production of equal exchange capacities, efficiencies are higher with the resins prepared from the sulfonic esters with the bulkier alcohol residues (*cf.* 1a with 2a or 1b with 4c). This may be because the bulkier alcohol residues directly assist in the formation of the loosely cross linked regions or it may be because the dependence of the hydrolysis rate of resin ester on local degree of cross linking is sharper with a bulkier alcohol group, so that the groups actually hydrolyzed are more closely limited to the regions of loose cross linking.

The group of resins show among themselves some specificities in their catalytic activity toward different esters, but these are not pronounced and show no obvious pattern. Thus most of the points of a plot (Fig. 1) in which the abscissa of a point is efficiency for the hydrolysis of methyl phenylacetate and the ordinate is efficiency for ethyl hexanoate lie along a single line, which may be taken as the norm, and similar results are obtained when any other pair of esters are compared in the same way. There are however exceptions; thus the point for resin 1b (the solid circle) lies decidedly below the normal line in Fig. 1. By itself this would have little if any significance but the data for this resin also deviate in the direction of a high efficiency for phenylacetate in all the comparisons involving this ester and do not deviate from the norm in comparisons which do not involve phenylacetate. The resin may therefore be said to show a positive specificity for phenylacetate. On the same basis it may be concluded that resin 3a shows a negative specificity for ethyl acetate and butyrate, and that resin 4a shows a negative one for phenylacetate, resin 5 a negative one for butyrate, and resin 1x a positive one for butyrate.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Chemisorption: Hydrogen on Nickel at Elevated Pressures

BY LAURI VASKA AND P. W. SELWOOD

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A volumetric method is described for gas adsorption on solids at adsorbate pressures above one atmosphere. The method is used for simultaneous measurement of hydrogen adsorption and of specific magnetization up to 140 atmospheres on a supported nickel catalyst. Some results are given in terms of magnetization–pressure and magnetization–volume isotherms, all at room temperature. At progressively higher pressures hydrogen adsorption causes a progressive though diminishing decrease of magnetization. The adsorption on particles which exhibit ferromagnetism at room temperature is essentially instantaneous and these data may be represented by a Langmuir adsorption isotherm. Chemisorption of hydrogen on nickel is essentially complete at about 100 atm. pressure.

Introduction

The purpose of this work was to extend our studies on the mechanism of chemisorption through use of the changes of magnetization which occur when hydrogen is chemisorbed on finely divided nickel.[1,2] The present paper is concerned with hydrogen adsorption at elevated pressures, and its correlation with the accompanying decrease of magnetization.

Experimental

Magnetic Measurements.—Magnetization changes as a function of hydrogen adsorption were observed on the low frequency a.c. permeameter previously described.[1] Minor modifications of the magnetization assembly included an enlarged primary solenoid of 5172 turns and a coaxial arrangement of the secondaries, of 44 turns each, as shown in Fig. 1. Convenience and precision were gained by placing a Leeds and Northrup Speedomax recorder (Type G) after the Hewlett-Packard 400-D millivoltmeter in the electrical circuit. A reverse e.m.f. was used to extend the zero of the recorder. The primary was operated at 0.70 amp., stabilized 60 cycle a.c. at *ca.* 230 v. The secondary e.m.f. produced by a typical reduced sample averaged about 1 to 2.5 mv. which was sufficient to obtain reproducible readings of the relative magnetization on the recorder within ± 0.02%.

High Pressure Adsorption Measurements.—Of the common methods available, the gravimetric one has been most often used to obtain the limited available data on adsorption at high pressures. Since the present investigation was concerned with simultaneous measurement of hydrogen adsorption and of magnetization, the gravimetric method could not be utilized. On the other hand, a moderately precise volumetric method for obtaining adsorption isotherms at high pressures, such as described by Doerner,[3a] requires a large adsorbent sample.[3b] This condition could not be observed in the present work, because the accuracy of magnetic measurements requires that the sample be situated in a relatively uniform magnetic field which is, of course, near the center of the primary solenoid. Consequently, for a given length of the primary, the choice of the catalyst sample size represents a compromise between the accuracy of magnetic and adsorption measurements. In view of this situation, a new volumetric method was adopted. This may best be described with reference to the diagram of the apparatus, shown in Fig. 2, and in terms of operations to obtain the adsorption isotherms.

