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WASHINGTON, D. C.

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THE ADSORPTION OF GASES BY METALLIC CATALYSTS.

BY HUGH STOTT TAYLOR AND ROBERT MARTIN BURNS.

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I. Introduction.

Theories of catalytic activity have been based frequently upon assumptions of adsorptive power on the part of the catalytic agent. Experimental investigation of such theories is in many cases possible, but hitherto a systematic attempt to apply such a test has not been undertaken. The selective action of catalytic agents suggests a starting point in such investigative work, and it is believed that a solution of the general problem of contact catalysis may be more readily attained when such a study has been accomplished. The data given in the literature for the "occlusion" of gases by the metallic elements are of little assistance because of the fact that these may cover cases of true solubility, of compound formation, and even of gaseous inclusions, whereas, in all probability, contact catalysis is concerned only with surface phenomena. Furthermore, these data generally refer to metals, the activity of which, as catalysts, has not been specifically determined for the material in the form used in the occlusion investigations.

The selective action of solid catalysts is clearly manifested in the action of catalytic poisons. Several instances of loss of catalytic activity have been found to result from the presence of certain impurities in the reactant gases. Harbeck and Lunge¹ have shown that carbon monoxide inhibits almost completely the catalytic action of platinum on a mixture of hydrogen and ethylene. Maxted² has found that palladium decomposes hydrogen sulfide, retains sulfur, and loses, thereby, the ability to adsorb hydrogen. Von Hemptinne³ was surprised to find that the presence of carbon monoxide decreased materially the adsorption of hydrogen by palladium at low temperatures.

It is, perhaps, natural that most observations of adsorption have been made with the platinum metals since these were among the earliest recog-

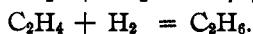
¹ Harbeck and Lunge, *Z. anorg. Chem.*, **16**, 50 (1898).

² Maxted, *J. Chem. Soc.*, **115**, 1050 (1919).

³ Von Hemptinne, *Z. physik. Chem.*, **27**, 429 (1898).

nized catalysts. On the other hand, since the development of the hydrogenation processes by Sabatier and his co-workers,¹ the use of other elements, notably nickel, for catalytic agents has suggested the importance of extending an investigation to include these. Indeed, the apparent simplicity of certain hydrogenation reactions has invited the present attempt to study the relation of adsorption to catalytic activity, and more particularly to cases of specific hydrogenation action.

From among reactions suitable for investigation, the following were chosen.



The metals used were nickel, cobalt, palladium, platinum, iron, and copper. All six of these catalyze the hydrogenation of ethylene, but with only the first three, nickel, cobalt and palladium, according to Sabatier, can the methanation reactions be accomplished.

A knowledge, then, of the adsorptions of hydrogen, carbon monoxide, carbon dioxide and ethylene by these metals might be expected to give some insight into the function of catalytic agents, and the mechanism of their action. Such a study of adsorptions should, moreover, contribute to the general theory of adsorption of gases by solids. Most observations hitherto have been made upon porous inert materials where capillarity and ease of liquefaction were important factors. In contrast to this, the present study has been confined to metals, substances which are chemically active, and which should therefore, display adsorptions of a specific nature.

II. Apparatus and Manipulation.

A diagram of the apparatus employed is shown in Fig. 1; it consists essentially of a Toepler vacuum pump, a gas buret, G, and an adsorption bulb, M, containing the metallic element to be investigated. Fig. 2 shows a simple type of Nichrome wire resistance furnace generally used, as described later, to prepare the sample. After being sealed to the system in Position M, the bulb containing the metal was evacuated at a temperature of about 444°, produced by bringing up a boiling sulfur bath. When the metal had been reduced from its oxide at 300°, or below, the temperature of evacuation was 305°, and was produced by boiling acetanilid. Exception to this rule was made in the experiments on platinum black, and palladium, when the highest temperature used was 110°. The evacuation process was, as a rule, concluded when the quantity of gas obtained during a 5-minute interval was less than 3 cu. mm. At this point the bath was removed and the adsorption bulb cooled to 25° by raising about it a large beaker of water maintained at this temperature. The gas, the adsorption of which was to be measured, was bubbled from the gas generator into the buret G, which contained conc. sulfuric acid. After washing out the delivery tube, which extended from the buret to the 3-way cock above the adsorption bulb, with the gas to be

¹ Cf. Sabatier, "La Catalyse en Chimie Organique," Librairie Polytechnique, Ch. Béranger, Éditeur, 1920.

used, the acid level in the open side arm was adjusted to that within the buret in order to make an initial reading at atmospheric pressure. The evacuated sample was then opened to the gas buret, and the amount of gas at atmospheric pressure required to fill the bulb containing the metal was determined. This gas was finally pumped off

