THE ADSORPTION OF CARBON MONOXIDE AND HYDROGEN BY PLATINIZED ASBESTOS

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The adsorption by colloidal platinum of substances which poison the hydrogen peroxide reaction has never been worked out even by qualitative experiments. That the determination of adsorption isotherms of gases in the presence of so-called catalytic poisons is necessary, to establish the generally accepted theory that this poisoning is due to the preferential adsorption of the poisons, has been pointed out by Bancroft.¹

Berliner² was one of the first to take up quantitatively the adsorption of gases by platinum, using platinum foil. He concluded that the catalytic action of the metal on oxyhydrogen gas is due invariably to the occlusion of hydrogen, which when occluded always seems to act like nascent hydrogen, as Graham³ had previously shown to be the case with hydrogen and palladium. Berliner pointed out that, when the metallic surface is not clean, catalysis still takes place at high temperatures, a fact which he attributed to the partial removal of the film of impurity by the action of heat.

In 1895, Mond, Ramsay and Shields⁴ studied the adsorption of gases by platinum black, using air, carbon dioxide, oxygen, and hydrogen. They called attention to precautions which are necessary to prevent the poisoning of the platinum black by contamination from greased stop-cocks and rubber connections. They found that platinum black may adsorb from two to fourteen volumes of carbon dioxide. They wrote as follows: "Platinum black dried at 100° C contains rather less than 100 volumes, or about 0.66 percent by weight, of oxygen. . . . The amount of hydrogen occluded by platinum black independent of that required to form water

¹ Jour. Ind. Eng. Chem., 13, 83 (1921).

² Wied. Ann., 35, 791 (1888).

³ Phil. Mag., 32, 503 (1866).

⁴ Phil. Trans., 186, 657 (1895).

with the oxygen already contained in it, is about 100 volumes for the best samples of black, the total amount of hydrogen adsorbed being about 310 volumes. This amount, however, is influenced very largely by the presence of accidental impurities, probably grease, etc. A portion of the hydrogen occluded by platinum black can be removed at the ordinary temperature by means of the pump alone, but not until the pressure has been reduced to about 300 millimetres. The bulk of the hydrogen can be extracted in vacuo at about 300°C , but a red heat is necessary for its complete removal. On heating platinum black charged with hydrogen in an atmosphere of hydrogen, a portion of the gas is immediately liberated, and in this respect it differs entirely from platinum black charged with oxygen." The hydrogen isotherms obtained by Ramsay and Shields are shown in Figure 1. The break in Curve II corresponds to a leakage into the pump.

Fig. 1
Isotherms by Ramsay and Shields

Harbeck and Lunge¹ found that platinum black adsorbs about sixty times its volume of carbon monoxide and they concluded that a true chemical compound is formed, since the carbon monoxide is not eliminated by the subsequent action of other gases such as hydrogen and since it is very stable but suddenly decomposes at 250°C into its constituents. They were unable, however, to isolate such a compound.

De Hemptinne² studied the catalytic action of platinum black and palladium at very low temperatures in the hope of settling the question of the formation of compounds, assuming that if the occlusion is due to the formation of a compound, it

¹ Zeit. anorg. Chem., 16, 15 (1898).

² Zeit. phys. Chem., 27, 429 (1898).

would be diminished greatly at low temperatures. His results are rather bewildering. He claims that in all cases the adsorption of hydrogen is greater at 15°C than at -78°C , while if the tube is allowed to regain slowly the higher temperature, a marked adsorption of the gas occurs at about -40°C . Results with carbon monoxide were completely analogous. These results raise the question as to whether the platinum had been previously reduced to eliminate the combined oxygen. For palladium and hydrogen, on the other hand, the adsorption was greater at low temperatures, but with palladium and carbon monoxide the results were similar to those with platinum.