The adsorbent chamber, a stainless steel autoclave, is shown in Fig. 1. This autoclave a (Fig. 2) is connected to a gas pipet b of steel tubing, *via* steel tubing j, the valve e_4, and a reducing coupling (not shown in the diagram). The pipet b is connected to a constant pressure gas source *via* valve e_2 and to a glass buret c *via* valve e_3 and kovar-to-glass seal f. The pressure of the gas in c is read from a constant-volume manometer d.

The valves, fittings and tubing of the high pressure equipment were obtained from Autoclave Engineers, Inc., Erie, Pa. Two kinds of valves and fittings were tried and used during the course of this work: (1) Tube Line valves and fittings (Bulletin 255) and (2) autoclave 30,000 p.s.i. valves and fittings (Bulletin 555). While the latter kind proved to be more satisfactory with respect to gas-tight seals, the Tube Line category was used exclusively for valves e_4, e_5 and tubing j because of the availability of $^1/_{16}$ in. i.d. tubing, which was necessary to minimize the free space of the catalyst chamber.

The free spaces of a (with reduced catalyst present), b

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[1] P. W. Selwood, THIS JOURNAL, **78**, 3893 (1956).

[2] E. L. Lee, J. A. Sabatka and P. W. Selwood, *ibid.*, **79**, 5391 (1958).

[3] (a) W. A. Doerner, "Diffusion and Adsorption of Hydrogen in a Porous Nickel Catalyst," Dissertation, University of Michigan, 1952; (b) Doerner used 370 g. of $Ni-SiO_2$ catalyst.

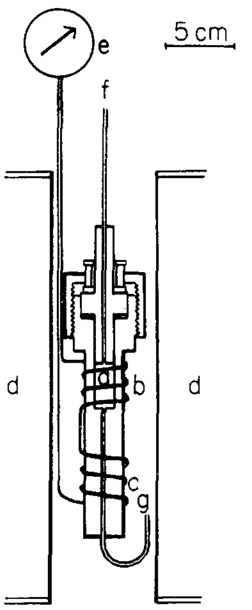

Fig. 1.—High pressure bomb assembly for simultaneous measurement of hydrogen adsorption and magnetization: a, adsorbent chamber; b, secondary coil; c, opposing secondary coil; d, primary solenoid; e, millivoltmeter; f, hydrogen in; g, hydrogen out.

and c were determined with purified helium before and after each run, or series of runs. As it is implicit in the method of adsorption measurement described below, the ratio of free spaces, b:c should be different at different ranges of pressure in order to obtain satisfactory precision. Consequently, this ratio was changed during the course of investigations by adjusting the length of tubing b. Alternatively, two pipets, having different volumes, were used in series. In theory, of course, one can have as many chambers in the pipet as desirable, all connected in series and also to the buret c. On the average, the free spaces both in a and b were *ca.* 5 cc., and that of c 1000 cc.

A full cylinder of Matheson hydrogen, Electrolytic grade (99.8% purity), was used as the high pressure hydrogen source. For measurements at medium pressures, the hydrogen was delivered from the cylinder through a High Pressure Automatic Regulator (Harris Calorific Co., Cleveland, Ohio), fitted with pressure gauges, and giving pressures as high as *ca.* 75 atm. To obtain higher pressures, up to 140 atm., the gas was charged from the cylinder directly into b *via* a needle valve on the cylinder and valve e_2. The pressure of hydrogen in the cylinder remained essentially constant during several successive withdrawals.

