\}$  taken from the nomogram for use should be subjected to direct tests by a definite procedure, to determine the accuracy of chlorine titrations in the concentrations to be employed and the rate of reaction of amounts of interfering substances likely to be encountered.

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[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

## The Sorption of Hydrogen on Supported Nickel

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### Introduction

In an earlier paper the writer<sup>1</sup> pointed out that the low-pressure increase in the adsorption of hydrogen by copper which had been poisoned with a small amount of carbon monoxide appeared to be due either to the ability of the monoxide molecule to link several hydrogen atoms to itself, or to an increased activity of the copper centers in proximity to the adsorbed monoxide. White and Benton,<sup>2</sup> after studying the poisoning action of a small amount of carbon monoxide on the adsorption of hydrogen by nickel, concluded that the increased adsorption of hydrogen caused by the monoxide was due to an increased activity of the most active centers of the metal, that is, an enlargement of the active areas following the poisoning. With both metals larger amounts of carbon monoxide caused a smaller increase of hydrogen adsorption, and, at higher pressures, the poison often decreased the adsorption. In both of the above studies the adsorption was of the activated type, the measurements being carried out at 0°.

In the extensive investigations of Benton and White on the sorption of gases at low temperatures<sup>3</sup> where the adsorption was largely of the physical type it was revealed that carbon monoxide caused an immediate decrease in the adsorption of hydrogen. Furthermore, at -183° this low-pressure decrease is exactly equal to the volume of poison employed provided, of course, the amount of poison used is not greater than the low-pressure adsorption of hydrogen itself. However, in their low temperature studies, Benton and

White did not use less than 1.0 cc. of the poison; and since previous experience had always shown that much more than 0.04 cc. of carbon monoxide caused a decrease in hydrogen adsorption, it seemed worth while to investigate the effect of a progressive poisoning of nickel with the smaller amounts of the monoxide at low temperature. In addition, by employing a supported nickel adsorbent two other points could be observed, namely, whether or not a supported sample shows the step-wise discontinuities which characterize many of the isotherms for gases on massive metals as shown by Benton and White, and the result of "experiments with temperature variation."<sup>4</sup>

### Experimental Part

The apparatus, the purification of hydrogen and the procedure for making a run have been described.<sup>5</sup> Helium, used as a reference gas, was purified by passing over hot copper and copper oxide and over active charcoal cooled in liquid nitrogen. The method of preparation of the supported nickel has been reported.<sup>6</sup> Fifty grams of brick was used to support the nickel in the ratio of two moles of nickel to a thousand grams of brick.

The low temperature measurements were carried out with the adsorbent in a bath of liquid nitrogen. The temperature was determined by use of a platinum resistance thermometer connected to a Leeds and Northrup Mueller type temperature bridge. The resistance thermometer was calibrated at 100, 25, 0° and at -78.5, -191.5 and -196°. The absolute temperature of the experiments at the lowest temperature may be in error by 0.5° or less, but variations in temperature amounting to 0.001° could be detected. The blade of the thermometer was approximately the same length as the bulb containing the adsorbent and was placed alongside the latter. For experiments at -78.5° solid carbon dioxide and alcohol were employed; for 0°, ice and water. The volume of the free

(1) Griffin, *THIS JOURNAL*, **49**, 2136 (1927).

(2) White and Benton, *J. Phys. Chem.*, **35**, 1784 (1931).

(3) Benton and White, *THIS JOURNAL*, **53**, 3301 (1931).

(4) Benton and White, *ibid.*, **54**, 1379 (1932).

(5) Pease, *ibid.*, **45**, 1196 (1923).

(6) Griffin, *ibid.*, **59**, 2431 (1937).

space for measurement at liquid nitrogen temperature was calculated from the helium values experimentally determined at  $-78.5$  and at  $0^\circ$ . No sorption was found for hydrogen on the brick itself at  $-196^\circ$ , although ethylene, for example, is considerably sorbed even at  $0^\circ$ .

### Results

At temperatures so low as  $-196^\circ$  a very large error is introduced in computing the adsorption if the temperature varies by a few tenths of a degree unless corrections are applied. This, however, may be done. In the seven runs made at  $-196^\circ$ , including three check runs, the initial temperature for the several runs varied up to  $0.4^\circ$  and, during any given run, the boiling point of the nitrogen varied a few tenths of a degree. However, for a given pressure the adsorption of hydrogen at  $-196^\circ$  and at  $-196 \pm 0.4^\circ$  cannot differ widely, and by using the proper, calculated helium value, based upon the observed temperature for each point, the precision secured for runs at low temperatures should be almost as great as that for measurements at higher temperatures. Since the platinum resistance thermometer indicated changes in temperature of  $0.001^\circ$ , the changing helium values for the slightly varying temperature could be computed precisely. The experimental accuracy<sup>3</sup> (p. 3307) is estimated to be about 0.05 cc. (The resistance thermometer, incidentally, is preferred by the author to the thermocouple since it gives the over-all average temperature of the liquid immediately surrounding the adsorbent rather than the temperature at a single point in the bath.)

