it difficult to verify the axial ratio by the use of electron micrographs.

Conclusion

A method has been developed for the preparation of fine iron powder of particle size suitable for permanent magnet applications. The method is simple and rapid and yields iron powder of purity higher than hitherto reported. In addition to the obvious use in the field of permanent magnets, this material may be useful in catalysis or in specialized powder metallurgy application.

Acknowledgment.—The authors take pleasure in acknowledging the work of Mr. E. W. Beiter who performed the chemical analyses of these samples.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Chemisorption: Hydrogen on Nickel. II

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Further work has been done on the magnetic changes which occur when hydrogen is chemisorbed on a nickel–silica catalyst. It has been shown that no simple relation exists between surface bond type and magnetic change, as observed in a variety of samples. The thermal transients which are observed on admission of hydrogen have been used to obtain the differential heat of adsorption. This has shown that, for the samples studied, the heat approaches zero for hydrogen pressures near one atmosphere. The slow, so-called activated, sorption of hydrogen on these samples has been shown to be a true chemisorption, but one which occurs on the smaller nickel particles. It has been confirmed that hydrogen adsorbed on these samples at room temperature gives a small positive, rather than a negative, change of magnetization if the magnetization is measured at liquid hydrogen temperature.

Introduction

The purpose of this work was to extend our studies on the mechanism of chemisorption through the use of magnetization–volume adsorption isotherms, as previously described.[1] In the present paper we take up four groups of observations, all of which relate to the chemisorption of hydrogen on supported nickel, and to the changes of magnetization, and hence presumably of d-band electron concentration, which occur during this process. The four groups of observations are, first, a series of exploratory measurements on the effect of changing experimental conditions; second, determination of the differential heats of chemisorption; third, a study of the "slow" process, that is, the slow take up of hydrogen which may be observed following the rapid chemisorption; and fourth, a further study of the "hydride" effect, namely, the apparent reversal of electron transfer which may be observed at very low temperatures.

Experimental

Magnetic Measurements.—All magnetic studies involving adsorbed hydrogen were made on the low frequency a.c. permeameter previously described.[1] Some modification of procedure was required for those runs in which hydrogen was adsorbed on the sample at room temperature but in which the magnetic measurements were made at liquid hydrogen temperature. For this purpose the Dewar flask situated inside the primary solenoid and around the sample and secondaries was fitted with a brass cap so that the whole internal Dewar assembly could be made air-tight. After the sample had been reduced, the secondaries, Dewar, and primary were all clamped in position and not moved until the completion of a series of measurements. This arrangement necessitated some means of evaporating liquid hydrogen and of bringing the sample up to room temperature without interminable delay. This was achieved by placing a small, non-magnetic, electric heating element just below the sample. In all runs a fraction of a mm. of purified helium was admitted to the sample to promote heat transfer. In the apparatus used the RMS field was about 90 oersteds.

A few measurements of specific magnetization in a helium atmosphere at relatively high field (6000 oersteds) were made on the Faraday balance.[2,3]

Catalyst Samples.—Measurements were made on several different samples of supported nickel catalysts. One group of samples was a coprecipitated nickel–silica prepared as described by Van Eyk Van Voorthuisjen and Franzen, and designated by them CLA 5421.[4] This catalyst was prepared in several different concentrations of nickel as indicated below. All are referred to as "coppt."

Another group of samples consisted of Universal Oil Products Company nickel–kieselguhr hydrogenation catalyst containing 52.8% Ni. Some of this catalyst was used as received (after reduction); this is referred to below as "U.O.P." Some of the U.O.P. catalyst was sintered at 600° for 3 hr. before use. It appeared to make little difference in the results if sintering were carried out in pure helium or in hydrogen. This sample is called "sintered U.O.P."

Another portion of U.O.P. catalyst was treated with carbon monoxide for the removal of part of the nickel. This was done in apparatus similar to that described by Schuit and DeBoer.[5] The sample was first reduced in hydrogen at 350° until no water could be collected at the exit end of the sample chamber. Commercial carbon monoxide was passed through a glass furnace at 300° to decompose iron carbonyl impurity. The purified carbon monoxide was then passed over the sample at 80°. The carbon monoxide plus nickel carbonyl emerging from the sample chamber was heated to 300° to decompose the carbonyl. The nickel thus deposited was determined gravimetrically as a check analysis and for evidence of completeness of reaction. The treated sample also was analyzed. After 80 hr. of such treatment the amount of nickel carbonyl coming off the sample was found to be negligible. In two typical runs the residual nickel content was found to be 29.0 and 34.5%, respectively, corresponding to the removal of nearly $^{2}/_{3}$ of the nickel in the original sample. Reduced samples of catalyst thus treated with carbon monoxide were not pyrophoric on exposure to air, whereas all other original samples (even including some sintered samples) became quite hot in contact with air. If, however, the sample treated with carbon monoxide was itself sintered it became, once more, mildly pyrophoric. Furthermore, after this sintering operation a moderate additional proportion of nickel was found to be removable with carbon monoxide. Samples treated with carbon monoxide (but not further treated by sintering) are referred to below as "CO-treated U.O.P."