Taylor and Burns¹ have determined the adsorption of gases by various metallic catalysts. They used the metals copper, cobalt, iron, palladium, platinum sponge, and platinum black, and the gases nitrogen, hydrogen, carbon dioxide, carbon monoxide, ethylene, and oxygen. Their apparatus consisted of an adsorption bulb connected to a measuring burette on one side for the introduction of known quantities of gas and to a Toepler vacuum pump on the other side for evacuating the cell and for measuring the gas withdrawn. An interesting detail of their work is the method of determining the free space of the adsorption bulb and the subsequent determination of isotherms at reduced pressures.

"The free space of the adsorption bulb was readily obtained from the nitrogen value since all available data confirmed the assumption that this gas is not measurably adsorbed, at least at these temperatures, by any of the six metals investigated. Calculations of this free space, made by weighing the amount of water required to fill the bulb after it had been evacuated, gave results which agreed with the nitrogen value. In the case of copper, the helium value obtained with a specially purified sample of the gas, obtained through the courtesy of Dr. R. B. Moore of the United States Bureau of Mines, served as additional evidence that the nitrogen value represents zero adsorption."

¹ Jour. Am. Chem. Soc., **43**, 1273 (1921).

The low adsorption values obtained by Taylor and Burns for platinum black with hydrogen seem to indicate that the metal contained impurities, possibly grease carried over from the stop-cocks, although no mention is made of the nature of the lubricant used.

EXPERIMENTAL PART

I. Platinum Black

At first, experiments were attempted using platinum black as the adsorbent in an apparatus shown later in Figure 2. This apparatus had no rubber connections and all stop-cocks were lubricated with phosphorus pentoxide in order to prevent the poisoning of the platinum by grease carried over from the stop-cocks by the gas.

The platinum black was prepared by the method used by Ramsay and Shields. A solution of chlorplatinic acid was evaporated to small volume and neutralized with sodium carbonate. The boiling solution was then poured into a five percent solution of sodium formate and allowed to stand over night. The platinum black was then filtered off and boiled eight or ten times with fairly large volumes of distilled water, and finally dried in a vacuum desiccator over sulphuric acid. In these preliminary experiments, six to seven grams of the platinum black was used.

The hydrogen was prepared electrolytically and purified by passing it through an alkaline pyrogallol solution and then over phosphorus pentoxide.

In two experiments, hydrogen was passed into the cell containing platinum black which had not been previously reduced with hydrogen. The cell was kept at 0° C by immersion in an ice bath. In one case a total "adsorption" of 291.8 volumes of hydrogen was obtained, and in the other, 369.9 volumes. The method and apparatus used, however, did not permit the determination of the amount of water formed, so that the amount of gas actually adsorbed was not determined.

In one experiment using platinum black which had previously been treated with hydrogen and evacuated at 250° C,

an adsorption of 84.8 volumes of hydrogen was obtained. This was probably considerably less than the amount of gas adsorbed in the previous experiments. It was found that the reduced platinum black could not be heated above 100°C without a marked decrease in the amount of hydrogen adsorbed. Apparently even moderate heating causes a very appreciable coalescence of the finely divided platinum when it is not more or less covered by an oxide film. In other words, the heating converted the platinum black to a certain extent into the form of platinum sponge which is known to have a lower adsorptive for gases. As all the work of the earlier investigators indicated that considerable heating was required to displace the adsorbed gas, it seemed probable that the duplication of results by successive runs with a given sample of platinum black would be impossible.

II. Platinized Asbestos

In the hope of securing platinum in a very active form and at the same time in a form which could be heated to a high enough temperature to remove the adsorbed gases without changing the physical nature of the platinum, platinized asbestos was substituted for platinum black. This form of the metal proved to have a higher adsorptive power than platinum black. In all of the experiments performed with platinized asbestos, the cell containing it has been evacuated at 400°C without any apparent reduction in the adsorptive power. Experiments with pure asbestos fibre alone showed no measurable adsorption of hydrogen.