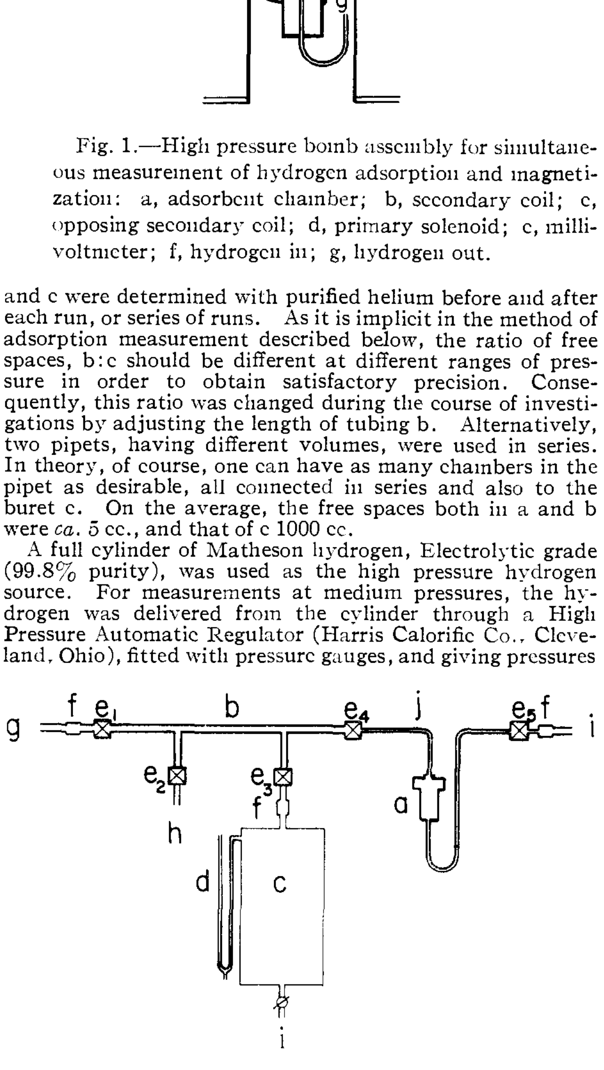

Fig. 2.—Gas handling assembly: a, adsorbent chamber (a stainless steel autoclave); b, gas pipet (stainless steel tubing $^1/_8$ inch i.d.); c, glass exhaust chamber serving as buret; d, open-arm manometer; e, steel valves; f, metal-to-glass seal; g, to low pressure adsorption assembly; h, to high pressure hydrogen source; i, to vacuum system; j, stainless steel tubing, $^1/_{16}$ inch i.d.

Operations to obtain adsorption data were as follows. Initially, all chambers were thoroughly evacuated and all valves closed. Then (1), hydrogen was admitted from the constant pressure source to b by opening valve e_2. Thereafter e_2 was closed and the gas expanded into c *via* valve e_3. From the pressure of hydrogen in c and b, and from the volumes of c and b, the original pressure of the gas as well as its original amount in b may be calculated; (2), after evacuation of chambers b and c, b was filled with the same amount of gas as before (from the constant pressure source). Then hydrogen was admitted to the adsorbent chamber a by opening the valve e_4. After allowing time for adsorption to take place, e_4 was closed and the pressure of the gas and its amount remaining in b determined *via* expansion into c as before. The latter pressure was the pressure of adsorption. From this pressure and the known dead-space in a the amount of gas remaining in a may be calculated. The difference between the original amount of hydrogen in b (amount of hydrogen used) and the sum of the amounts of hydrogen in b and a *after* adsorption (amount of gas not absorbed) gives the amount of hydrogen adsorbed by the adsorbent.

