2. Results with this method for nickel, copper, iron and zinc oxides have been presented.

3. Ferric oxide gel is reduced to ferroso-ferric oxide at 350° and to metallic iron at 450°. Ignited ferric oxide is not reduced at an appreciable rate at 350° and goes to metal at 450°.

4. Foreign metal interfaces with iron oxide accelerate the reduction to iron.

5. Alumina and chromium oxide greatly retard reduction of ferroso-ferric oxide.

6. Ferric oxide gels show the glow phenomenon in hydrogen at fairly low temperatures, but not in air or in vacuum.

7. The thermodynamics of zinc oxide reduction in the presence of copper have been worked out, giving an explanation in the formation of alpha brass.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 58]

ADSORPTION OF HYDROGEN BY NICKEL AT LOW TEMPERATURES[1]

BY ARTHUR F. BENTON AND T. A. WHITE

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Introduction

Although it is now recognized that the occurrence of catalytic reactions at solid surfaces is intimately connected with the nature and extent of the adsorptions of the reacting species and products, nevertheless, attempts to obtain a quantitative treatment of the relations involved have met with little success. The main difficulty appears to be the lack of an adequate general theory of adsorption at catalytically active surfaces.

Numerous adsorption measurements,[2] especially by Taylor and his co-workers, have shown that adsorption of gases may be accompanied by more or less "activation" of the adsorbed molecules, and that this activation is a prerequisite to any marked catalytic action of the solid. It is known that this activation is conditioned by the chemical rather than the physical properties of the substances involved, but its occurrence is unpredictable theoretically. Experimentally, however, the two limiting types of adsorption, the "secondary" type involving little or no activation and the "primary" type in which relatively great activation occurs, can be

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29–May 3, 1929.

[2] Critical summaries of the extensive work in this field may be found in the following papers: Taylor, *J. Phys. Chem.*, **28**, 897 (1924); **30**, 145 (1926); *Proc. Roy. Soc.* (London), **A113**, 77 (1926); Taylor and Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927); Langmuir, THIS JOURNAL, **38**, 2221 (1916); **40**, 1361 (1918).

readily distinguished by the fact that at moderate temperatures and pressures the extent of adsorption is much less dependent on these variables in the latter case than in the former. This fact is interpreted to mean that in primary adsorption even at low pressures the surface is largely covered with a unimolecular or monatomic layer of adsorbed gas, whereas in the secondary type either the unimolecular layer is far from complete or multimolecular layers are formed.

It appeared to us that considerable light might be thrown on these questions by carrying out adsorption measurements on an active catalyst under conditions where one type of adsorption merged into the other, a behavior which might be expected at low temperatures or at high pressures. The present paper deals with the adsorption of hydrogen by active nickel at pressures up to one atmosphere and over a range of temperatures down to 61°K.

The adsorption of hydrogen by nickel at temperatures above 0° has received some attention from numerous investigators. Gauger and Taylor,[3] using temperatures from 25 to 305° and pressures from zero to one atmosphere, found that the adsorption reached a constant value at relatively low pressures, but that this constant value decreased as the temperature was raised. Terwen[4] concluded from these data that at higher temperatures the amount adsorbed approached asymptotically a value half that at lower temperatures, and that the adsorption occurred as atoms at the higher temperatures and as molecules at the lower.

Although the adsorption of gases by charcoal has been measured at low temperatures, mainly in connection with the production of high vacua, little has been attempted along this line with catalytically active materials. Von Hemptinne[5] brought hydrogen, and in other experiments carbon monoxide, into equilibrium with platinum at −78° and then allowed the system to warm gradually to room temperature. From observations of the pressure at a series of temperatures, he concluded that the gas adsorbed at low temperatures is gradually evolved on warming, until a temperature of about −40° is reached, when a rapid increase in adsorption occurs. A similar phenomenon was observed with palladium and carbon monoxide. Nikitin[6] has recently reported adsorption measurements of hydrogen on nickel at three temperatures, −185, 19 and 336°, and finds that the adsorption is less at −185 than at 19°.