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

(2) P. E. Jacobson and P. W. Selwood, *ibid.*, **76**, 264 (1954).

(3) J. A. Sabatka and P. W. Selwood, *ibid.*, **77**, 5799 (1955).

(4) J. J. B. Van Eyk Van Voorthuisjen and P. Franzen, *Rec. trav. chim.*, **70**, 793 (1951).

(5) G. C. A. Schuit and N. H. DeBoer, *J. chim. phys.*, **51**, 9 (1954).

All samples were reduced prior to the magnetic studies by flowing hydrogen at 350° for 12 hr. Those samples used for adsorption studies were evacuated at 10^{-6} mm. for 2 hr. at 350°, then cooled to the temperature of measurement *in vacuo*.

Results

Exploratory Observations.—The first of this series consisted of three consecutive runs on the same sample of U.O.P. catalyst, heated and evacuated at 350° before each run. The purpose of this was to determine the reproducibility of the magnetization–volume isotherm. Conditions were: sample weight, 6.35 g.; temperature of adsorption and magnetization determination, 27°; dead space, 19.0 cc. The results are shown in Fig. 1. The levelling off noticed at relatively high (*ca.* 1 atm.) hydrogen pressure was found to depend on the time elapsing between admission of hydrogen and recording of pressure, as will be described more fully below. In some of our earlier work with the a.c. permeameter an iron screw was used in the opposing secondary in an effort to balance out the rather large secondary e.m.f. (*ca.* 10 mv.) produced by samples such as the U.O.P. But this procedure was found to distort the field and to produce undesirable phase changes leading to apparently nonlinear magnetization–volume isotherms, especially during the initial increments of hydrogen. This procedure was abandoned in favor of an external zero suppressor in the recorder circuit.

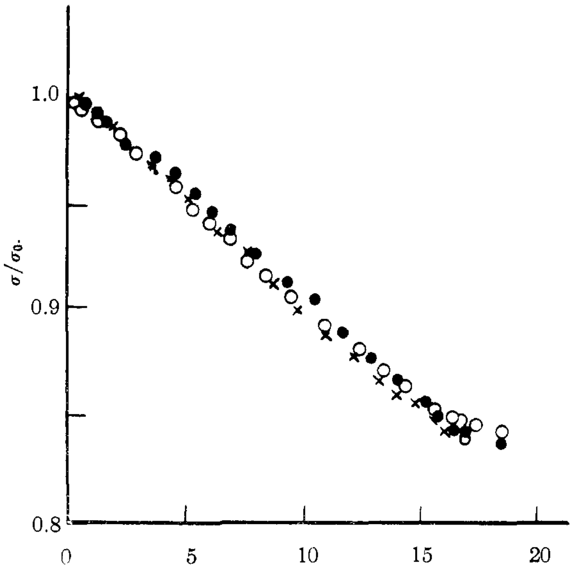

Fig. 1.—Three successive magnetization–volume isotherms on the same sample of nickel–kieselguhr at 27°. The sample was evacuated at 350° before each run.

Another group of measurements was made on sintered U.O.P. catalyst. It was found that while magnetization–volume isotherms were reproducible on any given sample, they were not reproducible on consecutive samples. In all cases the volume of hydrogen adsorbed to 1 atm. diminished as expected as sintering progressed. But the relative change of magnetization per cc. of adsorbed hydrogen was sometimes greater, sometimes less, than before sintering. Possible reasons for these peculiar results are discussed below.

The final group of measurements in this series was performed on the CO-treated U.O.P. catalyst sample. Figure 2 gives magnetization–temperature data for this sample, together with similar data for the same sample before treatment with carbon monoxide, and also for a sintered sample such as described in the preceding paragraph. It is well-established that treatment of nickel catalysts, such as those described, with carbon monoxide at 80° will remove some, but not all, of the nickel. It has been surmised that only the nickel most readily accessible to carbon monoxide is eliminated in this reaction.[5] A possible reason for this is that mentioned by Natta (ref. 5 Discussion), namely, that nickel carbonyl molecules cannot escape from the small pores in which the less accessible nickel is presumably located. The magnetic data in Fig. 2 show quite definitely that the nickel which is not removed by carbon monoxide consists of the smaller particles of nickel, but we have also found that the CO-treated catalyst is almost as effective for the hydrogenation of benzene as is the original U.O.P., and this leaves some doubt concerning the location of these particles.