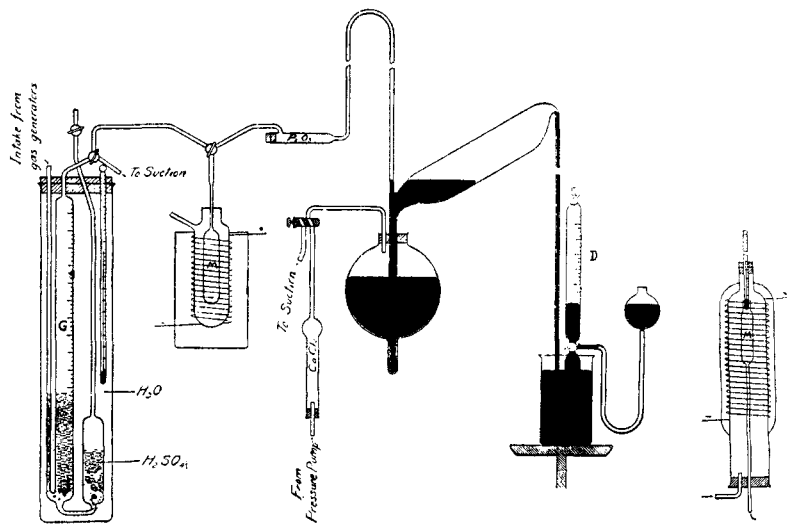


Fig. 1.

Fig. 2.

at the evacuation temperature, collected and measured in the buret D, which served as a control. The process was repeated, and the quantities of gas required to fill the bulb at 110° and 218° were measured. These temperatures were produced by boiling toluene and boiling naphthalene, respectively.

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 6 metals investigated. Calculation 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 U. S. Bureau of Mines) served as additional evidence that the nitrogen value represents zero adsorption.

III. Preparation of Gases.

Pure nitrogen was prepared by heating a solution made from equal parts of sodium nitrite, ammonium sulfate and sodium dichromate.

Carbon monoxide was obtained by dropping formic acid from a dropping funnel upon hot conc. sulfuric acid. Carbon dioxide was prepared by the action of hydrochloric acid on marble placed in a Kipp generator. Hydrogen was obtained electrolytically, and oxygen by the decomposition of potassium permanganate. Ethylene was prepared by dropping ethyl alcohol upon syrupy phosphoric acid which was maintained at a temperature of 220°.

Nitrogen, carbon monoxide, and hydrogen were dried by passing through phosphorus pentoxide, and were freed from traces of oxygen by passing over hot copper turnings. Carbon monoxide was passed through soda lime to remove any carbon dioxide

which it might contain. Carbon dioxide was passed through an absorption bulb containing water in order to prevent contamination of the gas by hydrogen chloride vapor. Ethylene was passed first through a tube cooled in a freezing mixture, and then through a train consisting of two bottles of conc. sulfuric acid and one containing a concentrated potassium hydroxide solution.

IV. Preparation of Metals.

A solid catalyst is supported, generally, on some inert porous material in order that it may present a maximum surface to the reacting substances. It was decided, however, in the present investigation to avoid the use of these supports owing to the possibility of their contributing specifically to the adsorptions. A comparison of our own results using pure nickel with the adsorptions found by Gauger and Taylor¹ who employed nickel on a porous support of Non-Pareil Diatomite brick suggests that this latter substance is not entirely without some influence in addition to that accruing from an increased surface.

Nickel, cobalt, iron and copper were all obtained by calcination of the pure nitrates of these metals at 300° to 400°, and subsequent reduction of the oxides, so produced, by a stream of dry hydrogen. In order to prevent oxidation of the finely divided metal, this reduction was carried out directly in the adsorption Bulb M, which was placed in the upright furnace as shown in Fig. 2. Completion of the reduction process was indicated when no further water was absorbed from the issuing hydrogen by a weighed tube of anhydrous calcium chloride. Before removing the reduced metal, the furnace was cooled and the hydrogen displaced by carbon dioxide. The wide end of the adsorption bulb was then quickly sealed off, and the bulb sealed on to the apparatus in the position shown in Fig. 1.

The first two nickel samples which appear in Table I were reduced from the oxide at 300°, Nickel I being subjected to this treatment for 48 hours, and Nickel II for 12 hours. Neither was completely reduced; the first still showed the formation of 2.4 mg. of water per hour, and the second, 1.8 mg. for the same period. This was to be expected, for as pointed out by Senderens and Aboulenc,² a temperature of 420° is necessary in order to obtain complete reduction of nickel. These two samples were, however, prepared in accordance with the known practise for preparation of an active nickel catalyst. The third sample of nickel was obtained by transferring Nickel II in an atmosphere of carbon dioxide to a quartz tube, reduction being then completed at 600° to 700°.