As is evident from this procedure, the method does not enable one to follow the pressure changes during the adsorption process. Some information about the rate of adsorption may, however, be obtained from series of experiments in which the time allowed for adsorption is varied. It might be thought that by repeating the operations (1) and (2) in a given run several times and thus applying successively higher pressures, one would obtain an adsorption isotherm of several points in a single experiment. This is true, of course, for the case when adsorption is allowed to proceed to equilibrium. But, for the non-equilibrium adsorption, only the first isothermal point represents a reliable value since further adsorption takes place during the time required for additional successive operations (1) and (2), and thus the amount of hydrogen present in the adsorbent chamber before the next addition cannot be known exactly. To overcome this limitation of the method, an isotherm was composed of the first points of several runs, in which different initial pressures were applied. Reproducibility of hydrogen adsorption in such measurements (20 to 70 atm.) was on the average within 1 cc./g. Ni.

In some experiments the changes of magnetization were measured as a function of pressure only, by increasing the pressure at intervals through the pressure regulator. Magnetization–time isotherms at constant pressures were obtained from the same experiments.

In the pV calculations at $p > 1$ atm. the compressibility of hydrogen was taken into account by making use of the data given by Doerner[3]: $1000(z - 1)/p = 0.600$ at 25°, where $z = pV/nRT$. It was assumed that the expansion of the steel tubing and the catalyst chamber due to high pressure hydrogen was negligible.

The most serious problem in this work was that of sensitivity of adsorption measurement at high pressures, which was, of course, due to the inherent limitation of all volumetric methods: namely, the large amount of gas in the dead space as compared to the amount of gas adsorbed.

In most experiments, low pressure adsorption isotherms up to 1 atm.) were determined before the catalyst sample was subjected to higher hydrogen pressures. For this purpose the steel chamber b was connected *via* valve e_1 and a kovar-to-glass seal f to a standard volumetric adsorption apparatus described previously.[1] The dead space in these runs was about 12 to 15 cc. For low pressure adsorption measurements, the electrolytic hydrogen was purified by silica gel at −78°. No significant difference in adsorption data was observed when the cylinder hydrogen was used without further purification.

Catalyst Samples.—All measurements were made on samples of Universal Oil Products Co. nickel–kieselguhr hydrogenation catalyst weighing *ca.* 5.5 g. and containing 52.8% Ni. Details concerning this catalyst which has a surface (B.E.T.N_2) of 175 m.^{2}/g., have been described earlier.[1,2] Reductions were performed *in situ* for 12 hr. at *ca.* 360° in flowing hydrogen, followed by evacuation at 10^{-5} mm. for 2 hr., and cooling *in vacuo* to 20°, which was the temperature of measurement in all experiments. As a rule, one sample was used in several runs, between which the catalyst was evacuated at elevated temperatures as above. A sleeve furnace surrounding the adsorbent chamber and extending to the lower part of the autoclave (Fig. 1) was used to obtain reduction and evacuation temperatures.

Results

Figure 3 shows rates of adsorption of hydrogen at various pressures in terms of automatically recorded changes of magnetization. The first instantaneous decrease of magnetization represented by the lower curve corresponds to addition of hydrogen to 70 mm.; the negative transient is the familiar thermal effect caused by the heat of chemisorption.[1,2] Subsequent portions of the curve are associated with adsorption taking place when the hydrogen pressure is raised to 1 atm. and then held constant for 100 min. by adding hydrogen from the buret. After the substantial fall of magnetization, occurring instantly, the curve gradually levels off and the magnetization approaches a constant value, although significant amounts of hydrogen are being adsorbed even during the period represented by the horizontal section of the curve. This slow adsorption has been found to occur preferentially on smaller particles of nickel which fail to show much ferromagnetism at room temperature and realizable fields.[2] When now the pressure is increased further, to 11 atm., a significant change of magnetization is observed. Maintaining this pressure causes some additional loss of magnetization, but a constant value is approached in a relatively short time. The upper curve in Fig. 3 shows again the effect of elevated hydrogen pressure on the magnetization of the nickel. Here, however, the situation is different in that only a limited amount of hydrogen is admitted to the adsorbent chamber. Thus, the pressure on the catalyst is falling during the adsorption. (This curve is displaced upward but has the same ordinate scale as the lower one).