Experimental Method and Apparatus

Apparatus and Procedure.—The method of measuring the adsorption was the usual one which consists in a comparison of the volume of the gas required to fill a bulb con-

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[3] Gauger and Taylor, THIS JOURNAL, **45**, 920 (1923).

[4] Terwen, *Chem. Weekblad*, **21**, 386 (1924).

[5] Von Hemptinne, *Z. physik. Chem.*, **27**, 429 (1898).

[6] Nikitin, *J. Russ. Phys.-Chem. Soc.*, **58**, 1081 (1926).

taining the adsorbent at a given temperature and pressure, with the corresponding volume of an unadsorbed gas, in this case helium, which is required to fill the bulb at the same temperature and pressure. A number of measurements were made with an apparatus of the type now commonly used, which has been described by Pease.[7] To obtain more certain protection against the possibility of leaks at stopcocks, however, a modified type was constructed and employed for all experiments subsequent to Run 33.

The new apparatus, shown in Fig. 1, differs from the type used in earlier investigations in this Laboratory mainly in that all stopcocks exposed to vacuum are replaced with mercury seals. Pyrex glass is used throughout, and the capillary parts are of 1 mm. bore. The adsorption bulb A, of approximately 50 cc. capacity, communicates by capillary tubing with the mercury seal C which leads to the Töpler pump, with the closed manometer B of 6 mm. bore, and with the mercury seal E, of 16 mm. bore, the essential purpose of which is to obviate the necessity of maintaining the stopcock G under vacuum for long periods of time. The capillary at E, sloping slightly downward to the left, facilitates admission of gas from F without danger of mercury droplets being driven into the capillary D. H is a water-jacketed buret in which gas volumes are determined by measuring on the closed manometer I (6 mm. bore) the pressure exerted when the gas fills the buret to a mark on the 6-mm. tubing immediately below the water jacket. The volume readings have been corrected for the small but varying amounts of gas retained in the calibrated capillary F. The manometers and mercury seals are operated by applying air pressure or vacuum to the bulbs below them.

The procedure in determining an adsorption isotherm consists in successively admitting known amounts of gas from H through FED to the previously evacuated bulb and, after bringing the mercury levels to b and D, respectively, measuring in each case the pressure produced at equilibrium. Equilibrium was considered to be established when the pressure readings remained constant for fifteen to thirty minutes, but this supposition was frequently checked by approaching the equilibrium from higher as well as lower pressures. Between such a "run" and the succeeding one the adsorbent was evacuated for about two hours, at 200° in the case of the former of the two nickel samples employed, and at 250° for the second.

Materials.—Hydrogen was prepared by electrolysis of 15% sodium hydroxide between nickel electrodes and purified by passage in succession over heated platinized asbestos, soda-lime, calcium chloride and phosphorus pentoxide. Helium used in the free space determinations was purified by passage over heated copper and copper oxide and over active charcoal cooled with liquid air.

The nickel adsorbent was obtained by dehydrating c. p. crystalline nickel nitrate in a current of dry, carbon dioxide-free air at temperatures up to 400°, transferring the nickel oxide thus produced to the adsorption bulb, which was then sealed to the apparatus, and reducing in a stream of hydrogen for about twenty-four hours at each of the three temperatures 200, 250 and 300°. The two samples of nickel were prepared from the same batch of oxide, but reduction was stopped when the amount of water given off per hour was 2.5 mg. in the former case and 3.6 mg. in the second. The weights of metallic nickel were 23.68 and 23.10 g., respectively.

Constant Temperature Baths.—The temperature range covered by these measurements was 110 to −210°. For 110 and 56.5° toluene and acetone, respectively, boiling under atmospheric pressure, were used. For temperatures from 0° down, Dewar flasks formed the bath containers: 0° was obtained with ice and water, −78.5° with solid carbon dioxide and alcohol. The intermediate temperature, −35°, was produced by periodically adding solid carbon dioxide to alcohol. For maintaining −183° liquid oxygen containing only a negligible quantity of nitrogen was employed, for −191.5°

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[7] Pease, THIS JOURNAL, **45**, 1197 (1923).

liquid air, while for lower temperatures liquid air was allowed to boil under a pressure of a few cm. of mercury.