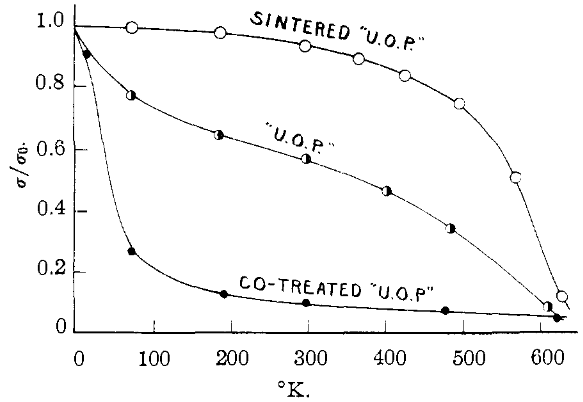

Fig. 2.—Relative magnetizations (per g. of Ni) *vs.* temperature for nickel-kieselghur before and after (1) sintering; and (2) treatment with carbon monoxide to remove part of the nickel.

After treatment with carbon monoxide the ability of the residual nickel to adsorb hydrogen was found to be considerably diminished. For instance, a sample of U.O.P. catalyst capable of adsorbing 16.9 cc. of hydrogen (S.T.P.) per g. of nickel at room temperature was found, after carbon monoxide treatment, to be capable of adsorbing only 7.1 cc. of hydrogen per g. of nickel. This change occurred concurrently with the removal of about 60% of the nickel as carbonyl. Another sample in which the nickel content was lowered from 52.8 to 34.5% was found to have had its ability to adsorb hydrogen lowered from 17.5 to 6.5 cc. per g. of nickel. For CO-treated U.O.P. the specific magnetization at room temperature is less than 1% of the magnetization of massive nickel and less than 2% of the magnetization of original U.O.P. But at 20°K. the magnetizations (per g. of nickel) are almost the same for all three. Magnetization–volume isotherms on CO-treated U.O.P. at room temperature show the expected linear drop of relative magnetization (σ/σ_0) with increments of hydrogen. The total loss of magnetization up to 1 atm. of hydrogen was nearly 50%, in spite of the comparatively low ability of this sample to chemisorb hydrogen.

Differential Heat of Chemisorption.—In a previous paper[1] it was shown how the magnetization of nickel–silica suffers a momentary excess loss when hydrogen is admitted. This effect was attributed to heating of the nickel during the adsorption process, and it was shown how these negative transients may be used to compute the integrated heat of chemisorption. In the present work hydrogen was added in small increments and the thermal transients were used to find the differential heats.

In a typical run 6.60 g. of U.O.P. catalyst was treated successively with approximately 6.0-cc. (S.T.P.) portions of hydrogen. With each addition the equilibrium value of the magnetization decreased, and the negative thermal transient also diminished in size. We know from the thermomagnetic curves such as are given in Fig. 2 that at room temperature the magnetization changes by about 0.1% per degree. The first increment of hydrogen gave an *excess* transient drop of magnetization corresponding to a temporary temperature rise of 9.9°. From the weight of nickel, silica and carbon in the sample, and from their respective specific heats, it may be calculated that this temperature rise would require 9.4 cal., and this yields a heat of chemisorption of 35 kcal. per mole of adsorbed hydrogen. A second run on U.O.P. catalyst gave 45 kcal. for the initial heat. The differential heats so obtained are plotted against volume of hydrogen adsorbed in Fig. 3. The magnetization–volume isotherm obtained simultaneously is shown also in Fig. 3 to make it clear that the heat of chemisorption reaches a negligible value, certainly no more than 1 kcal. per mole of hydrogen adsorbed, and that this occurs before the nickel surface is saturated with hydrogen. Similar results were obtained on a 37% coppt. catalyst. It may be mentioned that it is necessary to use a recorder of no more than 1 sec. full scale travel in order to observe these transient effects.

One further point may be mentioned. In an earlier paper[1] it was stated that if a hydrogenated nickel catalyst is pumped out at room temperature, and then hydrogen is readmitted, no thermal transient is observed. It is now found that if the pumping is prolonged a slight transient may be demonstrated under these conditions.

The Slow Process.—If hydrogen is admitted to a nickel catalyst at room temperature it will be found that a large volume of gas is adsorbed instantaneously, with simultaneous loss of magnetization as described above. It will now be found that hydrogen continues to be sorbed for a period of hours or days, the total of this "slow" process hydrogen amounting to an appreciable fraction of the whole. This section is concerned with the magnetic changes which occur during the slow process.

In a typical run 6.35 g. of U.O.P. catalyst at 27°, and in a dead space of 8.0 cc., was treated with hydrogen up to a pressure of 6 mm. The volume of hydrogen adsorbed was 12.1 cc. per g. of nickel. During this rapid process the relative magnetization fell to 0.893. The pressure was now held constant at 6 mm. (by manual admission of small hydrogen increments) until at the end of 133 minutes an additional 1.5 cc. of hydrogen per g. of nickel had been taken up and the relative magnetization had fallen to 0.887.

