3. An unsuccessful attempt was made to detect photo-electric conductivity in hydrogen bromide gas while illuminated by ultraviolet light.

4. The photographs of the spectra show no band structure,[14] but do exhibit continuous absorption extending from the limit of the quartz region in the ultraviolet to a long-wave limit (absorption limit). This limit has been found to be 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. The data support the hypothesis that a case of molecular absorption has been found in which the function of the radiation is not to produce a band spectrum, but to produce direct photochemical dissociation of the molecule into atoms.

5. Mechanisms for the photochemical decomposition of the hydrogen halides have been discussed. The mechanism of Warburg is consistent with all the evidence.

CAMBRIDGE A, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 96]

THE ADSORPTION OF GASES BY PLATINUM BLACK

BY ARTHUR F. BENTON

RECEIVED MARCH 19, 1926 PUBLISHED JULY 6, 1926

If adsorbed films of gases on solids are in general unimolecular, and if the forces involved are typical valence forces acting between individual molecules in the gas and individual atoms in the solid, then the possibility exists, as Langmuir[1] has pointed out, that the volumes of different gases adsorbed by a given surface may be related stoichiometrically. Thus, each atom in the solid surface might be capable of adsorbing one molecule of certain gases, two molecules of certain others, etc.; in still other cases, two or more atoms of the adsorbent might be equivalent to each molecule of gas. It is evident, however, that these stoichiometric relations could occur only if every atom in the surface of the adsorbent takes part in the process, or at least if the same fraction of the surface is active toward different gases. Pease[2] has shown that this condition is not fulfilled in the case of adsorptions on metallic copper, and Taylor[3] concludes that the same is probably true of contact catalysts in general. Nevertheless, when the forces are particularly powerful, as in the adsorption of numerous gases by platinum,

[14] Since this manuscript has been written, the absorption spectra of hydrogen bromide at different pressures have been photographed with a spectrograph of much greater dispersion. The photographs show no band structure and the spectra appear continuous. These additional data lend still more support to the assumption that the absorption spectra of the hydrogen halides are truly continuous.

[1] Langmuir, THIS JOURNAL, **40**, 1361 (1918).

[2] Pease, *ibid.*, **45**, 2296 (1923).

[3] Taylor, *Proc. Roy Soc.* (London), **108A**, 105 (1925).

one might anticipate a more uniform covering of the surface, and hence the possibility of adsorptions of different gases in stoichiometric ratios.

Langmuir's experiments[1] on the adsorption of gases at low pressures by a plane surface of platinum foil showed that the maximum volumes of carbon monoxide, oxygen and hydrogen adsorbed were roughly equal, and corresponded with the amount to be expected in a unimolecular layer. The main purpose of the present research was to find whether platinum in the form of platinum black also adsorbs approximately equal volumes of different gases.

This investigation was carried out during my appointment as National Research Fellow in chemistry, and was aided on the financial side by a grant to Professor A. A. Noyes from the Carnegie Institution of Washington.

Previous Work

The adsorption of gases by platinum black has been the subject of numerous investigations.[4] Most of the early work, however, is concerned with only a single gas, usually hydrogen, and as a rule the experimental technique employed was unsatisfactory. The first investigation which is not open to this criticism is that of Mond, Ramsay and Shields.[5] These authors found that similar samples of platinum black adsorbed, at room temperature, approximately equal volumes of hydrogen, oxygen, carbon monoxide and sulfur dioxide. In the method used, however, only one adsorption measurement could be made with a given sample of platinum black, and duplicate determinations with different samples often failed to check satisfactorily.

In an extended study of the adsorption of gases by contact catalysts, Taylor and Burns[6] included measurements on platinum black. The latter was first treated with hydrogen to remove the film of oxygen and then heated in vacuum to 110°, at which temperature it was hoped the hydrogen could be completely removed. However, the experiments reported in the present paper show that more than half of the hydrogen adsorbed by platinum black at room temperature is retained in a vacuum at 110°. It is therefore evident that, owing to reaction with, or displacement of, this large amount of hydrogen in subsequent experiments with other gases, the data obtained by these investigators do not represent the true adsorptions on platinum black. Taylor and Burns did show, however, that carbon monoxide could not be recovered by evacuation.