A spongy form of copper was prepared by complete reduction of the oxide at 250°.

Cobalt I was obtained by reducing cobalt oxide for 4 hours at a temperature of 400°. It was dark gray in color and contained a considerable quantity of oxide. Cobalt II was reduced in quartz at 600° to 700° until entirely free from oxide. Slight sintering occurred and the color became a bluish gray. Cobalt III consisted of 10% cobalt, and was prepared by impregnating porous brick with cobalt nitrate, calcining at 300° and reducing at 450°. It seems impossible to obtain complete reduction at this temperature, for at the end of 18 days, during which time there was no interruption of the hydrogen stream, the amount of water produced per hour had not fallen below 1.8 mg.

Finely divided iron was obtained by reduction at 450° of ferric oxide which had been made previously by calcination of ferric nitrate. Here again, there was, after 26 days of continuous reduction, enough oxide still present to yield 1.7 mg. of water per hour.

¹ Gauger and Taylor, *J. Ind. Eng. Chem.*, **13**, 75 (1921)

² Senderens and Aboulenc, *Bull. soc. chim.*, [4] **11**, 641 (1912).

It is probable that the oxide remaining in these cases of incomplete reduction is well within the interior of the masses. Ipatiew¹ claims that the activity of a nickel catalyst is due to the presence of oxide, but this has been disputed.²

Palladium sponge was prepared by reduction of palladious chloride at 125° with hydrogen. The chloride had been obtained from pure palladium foil.

Platinum sponge was prepared by gentle ignition of ammonium chloroplatinate which had been obtained in the usual way from the pure metal. For the preparation of platinum black, the method recommended by Mond, Ramsay and Shields³ was followed. This consists essentially in the reduction of a hot dilute solution of chloroplatinic acid by a solution of sodium formate, followed by a thorough washing of the precipitated platinum.

V. Discussion of Results.

Nickel.— The adsorption of hydrogen by Nickel I and Nickel II, both of them active catalysts, is shown by Table I to be of considerable magnitude, and to be practically independent of temperatures from 25° to 218°. The values given in this and subsequent tables have all been repeatedly checked.

TABLE I.

Metal.	Weight in G.	Gas.	Cc. required to fill bulb (reduced to N. T. P.).				Volumes of gas taken up by one volume of metal.			
			25°	110°	184°	218°	25°	110°	184°	218°
Nickel I	6.2000	N ₂	9.60	7.40	5.95
		H ₂	12.35	10.35	8.80	3.90	4.30	4.05
Nickel II	13.9422	N ₂	14.50	11.10	9.40	8.85
		H ₂	21.10	17.30	15.20	4.15	3.90	4.00
		CO ₂	16.35	11.90	9.50	1.15	0.50	0.40
		CO	15.00	3.50
Nickel III	13.5210	C ₂ H ₄	21.00	16.65	12.90	4.10	3.50	2.55
		N ₂	13.30	10.35	8.75	8.25
		H ₂	13.65	10.80	8.80	0.25	0.30	0.35
		CO ₂	13.60	10.45	8.30	0.20	0.06	<0.05
		CO	9.90	0.75
		C ₂ H ₄	14.30	10.90	8.50	0.65	0.35	0.15

The observations of early workers in the field are conflicting: Troost and Hautefeuille⁴ find 0.2 volume of hydrogen occluded by finely divided nickel; Neumann and Streintz⁵ find 16.9 to 17.6 volumes; Hempel and Thiele⁶ find none, while Baxter⁷ reports from 2 to 10 volumes. The technique employed by these investigators does not inspire complete

¹ Ipatiew, *J. Russ. Phys. Chem. Soc.*, **38**, 75 (1907); **39**, 693 (1907); **40**, 1 (1908).

² Senderens and Aboulenc, *Bull. soc. chim.*, **17**, 14 (1915).

³ Mond, Ramsay and Shields, *Phil. Trans.*, [A] **186**, 657 (1895).

⁴ Troost and Hautefeuille, *Compt. rend.*, **80**, 788 (1875).

⁵ Neumann and Streintz, *Monatsh.*, **12**, 675 (1891).

⁶ Hempel and Thiele, *Z. anorg. Chem.*, **11**, 93 (1896).

⁷ Baxter, *Am. Chem. J.*, **22**, 351 (1899).

confidence in their results. More recently, Mayer and Altmayer¹ report an occlusion of hydrogen by nickel at 360° which ranges from 5.5 volumes at one-fifteenth atmosphere pressure to 50 volumes at four-fifths atmosphere. Sieverts,² who has made a careful and exhaustive study of the solubility of gases in metals, found that nickel dissolves 0.18 volume of hydrogen at 200° and that solubility increases with temperature until at 1000° as much as one volume is absorbed.