Apparatus and Manipulation

The apparatus used was a modified form of the apparatus designed by Browne¹ and his co-workers in the study of pressure-concentration isotherms of certain ammonia systems. A diagram of the apparatus is shown in Figure 2. It consisted of a gas burette *A*, for measuring gas samples added or withdrawn and also serving as a pump for evacuating the cell,

¹ Jour. Am. Chem. Soc., **35**, 649 (1913).

connected with the cell *C* and a mercury manometer *M*. The cell *C* was a bulb of 150 to 200 cc capacity and was connected to the burette and the manometer through the small bulb *B* which was filled with phosphorus pentoxide to adsorb moisture resulting from the reduction of the platinized asbestos in the cell. The cell *C* was so placed that it could be immersed in an ice bath or could be surrounded by an electrically heated air oven.

Hydrogen was admitted to the apparatus at *E*, and carbon monoxide at *F*. All stop-cocks were lubricated with phosphorus pentoxide.

The empty cell was first sealed to the apparatus and the volume of the adsorption chamber determined by withdrawing measured volumes of air from the cell and observing the manometer readings. The total volume of the cell and tubes to the manometer and burette was thus

obtained either by plotting the pressure volume curve or by determining the total volume of air removed. During this calibration, the cell was immersed in an ice and water bath, as all of the experiments were performed with the cell at 0° C.

The cell was then broken off at (*a*), filled with platinized asbestos by blowing out the end of the tube (*b*), and resealed after the introduction of the material. The volume occupied by the platinized asbestos, computed from its density, subtracted from the previously determined volume of the cell gave the net volume or free space of the adsorption chamber. In some of the later runs, this net volume was determined by the method of Taylor and Burns already described, using the inert gas nitrogen.

Fig. 2

The gas to be investigated was drawn into the burette from the generator, measured, and passed into the cell. As soon as equilibrium had been reached, the manometer pressure was observed. From this pressure the volume of the gaseous phase (volume of gas occupying the free space in the cell) could be computed. The difference between this and the total volume of gas added represented the volume of adsorbed gas. This volume of gas in cubic centimeters could then be converted into volumes of platinum.

In the evacuation process, the cell was in every case heated to 400° C in an electric air oven. It was assumed that the adsorbed gases would be completely removed by evacuation at that temperature. Ramsay and Shields, however, found that about five volumes of hydrogen were retained by platinum black even at this temperature.

Materials

The platinized asbestos used was furnished by the General Chemical Company through the kindness of the late Mr. T. L. Briggs. It was prepared with especial care to give a catalyst of the maximum efficiency. It was reported to contain 15 percent platinum by weight. Its density was determined with a pyknometer to be 2.866.

The hydrogen, prepared electrolytically, was purified by bubbling it through alkaline pyrogallol and dried by passage through a tube of phosphorus pentoxide.

Carbon monoxide was prepared by heating potassium ferrocyanide with concentrated sulphuric acid to 160° C. The generation of gas in this way could not be controlled very readily so the method was later abandoned. Formic acid was used in place of potassium ferrocyanide. By means of a dropping funnel the formic acid could be added to the hot sulphuric acid to give carbon monoxide at the desired rate. This gas was passed through 1:1 potassium hydroxide solution and then through concentrated sulphuric acid and finally over phosphorus pentoxide.

Experiments

With the apparatus described a number of attempts were made, twelve or fourteen in all, to determine the adsorption isotherms for hydrogen and for carbon monoxide with platinized asbestos. Much trouble was encountered however with the stop-cocks lubricated with phosphorus pentoxide. After each addition of gas to the cell, it required from eight to twelve hours for the system to reach equilibrium. When exposed to a vacuum, or very low pressure, on one side, even the best stop-cock that could be obtained either leaked or set fast. No stop-cock was found that would function under these conditions long enough to permit the determination of a complete isotherm.

One carbon monoxide isotherm was determined from 0 to 400 mm pressure. The data are given in Table I. Curve 1 in Figure 4 shows these results.

The best results obtained with hydrogen are given in Table II and are plotted in Curve 1 in Figure 3.