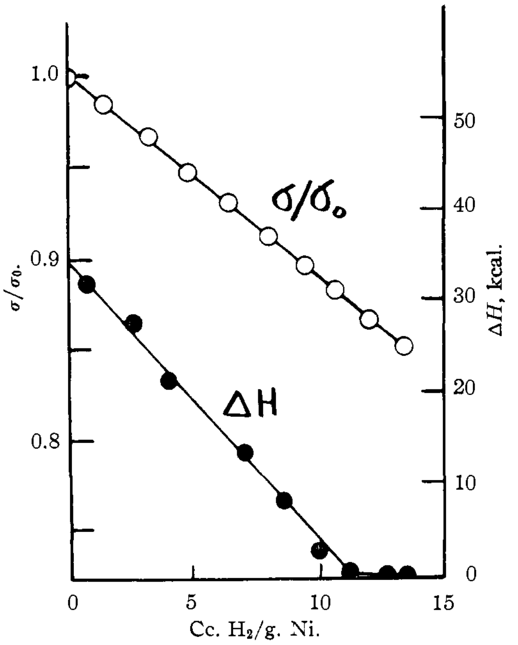

Fig. 3.—Differential heats of chemisorption for hydrogen on nickel–kieselguhr at room temperature calculated from the negative thermal transients observed magnetically when hydrogen is admitted. Relative magnetizations are also shown.

The sample was now evacuated at 350° and the experiment was repeated but with the pressure maintained at 144 mm. for 27 hr.; and a final run was made for 11 hr. at 1 atm. pressure. The results of these three runs are most conveniently shown in Fig. 4 which is actually a representation of the three successive runs with evacuation at 350° between each one.

Similar runs on other samples gave strictly comparable results. In all cases the magnetic change associated with the slow process was much smaller (per cc. of sorbed hydrogen) than that occurring with the fast process. In some runs at atmospheric pressure there seemed to be virtually no magnetic change during the slow process.

In view of these results (which seem to indicate little or no electronic interaction between hydrogen and nickel to be associated with the slow process) two further experiments were performed. In the first of these the slow process was continued for 11 hr. at 1 atm. until the total of "slow" hydrogen taken up was 2.13 cc. per g. of nickel. The system was pumped out for 2.5 hr. at room temperature, then hydrogen was readmitted at 1 atm. for 11 hr. The second "slow" hydrogen uptake was only 1.46 cc., thus showing that an appreciable fraction of the "slow" hydrogen is not removed by pumping at room temperature. (The same is, of course, true of the "fast" hydrogen, which is present in much greater amount.)

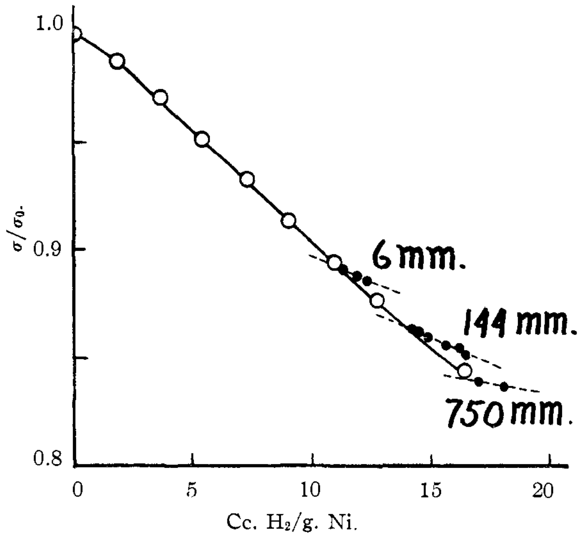

Fig. 4.—"Slow process" sorption of hydrogen as observed at three pressures. The figure is a superposition of three separate runs. The magnetic changes accompanying the slow process are shown thus (—●—).

The final experiment made on the slow process was one in which the process was allowed to go on until 1.5 cc. of "slow" hydrogen had been taken up at room temperature with an attendant drop of relative magnetization of only 0.002 below that produced by the "fast" hydrogen. The system was then cooled to −196° with no additional access of hydrogen. The purpose of this was to compare the loss of magnetization at low temperature with that at room temperature. The measured loss in σ/σ_0 at −196° was 0.057, that is, very much greater than at room temperature where only the relatively large nickel particles are ferromagnetic.

In all work on the slow process it is essential that the temperature of the sample be closely controlled, preferably by the use of a large liquid bath of say carbon tetrachloride which has been permitted to reach room temperature.

The Hydride Effect.—A 3.88-g. sample of coppt. catalyst containing 37.6% nickel, in a dead space of 7.0 cc., was treated with successive increments of hydrogen at 27°. Magnetic measurements after each increment were made at 27° and also at liquid hydrogen temperature. No additional access of hydrogen was admitted during the cooling of the sample except the very small fraction of a cc. present in the dead space for all except the last increment. The results for this tedious experiment are shown in Fig. 5. Some evidence was obtained that for some samples the change of magnetization at 77°K. on admission of hydrogen at 27° was less than expected. But in no case other than for the coppt. at 20°K. was an actual increase of magnetization observed.

Discussion

In this discussion we shall first consider our present understanding of the principal effect described, namely, the decrease of specific magnetization observed when hydrogen is admitted to a supported nickel catalyst. The slow process, and other related effects, will be taken up later.