Considerable difficulty was experienced in obtaining satisfactory thermostats at temperatures between −78.5 and −183°. For a temperature around −110° fair success was arrived at with a mixture of solid and liquid carbon disulfide, but it is difficult to maintain for long periods at the true melting-point (−111.6°). The solid carbon disulfide may be conveniently prepared by pouring the partially cooled liquid into liquid air, or vice versa. For temperatures between −160 and −170° the adsorption bulb was surrounded by a hollow cylinder, closed at top and bottom and constructed of 0.25-inch brass, which was wound externally with resistance wire, covered with alundum cement, and the whole immersed in liquid air. It was found that on passing a constant small current through the resistance wire, a fairly constant temperature could be maintained, and no temperature gradients could be detected inside the cylinder.

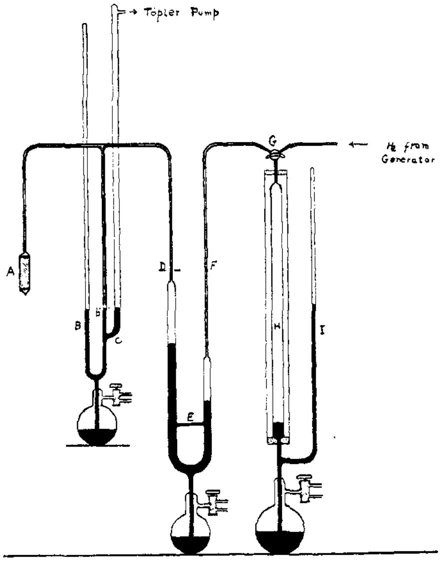

Fig. 1.—Apparatus.

Temperatures below 0° were determined with a copper-constantan thermocouple in connection with a Leeds and Northrup potentiometric temperature indicator. The couple was calibrated at 0, −78.5, −111.6 and −183°. Interpolation between these points and extrapolation below −183° were carried out with the help of a deviation curve prepared from the values given by Adams.[8] In spite of the fact that the deviations from Adams' values were very nearly a linear function of the observed e. m. f. down to −183°, continuation of the curve below this point led to a temperature of −193° for fresh liquid air, and temperatures below −200° determined in this way were obviously too low because in one experiment the calculated amount of free space exceeded the amount of gas actually in the bulb. For this reason the part of the calibration curve below −183° which we have adopted as most nearly correct, placing fresh liquid air at −191.5°, may be in error, but it is believed that this probably does not exceed ±0.5°.

Determination of Free Space.—The volume of the free space in the bulb and connecting tubing to the marks b and D, Fig. 1, was determined by filling with pure helium at each of the temperatures, 110, 0 and −78.5°; for the second adsorbent −109° was also used. Since it was feared small quantities of helium might be adsorbed at lower temperatures, the volume of gas required to fill the free space at these points was calculated by the use of the perfect gas law from each of the measurements at the higher temperatures, consideration being given to the fact that a small measured volume in the capillary tubing always remained at room temperature. The close agreement of the values calculated in this way from the various temperatures used experimentally indicates that helium is not appreciably adsorbed at the pressures employed at temperatures at least down to −109°.

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[8] Adams, "International Critical Tables," Vol. I, 1926, p. 58.

Experimental Results

Typical isotherms obtained at various temperatures are shown in Figs. 2–4. The ordinates represent volumes, in cc. at 0°, 760 mm., adsorbed by 23.68 g. of nickel in case of Sample I (Runs 1–23), or by 23.10 g. for Sample II (Runs 34–52); the abscissas are the corresponding pressures in cm. of mercury at 0°. It is impracticable to present in this form the results of the entire series of 42 runs. Of this number 13 were devoted to the determination of free spaces, and about half of the remainder were redeterminations of isotherms already obtained on one or the other sample. (Runs 24–33 are omitted since they were made for a different purpose.)

