havior on adsorption on alumina or (pure) silica of materials which yield a conjugate acid by simple proton addition, and materials which undergo more complex ionization with loss of water (or another polar molecule), may be had by shaking alumina or silica with an isoöctane solution of the leuco base of malachite green, *p,p'*-bis-(dimethylamino)-triphenylcarbinol, adsorption occurring as the green dye. A whole series of similar color changes has been observed by Weitz and Schmidt,[17] although their results may be complicated by the fact that their silica, since it adsorbed *p*-dimethylaminoazobenzene as its red form, must have contained some free acid.

This difference in behavior toward two classes of indicator suggests the possibility of still further characterizing surfaces by observing the color changes occurring with both (*e. g.*, a series of simple bases, and a series of triphenylcarbinols) and in turn relating the results to their catalytic behavior.

Summary

1. A definition of the acid strength of a solid surface is proposed as *the ability of the surface to convert an adsorbed neutral base as its conjugate acid.*

2. By observation of the colors of suitable adsorbed indicators the acid strengths of a number of materials have been semi-quantitatively determined.

3. Colors of the adsorbed indicators are, in every case, those of the indicator or its conjugate acid as observed in homogeneous solution. Further, acid strengths appear independent of the indicator employed, so the above definition appears a general and useful one.

4. Surface acid strengths depend somewhat upon the medium from which the indicator is adsorbed, and are decreased by the presence of weak bases, *e. g.*, acetone or water.

5. Although alumina and pure silica appear to have neutral surfaces, silica–alumina and silica–magnesia are strongly acid. Several surfaces containing strongly coördinating metal ions, *e. g.*, copper sulfate, silver chloride, etc., are also strongly acid.

6. The relation between surface acidity and certain examples of heterogeneous catalysis is discussed.

PASSAIC, NEW JERSEY RECEIVED OCTOBER 29, 1949

(17) Weitz and Schmidt, *Ber.*, **72B**, 1740, 2099 (1939).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Heterogeneity of Catalyst Surfaces for Chemisorption. III. Metallic Nickel

BY HUSSEIN SADEK[1] AND HUGH S. TAYLOR

In earlier communications[2] the heterogeneity of oxide catalysts for chemisorption has been demonstrated by a new technique in which adsorption was measured under constant pressure at different temperatures without intermediate evacuation. In this communication we present the results of parallel investigations on a series of nickel catalysts to indicate that similar behavior occurs both with oxide and metal catalysts.

Benton and White[3] early showed that a distinct minimum in the adsorption isobar of hydrogen on metallic nickel occurs, interpretable as a change from van der Waals adsorption to chemisorption, in their experiments in the temperature region −190 to −100°. On this interpretation, the activated adsorption above −100° was a rapid process. The researches of Beeck and his coworkers[4] have indicated that on evaporated nickel films the processes of chemisorption were rapid and complete down to temperatures of liquid nitrogen. Eucken and Hunsmann,[5] working with reduced nickel catalysts, found that van der Waals adsorption with a heat of adsorption of $\sim$1 kcal. occurred at liquid hydrogen temperatures; at 50°K. the heat of adsorption was indicative of a partial van der Waals adsorption and partial chemisorption, while at liquid-air temperatures and higher the process occurring was chemisorption with a heat of adsorption of $\sim$20 kcal. By a desorption technique these authors indicated that the surface of their nickel was heterogeneous so far as the adsorption process for hydrogen was concerned.

The aim of the present investigation was to examine a series of nickel catalysts by the adsorption technique developed by Taylor and Liang to determine how far different methods of preparation might influence the temperature range in which van der Waals adsorption of hydrogen changed to chemisorption and to reveal, by this newer technique, the extent to which heterogeneity of the catalyst surface might be present in each case. The results of the adsorption experiments were checked in two cases by studies of the hydrogen–deuterium reaction on the catalysts.

---

(1) This article is based upon a Thesis submitted by Hussein Sadek in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University, May, 1948.