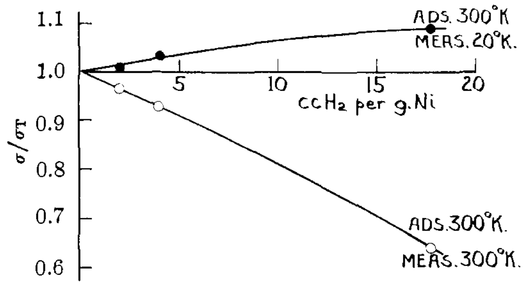

Fig. 5.—Magnetic changes observed at 300 and 20°K. for hydrogen adsorbed on nickel–kieselguhr at 300°K. The vertical axis shows magnetization after hydrogen adsorption divided by magnetization at the temperature of measurement prior to hydrogen adsorption.

The loss of magnetization which occurs for nickel has some analogy to the well-known loss of magnetic susceptibility when palladium sorbs hydrogen. The loss of susceptibility in palladium is linear with added hydrogen and the susceptibility reaches zero at an atom ratio of approximately $PdH_{0.6}$. This is taken to mean that palladium metal has, on the average, 0.6 unpaired electron per atom, and that the loss of susceptibility is due to filling of the d-band in palladium with electrons from the hydrogen, possibly through the formation of a covalent bond.

The nickel case also involves a linear change of magnetization with added hydrogen. This, from Fig. 1 and also from our earlier work,[1] is true (or very nearly so) for adsorptions within a fairly wide range of temperature although it is not true for adsorptions at temperatures so low that physical adsorption becomes important. There may be some deviation from linearity at pressures approaching 1 atm., but this is quite obviously due to intrusion of the slow effect. It might then be thought that extrapolation of the magnetization–volume isotherm to zero magnetization would show the nickel–hydrogen ratio corresponding to filling of the d-band in nickel. It is, of course, true that the saturation moment for nickel, determined at infinite field and 0°K. gives a magnetic moment of 0.6 Bohr magneton, corresponding to 0.6 unpaired electron spin (or electron hole) per nickel atom.

As recently shown by Broeder, *et al.*,[6] it should be possible to calculate the loss of magnetization from the volume of hydrogen adsorbed on the assumption that each surface atom of nickel in a particle adsorbs one hydrogen atom (at complete coverage), and that the fractional loss of magnetization so produced should be $\Delta\sigma/\sigma_0 = \pm n/0.6\ N$, where n is the number of nickel atoms on the surface and N is the total number in the particle. They find, however, that while the calculated loss of magnetization on a given sample saturated with hydrogen is 52%, the observed loss is only 22%.[7] This difference is used by Broeder, *et al.*, to estimate the departure from true homopolar bonding in Ni–H.

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(6) J. J. Broeder, L. L. van Reijen, W. M. H. Sachtler and G. C. A. Schuit, *Z. Elektrochem.*, **60**, 838 (1956).

(7) We believe that there is an arithmetical error in the paper referred to and that the calculated loss is only 44% for 50.6 cc. of H_2 adsorbed per g. Ni. This error does not invalidate the argument advanced by Broeder, *et al.*

In order to test this procedure we list in Table I samples in which the observed fractional loss of magnetization is compared with the loss calculated by the method of Broeder, *et al.*

TABLE I

COMPARISON OF OBSERVED AND CALCULATED LOSS OF MAGNETIZATION ON ADSORPTION OF HYDROGEN TO NEAR SURFACE SATURATION AT ROOM TEMPERATURE

Sample	Cc. H_2/g. Ni	$\Delta\sigma/\sigma_0$ Calcd.	$\Delta\sigma/\sigma_0$ Found
Broeder, *et al.* (coppt.)	50.6	0.52 (0.44)	0.22
37% coppt.	22.0	.19	.48
52.8% U.O.P.	17.4	.15	.13
29% CO-treated U.O.P.	6.5	.06	.50

An even more extreme case could be found by considering the sintered catalysts or, especially, a sample in which half of the nickel was in the form of the CO-treated U.O.P. and half was simply massive nickel. The magnetization of this sample at room temperature and realizable fields would be just a fraction of 1% over half that of massive nickel. It would adsorb *ca.* 3.25 cc. H_2 per g. Ni, and the change of magnetization would be less than 0.25%. To reconcile these divergent results it would be necessary to assume widely different bond types for the various samples and, in some cases, to assume more than one electron to be gained by the nickel for every hydrogen atom adsorbed.

The explanation for this difficulty almost certainly lies in the particle size distribution and in the failure of very small particles of nickel to be ferromagnetic at room temperature, as was pointed out by Michel and later by ourselves.[8,9] In a typical coppt. sample little more than 10% of the nickel is ferromagnetic at room temperature and realizable fields yet all the nickel participates in the adsorption of hydrogen. The fraction of hydrogen taken up by the smaller particles may not, according to our results on CO-treated U.O.P. be so large as expected, but it must nevertheless be substantial. It is meaningless to compare hydrogen uptake with loss of magnetization unless one knows the amount of hydrogen taken up by the particles actually under observation, that is, exhibiting ferromagnetism at the temperature of measurement.