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[4] For a list of references up to the year 1900, see Bose, *Z. physik. Chem.*, **34,** 710 (1900).

[5] Mond, Ramsay and Shields, (*a*) *Phil. Trans.*, **186A,** 657 (1895); (*b*) **190A,** 129 (1897). These papers may also be found in *Z. physik. Chem.*, **19,** 25 (1896) and **25,** 657 (1898), respectively.

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

Pollard[7] has attempted to measure the adsorption of hydrogen and carbon monoxide by platinized asbestos, but the results appear rather doubtful. He claims to have been able to pump off these gases completely at 0°, if sufficient time was allowed. This result is at variance with all other work in this field, and it seems probable that part of the gas apparently recovered from the platinum was in reality air which had leaked into the apparatus through the stopcocks lubricated with phosphorus pentoxide.

Boswell and McLaughlin[8] have recently published a paper dealing with the adsorption of hydrogen and oxygen by platinum black, in which some extraordinary results are reported. However, a careful consideration of the experimental part of their paper, together with Boswell's previous work[9] on nickel, suggests very strongly that their results were vitiated by the escape of hydrogen from their apparatus through the numerous rubber connections.

Experimental Part

Method.—A survey of previous work in this field shows that it is impossible to free platinum black completely from adsorbed gases without heating it to temperatures at which the black is converted into sponge. Mond, Ramsay and Shields[5] overcame this difficulty to some extent by using a new sample of platinum black for each experiment. In the investigation here reported, on the other hand, the same sample of platinum was used throughout. Care was exercised, however, to avoid the errors of much recent work on this subject, and it is believed that correct measurements of the relative adsorptions of different gases by the same sample of platinum black have been obtained for the first time.

An outline of the method, which is somewhat similar to that employed by Langmuir in his studies[1] on platinum foil, is as follows. The bulb containing the platinum black was exhausted, filled with hydrogen to remove the oxygen previously adsorbed, and then again exhausted for a long time at 110°, in order to complete as far as possible the sintering process which occurs under these conditions. The remaining hydrogen was then removed by treatment with an excess of oxygen and exhaustion to remove the water thus formed. After this treatment oxygen is left on the platinum, and this was eliminated by introducing an excess of carbon monoxide. The bulb was then again evacuated at 110°, and the amount of carbon dioxide formed determined by analysis of the recovered gases. Half this volume of carbon dioxide represents the volume of oxygen previously present. Also, by subtracting the volume of carbon dioxide formed from the volume of carbon monoxide disappearing, the amount of

[7] Pollard, *J. Phys. Chem.*, **27,** 356 (1923).

[8] Boswell and McLaughlin, *Trans. Roy. Soc. Can.*, [3] **17,** Sec. III, 1 (1923).

[9] Boswell, *ibid.*, [3] **16,** Sec. III, 1 (1922).

carbon monoxide remaining in vacuum at 110° may be calculated. On again introducing carbon monoxide, the total adsorption of this gas under any given conditions could be readily obtained. An analogous procedure was used in determining the adsorptions of oxygen and hydrogen. Thus, for example, the volume of oxygen required to react with the known amount of carbon monoxide remaining in vacuum at 110°, subtracted from the total volume of oxygen disappearing, gave the volume of oxygen retained by the platinum.