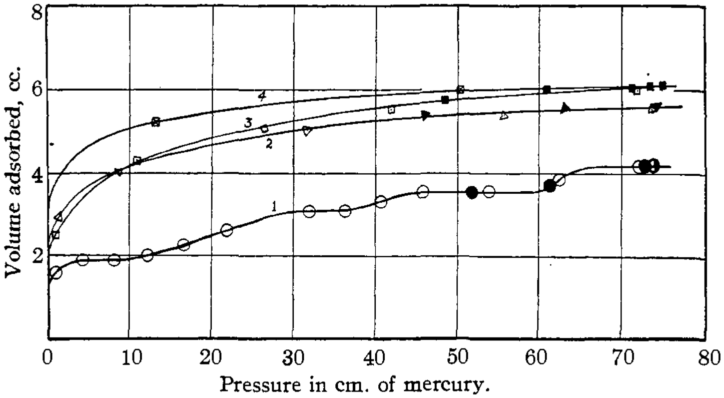

Fig. 2.—Adsorptions of hydrogen on nickel, Sample I. Curve I, −191.5° (Run 13); Curve 2, 56.5° (Run 15); Curve 3, 110° (Run 12); Curve 4, −35° (Run 16).

Reversibility with Respect to Pressure Changes.—In the majority of runs, after measurements had been made nearly up to atmospheric pressure, as large a portion of gas as practicable was withdrawn from the bulb and the course of the isotherm retraced to its upper end. In some cases this process was repeated several times. The values thus obtained are indicated in Figs. 2–4 by full black circles, triangles, etc. It will be observed that, while the exact equilibrium value was not always reached on first ascending the isotherm, nevertheless the values obtained from higher and from lower pressures agree so closely that the equilibrium isotherm can be drawn in every case with considerable confidence. This is especially true at the lower temperatures, where no evidence of hysteresis was ever observed. It is clear, therefore, that with respect to changes in pressure the adsorptions are strictly reversible.

Rate of Adsorption.—The rate of approach to equilibrium depended greatly on the experimental temperature and pressure. It is a remarkable fact that at −183 and −191.5° the pressure in the bulb became constant almost immediately after admitting the gas, whereas at both higher and lower temperatures considerably longer periods were required. It was also observed that in the higher temperature range equilibrium was reached less quickly at low pressures than at higher pressures. In the latter range times of the order of an hour were usually required, but as much as two hours was often necessary at pressures below 200–300 mm. However, at those points where the entire quantity of gas admitted to the bulb was adsorbed with a value of the final pressure practically equal to zero, shorter times were again required, of the order of half an hour.

Accuracy of Individual Isotherms.—The accuracy of any particular isotherm depends on the conditions employed. Volumes and pressures involve errors which are negligible in comparison with other factors. In those cases where the temperature remained definitely constant for long periods, as at −183, −78.5, 0, 56.5 and 110°, the limiting uncertainty is that involved in the exact establishment of equilibrium, amounting to not more than 0.1–0.2 cc. even at the higher temperatures. At the other temperatures, and particularly below −191.5° where the volume of gas in the free space is very large compared to the volume adsorbed, the limiting factor is the constancy and accuracy of the temperature. In these cases the temperature could be held constant within ±0.5°. Although the error in a single adsorption measurement produced by such a variation amounts to only 0.3 cc. at −110° and one atmosphere and proportionately less for lower pressures, nevertheless at −210° the uncertainty rises to nearly 2 cc.