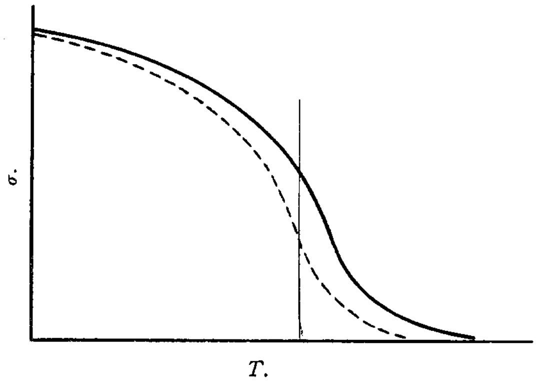

Fig. 6.—Assumed effect of chemisorption on the magnetization of a particle of nickel. The observed magnetization at temperature *T* may diminish both because the saturation moment is lowered and because the Curie temperature is depressed.

Another aspect of the problem is the virtual certainty that the pairing of all electrons in the surface atoms of a particle will lead to some lowering of the Curie point. Thus a particle which is ferromagnetic at room temperature might lose all its ferromagnetism by surface saturation with hydrogen, simply by lowering of the Curie point by a few degrees (Fig. 6). The reason for making this statement is that the dilution of a ferromagnetic such as magnetite or nickel by a diamagnetic such as zinc oxide or copper, respectively, always lowers the Curie point. This effect almost certainly contributes to the lowering of magnetization accompanying the chemisorption of hydrogen. How much it contributes will depend on the detailed distribution of particle sizes, with special reference to those which have Curie points just above room temperature.

It appears from this that the only way to make a valid comparison of electrons gained by the nickel per atom of hydrogen adsorbed is to obtain the saturation moments at 0°K. in the accepted way[10] for a sample both with and without hydrogen. A preliminary attempt[11] to obtain these data yielded a ratio *e/H* of 0.084/0.11. The determination is complicated by the so-called hydride effect, but more precise measurements are in progress.

A remaining question to be considered in this section is whether the magnetic change, as measured above 0°K. is the same, except possibly as to sign, for any bond between nickel and a chemisorbed atom. This question is of considerable interest if we wish to compare the number of bonds formed by hydrogen and nickel with, say, those between ethylene and nickel. In the absence of more specific information we[12] have assumed that *if on a given catalyst sample and at the same temperature* a molecule of ethylene gives the same magnetic change as a molecule of hydrogen, then we may say that the ethylene is held to the surface by two-site attachment. In support of this view it may be said that in all the literature of magnetochemistry it is hard to find any example which might be called "partial pairing" (or partial unpairing) of an electron. When the formation of a chemical bond leads to a change of magnetic moment it always appears to do so by units equivalent to whole number multiples of one electron spin. Thus magnetic moments have often been used to determine bond-type in coördination compounds; but the magnetic distinction always has been between completely covalent and completely ionic (or more recently, strong and weak covalence) but not between completely covalent and partially covalent.

The Heat of Chemisorption.—The method described here for obtaining differential heats of chemisorption has the unique feature that the nickel

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[8] A. Michel, R. Bernier and G. LeClerc, *J. chim. phys.*, **47**, 269 (1950).

[9] P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955); in a recent paper Michel, *Compt. rend.*, **243**, 373 (1956), suggests that we should have used $T/T_0 = \sqrt{Z'/Z}$ instead of $T/T_0 = Z'/Z$ to calculate Curie points T from average coördination number Z' in small particles.

[10] R. M. Bozorth, "Ferromagnetism," D. Van Nostrand Co., Inc., New York, N. Y., 1951.

[11] L. E. Moore and P. W. Selwood, THIS JOURNAL, **78**, 697 (1956).

[12] P. W. Selwood, *ibid.*, **79**, 3346 (1957).

is made to act as its own thermometer. The method has also the feature that the heat liberated is measured before the "slow" process has time to interfere. It is, therefore, of considerable interest to see how the data compare with those obtained by other direct or indirect procedures. Qualitatively, the data given in Fig. 3 are in agreement with other values so far as the initial heat at zero coverage is concerned, and with the approximate linear decrease of heat with increasing coverage.

The work on systems most nearly comparable with those studied here is that of Schuit and DeBoer[13] who used, among others, coppt. catalysts of identical preparation with our own, and containing 43.7% nickel. The reduction was at 500° for 16 hr. which, according to Heukelom, *et al.*,[14] is not only more than enough to ensure complete reduction, but sufficient to cause some sintering. This is confirmed by our own magnetic measurements on the same system. The Schuit and DeBoer heats of adsorption were determined indirectly from the dependence of amounts of hydrogen adsorbed on the pressure and the temperature. The results (their Fig. 3) show a nearly linear decrease of heat from about 24 kcal. per mole of hydrogen adsorbed at zero coverage down to about 9 or 10 kcal. at complete coverage. The serious disagreement with our own results is that we found effectively zero heat at, or near, complete coverage.