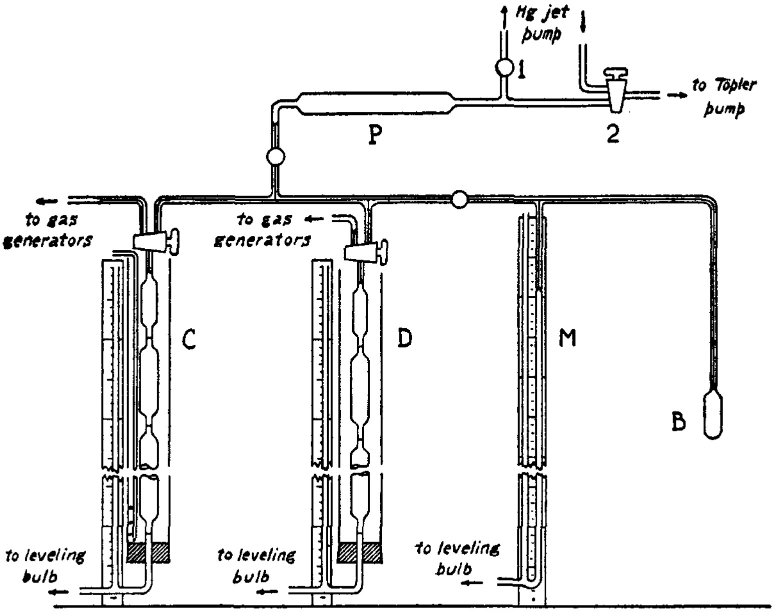

Fig. 1.—Diagram of apparatus.

Apparatus.—The apparatus (Fig. 1) consisted essentially of a bulb (B), containing the platinum black, a constant-volume manometer (M), two gas burets (C,D) connected with the gas generating and purifying lines, a Töpler pump and a mercury-vapor pump. The Töpler pump was so arranged that it could be operated either alone or as fore vacuum for the vapor pump. It was provided with a third gas buret (not shown) for measuring the gases collected, and this in turn communicated with gas analysis apparatus of a modified Orsat type. The pumps were protected from water vapor by the phosphorus pentoxide tube P. Gas volumes were determined in the calibrated burets by bringing the mercury level to the most convenient mark, and measuring the pressure exerted by the gas. Fused glass joints were used throughout. The stopcocks marked 1 and 2 were greased with the usual rubber stopcock grease. All others were lubricated with white vaseline which had been heated for some time in a vacuum at 120°. As a lubricant this material proved unsatisfactory on continued use, but it was considered desirable to avoid contamination of the platinum as far as possible.

Materials.—The platinum used in this investigation was freed as far as practicable from all impurities, including iridium. After various unsuccessful attempts with other methods, the separation of the latter metal was effected by repeated fractional precipitation of ammonium chloroplatinate, followed each time by ignition and fractional solution in aqua regia. This cycle of operations was repeated four times.

The platinum black was prepared by slowly adding hot 6% chloroplatinic acid solution, neutralized with sodium carbonate, to an equal volume of boiling 5% sodium formate solution. The precipitate was washed by decantation with hot water until no further test could be obtained for chloride ion. In the first four or five washings a small amount of platinum was removed, due to the fact that it failed to settle within a reasonable time. The product was finally dried on a water-bath and transferred to a bulb, which was sealed to the apparatus as shown in Fig. 1. In this condition the sample weighed 4.316 g. By analogy with similar material prepared by Mond, Ramsay and Shields, it was estimated to contain 0.5% of water and 0.6% of oxygen, and therefore 4.269 g. of platinum.

The gases used in this work were prepared as follows. Hydrogen and oxygen were generated by electrolysis of sodium hydroxide solution between Chromel electrodes, and were purified by successive passage over soda lime, hot copper (copper oxide in case of oxygen) and phosphorus pentoxide. Carbon monoxide was obtained by dropping formic acid on warm, concd. sulfuric acid, and passing the gas over soda lime and phosphorus pentoxide. Carbon dioxide was generated by the action of sulfuric acid on sodium carbonate solution, and purified by conducting it through separate tubes of calcium chloride and phosphorus pentoxide. Helium from a tank was freed from impurities by passage over hot copper oxide, and through active charcoal cooled with liquid air. No rubber connections were used on any of the gas-purifying lines, except rubber stoppers on the generating flasks, and adequate displacement of air before collecting gas was always provided.