The adsorption of hydrogen on the supported nickel at  $-196^\circ$  is represented by Curve 1 of Fig. 1. The open circles and triangles of the curves indicate points obtained in going from lower to higher pressures; full black circles and triangles, from higher to lower. Curve 2 resulted from measurements made by poisoning the nickel with 0.12 cc. of carbon monoxide before admitting hydrogen to the bulb. This run was extended to atmospheric pressure (as was the run of Curve 3) but only a portion is shown since the points at higher pressures for the four curves become crowded. Curve 3 resulted from the use of 0.23 cc. of poison while Curve 4 was obtained after introducing 0.60 cc. of the monoxide.

All of the isotherms indicate the same sort of step-wise adsorption that Benton and White found for massive nickel. According to the hypothesis of concentric rows<sup>3</sup> (p. 3309), the fact

that the supported nickel of this study shows a fewer number of steps than the massive nickel used by Benton and White suggests that the nickel crystals upon the brick support are considerably smaller than the crystals in their adsorbent. This may well be true for a supported sample of nickel.

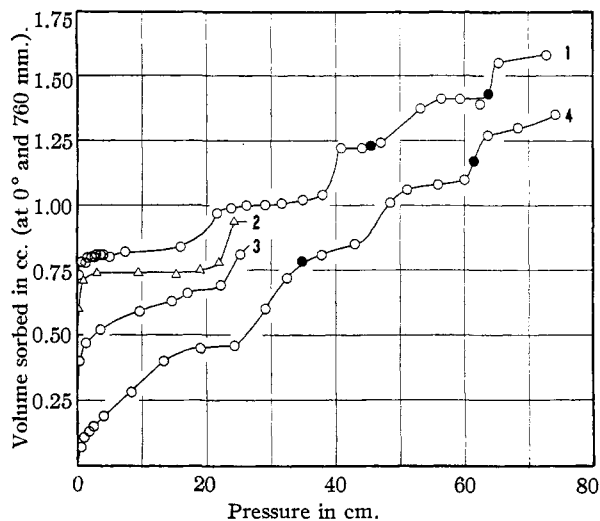


Fig. 1.—Sorption of hydrogen on supported nickel, two moles of nickel per 1000 g. of brick, poisoned with carbon monoxide at  $-196^\circ$ : curve 1,  $H_2$  with no poison; 2,  $H_2$  with 0.12 cc. CO; 3,  $H_2$  with 0.23 cc. CO; 4,  $H_2$  with 0.60 cc. CO.

The smallest amount of poison used was 0.039 cc. No curve is shown for this run, the reason being that the points all fall within a few hundredths cc. of Curve 1 with no point above this curve. Thus, although the presence of a finite sorption at zero pressure, as indicated by Curve 1, implies that there is some activated adsorption taking place in addition to physical adsorption, the effect of 0.039 cc. of poison differs from its influence when employed at higher temperatures where little or no physical adsorption is at play. It is also seen from Fig. 1 that the decrease in adsorption is very nearly equal in every case to the amount of poison used. This is quite evident at low pressures; nearer atmospheric pressure there is a drawing together of the pure and the poison isotherms. This drawing together can be explained if, at higher pressures, hydrogen is more and more adsorbed as a second layer above the carbon monoxide. It is reasonable to believe that the poison is adsorbed by the most active part of the nickel crystal, say the atoms forming the outside row of a crystal, while the hydrogen later ad-

mitted is adsorbed on the inside rows of nickel atoms. Finally, at higher pressures, the hydrogen begins to cover the monoxide so that the two isotherms draw together and should, at a pressure greater than atmospheric for the nickel of this study, coincide.

The rate of adsorption at  $-196^{\circ}$  was found to be very rapid; equilibrium was established practically instantaneously from both sides. The rapid rate, of course, was to be expected since physical adsorption predominates at this temperature.