There seems to be no doubt that Sieverts is dealing with true solubility rather than adsorption. The metal samples which he employed were heated to high temperatures in hydrogen, and show, as a result, an absorption which is independent of the size of the surface, and which is directly proportional to the square root of the gaseous pressure.

Nickel III, as already stated, was obtained from Nickel II by continuing its reduction at 600° to 700°. It is seen at once that there is a decrease in the adsorptions of all four gases which runs from 80 to 97%. According to Sabatier,³ nickel reduced at 700° is practically inert as a catalyst. There is, thus, a striking parallelism in this case between adsorption and catalytic activity.

It will be observed that the results obtained by us with active nickel catalysts show an adsorption of hydrogen which is of a higher order of magnitude, entirely, than Sieverts' solubility determinations. Our Nickel III is a much closer parallel to the samples used by Sieverts, although even in this case we obtained measurable adsorptions, whereas Sieverts specifically states⁴ in one case that there was no difference between the hydrogen and nitrogen values of his sample. The higher temperatures used by him in the preparation of his samples may account for this in part. The surface of Sieverts' material was probably less extensive than ours, and his experimental accuracy not quite so great. Possibly the variable values hitherto recorded for nickel may be attributed in part to the varying modes and temperatures of preparation. They are also due in part, doubtless, to the presence of unreduced oxide. We found, in this connection, that it was impossible to pump off all of the hydrogen which was taken up by Nickel II. The same was true, but to a less extent, in the cases of Nickel I, Cobalt I, and iron. It was also not possible to recover entirely all of the carbon dioxide in cases where oxide was known to be present. There was evidence of reduction in the first case, and in the second it may have been that there was a formation of carbonate by the action of carbon dioxide on the metallic oxides. It should be noted that in all of these cases the recovered volumes of gases were used in order to

¹ Mayer and Altmayer, *Ber.*, **41**, 3062 (1908).

² Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).

³ Sabatier, *op. cit.*, p. 134.

⁴ Sieverts, *Z. physik. Chem.*, **60**, 171 (1907).

calculate the adsorptions. The occurrence of a discrepancy between volumes recovered was an important indication of interaction.

In order to investigate the adsorption of hydrogen by Nickel I at pressures of less than one atmosphere, mixtures with nitrogen were used. The results are given in Table II, and are shown graphically in Fig. 3, by Curve I. In determining the points on this curve, correction was made for the small lowering of the partial pressure of hydrogen in the gas phase which occurred as a result of its adsorption from the gaseous mixture. The amount of hydrogen consumed in reduction of Nickel I had been shown previously to be so small at 25° as not to prove a complicating factor in the experiments.

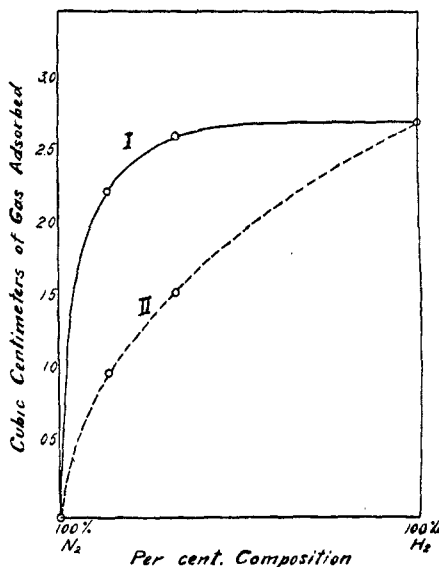


Fig. 3.

TABLE II.

Hydrogen %	Partial pressure of hydrogen. mm.	Hydrogen (N.T.P.) adsorbed at 25° 760 mm. Cc.	Calculated adsorption if proportional to the square root of hydrogen pressure.
100.	760.	2.72
32.4	246.2	2.62	1.55
13.5	102.6	2.25	1.00

It is thus shown by Curve I that the adsorption of hydrogen is almost independent of its partial pressure for pressures above a third of an atmosphere. If adsorption were proportional to the square root of the hydrogen pressure, as found by Sieverts for solubility, the results obtained should have followed the dotted Curve II. Sieverts believes that his results indicate a dissociation of molecular hydrogen, and subsequent solution in the atomic form.

Thomas,¹ and also Lewis,² from a consideration of the ability of nickel to dissociate hydrogen, as calculated from Sieverts' solubility data, reach a conception of the catalytic mechanism involved in the hydrogenation of olein. It is significant that the nickel employed by Sieverts could not have been catalytically active owing to its antecedent treatment. The calculations based on results obtained from such metals are consequently

¹ Thomas, *J. Soc. Chem. Ind.*, 39, 10T (1920).