(2) (a) Taylor and Liang, THIS JOURNAL, **69**, 1306, 2989 (1947); (b) Taylor, "Advances in Catalysis," Vol. I, Academic Press, New York, N. Y., 1948, Chap. 1, pp. 1–26.

(3) Benton and White, *ibid.*, **52**, 2325 (1930).

(4) Beeck, Smith and Wheeler, *Proc. Roy. Soc.* (*London*), **177A**, 62 (1940); Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

(5) Eucken and Hunsmann, *Z. physik. Chem.*, **B64**, 163 (1939).

TABLE I

ADSORPTION ISOBARS IN CC./G. AT $P = 1$ ATM. AFTER 1000 MINUTES

Temp., °C.	Ni–Cr_2O_3, 6.03 g., V_m 36.4 cc.		Ni–Kieselguhr, 1.47 g., V_m 34.0 cc.		Ni–Kieselguhr, du Pont, 2.55 g., V_m 50 cc.		Cat. 6545, 3.5 g., V_m 111.6 cc.		Ni–ThO_2, 21.2 g., V_m 29.8 cc.		Ni–BeO, 2.58 g., V_m 39.9 cc.	
−195	4.296		5.74	10.32	8.17	14.2	10.96	12.31	1.06	1.39	6.08	8.23
−126.5	...		..	..	5.65	7.57	1.38	2.49	0.81	1.12	1.17	2.83
− 95	...		..	..	6.15	7.5	1.35	2.38	.75	1.10	0.85	2.52
− 78	2.285		2.63	4.59	6.35	7.34	1.53	2.40	.81	1.09	0.65	2.4
0	1.954	3.329	4.02	4.08	5.84	6.60	1.52	2.12	.91	1.01	0.69	2.19
56	2.012	3.16	3.54	3.57	5.45	5.86	1.39	2.01	.87	0.97	1.08	2.04
80	1.976	3.11	3.34	3.32	5.06	5.35	1.46	1.96	.89	.94	1.23	2.03
110	2.15	3.04	2.98	3.05	4.52	4.88	1.41	1.89	.86	.92	1.23	1.97
184	2.25	2.92	2.15	2.43	3.33	3.58	1.44	1.75	.82	.85	1.08	1.74
218	2.36	2.76	1.91	2.13	2.76	2.94	1.42	1.63	.77	.80	1.12	1.58
256	2.41	2.64	1.79	1.95	2.32	2.52	1.36	1.50	.71	.73	1.01	1.29
302	2.42		1.65		2.01		1.41		.64		1.13	

Experimental

Apparatus.—The adsorption apparatus used was a modification of that employed by Taylor and Strother.[6] The pressure could be maintained sufficiently constant by hand-regulation without the use of the automatic regulation of these authors.

Gases.—Helium, nitrogen and hydrogen from commercial cylinders were used with suitable purification over hot copper at 450° followed by a drying train of calcium chloride, ascarite and phosphorus pentoxide. In the case of helium, the gas was freed from nitrogen by passage through a previously evacuated charcoal trap, kept at liquid-air temperatures as helium was passed slowly through the trap.

Catalysts: (a) **Nickel–Chromium Oxide.**—A pelleted nickel catalyst obtained by precipitation from appropriate solutions and containing 80% nickel by weight, the residue being chromic oxide, was reduced in a current of hydrogen at 400° for twenty-one hours and evacuated for ten hours at 450°.

(b) **Nickel–Kieselguhr.**—This was prepared by adding a weighed quantity of purified kieselguhr to a solution containing a known weight of pure nickel nitrate. Dilute sodium hydroxide was gradually added with continuous stirring until the solution was alkaline to litmus. The precipitate was washed by decantation at intervals for one week. The product was dried at 110° and reduced in a current of hydrogen at 450°. It contained 19.1% nickel by weight.

(c) **Nickel–Kieselguhr du Pont.**—This was a part of a du Pont preparation used in many researches in this Laboratory. It was a pelleted catalyst containing 15% nickel.

(d) **Catalyst no. 6545.**—This catalyst, of German origin, contained nickel distributed on a hard siliceous support material, had been prepared to produce exchange reaction between the deuterium content of hydrogen and water, reputedly with good efficiency.