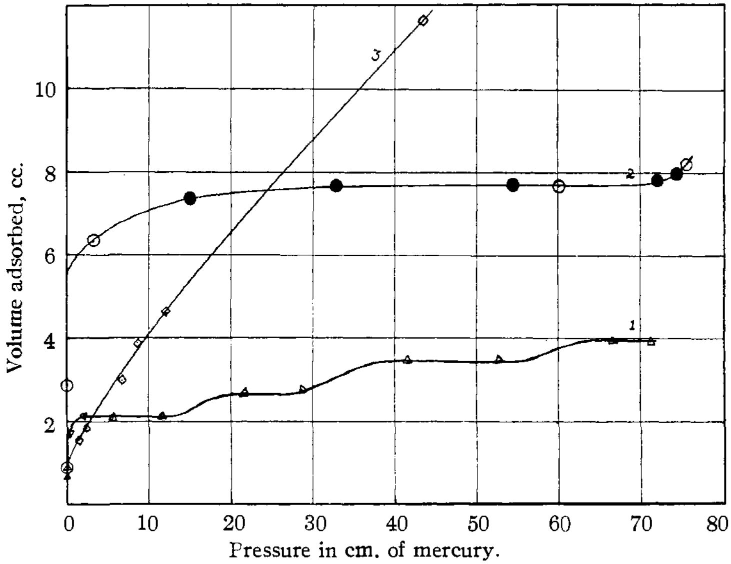

Fig. 3.—Adsorptions of hydrogen on nickel, Sample II. Curve 1, −191.5° (Run 39); Curve 2, −78.5° (Run 47); Curve 3, −209° (Run 49).

at atmospheric pressure. At this temperature there is an additional uncertainty, which is probably of even greater magnitude, in determining the absolute value of the temperature from the thermocouple calibration. For these reasons measurements below −200° must be regarded as fair approximations only, except at the lower pressures, yet the general trend of the true isotherms cannot differ greatly from those we have obtained. At all higher temperatures the accuracy is probably at least as great as that with which Figs. 2–4 can be read.

Comparison of Results for Different Temperatures.—In order to determine to what extent the values obtained for a given sample are reproducible, a large proportion of the runs (which are numbered serially in the order in which they were made) were devoted to checking earlier determinations. It was found that only a very small change in adsorption occurred in the case of Sample II. Thus the first run (34) and one near the end (50), both at 0°, gave exactly similar curves and differ only in the fact that in Run 50 about 0.3 cc. more hydrogen was adsorbed at all pressures than in Run 34. It is felt, therefore, that for this sample changes in activity with time are of the same order of magnitude as the probable error of the individual isotherms. Sample I, however, showed a steady and fairly considerable decrease in adsorptive capacity throughout, although here also only the absolute values were affected and not the shape of the isotherms. This change should be considered in comparing the curves of Fig. 2. While sufficient data have been obtained to correct systematically for this variation, it appears unnecessary to do so, since all the temperatures at which Sample I was investigated were also used with Sample II, except −35, 56.5 and 110°.

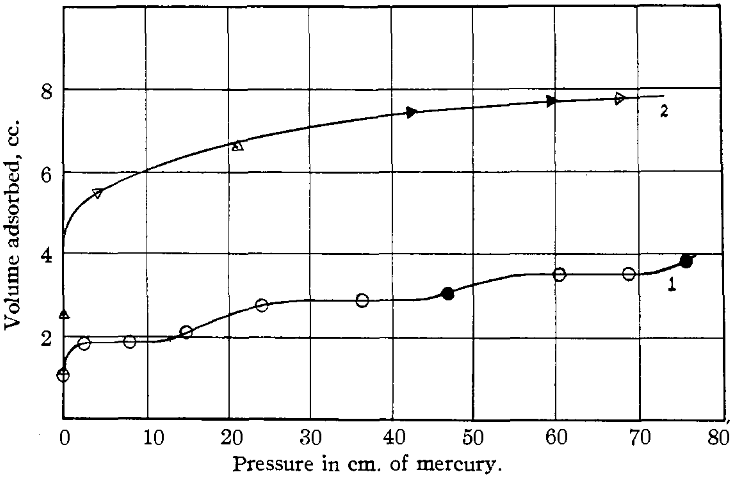

Fig. 4.—Adsorptions of hydrogen on nickel, Sample II. Curve 1, −183° (Run 52); Curve 2, 0° (Run 50).