² Lewis, *J. Chem. Soc.*, 117, 623 (1920).

of doubtful value. Furthermore, the adsorption of hydrogen at various partial pressures by catalytically active nickel does not, as just shown, agree with Sieverts' solubility data. Catalytic studies or reaction kinetics should not, therefore, it is concluded, show agreement with such solubility data.

TABLE III.

Metal.	Weight. G.	Gas.	Cc. required to fill bulb (reduced to N. T. P.).			Volumes of gas taken up by one volume of metal.		
			25°	110°	218°	25°	110°	218°
Copper	22.8550	N ₂	22.40	17.45	13.90
		H ₂	22.40	17.55	13.90	<0.05	<0.05	<0.05
		CO ₂	22.55	17.50	13.90	0.06	<0.05	<0.05
		CO	23.90	18.10	13.90	0.60	0.25	<0.05
		C ₂ H ₄	24.10	18.10	13.90	0.65	0.25	<0.05
		O ₂	22.35	<0.05
Cobalt I	19.7600	He	22.35
		N ₂	11.70	9.10	7.00
		H ₂	11.60	9.10	<0.05	<0.05
		CO ₂	16.30	10.30	9.10	2.00	0.50	<0.05
		CO	28.60	11.90	9.20	7.35	1.20	0.95
Cobalt II	35.1750	N ₂	24.00	18.70	15.20
		H ₂	24.20	18.95	15.30	0.05	0.06	<0.05
		CO ₂	26.00	18.85	15.50	0.50	<0.05	0.05
		CO	30.40	21.20	16.70	1.55	0.60	0.35
		C ₂ H ₄	25.50	19.10	15.10	0.35	0.10	<0.05
Cobalt III	0.7500	N ₂	21.25
		H ₂	21.40	1.70
Iron	13.1030	N ₂	8.65	6.75	5.45
		H ₂	8.75	6.80	5.50	0.05	<0.05	<0.05
		CO ₂	9.05	6.80	5.45	0.25	<0.05	<0.05
		CO	9.80	7.05	5.65	0.70	0.20	0.10
		C ₂ H ₄	9.10	6.80	5.45	0.30	<0.05	<0.05
		N ₂	1.60	1.30
		H ₂	40.90	29.50	753.25	540.50
Palladium	0.6000	CO ₂	1.60	1.30	<0.05	<0.05
		CO	2.35	2.05	14.40	14.40
		O ₂	2.20	1.90	11.50	11.50
		N ₂	3.45	2.60	2.10
		H ₂	4.40	3.65	3.25	4.05	4.50	4.90
Platinum Sponge	5.0000	CO ₂	3.30	2.60	2.10	<0.05	<0.05	<0.05
		CO	3.50	2.80	2.20	0.20	0.85	0.45
		C ₂ H ₄	3.45	2.60	2.05	<0.05	<0.05	<0.05
		O ₂	3.90	3.25	3.10	1.90	2.80	4.30
		N ₂	4.90	3.90
Platinum Black	2.5000	H ₂	5.70	4.60	6.85	6.00
		CO ₂	5.10	4.00	1.70	0.85
		CO	7.00	6.20	18.00	19.70
		C ₂ H ₄	5.80	4.60	7.70	6.00
		O ₂	8.00	6.95	26.50	26.10

We next found that Nickel II showed large adsorptions of ethylene and carbon monoxide. The single temperature of 184° was chosen for measurement of the latter since it is within the range in which carbon monoxide is readily hydrogenated, and above that in which nickel carbonyl is stable. The amount of carbon dioxide which nickel adsorbs is seen to be about one-fourth that of the other three gases, and further, to diminish rapidly with increasing temperature.

Copper.—Adsorptions by copper were found to be of a lower order of magnitude than those of nickel, and in no case were they measurable at 218°.

From Table III it is seen that the hydrogen values for copper are in agreement, practically, with those of nickel. Those who have studied the occlusion of hydrogen by copper report anywhere from 19.8 volumes¹ to nothing.² Sieverts found no measurable solubility of hydrogen below 400°.

Ethylene and carbon monoxide were both found to be considerably adsorbed at 25°, and less so at 110°. Sieverts and Krumbhaar³ state that copper neither absorbs nor reacts with carbon monoxide.

It was possible to measure the adsorption of carbon monoxide by copper under reduced pressures at 25°, by the method previously outlined for hydrogen on nickel. Carbon monoxide is not hydrogenated by copper, and therefore mixtures of the gas with hydrogen could be used. The results are recorded in Table IV.

TABLE IV.