### Experiments with Temperature Variation

Following the interesting procedure of Benton and White, working with massive copper<sup>4</sup> (p. 1373), the adsorbent was brought to a temperature of  $-78.5^{\circ}$  and hydrogen was admitted. After equilibrium, very rapid also at  $-78.5^{\circ}$ , the pressure was recorded and the system was quickly brought to  $0^{\circ}$ . This resulted in a greater increase in pressure than the higher temperature alone would cause, indicating desorption of some of the hydrogen. Benton and White found that this increase in pressure at  $0^{\circ}$  was followed by a slow decrease until the gas sorbed was approximately equal to the amount ordinarily taken up at  $0^{\circ}$ . On cooling again to  $-78.5^{\circ}$  they found the adsorption was greater than originally prevailed at that temperature—greater by an amount approximately equal to the volume slowly taken up at  $0^{\circ}$ . Their interpretation of this behavior is a convincing argument that the slow sorption occurring after warming to  $0^{\circ}$  consists of solution

of hydrogen in the metal. With *supported* nickel no solution was expected. As a matter of fact, however, there was a small but quite distinct, slow decrease in pressure following the initial increase after warming to  $0^{\circ}$ . This means that even with supported nickel there is a small but significant amount of hydrogen which dissolves in the metal. The results of three such experiments are brought together in Table I and give an interesting comparison with Table II for the similar experiment on Benton and White's<sup>4</sup> (p. 1373) massive copper.

TABLE I

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY SUPPORTED NICKEL (5.87 G. OF NICKEL ON 50 G. OF BRICK)

(1) Gas taken up at $-78.5^{\circ}$	Pressure	40.2	422.8	508.2
	Volume	1.92	2.45	2.48
(2) Initial values after warming to $0^{\circ}$	Pressure	57.4	594.6	714.5
	Volume	1.83	2.16	2.14
(3) Total sorption at $0^{\circ}$ at pressures given in (2)		1.84	2.25	2.27
(4) Difference of (2) and (3)		0.01	0.09	0.13
(5) Final values reached at $0^{\circ}$	Pressure	56.9	593.8	712.9
	Volume	1.87	2.21	2.26
(6) After cooling to $-78.5^{\circ}$	Pressure	39.9	421.8	507.2
	Volume	1.95	2.55	2.58
(7) Direct values at $-78.5^{\circ}$ at pressures given in (6)		1.91	2.45	2.47
(8) Difference of (6) and (7)		0.04	0.10	0.11

The values given in Row (2) of Table I represent the adsorptions at  $0^{\circ}$  (provided no solution was present at  $-78.5$ , which seems likely). The differences given in Row (4) represent the volumes of hydrogen dissolved at  $0^{\circ}$  at pressures of Row (2) while the differences given in Row (8) are the volumes of gas dissolved at  $0^{\circ}$  and at pressures of Row (5). The sums of adsorption and solution at  $0^{\circ}$  are given in Rows (3) and (5).<sup>7</sup>

These data are shown graphically in Fig. 2. Curve 1 is the isotherm for  $-78.5^{\circ}$ . Curve 2 is that for  $0^{\circ}$ . The hydrogen dissolved at  $0^{\circ}$  is shown in curve 4. By subtracting the amount of dissolved hydrogen from the total sorption at  $0^{\circ}$  curve 3 results and this represents the adsorption at  $0^{\circ}$  (plus solution at  $-78.5^{\circ}$ , if any). It is interesting to note that these isotherms more nearly reach saturation limits than those found by Benton and White with massive copper. This is to be expected of an adsorbent which dissolves the hydrogen to such a lesser extent. It is of further interest that this sample of supported nickel sorbs more than half as much hydrogen at  $-196$  as at  $0^{\circ}$ , whereas Benton and White<sup>8</sup> with massive

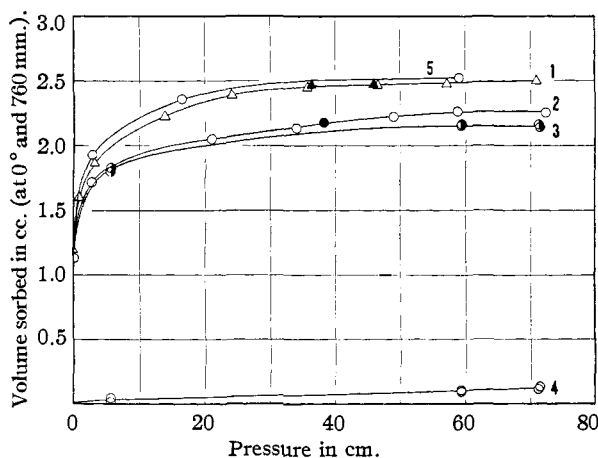


Fig. 2.—Sorption of hydrogen on supported nickel, two moles of nickel per 1000 g. of brick: curve 1, total sorption at  $-78.5^{\circ}$ ; 2, total sorption at  $0^{\circ}$ ; 3, adsorption at  $0^{\circ}$ ; 4, solution at  $0^{\circ}$ ; 5, sorption at  $-78.5^{\circ}$  after poisoning with 0.039 cc. CO.