TABLES I-II

Cell Data

Volume of Cell.....	226.6	cc
Weight of Platinized Asbestos.....	11.3145	gm
Volume of Platinized Asbestos.....	3.95	cc
Net Volume of Cell.....	222.65	cc
Weight of Platinum.....	1.6972	gm
Volume of Platinum.....	0.08	cc

TABLE I

Carbon Monoxide at 0° C

Equilibrium pressure (mm Hg)	Reduced volume of CO added (cc)	Reduced volume of CO remaining (cc)	Volume of adsorbed CO	
			Cc	Vol.CO/vol.Pt
5.5	4.50	1.80	2.70	33.1
20.0	9.00	5.90	3.20	40.0
36.0	14.20	10.55	3.65	45.8
51.0	19.20	14.90	4.30	53.8
68.5	24.10	20.10	4.00	50.0
85.1	29.65	24.90	4.75	59.0
116.6	38.95	34.20	4.75	59.0
160.7	52.85	47.10	4.75	59.0
274.2	86.90	80.90	6.00	75.0
402.8	125.80	118.00	7.70	96.3

TABLE II
Hydrogen at 0° C.

Equilibrium pressure (mm Hg)	Reduced volume of H ₂ added (cc)	Reduced volume of H ₂ remaining (cc)	Volume of adsorbed H ₂	
			Cc	Vol. H ₂ /vol. Pt
9.0	4.60	2.60	2.00	25.0
19.7	9.20	5.80	3.40	42.6
32.3	13.90	9.50	4.40	55.0
46.7	20.50	13.70	6.80	85.0
57.0	25.10	16.70	8.40	104.2
71.0	29.90	20.90	9.00	112.5
83.9	34.65	24.60	10.05	125.6
99.0	39.55	29.00	10.55	132.0
114.2	44.75	33.45	11.30	141.0
130.0	50.30	38.10	12.20	152.5

The use of a good rubber-vaseline lubricant was then attempted. The results showed very conclusively the "poisoning" effect of such a lubricant. The results of two successive experiments are shown in Curves 2 and 3 of Figure 3.

A modification was next made in the apparatus by the insertion of a trap between the burette and the phosphorus pentoxide tube above the cell to remove as completely as possible the volatilized impurities carried over in the gas from the greased stop-cock. This trap consisted of a deep U shaped tube of ordinary sized glass tubing, packed with fine glass wool and so arranged that it could be surrounded by a Dewar flask containing liquid air.

A series of hydrogen isotherms was run, the data for which are given in Table III, and curves 4 and 5 in Figure 3. By keeping liquid air around the trap the poisoning effect of greasy impurities was reduced materially. It is very evident however on comparing Tables II and III that while the liquid air eliminates part of the grease, it does not by any means remove it completely.

Similarly, a series of carbon monoxide isotherms were determined, the data for which are given in Table IV and curves 2 and 3 in Figure 4.

In connection with these experiments, an attempt was made to show definitely whether or not hydrogen and carbon monoxide formed compounds with the platinum and whether or not the process of adsorption in these cases is to some extent irreversible as the results of certain earlier workers seem to

Fig. 3
Adsorption of Hydrogen by Platinized Asbestos

indicate. Ramsay and Shields, as has been pointed out, state that only a portion of the adsorbed hydrogen can be removed by evacuation. Their adsorption isotherms, shown in Figure 1, represent an adsorption of about 35 volumes of hydrogen at zero pressure. With carbon monoxide, the statement of Harbeck and Lunge, that a compound with platinum is

formed which decomposes suddenly when heated to 250°C , has never been clearly disproved.