This discrepancy apparently is due chiefly to a lack of agreement on what constitutes complete coverage. The Schuit and DeBoer measurements were carried up only to 100 mm. pressure, while our own were taken to 1 atm. During the rise from 100 to 760 mm. an additional 18% of hydrogen was chemisorbed as shown by the continuing loss of magnetization. It was during these final few increments of hydrogen that no thermal transients could be observed. It may be objected that our relatively low (350°) reduction temperature left some unreduced oxide on the nickel surface and that the last increments of hydrogen and the zero heat were somehow connected with this surface contamination. But it must be pointed out that the magnetization continued to fall even after the heat had reached zero, showing that the final increments of hydrogen were indeed chemisorbed.

Similarly the results of Kwan[15] on reduced nickel, although terminated at about 0.6 surface coverage, suggest a negligible ΔH at complete coverage.

It may be objected that the diminishing transients observed with increasing admission of hydrogen may be related to the thermal conductivity of the hydrogen. But it should be pointed out that the measurements were made in the presence of about 0.1 mm. of helium, the only function of which appeared to be to ensure that the initial temperature of the nickel was that of the surrounding bath. The presence of this helium did not perceptibly diminish the transient loss of magnetization on admission of hydrogen.

In this connection it should be mentioned that the concept of complete surface coverage is far from being understood. With every increase of pressure a slight (though diminishing) increase occurs in the volume of hydrogen adsorbed and this additional hydrogen causes a further loss of magnetization. It seems impossible to choose any particular point and to say that at this point surface coverage is complete.

The Slow Process.—In spite of much debate there is still no general agreement on the nature of the slow process. The results presented here show that at low surface coverage the slow process is a true chemisorption resulting from electronic interaction between hydrogen and nickel in much the same way as occurs for the fast process. But, as surface coverage increases the magnetization becomes progressively less affected by the slow hydrogen. This could mean that adsorption may occur by some process not involving a net gain of electrons by the d-band of the nickel, or it could simply mean that the slow hydrogen at nearly complete surface coverage is going on to smaller particles of nickel which are not ferromagnetic at room temperature. That the latter explanation is correct is shown by the fact that slow hydrogen which produces a negligible magnetic effect at room temperature produces a substantial effect at −196°. It may therefore be stated that the slow process as it occurs in the catalyst systems studied is essentially the same as the fast process, namely, a true chemisorption, but that it occurs on the smaller (and presumably less accessible) particles of nickel. This conclusion is in agreement with that reached by Rideal[16] for the slow process on nickel films. We have no new information concerning the reason for the "slowness" of the process, but our results are consistent with the evidence and conclusion developed by Doerner[17] for a similar catalyst, under high hydrogen pressures, namely, that the slow process is due to diffusion in the catalyst micropores.

These conclusions are not in agreement with the view[18] that the slow process is due to reaction of the hydrogen with a surface contamination of oxygen in the form of oxide. It is difficult to see how such a process could result in a decrease of magnetization.

The Hydride Effect.—In an earlier paper we showed that with decreasing temperature smaller particles of nickel should become ferromagnetic and hence contribute more to the observed magnetization. Small particles should also show a greater loss of magnetization on exposure to hydrogen, because of the proportionally larger number of gas molecules which may be accommodated on the surface. In view of this it was thought that measurements at low temperatures on samples to which hydrogen had been admitted at room temperature would show progressively larger fractional losses of magnetization. This actually occurs for samples

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[13] G. C. A. Schuit and N. H. DeBoer, *Rec. trav. chim.*, **72**, 909 (1953).

[14] W. Heukelom, J. J. Broeder and L. L. van Reijen, *J. chim. phys.*, **51**, 474 (1954).

[15] T. Kwan, *J. Research Inst. Catalysis, Hokkaido Univ.*, **1**, 81 (1949).

[16] M. McD. Baker, G. I. Jenkins and E. K. Rideal, *Trans. Faraday Soc.*, **51**, 1592 (1955).

[17] Wm. A. Doerner, Thesis, "Diffusion and Adsorption of Hydrogen in a Porous Nickel Catalyst," University of Michigan D. Sc., Ann Arbor, 1952.

[18] G. C. A. Schuit and N. H. DeBoer, *Rec. trav. chim.*, **70**, 1067 (1951).

measured down to −196°, but at 20°K. the magnetization of a hydrogenized sample was found to be about the same as prior to the admission of hydrogen. It was surmised that this effect might be due to a reversal of electron transfer leading to the formation of hydride ions on the nickel surface.