Procedure.—Before starting a run the bulb containing the platinum was exhausted at 110° (boiling toluene) until the amount of gas obtained at this temperature in five minutes did not exceed 20 cu. mm. The bulb was then cooled and immersed in a bath at 25°. Evacuation was continued for some time in order to make certain that no leak existed. The line to the pumps was then closed and the gas to be tested was admitted to the bulb from C or D, up to approximately atmospheric pressure. The volume of gas so admitted was accurately measured, and the time of admission was noted. Manometer readings were then made at frequent intervals, usually for a period of 30–50 minutes. The possibility of leak was then again tested for by operating the Töpler pump. The bulb and connecting tubing were next exhausted, at 25° until a good vacuum was obtained, and finally at 110°. The gases pumped off were collected and measured, and analyzed when necessary for carbon dioxide and other gases.

Experimental Results.—The data obtained are summarized in Table I, where the experiments are listed in the order in which they were made. The several columns give (1) the run number, (2) the gas used, (3) the volume admitted to the bulb, (4) the total volume pumped off, (5) the volume of carbon dioxide pumped off (when analysis was made), (6) the volume of gas remaining adsorbed on the platinum in vacuum at 110°, (7) the equilibrium pressure (in mm. of mercury at 0°), (8) the volume of gas in the free space at this pressure, and (9) the volume of gas adsorbed

TABLE I

ADSORPTION DATA

Weight of Pt = 4.269 g.

Run	Gas used	Volume in, cc.	Volume out, cc.	CO_2 out, cc.	Volume remaining at 110°, cc.	Pressure (extrapolated), mm.	Volume in free space, cc.	Volume adsorbed at 25°, cc.
3	O_2	16.39	9.30	...	3.95	688	8.96	4.38
4	H_2	25.14	12.96	...	4.28	743.6	9.69	7.55–7.85
5	H_2	13.09	13.16	...	4.21	755.3	9.84	7.53
6	H_2	12.92	12.97	...	4.16	737.7	9.61	7.52
7	O_2	16.62	9.83	...	4.71	728	9.48	4.96
8	H_2	26.72	13.23	...	4.07	774.3	10.09	7.21–7.51
9	H_2	13.27	13.32	...	4.02[a]	768.0	10.00	7.34
10	CO	15.88	12.19	...	6.21[b]	776	10.11	?
11	O_2	12.53	11.58	6.21	3.34	769.2	10.02	3.39
12	CO	18.12	11.38	6.68	6.74 6.51	766.6	9.98	?
13	CO	11.13	11.17	<0.1	6.70 6.47	770.5	10.04	7.72
14	CO	11.27	11.25	0.00	6.72 6.49	783.9	10.21	7.65
15	O_2	11.49	10.92	6.49	3.81	733.8	9.55	3.88
16	He	9.85	9.89	...	...	756.7	9.85	...
17	O_2	10.04	9.86	0.00	3.99	746.0	9.72	4.13
18	H_2	24.97	12.87	...	4.12	765.4	9.97	7.02–7.32
19	CO_2	13.46	10.61	10.59	(2.85)[b]	781.7	10.18	(3.28)[b]
20	CO_2	10.56	10.34	...	(3.07)[b]	754.4	9.83	(3.58)[b]
21	CO	14.06	11.12	0.0	6.33[b]	766.8	9.99	?
22	O_2	...	...	6.33	...	...	...	...

[a] Between Runs 9 and 10 a slight leak (air) removed 0.08 cc. of hydrogen.

[b] These values are exclusive of the volumes of hydrogen also present. The latter were: in Run 10, 1.42 cc.; in Runs 19 and 20, 4.12 cc.; in Run 21, 0.83 cc.

at 25° and the equilibrium pressure. All volumes are expressed in cc. at 0° and 760 mm. The methods of obtaining the values in Cols. 6–9 are explained below.