TABLES III-IV

Cell Data

Volume of Cell.....	229.22	cc
Weight of Platinized Asbestos.....	15.5583	gm
Volume of Platinized Asbestos.....	5.43	cc
Net Volume of Cell.....	223.8	gm
Weight of Platinum.....	2.3337	gm
Volume of Platinum.....	0.11	cc

TABLE III

Hydrogen at 0°C

Equilibrium pressure (mm Hg)	Reduced volume of H ₂ added (cc)	Reduced volume of H ₂ remaining (cc)	Volume of adsorbed H ₂	
			Cc	Vol.H ₂ /vol. Pt
Run 1				
14.5	7.0	4.5	2.5	22.8
36.4	13.9	11.3	2.6	23.4
61.5	21.7	19.1	2.6	23.4
89.6	30.0	27.3	2.7	24.1
139.0	46.9	43.1	3.7	33.5
170.3	56.5	52.9	3.6	32.5
203.0	66.6	63.0	3.6	32.5
239.8	77.6	74.4	3.2	28.6
207.2	86.9	83.9	3.0	27.2
299.6	96.3	93.0	3.3	30.0
342.8	110.0	106.4	3.6	32.0
654.7	212.6	203.2	9.4	84.5
718.2	246.2	222.9	23.3	209.3
Run 2				
157.5	49.9	47.5	2.4	21.4
338.7	104.3	102.1	2.2	20.0
515.6	158.6	155.5	3.1	27.7
672.3	207.1	202.8	4.3	38.5
750.7	231.5	226.4	5.1	46.4
731.3 ¹	231.5	220.6	10.9	99.0
510.3	164.6	153.9	10.7	96.4
347.5	117.7	104.8	12.9	115.9
51.7	31.1	16.2	14.9	135.5
1.4	13.0	0.4	12.6	112.8

Run 3

55.4	18.3	16.7	1.5	13.9
108.3	34.8	32.6	2.2	20.0
520.7	159.2	157.0	2.2	20.0
655.0	200.7	197.5	3.2	28.7
762.2	234.7	229.2	5.5	50.0
759.9 ¹	234.7	229.2	5.5	50.0
550.8	168.7	166.2	2.5	22.9
384.0	118.0	115.8	2.2	20.0

TABLE IV
Carbon Monoxide at 0° C

Equilibrium pressure (mm Hg)	Reduced volume of CO added	Reduced volume of CO remaining	Volume of adsorbed CO	
			Cc	Vol.CO/vol.Pt
		Run 1		
31.8	14.5	9.6	4.9	44.5
90.7	32.3	27.4	4.9	44.5
155.8	54.5	47.0	7.5	68.2
229.6	77.1	69.3	7.8	70.1
289.4	95.9	87.3	8.6	77.3
342.4	114.5	103.3	11.2	101.0
546.5	182.0	164.8	17.2	154.5
751.0	246.1	226.5	19.6	176.4
745.8 ²	246.1	224.9	21.2	190.3
529.9	178.6	159.9	28.7	261.0
382.2	130.4	115.3	15.1	128.6
272.6	95.1	82.0	13.1	117.5
193.1	70.1	58.2	11.9	108.2
139.5	52.4	42.1	10.3	92.7
99.0	39.8	29.8	10.0	90.1
82.8	29.7	25.0	4.7	42.7
Run 2				
49.2	19.1	14.9	4.2	37.6
260.6	88.0	78.6	9.4	84.5
404.6	135.4	122.0	13.4	120.0
544.1	179.5	164.1	15.4	138.2
39.4 ²	17.9	11.9	6.0	54.5
35.4	15.5	10.6	4.9	44.5
16.0	8.3	4.8	3.5	31.9

¹ The system was allowed to stand several days and then the gas was withdrawn in stages.

² The system was allowed to stand several days and then the gas was withdrawn in stages.

In order to obtain evidence for or against these ideas, after determining the adsorption isotherm up to about one atmosphere by gradual addition of gas, the isotherm was re-determined by the gradual removal of gas. With both hydrogen and carbon monoxide, it was found that the two curves so obtained did not coincide. In the case of hydrogen the digression was very marked in some experiments, as is shown by

Fig. 4

Adsorption of Carbon Monoxide by Platinized Asbestos

the dotted curve 5' in Figure 3. The adsorbed gas was apparently not liberated until the greater part of the gas phase had been removed. The amount of adsorbed gas seemed to increase to a higher value, and then, when the pressure was decreased below 50 mm, to decrease rapidly. It was found that by allowing sufficient time to elapse, the adsorbed gas can be removed completely.