(7) For a detailed explanation of these statements see ref. 4, p. 1380.

(8) Benton and White, *THIS JOURNAL*, 52, 2325 (1930).

nickel found less than half the sorption at  $-191.5$  and at  $-183^\circ$  as at  $0^\circ$ . The probable explanation is that the greater solution taking place with massive nickel at  $0^\circ$  makes the differences in sorption at the higher temperature and at the lower temperatures greater with massive than with supported metal where solution is markedly less.

The rates of sorption at  $0$  and at  $-78.5^\circ$  on the supported nickel were not so slow as many workers have found for activated adsorption. This leads to the question whether many cases of slow attainment of equilibrium in sorption measurements might not be due more to solution than to activated adsorption.

The final run in this series was one in which 0.039 cc. of carbon monoxide was introduced to the adsorbent at  $-78.5^\circ$  a half an hour before hydrogen was admitted. Only three points were taken in this run and as seen in curve 5 they all fall slightly above the isotherm for the unpoisoned run. Thus at  $-78.5^\circ$ , as at  $0^\circ$ ,<sup>6</sup> where also activated adsorption takes place, carbon monoxide

used in very small quantity slightly increases the adsorption.

The author wishes to thank Dr. L. M. Willey of the General Electric Company for supplying the liquid nitrogen used in this investigation, and Miss Isabel Mills of the faculty of Vassar College for assistance in temperature control.

### Summary

Sorption measurements of hydrogen on supported nickel have been made at  $0$ ,  $-78.5$  and  $-196^\circ$ . A step-wise increase of adsorption with pressure was found at  $-196^\circ$ . Poisoning with carbon monoxide at  $-196^\circ$  decreases the low-pressure adsorption by an amount approximately equal to the quantity of poison used. Experiments at  $-78.5$  and at  $0^\circ$  indicate the process of solution takes place to a very slight extent at the latter temperature. A small amount of carbon monoxide causes a slight increase in hydrogen adsorption at  $-78.5^\circ$ .

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## The Photolysis of the Aliphatic Aldehydes. VII. Crotonaldehyde at Elevated Temperatures

BY FRANCIS E. BLACET AND JAMES E. LU VALLE

In view of the fact that crotonaldehyde is very stable at room temperature when exposed to ultraviolet light,<sup>1</sup> it has seemed advisable to continue the photochemical study of this compound at higher temperatures.

### Experimental Methods

The quartz reaction tube was enclosed in an electric furnace in essentially the same manner as that described in a report on the photolysis of the butyraldehydes.<sup>2</sup> By using a single junction copper-constantan thermocouple and manually controlling the input of electrical energy, no difficulty was experienced in keeping the temperature of the furnace constant within  $1^\circ$ .

Since it is impossible to use a thermopile near a cell which is at the temperatures used in this study, the amount of radiant energy absorbed by the aldehyde was determined in the following way. After suitably protecting the thermopile from the furnace by a distilled water filter, it was found that for a given concentration of crotonaldehyde in the reaction cell the fraction of light of several different wave lengths absorbed by the vapors was independent of

temperature in the range  $30$  to  $300^\circ$ . Beer's law had been shown previously to apply to this compound at room temperature.<sup>3</sup> In view of these facts it was assumed that the character of the absorption process did not change with temperature. Next, working at room temperature the fractions of light absorbed at several different concentrations were determined for all the wave lengths used in this study. A plot of these values gave the fraction absorbed at any concentration which might be used. Then from a series of measurements it was found that by manually controlling the amperage of the mercury arc the energy output could be kept constant to within about 2%. With these facts it was possible to get the energy absorbed during a given run simply by measuring the energy entering the cold, empty reaction tube. After this had been done the shutter was closed, the furnace brought to the desired temperature, the gas introduced and brought to the desired concentration and, finally, the exposure made.

Owing to fluctuation of the temperature of the system no attempt was made to follow the slight pressure change which took place during a run. The source of monochromatic radiation and the methods of analysis of the reaction products are adequately referred to in the previous articles of this series.

(1) Blacet and Roof, *THIS JOURNAL*, **58**, 73 (1936).

(2) Leighton, Levanas, Blacet and Rowe, *ibid.*, **59**, 1843 (1937).

(3) Blacet, Young and Roof, *ibid.*, **59**, 608 (1937).