A consideration of Runs 12, 11, 10, 9 and 8 will illustrate the method of calculating the values in Col. 6. Thus in Run 12, of the 18.12 cc. of carbon monoxide introduced, 11.38 cc. was recovered, partly as carbon monoxide and partly as carbon dioxide formed by interaction of the monoxide with oxygen remaining from Run 11. The difference, or 6.74 cc., represents the volume of the monoxide which remained adsorbed on the platinum in vacuum at 110° at the conclusion of this run. (The value, 6.51 cc., also given for this run in Col. 6, was obtained by calculating back from the results of Runs 15, 14 and 13.) Furthermore, since 6.68 cc. of carbon dioxide were obtained in Run 12, the volume of oxygen remaining in vacuum at the end of Run 11 must have been half of this value, or 3.34 cc. In Run 11, 6.21 cc. of carbon dioxide was formed and, therefore, this quantity of carbon monoxide must have remained from Run 10. The amount of oxygen recovered as such in Run 11 was 11.58–6.21, or 5.37 cc. Hence the loss of oxygen was 12.53-5.37, or 7.16 cc. But 3.34 cc. was left on the platinum and 3.11 cc. reacted to form carbon dioxide. Therefore, 7.16–3.34–3.11, or 0.71 cc., reacted with hydrogen which had remained from Run 9, incompletely displaced by carbon monoxide in Run 10. Hence at the end of this run the platinum retained 1.42 cc. of hydrogen and 6.21 cc. of carbon monoxide. Accordingly, of the 15.88 cc. of the monoxide introduced in this run, 6.21 cc. was not recovered. The 12.19 cc. of gas pumped off must have consisted, therefore, of 15.88–6.21, or 9.67 cc., of carbon monoxide and 2.52 cc. of hydrogen. Consequently the hydrogen present at the start of Run 10 amounted to 2.52 plus 1.42, or 3.94 cc. Since 0.08 cc. of hydrogen was accidentally removed by a slight leak before this run, the volume of hydrogen remaining at the conclusion of Run 9 was 4.02 cc., as given in Col. 6. In Run 9, 0.05 cc. of hydrogen was pumped off in excess of the amount introduced, and therefore 4.07 cc. of hydrogen must have remained in vacuum at 110° at the end of Run 8. It will be unnecessary to illustrate for the other runs the relatively simple calculations needed to obtain the values given in Col. 6.

To obtain the equilibrium pressures tabulated in Col. 7, Table I, the pressures in the bulb, obtained from the manometer readings, were plotted against the reciprocals of the corresponding times, and the curves extrapolated to infinite time. Some typical curves are shown in Fig. 2. The volumes of gas in the free space of the bulb at these extrapolated equilibrium pressures were then calculated (Col. 8, Table I), making use of the helium experiment (Run 16) on the assumption that this gas was not appreciably adsorbed. In those cases where the same gas was used as in the previous run, the volumes adsorbed at 25° and the equilibrium pressure (Col. 9) were obtained by adding to the volume remaining from the previous run (Col. 6) the volume taken up in the run in question, that is, the difference between Cols. 3 and 8. Thus, for example, in Run 13, 11.13–10.04, or 1.09 cc. of gas was taken up; since 6.63 cc. (average of two values given in Col. 6) was already present as a result of Run 12, the total adsorption in Run 13, at 25° and the equilibrium pressure, was 7.72 cc.

When the gas being tested was different from that used in the previous run, the volume adsorbed at the equilibrium pressure could not ordinarily be calculated, since in these cases the free space was filled with a mixture of two gases. Thus, in Runs 10 and 21 carbon monoxide and hydrogen, and in Run 12 carbon monoxide and dioxide, were present in the free space in undetermined proportions. Similar, but much less uncertainty exists in Runs 4, 8 and 18, where the mixture consisted of hydrogen and water vapor. The two values given in these cases for the adsorption at 25° (Col. 9, Table I) were calculated on the assumption that the free space was free from water vapor, and saturated at 25°, respectively.

The mean of these two is probably not far from the true value. This difficulty may be avoided in Runs 3 and 7, since it was found that the volume of oxygen pumped off was the same, within experimental error, as the volume required to fill the free space at the last measured pressure. Hence, no adsorbed oxygen could be removed by exhaustion at 110° and, therefore, the values given in Col. 6 for Runs 3, 7, 11 and 15 represent also the amounts of oxygen actually adsorbed at 25° and the last measured pressure. The adsorptions at 25° and the equilibrium pressure (Col. 9) were obtained by adding to these values the small additional quantities which would have been taken up on standing indefinitely. For example, in Run 7 the last measured pressure was 746.6 mm., and by extrapolation (Curve 7, Fig. 2) the equilibrium pressure was estimated as 728 mm. This decrease of 18.6 mm. corresponds to a further adsorption of 0.25 cc., and consequently the total adsorption at equilibrium would have been 4.71 + 0.25, or 4.96 cc. It may be noted that Runs 3 and 7 were unique in the slowness with which equilibrium was approached.