With carbon monoxide, although the difference between the two curves was less marked, nevertheless, no matter how

long a time was allowed for equilibrium to be reached after adding the gas, the isotherm plotted upon the removal of gas always gave higher adsorption values. In Figure 4, curves 2 and 2', 3 and 3' show this relation. As in the case of hydrogen, however, it was found that the adsorbed gas was completely removable if sufficient time was allowed, two or three days being required to give true equilibrium.

These results seem to establish two things. First, the difference in adsorption upon the addition and removal of gas indicate that for some reason (other than the time factor) the full adsorption capacity of the platinum was not being reached in these experiments. The conclusion reached was that, while the cooling of the incoming gases with liquid air froze out part of the impurities carried over from the stop-cocks, these were not completely removed. Although such an impurity inhibits the adsorption, it does not influence strongly the liberation of the gas once it has been adsorbed.

Secondly, the results show conclusively that the combination of these gases with finely divided platinum is an adsorption phenomenon, and is not due in any way to the formation of definite homogeneous compounds with the platinum.

Although the use of a trap surrounded with liquid air seemed to cut down the poisoning effect of the grease from stop-cocks, it was evident from the data that this arrangement only eliminated the trouble partially. Another set of experiments was therefore attempted to determine the adsorption of hydrogen and of carbon monoxide from mixtures of each of these gases with nitrogen. Preliminary tests were made with pure nitrogen to check up the results of Taylor and Burns which showed that nitrogen was not adsorbed. These results were confirmed.

Nitrogen was prepared by adding a saturated solution of sodium nitrite from a dropping funnel to a flask containing a hot solution of ammonium chloride. The gas was dried by bubbling it through wash bottles containing concentrated sulphuric acid. It was then passed through a tube containing finely divided copper heated to about 300° C to insure the

removal of any possible traces of oxides of nitrogen. Finally it was passed through a tube of phosphorus pentoxide.

Hydrogen and nitrogen were added in varying proportions to the freshly evacuated cell of a second apparatus until approximately an atmosphere of gas was present. By working at ordinary pressures in this way it was possible to use phosphorus pentoxide on the stop-cocks without danger of leakage. The data for the adsorption of hydrogen from hydrogen-nitrogen mixtures are given in Table V. These results did not give as smooth adsorption isotherms as the previous experiments had, but this was not to be expected since each point had to be determined by a separate experiment, heating the cell to 400° C and evacuating it at that temperature before each mixture was added to the cell. Fairly consistent checks were obtained, however. The results are given in Table V and the mean values are shown in curves 6 and 7 in Figure 3. The corresponding data and curves for carbon monoxide are given in Table VI and Figure 4.

TABLE V
Mixtures of Hydrogen and Nitrogen at 0° C

Hydrogen partial pressure	Volume of adsorbed gas	
	Cc	Vol. H ₂ /vol. Pt
44.6	10.6	133
75.0	11.5	144
148.3	11.9	149
160.0	12.3	154
279.0	11.8	148
350.5	12.2	152
416.0	12.9	161
462.1	13.4	167
463.6	11.6	145
470.0	13.2	165
481.1	12.3	154
502.4	11.8	148
632.1	12.2	152
671.1	18.7	159
672.7	12.3	154
696.5	15.1	188

TABLE VI
Mixtures of Carbon Monoxide and Nitrogen at 0° C

Carbon monoxide partial pressure	Volume of adsorbed gas	
	Cc	Vol. CO/vol. Pt
59.5	9.0	113
63.6	7.8	98
95.7	17.5	219
180.6	21.3	266
195.1	21.9	274
231.7	19.2	240
544.6	23.8	297
648.7	23.2	290
681.0	23.9	298

The adsorption values obtained by this last method are consistently higher for both hydrogen and carbon monoxide than are the values obtained in any of the earlier methods used and the indications are that they represent more nearly the true adsorption of these gases by the form of platinum used. These determinations were made with a sample of platinized asbestos that had not been used previously. They were carried out in an entirely new apparatus to eliminate as far as possible the presence of any impurities which might contaminate the gases or the platinum.