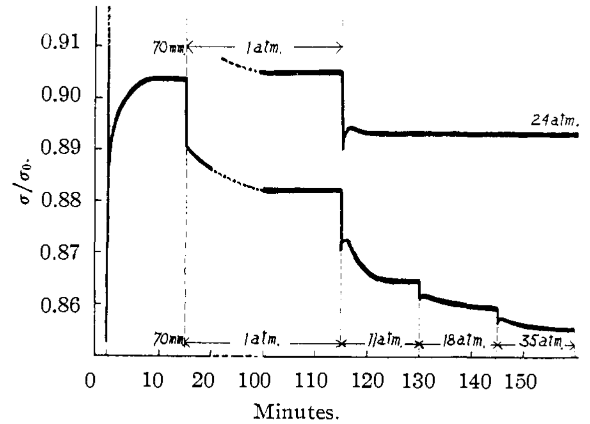

Fig. 3.—Recorder tracings of relative magnetization, σ/σ_0, *vs.* time following introduction of hydrogen.

Figure 4 shows a magnetization–pressure isotherm indicating that definite though diminishing changes of magnetization occur at least up to 100 atm. pressure. A magnetization–pressure isotherm for helium is given for comparison.[4]

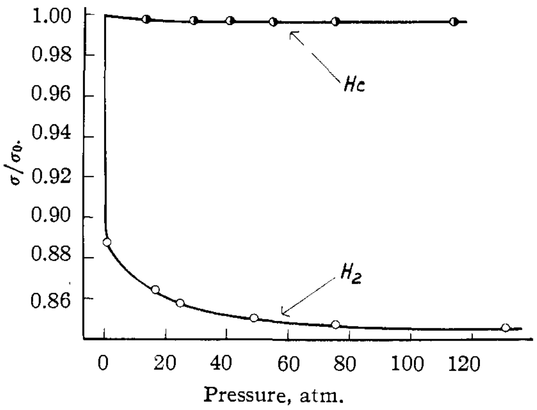

Fig. 4.—Magnetization–pressure adsorption isotherms for helium and for hydrogen on nickel–silica at room temperature.

The relationship between changes of magnetization and high pressure hydrogen is most clearly demonstrated by a semi-logarithmic graph such as shown in Fig. 5. The magnetization values used were taken from the recorded plot (Fig. 3) 15 min. after each pressure had been applied. When this isotherm is extended to include points between pressures of 10^{-4} to 100 atm. we obtain a linear relation between magnetization and log pressure between 10^{-3} and 10 atm., while both ends of the curve, 10^{-4} to 10^{-3} atm., and 10 to 100 atm., have a concave shape. It should be noted that the extended magnetization–log pressure isotherm has a striking resemblance to the volume–log pressure isotherms of Doerner (ref. 3, Fig. 6) who investigated hydrogen adsorption on a similar catalyst up to 30 atm. pressure.

A typical magnetization–volume isotherm is shown in Fig. 6 which includes also the corresponding pressure–volume data. As should be expected, the location of magnetization–volume points in the high pressure range was observed to be somewhat dependent on the time elapsed between addition of hydrogen and recording the pressure. The magnetization was not noticeably affected by the time allowed for adsorption (see upper curve in Fig. 3), so that the slight displacement of the isothermal

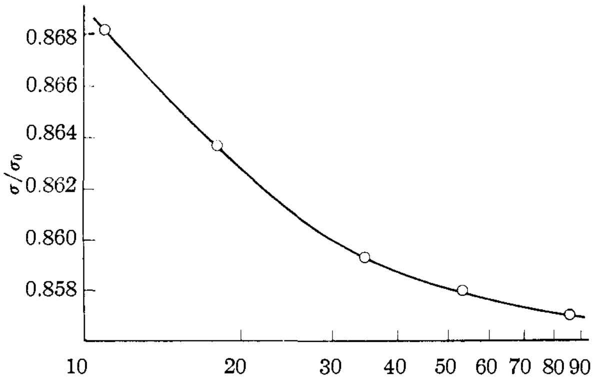

Fig. 5.—Magnetization–pressure (log scale) adsorption isotherm for hydrogen on nickel–silica at room temperature, from 11 to 85 atm.