(e) **Nickel–Thoria.**—A nickel catalyst promoted with 2% thoria was prepared according to the directions of Russell and Taylor.[7] The sample was reduced at 300° before adsorption experiments were performed.

(f) **Nickel–Beryllia.**—This catalyst was prepared according to the directions of Herbo and Hauchard.[8] The sample contained 39.6% nickel.

Procedure: (i) **Adsorption.**—The dead space was measured with helium. Surface areas were determined by the BET method with nitrogen at liquid nitrogen temperatures. The adsorption of hydrogen was measured, after equilibration of the whole adsorbent to the working temperature, at −195, −126, −95, −78, 0, 56, 80, 110, 184, 218, 250 and 302°. Above 0° suitable vapor-baths were used, and liquid nitrogen for −195°. The temperatures of −126 and −95° were maintained with solid methylcyclohexane and toluene melting, respectively, in their own liquids. Solid carbon dioxide and ice gave the temperatures of −78 and 0°.

(ii) **Isotope Exchange Reaction.**—Deuterium was generated electrolytically from a cell in which a sodium hydroxide solution was obtained by treating 1 g. of metallic sodium with ~10 cc. of 99.9% D_2O. The gas was freed from oxygen over copper at 450° and dried with calcium chloride. Hydrogen from commercial cylinders was similarly purified and dried in a calcium chloride, ascarite, phosphorus pentoxide train. The hydrogen and deuterium were mixed in ratios calculable from a flow meter reading of the former and by the current consumed in electrolyzing the heavy water. Analyses of the product of reaction were made on the mass-spectrometer. Six standards containing known quantities of HD in equilibrium with hydrogen and deuterium were used as calibration for the spectrometer. The percentage of HD formed in the exchange reaction could be read directly for the observed spectrometer reading of the analyzed sample, from a plot of the data for the six calibration samples. The standards were prepared by Mr. M. M. Wright of this Laboratory by the interaction of hydrogen with heavy water vapor of different concentrations over a platinum catalyst at 80°.

Experimental Results and Discussion

The amounts of hydrogen adsorbed per gram of catalyst after one thousand minutes contact at 1-atm. pressure are shown in Table I. Under each heading the data in the first column are those obtained as the temperature is raised in steps from the lowest temperature, *i. e.*, −195°. The second column in each case gives the data for adsorption as the temperature is lowered in steps from the highest temperature of 302°.

Discussion of the One Thousand-Minute Isobars.—(a) **Nickel–chromia** is significantly different from all the others. On raising the temperature, decrease in adsorption continues up to 0°. It is then followed at higher temperatures by adsorption increasing in amount continuously to 256°. The descending curve shows marked increments in adsorption paralleling those found on oxides by Taylor and Liang. Indeed, the whole isobar can be considered as a combination of chemisorption on a nickel surface and on chromium oxide.

(b) **Nickel–kieselguhr** gives an isobar very similar to that of Benton and White with the

---

[6] Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

[7] Russell and Taylor, *J. Phys. Chem.*, **29**, 1325 (1925).

[8] Herbo and Hauchard, *Bull. soc. chim. Belg.*, **55**, 177 (1946).