Carbon monoxide. %.	Partial pressure of carbon monoxide. mm.	Cc. of carbon monoxide (N.T.P.) adsorbed at 25°, 760 mm.	Calculated adsorption if proportional to partial pressure of carbon monoxide.
100	760	1.5	...
47	357.2	1.3	0.92
13.5	102.6	0.9	0.26

If these data are plotted on coördinate paper, the adsorption curve for carbon monoxide on copper follows closely that for hydrogen on nickel shown by Curve I in Fig. 3. That is, here again, adsorption increases very rapidly at low pressures and becomes practically independent of pressure between 0.5 and one atmosphere. This point is of especial significance in the kinetics of hydrogenations involving these gases, and will receive further investigation in this laboratory. The results of Grassi⁴ on the kinetics of hydrogen addition to ethylene in the presence of copper are inadequate to a full comprehension of the prevailing factors.

¹ Melsens, *Ann. chem. phys.*, [3] 8, 205 (1845).

² Hampe, *Z. anal. Chem.*, 13, 362 (1874).

³ Sieverts and Krumbhaar, *Ber.*, 43, 893 (1910).

⁴ Grassi, *Nuovo cimento*, 11, 147 (1916).

Ethylene is hydrogenated, according to Grassi, above 150°, and proceeds rapidly at 200°. At this latter temperature the adsorption of ethylene has become immeasurably small, a fact to which we will especially refer later.

Cobalt.—No adsorption of hydrogen by Cobalt I could be detected, although a slight amount was noticeable with Cobalt II, where a large sample was used; and there was unmistakable evidence of adsorption by Cobalt III, this being due, no doubt, to the large surface exposed. Solubility of hydrogen in cobalt is first measurable at 700°, and reaches a value of 0.4 volume at 1000°.¹

Cobalt was found to show considerable adsorption of carbon monoxide when prepared by reduction at 400°, and, confirming the experience with nickel, this became much less when the metal was prepared at 600°. Ethylene is seen to be adsorbed at 25° and 110°. In the case of carbon dioxide, some of the adsorption shown by Cobalt I may have been due to the formation of cobalt carbonate by association with cobalt oxide present.

Iron.—The adsorptions by iron were small; only at 25° were there measurable values for hydrogen, carbon dioxide and ethylene. Neumann² found the solubility of hydrogen in iron to be about 0.04 volume at 400°, and this is confirmed by Sieverts.³ The high adsorption of carbon monoxide which we found is not surprising in view of the fact that iron forms carbonyl compounds. Stoffel⁴ has shown that the iron pentacarbonyl formed by the action of carbon monoxide on iron is adsorbed by the iron, and that it forms a protective film over the surface of the metal.

Palladium.—Palladium took up large quantities of hydrogen, 753 volumes at 25°, and over 540 volumes at 110°. It is interesting to note that the presence of less than 0.5% of water vapor in the hydrogen had the effect of markedly diminishing the rate at which the hydrogen was adsorbed by the palladium, although it did not affect the total amount taken up.⁵

Palladium was found to take up large quantities of carbon monoxide and oxygen. It was impossible to pump off either of these gases entirely at 110°, and it was therefore, necessary to wash the metal with hydrogen after each successive determination. Mond, Ramsay and Shields⁶ believe that palladium forms a definite oxide and that this is dissociated suddenly at higher temperatures.

¹ Sieverts, *Z. physik. Chem.*, **60**, 129 (1907).

² Neumann, *Stahl u. Eisen*, **34**, 252.

³ Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).

⁴ Stoffel, *Z. anorg. Chem.*, **84**, 56 (1913-14).

⁵ Cf. Taylor, *Trans. Am. Electrochem. Soc.*, **36**, 152 (1919).

⁶ Mond, Ramsay and Shields, *Phil. Trans.*, [A] **191**, 105 (1898).

Platinum.—Platinum black is seen from Table III to take up considerably larger quantities of gases than does the spongy form. It is, too, the more active catalyst. There is evidently some inherent difference between these two forms of platinum since the ratio of adsorptions of the different gases by platinum black does not follow that shown by platinum sponge. For instance, while the adsorption of hydrogen by the former is only one-third more than by platinum sponge, the amount of oxygen taken up is from 10 to 15 times greater. Confirming Gutbier and Maisch,¹ we have found that the quantity of hydrogen taken up by spongy platinum increases slightly with temperature, whereas the reverse is true for platinum black. Finally, the hydrogen value is greater than that for carbon monoxide in the case of the sponge, but less than that of carbon monoxide for platinum black.