Finally, having determined satisfactorily the adsorption isotherms for carbon monoxide and for hydrogen, the adsorption of gas from mixtures of the two was investigated as follows.

The cell was filled with hydrogen and allowed to come to equilibrium so that the hydrogen adsorption was known. Then a certain volume of hydrogen was withdrawn and an approximately equal volume of carbon monoxide was added. When the system had come again to equilibrium, the volume of adsorbed gas was computed in the usual way. In order to determine the composition of this adsorbed gas, a sample of the gas phase was withdrawn and analyzed. About 70 cc of gas was withdrawn quickly from the cell and divided into two portions for analysis. The composition was determined by burning

the sample with oxygen in a Hempel combustion pipette and subsequently determining the carbon dioxide by adsorption over caustic alkali solution. As the volume of the free space of the cell at the equilibrium pressure was known, it was possible from this analysis to calculate the amount of each gas present in the gaseous phase. The difference between this amount and the amount of that gas introduced into the apparatus gave the volume of the gas adsorbed. The results of a number of such experiments are given in Table VII. Although the cell had been evacuated after the experiments of Table VI the trace of carbon monoxide left in the platinum cut down the hydrogen adsorption from over 150 volumes to about 50 volumes.

TABLE VII
Adsorption of Mixtures of Hydrogen and Carbon Monoxide₁ by
Platinized Asbestos

Run 1	
Initial volume of hydrogen.....	212.24 cc
Equilibrium pressure.....	767.20 mm
Volume of cell.....	208.64 cc
Volume of adsorbed hydrogen }	3.60 cc
	45.00 vol. Pt
Volume of hydrogen removed.....	46.84 cc
Volume of carbon monoxide added.....	46.18 cc
Final volume of hydrogen.....	165.40 cc
Final volume of carbon monoxide.....	46.18 cc
Total volume of gas present.....	211.58 cc
Equilibrium pressure.....	718.06 mm
Volume of cell corresponding.....	195.27 cc
Volume of adsorbed gas }	16.31 cc
Analysis of gas phase }	204.00 vol. Pt
Hydrogen.....	80.4%
Carbon monoxide.....	20.0%
Volume of hydrogen in gas phase.....	166.22 cc
Volume of carbon monoxide in gas shape...	29.05 cc
Volume of adsorbed hydrogen }	-0.78 cc
	-9.70 vol. Pt
Volume of adsorbed carbon monoxide } ..	17.13 cc
	214.10 vol. Pt

Run 2

Volume of hydrogen.....	150.83 cc
Volume of carbon monoxide.....	62.29 cc
Total volume of gas present.....	220.12 cc
Equilibrium pressure.....	777.70 mm
Corresponding volume of cell.....	211.49 cc
Volume of adsorbed gas }	8.63 cc
Analysis of gas phase }	108.00 vol. Pt
Hydrogen..... 71%	
Carbon monoxide..... 29%	
Volume of hydrogen in gas phase.....	150.16 cc
Volume of carbon monoxide in gas phase..	61.33 cc
	0.67 cc
Volume of adsorbed hydrogen }	8.40 vol. Pt
	7.96 cc
Volume of adsorbed carbon monoxide } ..	99.50 vol. Pt