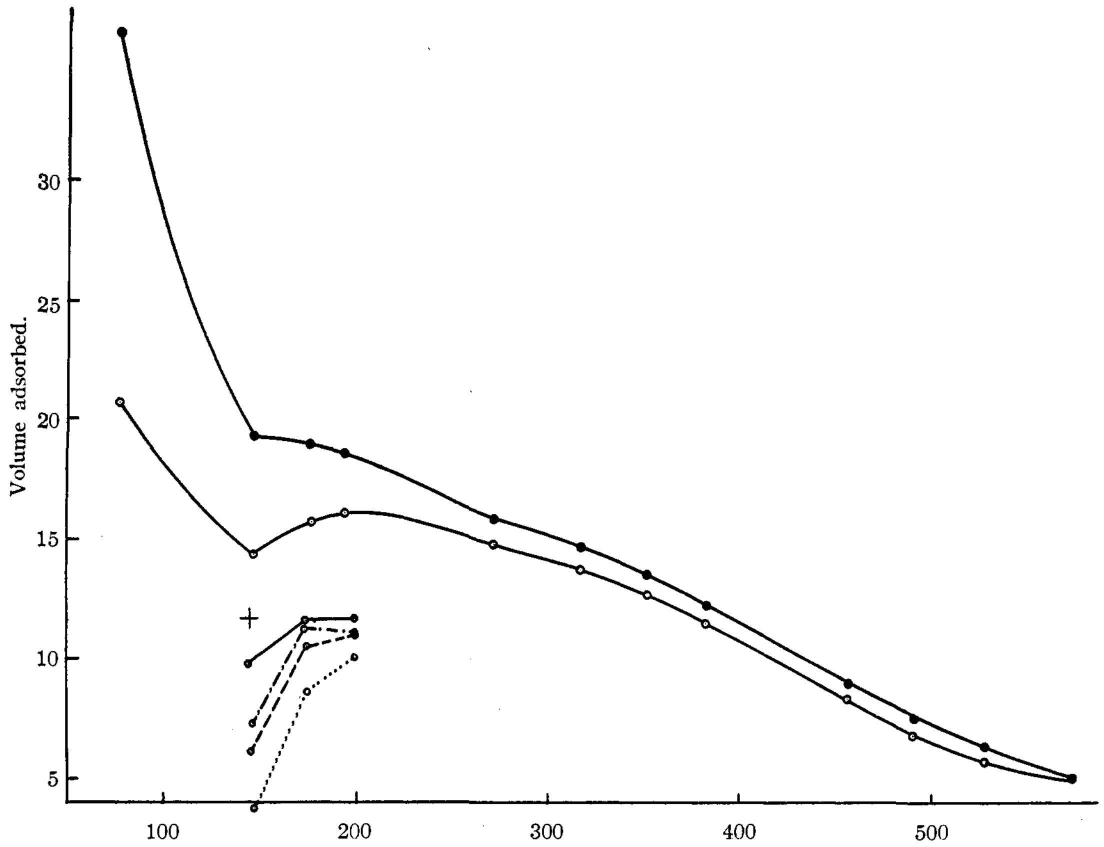

Fig. 1.—Hydrogen adsorption isobar on Ni–Kieselguhr du Pont, V_m = 50 cc.: ··········, after 10 min.; - - - - - -, after 60 min.; —·—·—·—, after 120 min.; ———, after 250 min.; +, after 400 min.

minumum at about −78° and a sharp rise in adsorption from −78 to 0°. In this same temperature range, as the data for descending temperatures indicate, the desorption–readsorption phenomenon of a heterogeneous surface is occurring. The increase of 0.51 cc. adsorption in this range is much larger than the probable van der Waals adsorption in this range

(c) **Nickel–kieselguhr du Pont** shows a shallow minimum in the ascending isobar at −126.5° with chemisorption increasing in the range −126.5 to −78° followed by a progressive decline in total adsorption at the higher temperatures. The descending isobar deviates progressively from the ascending isobar, the greatest divergence occurring from 0 to −126.5°, the divergencies being relatively small above 0°.

In the region −126.5 to −78° the rate of chemisorption is measurable on this catalyst. This is shown by the data in Table II for adsorptions at times up to three and one-half hours on surfaces cleaned by prior evacuation at 450°. Some points from these data are plotted in Fig. 1. Examination of Table II indicates that van der Waals adsorption at −126.5° must be less than 3 cc. since this type of adsorption is rapid and must have occurred prior to the five-minute reading recorded. An additional 4 cc. was chemisorbed over the succeeding two hours. The data at −95° reveal that, at this temperature, the chemisorption is more rapid since, already after two minutes, some 6.3 cc. is adsorbed while the van der Waals adsorption must be less than the upper limit of 3 cc. found at −126.5°. The table and Fig. 1 show that the

TABLE II

RATE OF ADSORPTION OF HYDROGEN ON CLEAN SURFACE OF NI–KIESELGUHR DU PONT[a]