In order to make the values for Sample I at these temperatures suitable for comparison with the data at other temperatures for Sample II, we have assumed that the ratio of the adsorptions at two temperatures is the same for each sample. This is closely the case for temperatures at which both samples were actually studied. Since several runs at 0° were made at wide intervals on each sample, this is a convenient temperature at which to make the comparison. The method will be clear from the following example. At 110° and 600 mm. pressure 7.77 cc. was adsorbed in Run 6 and 5.85 cc. in Run 12. At 0° and 600 mm. the adsorptions were 6.93 cc. in Run 11 and 6.25 cc. in Run 14. Hence at this time the decrease in adsorption amounted to about 0.3 cc. per run at this pressure. If Run 12 could have been made at the same time as Run 14, we should expect, therefore, that 5.85 − 0.6 = 5.25 cc. would have been adsorbed. Hence for Sample I the corrected value for 110° is 5.25/6.25 times the value at 0°. If we assume that this same ratio holds for Sample II, which in Run 50 took up 7.70 cc. at 0° and 600 mm., the adsorption at 110° and 600 mm. would be 5.25/6.25 × 7.70 = 6.49 cc.

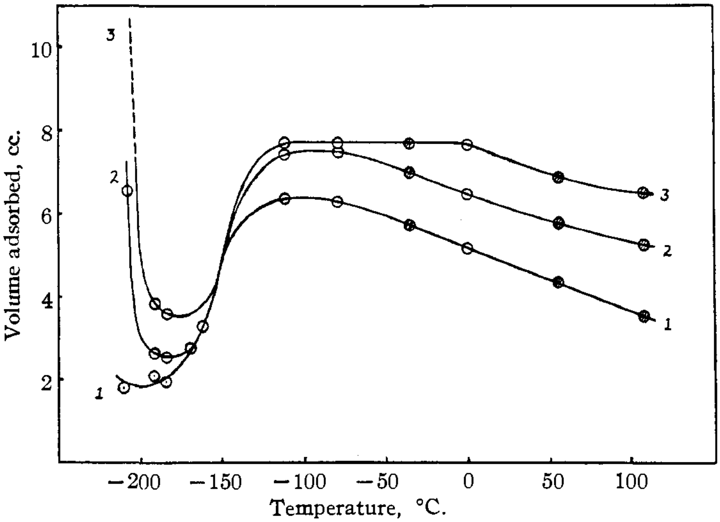

Fig. 5.—Isobars for hydrogen on nickel: Curve 1, at 2.5 cm. pressure; Curve 2, 20 cm.; Curve 3, 60 cm.

Similar calculations have been made for 25, 200 and 600 mm. pressure at the three temperatures −35, 56.5 and 110°. The values so obtained, together with those interpolated from the experimental isotherms for Sample II, are included in Fig. 5, in which the ordinates represent volumes adsorbed and the abscissas temperature, and the three curves are the isobars for 25, 200 and 600 mm., respectively.

Test of Reversibility with Respect to Temperature Change.—At the conclusion of the experiments described above, a working hypothesis to account for the observed variation of adsorption with temperature led us to an attempt to follow the equilibrium from higher to lower temperatures without intervening evacuation. In a run made at 0° in the regular way 7.40 cc. of hydrogen was adsorbed at a pressure of 651.4 mm. Without altering the amount of gas in the bulb the latter was then cooled to liquid air temperature. After apparent equilibrium had been reached, it was found that 9.85 cc. was now adsorbed at a pressure of 184.1 mm., whereas in a run (Run 39, Fig. 4) in which the gas was directly admitted to the bulb at this temperature, only 2.5 cc. was taken up at 184.1 mm. The same gas was then allowed to remain in contact with the nickel at room temperature for twenty-one hours. Following this, a remeasurement at 0° showed 8.22 cc. adsorbed at 636.2 mm., the increase over the previous value at 0° probably being due to a very slow solubility of hydrogen in the nickel. On cooling to $-186°$ the pressure became constant at 189.8 mm., at which 10.50 cc. was taken up. This increase of adsorption on cooling, 2.28 cc., agrees fairly well with the 2.45 cc. found in the previous part of the experiment. Subsequently additional gas was admitted to the bulb at $-186°$ and then withdrawn in stages. The following adsorptions were found: at 359.9 mm., 10.47 cc.; at 148.2 mm., 10.06 cc.; at 74.2 mm., 9.72 cc.