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[4] Matheson helium, specified as 99.9% pure, was used without further purification.

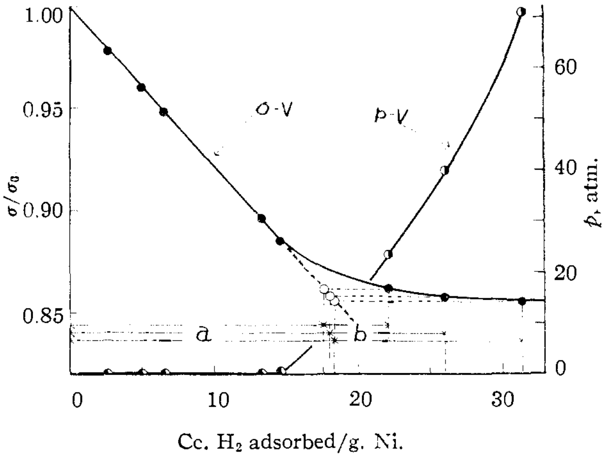

Fig. 6.—Method for determining fast chemisorption by extrapolating σ-v isotherm: a, fast chemisorption; b, physical adsorption plus slow sorption.

points on the graph by time occurred horizontally. Quantitative determination of rates of adsorption in terms of quantities of hydrogen adsorbed was not feasible. It appeared, however, that a substantial fraction of hydrogen was adsorbed relatively rapidly at each pressure. The magnetization–volume points on Fig. 6 were obtained after adsorption had proceeded for about 1 min. Shorter adsorption times down to 5 sec. gave essentially the same results, while only a relatively minor additional fraction of hydrogen was taken up when the time interval was extended to 30 min. Interpretation of the isotherms in Fig. 6 is given below.

Discussion

The principal result of these studies was the observation that at progressively higher pressures hydrogen sorption causes a progressive decrease of magnetization of nickel.

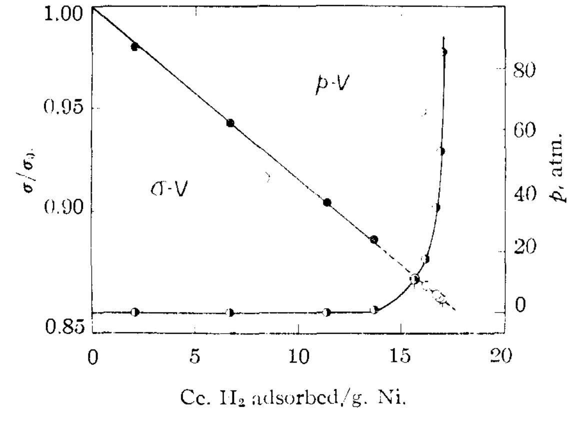

Fig. 7.—Corrected magnetization–volume and pressure-volume isotherms (fast chemisorption only) for hydrogen on nickel–silica at room temperature.

First we shall attempt to account for the fact that hydrogen uptake by the nickel–silica catalyst as a function of pressure goes far beyond the conditions which are commonly believed to be sufficient to saturate a surface. We find, for example, that the quantity of hydrogen sorbed at 70 atm. is twice the amount which is taken up at 1 atm. (Fig. 6). Although the extent of van der Waals adsorption is generally insignificant above the critical temperature of the adsorbate, particularly for hydrogen at room temperature,[5] there appear to be no experimental data available for such adsorption at high absolute pressures. Van der Waarden and Scheffer[5] found that pressure–volume isotherms for hydrogen adsorption on silica gel were linear to 1 atm. The amount taken up at 0° and 760 mm. by the adsorbent (area = 614 m.^{2}/g.) was 0.255 cc./g.