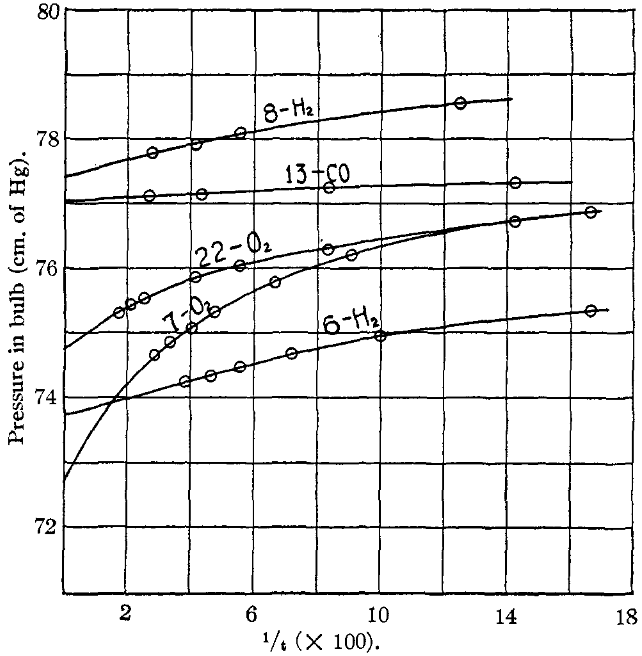

Fig. 2.—Rate of approach to equilibrium. (The curves are numbered to correspond to the run numbers in Table 1.)

Parentheses have been placed around the carbon dioxide adsorptions in Runs 19 and 20 to indicate that these values are doubtless affected by the hydrogen also present (Table I, Note *b*). In fact it seems not improbable that the carbon dioxide and hydrogen interacted to form a very stable surface complex, since it is difficult to account otherwise for the fact that in Runs 19 and 20, only 0.07 and 0.06 cc., respectively, of carbon dioxide were given off in vacuum after the temperature had been raised to 110°.

For the sake of completeness it should be mentioned that the first run with this sample of platinum (Run 1) was made with oxygen, and Run 2 with hydrogen. The results are omitted from Table I because the recovered volumes were not determined. From the volume introduced in Run 2 it was found that the amount of hydrogen adsorbed plus the amount equivalent to the oxygen remaining from Run 1, equaled 45.17 cc. The corresponding value for similar runs made later was, on the average, 15.7 cc., indicating the great sintering effect produced when platinum black is heated to 110° in hydrogen for the first time.

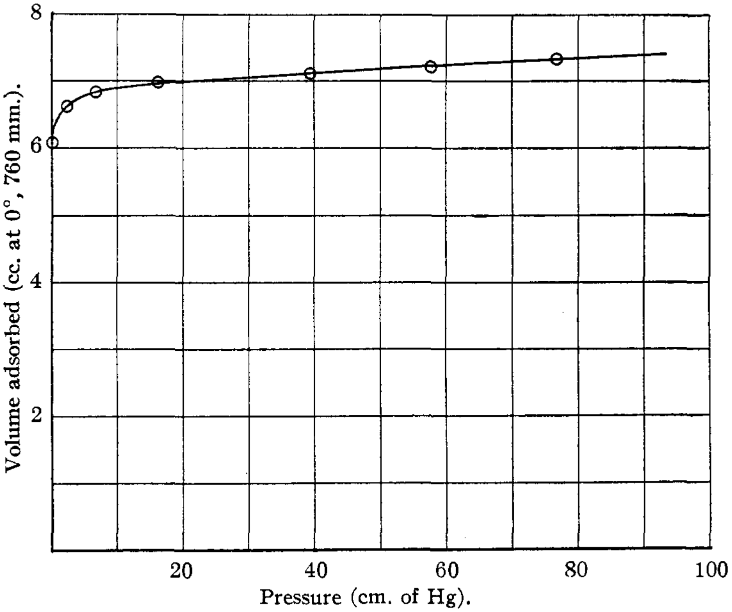

Fig. 3.—25° isotherm for hydrogen.