Carbon monoxide was found to adhere tenaciously to platinum, and it was necessary to burn it off with oxygen and then remove the excess of oxygen with hydrogen. The hydrogen could then be removed by heating in a vacuum. We regard these results with carbon monoxide as a most significant fact, especially when contrasted with the behavior of palladium, from which carbon monoxide can be removed readily by hydrogen at ordinary temperatures. When it is remembered that palladium is a good methanation catalyst at ordinary temperatures and that platinum even in its most active form cannot be used to effect this reaction,² the importance of this factor will readily be realized. When platinum black was not subjected to treatment with oxygen after having been exposed to carbon monoxide, but was merely evacuated, a subsequent measurement of hydrogen adsorptions showed 3 volumes at 25°, and 2.6 volumes at 110°, whereas the true values on a clean surface were 6.85 and 6.00 volumes, respectively. This is a decrease of approximately 57%. In an analogous way the adsorption of carbon monoxide itself at 110° declined from 19.17 volumes on a clean surface to 7.3 volumes, a decrease of 63%, when the surface had been exposed previously to carbon monoxide, and then only evacuated. This would indicate that it is possible to render only about 40% of the platinum surface free from carbon monoxide even by heating the metal to 110° in a vacuum. In this case, as in the usual practise, the evacuation was continued until the quantity of gas which could be obtained during a five minute interval was less than 3 cu. mm. This was calculated to be equivalent to a pressure of less than 0.002 mm. of mercury. Consequently, even when pressures of carbon monoxide not exceeding a few centimeters exist, it is reasonable to suppose that the platinum surface remains so thoroughly covered with carbon monoxide

¹ Gutbier and Maisch, *Ber.*, **52B**, 1368 (1919).

² Sabatier, *op. cit.*, p. 197.

that hydrogen or other gases are unable to reach it. Bancroft has already predicted¹ that carbon monoxide would tend to prevent the adsorption of hydrogen by platinum. In confirming this view, our experiments demonstrate the cause of the inhibition noted by Harbeck and Lunge² when carbon monoxide was present in the hydrogenation of ethylene.

Platinum sponge showed no adsorption of either ethylene or carbon dioxide. On the other hand, platinum black adsorbed more ethylene than hydrogen, and even adsorbed appreciable quantities of carbon dioxide.

VI. Conclusion.

From the experimental work here recorded we feel that certain important conclusions relative to the adsorption theory of contact catalysis have obtained decisive demonstration. Furthermore, we believe that the experiments are of importance in the general problem of adsorption, and disclose the operation of other factors, the significance of which, in reference to catalysis, needs special emphasis.

Investigations of catalytic adsorbents of the type dealt with in these experiments show results which are in marked contrast to the results of adsorption measurements in which porous, chemically inert, materials such as charcoal and silica gel are used. In the case of metallic catalytic agents the adsorption is pronouncedly specific. In one of such cases hydrogen is more markedly adsorbed than other gases. For example, nickel adsorbs more hydrogen than carbon monoxide. On the other hand, the reverse is the case with iron and cobalt, these metals showing hydrogen adsorptions which are decidedly smaller than those of the other gases. The parallelism observed in the case of porous, inert adsorbents, such as charcoal, between adsorption, compressibility, and ease of liquefaction of the gas does not appear to hold in the case of adsorption by the metal catalysts which we have studied. The adsorption isotherms are also different, saturation capacity of the adsorbent being attained at rather low partial pressures of the gases.

All of this evidence is in agreement with the view that adsorption in the case of metal catalysts is a surface phenomenon somewhat chemical in nature, possibly involving rearrangements of electrons in both the adsorbent and the gas. In the case of bodies like charcoal and silica gel, the phenomenon may be attributed frequently to the presence of pores which fill gradually with liquid, although covering of the surface by an adsorbed gas film can undoubtedly occur in this case also. At any rate, the experiments which have been performed demonstrate that the problem of adsorption by *solid* adsorbents is a far wider one than hitherto indicated, and that it promises to be more interesting by reason of the wide range of

¹ Bancroft, *J. Phys. Chem.*, **21**, 734 (1917).

² Harbeck and Lunge, *loc. cit.*

possibilities. A comprehensive scheme of study in this field has been planned and undertaken.

The measurements with active nickel catalysts and with inactive nickel obtained by reduction of the oxide at elevated temperatures form, we believe, convincing experimental demonstration that the destruction of catalytic activity is accompanied by an almost complete suppression of adsorptive power. In addition, these results clearly indicate one reason for variability in catalytic behavior with variation in mode of catalyst preparation, a phenomenon widely known, but hitherto little understood. The varying adsorptive capacity of the material would account for such variable catalytic behavior. The results suggest, moreover, the necessity of obtaining, in the kinetic studies of catalytic action, the actual behavior of the catalytic agent as an adsorbent.

From an examination of our adsorption measurements, it is evident that maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. Indeed, in the case of copper, the hydrogenation of ethylene begins only at a temperature where the adsorption of ethylene is ceasing to be a measurable quantity. It is true that nickel begins to hydrogenate ethylene at ordinary temperatures, where adsorptions are very large, but it will be observed that at the optimum temperature for this reaction, 130° to 150° , the adsorption of ethylene is considerably less than that at the temperature at which reaction commences. Similar observations may be made with respect to a cobalt catalyst with carbon monoxide and hydrogen, and with nickel in the case of carbon dioxide and hydrogen.