In order to obtain an estimate of the hydrogen physically adsorbed on the nickel–kieselguhr catalyst at higher pressures, we may extrapolate the linear low pressure isotherm on silica to, say, 23.4 atm. (There is, of course, no strictly valid basis for this extrapolation.) Then, on a nickel–kieselguhr surface of 175 m.^{2} the physical adsorption of hydrogen at room temperature will be in the neighborhood of $0.255 \times 23.4 \times 175/614 = 1.7$ cc. or about 3.2 cc. per g. of nickel. The observed sorption under these conditions was 22.1 cc. Correction for the estimated physical adsorption leaves 18.9 cc., which is still 4.3 cc. more than the total adsorption at 1 atm.

We must, therefore, look to the "slow" process for the major part of the increase of sorption observed at higher pressures. By observing the variation of pressure during the course of hydrogen adsorption, Doerner[3] concluded that the adsorption was about 50% complete instantaneously and that the slow adsorption was due to the diffusion in the catalyst micropores. He also found that at elevated pressures equilibrium conditions were established in about an hour while at pressures below 1 atm. the equilibrium was not reached even after several days. It follows from this that the slow diffusion-controlled adsorption at low pressures becomes faster, so to speak, as the pressure is raised; and thus we have an explanation for our observation of an increased hydrogen uptake.

The arguments set forth above neglect the fact that adsorption at high pressures is accompanied by an additional decrease of magnetization of nickel, since the major fraction of hydrogen taken up by the slow process is being adsorbed by the particles which are not appreciably ferromagnetic at room temperature[2] (see also Fig. 3). Consequently, an additional process, responsible for the observed change of magnetization, must occur on ferromagnetic, *i.e.*, larger particles. In order to assign a meaning to the fall of magnetization, we need to know the quantity of hydrogen taken up by the ferromagnetic particles only. According to the results obtained by treating this catalyst with carbon monoxide,[2] the larger particles are more readily accessible to adsorbate molecules, and this agrees with our present observation that adsorption occurring simultaneously with magnetic changes observable at room temperature is essentially instantaneous. It was mentioned above that it was not possible to determine experimentally this instantaneous adsorption at high pressures before the "slow" process begins to interfere. We may, however, make a rough estimate of the fractional

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(5) M. van der Waarden and F. E. C. Scheffer, *Rec. trav. chim.*, **71**, 689 (1952).

uptake representing instantaneous chemisorption by using Doerner's figure of 50% (Table I).

TABLE I

Obsd. sorption at 23.4 atm. and 20°, cc./g. Ni	22.1
Estimated physical adsorption (at 23.4 atm.)	3.2
Sum of fast and slow chemisorption 22.1 − 3.2 =	18.9
Total sorption at 1 atm. and 20°	14.6
Chemisorption at 1 atm. and 20°	14.5
Additional chemisorption from 1 atm. to 23 atm. 18.9 cc. − 14.5 cc. =	4.4
50% (from Doerner) of 4.4 cc.	2.2
Instantaneous chemisorption at 23.4 atm. 14.5 + 2.2 =	16.7

Another approach to this problem is possible: we know from earlier work[1,2] that the low pressure part of the magnetization–volume isotherm is a straight line, and that this part is almost certainly concerned solely with the instantaneous chemisorption. It is reasonable to assume that more instantaneous chemisorption, so far as it may occur at higher pressures, will continue the straight-line isotherm. We extrapolate the isotherm, therefore, until it covers the observed magnetization range, and read off directly the volume corresponding to instantaneous chemisorption at any desired pressure. This is shown in Fig. 6 where, for instance, the instantaneous chemisorption at 23.4 atm. is found to be 17.6 cc. (the agreement between this and the estimated value 16.7 cc. shown in Table I is satisfactory, considering the reproducibility of the adsorption data) per g. of nickel, while at 71 atm. it is 17.9 cc.