These results show that, contrary to what would be expected from a consideration of the individual isotherms, hydrogen adsorbed at 0° is not evolved on cooling to $-190°$, at least at an appreciable rate, but instead an increased adsorption occurs. This increase, 2.45 cc. and 2.28 cc. in the two trials, is of the same order of magnitude as the entire adsorption found at $-191°$ when the gas is admitted directly at this temperature. These facts strongly suggest that hydrogen can be adsorbed by nickel in two different ways, a strong binding being characteristic of the higher temperature range and a looser binding at low temperatures. The rate of change of the adsorbed gas from one form to the other is inappreciable at low temperatures.[9] For this reason either the low-temperature isotherms directly determined, or the values obtained after cooling from 0°, or perhaps both, represent metastable equilibria. It appears that the only hope of determining experimentally the values which correspond to true thermodynamic equilibrium at temperatures below $-110°$ lies in greatly extending the times of observation.

However, the fact that the isotherms are completely and quickly reversible with respect to pressure changes indicates that the metastable states are perfectly definite and in no sense mere accidental stopping-places on the

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[9] More recently we have found that the equilibrium, which is almost immediately established at $-183°$ when hydrogen is directly admitted at this temperature, remains unchanged for at least seventy hours.

way to true equilibrium. In this respect the situation appears to be analogous to the numerous cases of chemical reactions, such as the addition of hydrogen to benzene to form cyclohexane, where the reactants and products quickly reach a definite equilibrium of undoubted significance in spite of the fact that one or more of the reacting substances is itself unstable with respect to other possible reactions.

Discussion

The major results of this investigation can readily be accounted for on the hypothesis that at the lowest temperatures the adsorption is of the secondary type, involving hydrogen molecules whose configuration is little if at all altered by the process, whereas at temperatures above $-100°$ only primary adsorption occurs, in which the adsorbed molecules suffer a marked activation and perhaps even complete dissociation. The flatness of the 60-cm. isobar from -110 to $0°$ is strongly suggestive of the idea that here the nickel surface is entirely saturated with a single layer of these activated molecules. At temperatures above $0°$, pressures higher than 60 cm. would evidently be necessary to complete the layer. On this view the additional hydrogen which is taken up at low temperatures after the nickel has been saturated at $0°$ corresponds to the partial formation of a second layer. The isothermal results at temperatures below $-191°$ suggest that at still lower temperatures multimolecular layers are also capable of existence.

Between -100 and $-191°$ the adsorption appears to consist of both types. It is obvious, however, that in this range the observed values cannot be accounted for on the basis of an equilibrium between the two types since the experiments described in the last section show that the rate at which this equilibrium is established is negligibly small. For the same reason it is impossible to consider that the results in this region represent a continuous variation in the degree of activation of the adsorbed molecules. It must be supposed that primary and secondary adsorption constitute, at least in the present example, separate and distinct types, and not merely limiting cases of a continuously variable property. (It is not meant to be implied, however, that all the hydrogen held by primary adsorption necessarily has the same chemical reactivity.) We believe that the values obtained in this intermediate range are best explained by assuming that, as the temperature is raised, a larger and larger fraction of the nickel surface is capable of producing activation in the adsorbed molecules. At the same time the secondary adsorption, which falls off much more rapidly with decreasing pressure than the primary, is continuously decreasing. The opposition of these two effects results in a minimum in the isobars, which lies at temperatures which are lower the lower the pressure.

The isotherms for temperatures above $-110°$ show nothing unexpected except that above $0°$ they are considerably less flat than those obtained by

Gauger and Taylor.[3] As the temperature is raised in this region, higher and higher pressures are required to produce saturation of the surface, and a progressive change in the shape of the isotherms occurs. The curves for temperatures below −200° are typical of adsorption without activation, except that about 1 cc. of gas is adsorbed at zero pressure, a fact which presumably indicates that even at these temperatures nearly one-eighth of the surface is capable of activating the hydrogen.