Isotherms.—In Run 9 the hydrogen was withdrawn in stages, in order to secure data for the 25° adsorption isotherm for this gas. The results are given in Table II, and plotted in Fig. 3.

Complete isotherms were not determined for the other gases, but their general trend may be estimated for carbon monoxide and oxygen. Thus in Runs 13 and 14 the adsorption of the monoxide at approximately atmospheric pressure was 7.72 and 7.65 cc., respectively; the volumes not recovered by evacuation at 25° were 7.20 and 7.22 cc. Though not strictly equilibrium values, the latter could probably have been reduced

Table II

Isotherm for Hydrogen at 25°

Pressure (extrapolated), mm.	Total volume in bulb, cc.	Volume in free space, cc.	Volume adsorbed, cc.
768	17.34	10.00	7.34
577	14.73	7.52	7.21
393	12.27	5.15	7.12
162.4	9.10	2.13	6.97
67.8	7.71	0.88	6.83
23.5	6.94	.31	6.63
1.1	6.07	.01	6.06

but slightly by continued pumping, since only about 0.6 cc. more was removed by exhaustion at 110°. Hence, it is evident that the isotherm for carbon monoxide is even flatter than that for hydrogen. The adsorption of oxygen appears to be completely irreversible, since none was removed by evacuation either at 25° or at 110°.

Discussion

Considering the nature of the experiments, the checks obtained in different runs with hydrogen or with carbon monoxide are regarded as satisfactory. A general tendency may, however, be noted for the adsorption to decrease slightly in successive runs, probably owing to a gradual sintering of the platinum.

In Table III are given the average volumes of the different gases adsorbed by unit volume of platinum, assuming the density of the latter to be 21.0. It will be observed that at 25° and one atmosphere, hydrogen and carbon monoxide are adsorbed to practically the same extent, while the adsorption of oxygen is somewhat more than half as great.

Table III

Average Adsorption per Unit Volume of Platinum

Gas	H_2	CO	O_2
At 25° and 1 atm. (approx.)	36.7	37.8	20.4

The question arises as to the effect of temperature and pressure changes on these adsorptions; for evidently a surface can not be regarded as completely covered with a unimolecular gas film, under given conditions, if a small change in temperature or increase in pressure materially increases the adsorption. Conversely, failure of moderate pressure and temperature changes to alter the volume of gas adsorbed would furnish strong evidence in support of the one-layer hypothesis. From a consideration of the isotherms previously discussed, it is plain that the adsorptions of all these gases are affected but little by moderate changes in pressure. The effect of temperature, however, requires further comment.

Numerous investigators have studied adsorptions, especially of hydrogen, by platinum black at different temperatures, but for the most part without concordant results. Nearly all these experiments are unsatisfactory for the present purpose because the samples of platinum used at the lower temperatures had not previously been heated so hot as those employed at higher temperatures, and hence it was to be expected that the latter would have a smaller adsorption capacity.[10] The results of Taylor and Burns[6] are not open to this criticism, and it should be noted that the objection to their work with platinum black previously discussed, namely, the initial presence of hydrogen on the surface, applies equally to the measurements at different temperatures. Therefore, the fact that these authors found almost identical hydrogen adsorptions at 25° and 110° shows that the total adsorption of this gas on a bare surface is likewise nearly independent of temperature in this range. Such data as exist for carbon monoxide indicate that the adsorption of this gas is also affected but little, if at all, by a temperature change from 25° to 110°. As for oxygen, Mond, Ramsay and Shields[5] found the adsorption increased with temperature and Langmuir[1] has made a similar observation for this gas on platinum foil.