Run 3

Initial volume of hydrogen.....	209.83 cc
Equilibrium pressure.....	761.22 mm
Corresponding volume of cell.....	206.57 cc
	3.26 cc
Volume of adsorbed hydrogen }	40.70 vol. Pt
Volume of hydrogen removed.....	49.02 cc
Volume of carbon monoxide added.....	50.03 cc
Final volume of hydrogen.....	160.81 cc
Final volume of carbon monoxide.....	50.03 cc
Total volume of gas present.....	210.84 cc
Equilibrium pressure.....	749.96 mm
Volume of cell corresponding.....	203.52 cc
Volume of adsorbed gas }	7.32 cc
Analysis of gas phase }	91.50 vol. Pt
Hydrogen..... 78.3%	
Carbon monoxide..... 21.7%	
Volume of hydrogen in gas phase.....	159.36 cc
Volume of carbon monoxide in gas phase..	44.16 cc
	0.45 cc
Volume of adsorbed hydrogen }	5.60 vol. Pt
	6.87 cc
Volume of adsorbed carbon monoxide } ..	86.00 vol. Pt

These experiments show conclusively that carbon monoxide will displace adsorbed hydrogen practically completely from the platinized asbestos. Taking into consideration the volume of the cell (about 200 cc), and the volume of gas taken for an individual analysis (30 to 40 cc), it will be seen that an error

in reading of 0.1 cc during the analysis would amount to more than the final volume of adsorbed hydrogen obtained in any of these experiments. Therefore, it may be said that, within the limits of experimental error, the carbon monoxide displaces the adsorbed hydrogen completely.

This displacement of hydrogen by carbon monoxide bears out the principle that adsorption is purely a selective phenomenon. It furnishes, likewise, much needed experimental evidence concerning the problem of catalytic poisons and supports strongly the hypothesis advanced by Bancroft¹ "that all substances which poison catalytic agents do cut down the adsorption of the essential reacting substances." Since it has now been shown that carbon monoxide does actually displace adsorbed hydrogen from platinum, it is possible to account for the fact that carbon monoxide is a catalytic poison in many hydrogenation processes carried out with platinum.

The results of this investigation may be summarized as follows:

1. The adsorption of hydrogen, carbon monoxide, and mixtures of these gases by platinized asbestos has been determined at 0° Centigrade and for pressures up to one atmosphere.

2. The determination of the actual adsorption isotherms is made difficult by the fact that minute quantities of impurities such as may be entrained by passing the gases through stop-cocks lubricated by grease, decrease greatly the adsorptive power of the platinum. The observations of Berliner in this regard have been amply confirmed. It seems probable that all determinations of the adsorption of gases by platinum are untrustworthy and the results are too low unless scrupulous care be taken to eliminate all possible contamination of the adsorbent.

3. The adsorption process is a reversible one providing sufficient time is allowed to elapse so that equilibrium may be

¹ Jour. Phys. Chem., 21, 571 (1917).

established. The adsorbed gas may be removed completely from the platinum merely by long continued pumping-out at 0° Centigrade.

4. No evidence has been found to support the contention that the gases mentioned above form definite solid compounds with platinum at this temperature.

5. When contamination of the adsorbent is most effectively prevented platinized asbestos as used in this work is able to adsorb 200 volumes of hydrogen or 300 volumes of carbon monoxide at 0° C and atmospheric pressure, the volumes of gas being expressed in terms of the volume of platinum actually present.

6. Carbon monoxide, added in relatively small amounts to the system hydrogen and platinized asbestos in equilibrium, is able completely to displace the adsorbed hydrogen from the platinum. This evidence supports directly Bancroft's theory of catalytic poisoning and accounts for the fact that carbon monoxide is known to be a poison toward platinum in certain catalytic hydrogenations.

7. The adsorption coefficient of 200 volumes of hydrogen is greater than that obtained by previous investigators, who used platinum black instead of platinized asbestos. The greater value of the coefficient now reported is without doubt the result, at least partly, of the greater precautions taken in this investigation to prevent contamination of the catalyst, but it may also indicate that platinum in the form of platinized asbestos has a greater specific surface than platinum as platinum black.

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