Whatever may be the explanation, the existence of the effect is confirmed by the present work (Fig. 5), in which a small but definite increase of magnetization was found to occur. The attribution of this effect to hydride ion formation receives some support from the results of hydrogen adsorption on a CO-treated U.O.P. sample. Such a sample, containing a relatively small fraction of the nickel in large particles, was found to have less than half the ability (per g. of nickel) to adsorb hydrogen as compared with the original U.O.P. sample. This peculiar effect could be attributed to the larger size of hydride ions and hence to the diminished number which could be accommodated on a surface, as compared with hydrogen atoms. The fact that the 1% of nickel which is ferromagnetic at room temperature, in the CO-treated U.O.P., gives a negative change of magnetization on exposure to hydrogen is, of course, of no significance in this discussion.

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The Kinetics of the Reaction of Sulfite and Bromate[1-2]

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The oxidation of sulfur(IV) by bromate results, very largely, in the formation of sulfate; a deviation of the stoichiometry from that corresponding to sulfate production suggests the formation of a small amount of sulfur(V), presumably dithionate ion. The rate of disappearance of sulfur(IV) has been determined over the *p*H value ranges 3.4–7.4 at 25° and 1.7–4.5 at 0°. The rate data indicate that in the *p*H range studied the reaction proceeds *via* two different transition states with the compositions $[HSO_3{\cdot}BrO_3^{=} + nH_2O]^{\mp}$ and $[SO_2{\cdot}BrO_3^{-} + mH_2O]^{\mp}$.

The oxidation of sulfur(IV)[4] by bromate ion in neutral or mildly acidic aqueous solution proceeds at a conveniently measurable rate at 25.0°. Among the facets of this reaction which are of interest is the *p*H dependence of the rate. The reported acid dissociation constant for sulfurous acid are $K_1^0 = 1.72 \times 10^{-2}$ and $K_2^0 = 6.24 \times 10^{-8}$ at 25°.[5] These values, although not valid for a medium with Γ[6] equal to 4.20 (the value for most of the solutions studied in this work), do allow the establishment of the approximate hydrogen ion concentration limits in which each of the sulfur(IV) species are predominant. ·Thus the equations for the net reactions producing sulfate, the principal product of the oxidation of sulfur(IV), are[7]

$$\text{at } (H^+) > K_1,\ 3H_2SO_3 + BrO_3^- \longrightarrow 3HSO_4^- + Br^- + 3H^+ \quad (1)$$

$$\text{at } K_1 > (H^+) > K_2,\ 3HSO_3^- + BrO_3^- \longrightarrow 3SO_4^{=} + Br^- + 3H^+ \quad (2)$$

$$\text{and at } K_2 > (H^+),\ 3SO_3^{=} + BrO_3^- \longrightarrow 3SO_4^{=} + Br^- \quad (3)$$

Over a significant fraction of the hydrogen ion concentration range studied, hydrogen ion is produced in the reaction; since the rate is hydrogen ion dependent, buffers were used to maintain the hydrogen ion concentration approximately constant during the course of a kinetic run. Because of the high rate of reaction, kinetic studies were not made in the region $(H^+) > K_1$ (eq. 1).

The reaction has been found to be first order in bromate ion, first order in total sulfur(IV) and exhibits a hydrogen ion dependence which indicates that the reaction proceeds *via* two different activated complexes. The rate law is a four parameter equation

$$-\frac{d(S^{IV})}{dt} = (BrO_3^-)(S^{IV}) \left\{ \frac{k_1 + k_2(H^+)}{K_1^{-1}(H^+) + 1 + K_2(H^+)^{-1}} \right\} \quad (4)$$

the parameters K_1 and K_2 being identified as the first and second ionization quotients for sulfurous acid.

Experimental

Reagents.—All solutions were prepared using doubly distilled water, the second distillation being carried out in the presence of alkali and permanganate from Pyrex glass apparatus. Reagent grade chemicals were used without further purification with the exception of the sodium perchlorate which was C.P. grade and was recrystallized from water before use. Kinetic runs using completely independent sources of reagents yielded essentially the same value

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[4] In this paper, sulfur(IV) refers to the equilibrium mixture of sulfur(IV) species while sulfur dioxide, sulfurous acid, hydrogen sulfite ion and sulfite ion refer to the individual species. These species are in equilibrium with one another. Although the hydration of SO_2 has a measurable rate ($t^1/_2 \cong 10^{-3}$ sec., from work of G. v. Bunau and M. Eigen, *Z. physik. Chem.* (*Frankfurt*), **7**, 108 (1956)), it is large compared to the rates under consideration in this work.

[5] H. V. Tartar and H. H. Garretson, THIS JOURNAL, **63**, 808 (1941).

[6] The ional concentration Γ is defined, $\Gamma = \Sigma C_i Z_i^2$, where C_i is the molar concentration of i-th species and Z_i its charge. The ional concentration differs by a factor of *approximately* two from the ionic strength, the difference being only *approximate* because the ionic strength involves the molal concentration scale.

[7] Since K_2 for sulfuric acid is approximately equal to K_1 for sulfurous acid, three equations are sufficient to summarize all of the net reactions.