We regard this evidence concerning diminishing adsorption and increasing catalytic activity with temperature as demonstrating the necessity, in many catalytic reactions, of a free evaporation of both reactants and resultants from the catalyst surface. A strong or irreversible adsorption of any of the participants in a reaction undoubtedly tends to render the catalyst surface inactive. At the same time it is possible that such an irreversible adsorption may, in certain cases, lead to a reaction between gases which only occurs with difficulty in the gas phase. Our experiments with palladium and platinum with carbon dioxide and hydrogen may be cited in illustration. The experimental data show that carbon monoxide is tenaciously adsorbed by both metals, and that at moderate partial pressures the gas probably covers the metal surface. In such case, hydrogen, in presence of carbon monoxide, can be adsorbed only on a surface of carbon monoxide and not on the metal. The union of carbon monoxide with palladium to form a Pd-CO surface complex is apparently such that at ordinary temperatures the reactivity of the carbon is enhanced, and with hydrogen, methanation results. With platinum, on the other hand,

no reaction occurs at any temperature and the Pt-CO surface complex remains undecomposed. The evidence cited by von Hemptinne¹ as to the behavior of Pd-CO surface complexes at low temperatures, (-20° and lower) is quite parallel to that occurring with Pt-CO complexes at all temperatures within the range investigated. There is evidence that the production of sulfur trioxide in presence of platinum is caused by the interaction of a Pt-O surface complex with sulfur dioxide molecules. In this case the slight tendency of sulfur trioxide molecules to evaporate constitutes a complicating factor.

When such strong or irreversible adsorptions are not present, when evaporation of the reacting gases is relatively rapid, the conclusion seems inevitable that the condensation process disturbs the electron field of one or the other, or both of the reacting gases, thus bringing them into a reactive condition. Subsequently, on evaporation, by readjustment of the electron field, the active molecules may either regain their normal state, or, on the other hand, may collide with other molecules bringing about reaction. That the adsorption effect is not singly the cause of reaction has been suggested in the preceding paragraphs. We are disposed, therefore, to consider reaction as the resultant of at least two factors, the adsorption factor and the temperature factor. There is evidence as to how these two factors operate. For example, it is known that ethylene and hydrogen can be caused to react by purely thermal means. The temperatures required are high, being in the region of 500° . With a nickel catalyst present reaction occurs from room temperatures upward, and strong adsorption of both gases is shown by nickel. With copper a temperature of 150° is required for incipient action, and adsorption by this metal is much less pronounced than in the case of nickel. Similar observations hold in respect to the conversion of carbon monoxide and hydrogen by means of nickel and cobalt, the temperature required in the case of cobalt, the less efficient adsorption agent, being some 90° higher than with nickel for similar rates of reaction.

It would, therefore, appear that the adsorptive capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong we have, presumably, a more marked or more frequent displacement of the stable configuration of the molecule than with a weak adsorption. Consequently, a lower temperature will effect interaction. In such manner it is possible to correlate, qualitatively at least, the present data on adsorption with the known catalytic activity of the metals in the reactions chosen for study. The importance of this conclusion is sufficient to warrant a detailed study of the same with a view to obtaining a quantitative relationship between the temperature factor and the adsorption

¹ von Hemptinne, *loc. cit.*

factor. Such a study undoubtedly involves an analysis of catalytic action in its relation to radiation theories. An experimental investigation upon such lines is in progress.

VII. Summary.

(1) Measurements of the adsorption of hydrogen, carbon monoxide, carbon dioxide, and ethylene by finely divided nickel, cobalt, iron, copper, palladium and platinum have been made for the purpose of finding what relation this phenomenon might bear to catalytic activity, and particularly to the mechanism involved in hydrogenation reactions.

(2) It has been shown that adsorption by such metals is a specific property quite different in nature from adsorption by inert adsorbents such as charcoal.

(3) The extent of adsorption has been shown to be a function of the mode of preparation, and is especially less pronounced the higher the temperature at which the reduced metal is prepared. The analogy of this fact with the corresponding facts of catalytic behavior has been emphasized.

(4) Adsorption isotherms have been studied in two cases, nickel and hydrogen, and copper and carbon monoxide. In both cases, adsorption increases rapidly with increasing partial pressures below 300 mm., and becomes practically independent of pressure beyond this pressure.

(5) The significance of irreversible adsorptions of gases by metallic catalysts has been studied in more detail than hitherto, and the reasons for divergencies between different catalysts have been suggested.

(6) The necessity, in elucidating catalytic action, of considering a factor in addition to the adsorption factor has been indicated. It has been shown that a combination of the temperature factor with the adsorption factor in a catalytic action suggests a possibility of explanation of the divergence between the catalytic activities of various metals.