From the data so obtained one may plot a pressure–volume isotherm, as in Fig. 7, where the volume corresponds solely to the hydrogen which is chemisorbed instantaneously. The validity of this procedure may be tested by replotting the data of Fig. 7 according to the linear form of the Langmuir equation[6]

$$p/n = 1/Kn_{\mathrm{m}} + 1/n_{\mathrm{m}}p$$

where n represents moles of gas adsorbed per gram of adsorbent and n_{m} is the number of moles required to cover the surface with a complete monomolecular layer. The result is a straight line and this is in agreement with Doerner's Langmuir adsorption isotherms at 200° and 300° extending to 30 atm. pressure (ref. 3, Fig. 8). At such high temperatures the van der Waals adsorption is definitely negligible[4] even at higher pressures, which is, of course, confirmed by the linearity of the isotherms. Another point should be made in connection with our interpretation. The Langmuir equation is derived for equilibrium conditions and the latter are observed also by Doerner. One may question the meaning of our Langmuir plot since we used nonequilibrium data. The explanation for this seeming contradiction is simply the fact that we are considering adsorption only on such particles on which equilibrium is established in a very short time.

The surface area of nickel, calculated from the slope of the Langmuir adsorption isotherm (Fig. 8), $1/n_{\mathrm{m}}$, and the area per H atom site,[7] 6.1 Å.,[2] was found to be 57.4 m.^{2}/g. The amount of hydrogen adsorbed at 1 atm., 14.6 cc., gives an area of only 47.8 m.^{2}/g. Ni. The observed adsorption data at high pressures are also shown in Fig. 8. Although this isotherm does not indicate surface saturation, it is of interest to estimate the area of the adsorbent by using the average slope between the last two points of the curve. We obtain 140 m.^{2}/g. Ni, or 70 m.^{2}/g. catalyst. It should be noted in this connection that the total quantity of hydrogen taken up varied slightly from sample to sample and it was also dependent upon the pretreatment of the catalyst as has been described previously.[1,2]

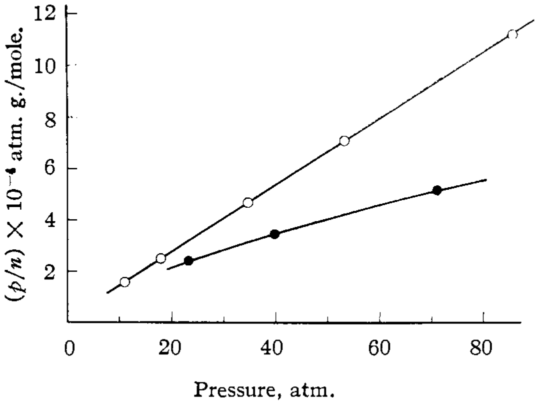

Fig. 8.—Langmuir isotherm plot of observed (●) adsorption and of corrected fast chemisorption (○).

In conclusion, the results of these studies demonstrate that the monolayer of chemisorbed hydrogen on the surface of nickel in the silica-supported catalyst is not complete at 1 atm., but, for all practical purposes, the saturation is reached at about 100 atm. It may be estimated from Fig. 7 (in connection with Fig. 5) that the increase of instantaneous chemisorption caused by increasing the pressure from 100 to 200 atm. would be only *ca.* 0.1 cc./g. We have not developed any direct evidence concerning possible penetration of hydrogen into the nickel lattice at high pressures, but the fact that the data can be represented by the Langmuir monolayer equation and the shape of the magnetization–time curves (Fig. 3), together with the arguments advanced by Doerner (ref. 3, p. 38) all tend to show that if such penetration occurs it must be an extremely slow process.

The present work confirms our earlier conclusions that the change of magnetization of nickel is a definite and direct measure of the quantity of hydrogen chemisorbed, and thus a new and reliable tool for investigating chemisorption.

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EVANSTON, ILLINOIS

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(6) I. Langmuir, THIS JOURNAL, **40**, 1361 (1918).

(7) O. Beeck, "Advances in Catalysis," Academic Press, New York, N. Y., Vol. II, 1950, p. 161.