The isotherms obtained at −183 and −191° warrant special mention. Owing to the almost instantaneous establishment of equilibrium and the extreme constancy of the temperature at these points, the individual values found here are probably more precise than at any other temperature. Nevertheless, smooth curves cannot be drawn through the experimental points within the limit of accidental error, which probably does not exceed 0.05 cc. Systematic errors, such as would result from deviations from the gas laws or uncertainty in determining the absolute temperature, could not account for the observed behavior. Furthermore, the anomaly is found in every isotherm at these temperatures, and only at these temperatures. For these reasons it appears that the stepwise increase of adsorption with pressure must have some physical significance. It should be pointed out, however, that the data obtained are insufficient to locate the exact course of the curves between steps, a point which is still under investigation.

The following tentative interpretation of this phenomenon may be proposed. At either temperature a fraction of the adsorbing surface, equivalent to about 1.5–2.0 cc. of gas, holds hydrogen by primary adsorption to an extent practically independent of pressure. On top of this and on the remainder of the surface, adsorption of the secondary type occurs, as indicated by its reversibility, which experiment shows does not occur at these temperatures for the primary type. It appears also that the surface is a composite one, which may perhaps be thought of as presenting a number of distinct regions of different adsorptive capacity. On each of these regions the adsorption represents an equilibrium between condensation and evaporation. If it be assumed that the rate of evaporation is very great for isolated molecules but much less when a number are adsorbed side by side, it follows that scarcely any adsorption would occur on a given region until the pressure reached a point at which the rate of condensation was sufficiently high to produce patches of neighboring adsorbed molecules. At this point further increase of pressure would quickly lead to the formation of a saturated layer. It appears that a summation of such effects on the different regions of the surface would result in an isotherm of the form found experimentally.

Summary

The adsorption of hydrogen by two samples of reduced nickel has been studied at pressures from zero to one atmosphere and at eleven tempera-

tures from 110 to −210°. The apparatus employed involves no stopcocks that are required to remain under vacuum more than momentarily.

At a given pressure the adsorption is relatively large at the lowest temperatures, decreases to a minimum at −200 to −175° depending on the pressure, then rises to a maximum in the neighborhood of −100°, and finally decreases again at higher temperatures. The fact that at 600 mm. the adsorption is independent of the temperature from −110 to 0° is taken as evidence that here a completely saturated single layer is formed.

It is shown that the values obtained are reproducible, and readily reversible with respect to changes of pressure, particularly at the lower temperatures. However, on cooling to about −190° a sample previously brought to equilibrium at 0°, the adsorption does not decrease to the value obtained isothermally at −190°, but reaches a new reversible equilibrium at which larger quantities of gas are adsorbed than at 0°.

At −191 and −183° the adsorption increases with pressure in a discontinuous manner, an observation whose explanation is somewhat obscure.

The major results of the work are interpreted on the hypothesis that at the lowest temperatures the adsorption is of the "secondary," or ordinary molecular type, while at higher temperatures a progressively larger fraction of the nickel surface is capable of holding the hydrogen by adsorption of the "primary" type, involving a marked activation of the gas.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

THE INCOMPATIBILITY BETWEEN ANY THEORY OF COMPLETE DISSOCIATION AND MIGRATION DATA

BY JAMES W. McBAIN AND PIERRE J. VAN RYSSELBERGE

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Inspection of the migration data for solutions of pure single electrolytes cannot, in general, give very conclusive evidence for or against the existence of any but the simplest ions in such solutions. In general, migration ratios are not constant throughout a range of concentrations, but it is a matter of rather arbitrary interpretation as to whether this is due to the ions being unequally affected by increase of concentration or whether the appearance of new (complex or intermediate) ions is assumed to account for the change in the gross transport number. It is only in the few rare instances, such as the well-known case of cadmium iodide where the change in transport number becomes so great that the sign of the migration is actually changed, that this method yields any conclusive proof of the existence or presence of complex ions.

It is evident that, if the migration number of a salt such as potassium chloride changes somewhat upon concentration, the change would most