−195°		−126°		−95°		−78°	
Time	$V_{ads.}$	Time	$V_{ads.}$	Time	$V_{ads.}$	Time	$V_{ads.}$
2	17.39	5	3.08	2	6.31	2	7.81
5	18.12	10	3.81	5	7.79	5	9.28
10	18.31	15	4.41	10	8.74	10	10.23
25	18.39	25	4.78	25	9.82	25	10.60
35	18.49	30	5.14	35	10.22	35	10.91
45	18.63	40	5.57	45	10.50	45	11.01
55	18.67	50	5.92	60	10.79	60	11.15
65	18.67	60	6.10	130	11.16	75	11.20
85	18.70	70	6.30	150	11.26	90	11.26
100	18.70	100	6.77	180	11.38	120	11.33
130	18.85	130	7.32	210	11.50	150	11.44
170	18.85					180	11.53

[a] Times are expressed in minutes, adsorbed volumes in cc. on 2.55 g. of catalyst V_m = 50 cc.

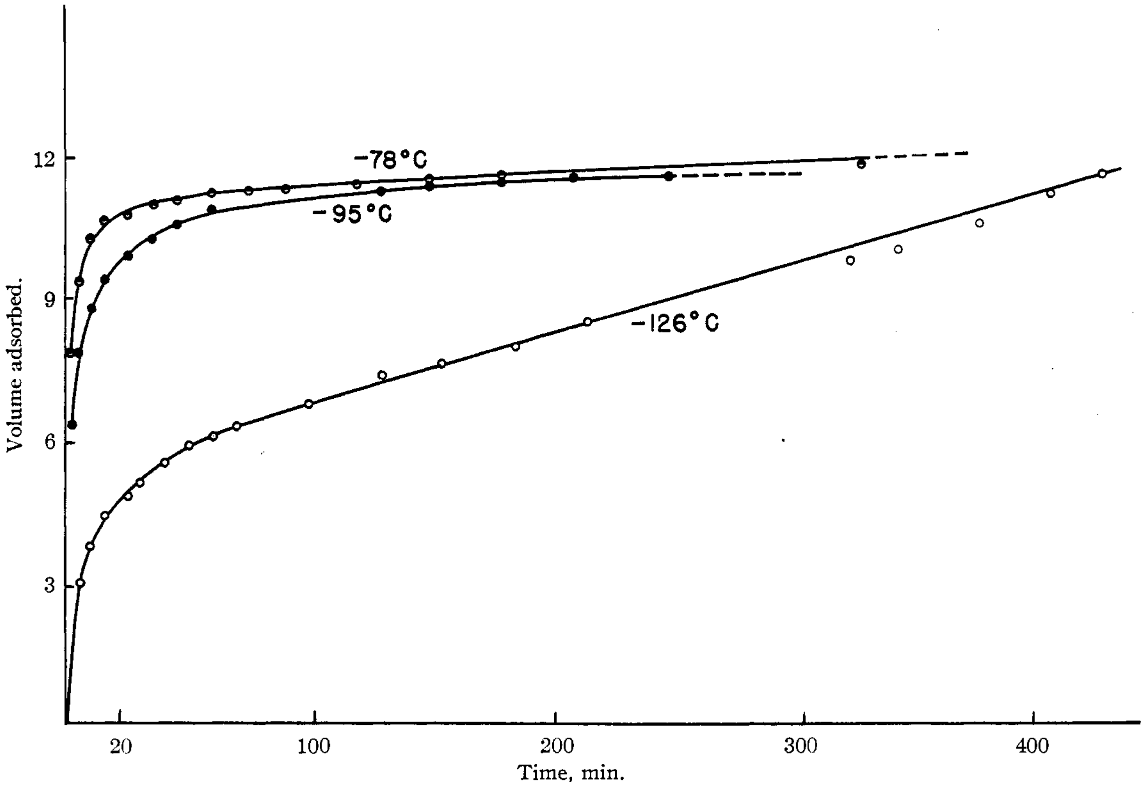

Fig. 2.—Rate of adsorption of hydrogen on clean surface of Ni–Kieselguhr du Pont, V_m = 50 cc.

change in temperature produces its most marked effect in the quantity of gas adsorbed in the first minutes, gas which for the reasons given must be chemisorbed. The data lend themselves to a calculation of apparent activation energy of adsorption which is found to be 3.5 kcal. per mole.