These considerations lead to the conclusion that if the experiments recorded in this paper were repeated at somewhat higher temperatures, the carbon monoxide and hydrogen adsorptions would remain unchanged, but the oxygen value would increase. It is perhaps questionable whether the oxygen adsorption would finally become equal to the values for carbon monoxide and hydrogen, but the results for the two latter gases are clearly in harmony with the view that they form on platinum black "saturated" unimolecular layers.

If this view is correct, the surface area of a given quantity of the platinum black may be roughly calculated. The molar volume is approximately 9.30 and, therefore, the volume occupied by each platinum atom is 1.53×10^{-23} cc., and the area assignable to each atom in a platinum surface is 6.2×10^{-16} sq. cm. There are then 1.6×10^{15} atoms per sq. cm., and if the assumption be made that each platinum atom on the surface holds one *atom* of adsorbed gas, there must be 0.80×10^{15} molecules of hydrogen or carbon monoxide adsorbed per sq. cm. of surface. In other words, 3.0×10^{-5} cc. of gas is required to form one sq. cm. of such an adsorbed layer. Since in the present experiments an average of 37.3 cc. was needed per cc. of platinum, it appears that the sample used had a surface area of 1.3×10^{6} sq. cm. per cc., or 6.0 sq. m. per gram.

Summary

The adsorption of hydrogen, carbon monoxide and oxygen by platinum black has been measured at 25° and one atmosphere pressure, and the

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[10] This applies, for example, to the isobars of Mond, Ramsay and Shields (Ref. 5), and to those of Gutbier and Maisch [*Ber.*, **52B,** 1368 (1919)].

25° isotherm for hydrogen has been determined. The method employed is believed to be free from the serious errors of other work in this field.

It was found that hydrogen and carbon monoxide were adsorbed to practically the same extent, while the oxygen adsorption was only about half as great. A consideration of the effect of temperature on these adsorptions leads to the conclusion that at somewhat higher temperatures all three gases would be adsorbed in more nearly equal amounts.

Of especial interest is the fact that the results support the hypothesis of unimolecular (or monatomic) adsorbed films.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 97]

THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES
VI. THE IONIZATION AND IONIZATION CONSTANTS OF MODERATELY IONIZED ACIDS

BY MILES S. SHERRILL AND ARTHUR A. NOYES

RECEIVED MARCH 23, 1926 PUBLISHED JULY 6, 1926

Principles of the Method

The theory of inter-ionic attraction developed by Milner and by Debye and Hückel[1] has been tested and found to account satisfactorily, at any rate at low concentration, for the anomalous behavior of salts, acids and bases which may be assumed to be completely ionized. In case of slightly ionized acids or bases, the effect of ion attraction is small on account of the low ion concentration in such solutions. In the case of acids or bases which lie between these two extremes (the so-called half-electrolytes) the effect is large; and it is the purpose of this paper to apply certain principles derived from the theory to the evaluation from conductance data of the true ionization and of the ion activity of such substances.

The usual method of calculating the ionization of acids from the conductance ratio Λ/Λ_0 becomes inexact in case of moderately ionized acids, since according to the inter-ionic attraction theory the mobility of the ions decreases when their concentration increases. The exact mathematical treatment of this effect has been developed by Debye and Hückel, and they have derived an expression for the ratio of the mobility of a given ion in a solution of (small) ionic strength[2] to the mobility of that ion at zero

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[1] (a) Milner, *Phil. Mag.*, **23**, 551 (1912). (b) **25**, 742 (1913). (c) Debye and Hückel, *Physik. Z.*, **24**, 185, 334, 305 (1923). See also (d) Noyes, THIS JOURNAL, **46**, 1080, 1098 (1924); and (e) Hückel, "Zur Theorie der Elektrolyte," *Ergebnisse der exakten Naturwissenschaften*, Julius Springer, Berlin, **1924**, vol. 3, pp. 256–275.

[2] The term ionic strength is here used, as defined by Lewis and Randall [THIS JOURNAL, **43**, 1141 (1921)], to denote one-half of the sum, taken for all the kinds of ions in the solution, of the products of the molal concentration c of each ion by the square of its valence, z, that is, to be equal to $\frac{1}{2}\Sigma(cz^2)$.