Evacuation at the same temperature of the gas adsorbed on a clean surface at −195° and measurement of the quantity then readsorbed gave a value of 16.65 cc. This is a maximum value for the van der Waals adsorbed gas at this temperature since some chemisorbed gas might be removed by the evacuation at temperature. This indicates therefore that some chemisorption also occurs at −195°, since the amount adsorbed after one hundred and seventy minutes at this temperature is 18.85 cc. The data of the descending isobar confirm the value of ∼16.7 cc. for van der Waals adsorption and easily reversible chemisorption. Some 2 cc. of gas is therefore chemisorbed at −195° in a time interval in which more than 4 cc. is adsorbed at −126° and more than 8 cc. at −95°. This is typical of slow activated adsorption occurring here on *metal* catalyst surfaces paralleling that shown by oxide catalysts in the range of temperatures above 0°. We have plotted some of the rate data in Fig. 2.

A further interesting feature is to be noted. The amount of gas adsorbed on a clean surface at −126.5° after four hundred minutes (12 cc.) proved to be less than that adsorbed at the same temperature, after only one hundred and fifty minutes, when the catalyst saturated at −195° was raised in temperature to −126.5° (14.4 cc.). This suggests that the rate of chemisorption may be determined by the concentration of gas on the surface bound by van der Waals forces and that this is favored by saturation at the lower temperature followed by temperature increase rather than through operation on a clean surface at the higher temperature where van der Waals adsorption is correspondingly smaller.

(c-1) **Sintered Nickel–Kieselguhr du Pont.**—The catalyst just considered was subjected to a heat treatment at progressively higher temperatures (up to 500°) until its monolayer volume had decreased from the initial V_m = 50 cc. to a value of 33.8 cc. It is of the nature of such heat treatment that the activity of the metal catalyst would suffer severe decrease. The adsorption isobar of this sintered catalyst is shown in Fig. 3. The most striking divergence from the data on the unsintered catalyst plotted in Fig. 1 is seen in the adsorption at −126.5°. This has decreased to one-fifth the value for the unsintered catalyst while at −78° and higher temperatures the chemisorption has only decreased by one-half. This means that the heat treatment has destroyed those areas on which chemisorption was occurring measurably at −126.5°, higher temperatures being required for the necessary activation energy. The descending isobar shows an increased adsorp-

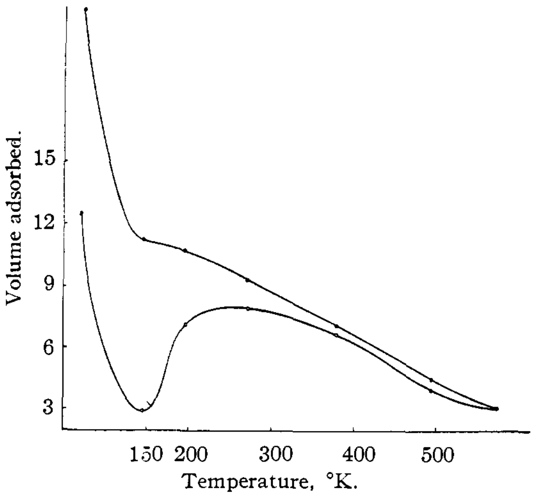

Fig. 3.—Adsorption isobar of hydrogen on sintered Ni-Kieselguhr du Pont, V_m = 33.77 cc.

tion of more than 2 cc. between 0 and −126.5° which measures the surface laid bare of chemisorbed gas in the same interval in the ascending isobar,[1] most of this occurring in the interval −78 to 0°. For reasons given in the following discussion, the van der Waals readsorption in this same temperature interval is of the order of 0.1 cc.

(d) **Catalyst No. 6545.**—The isobar recorded for 1-atm. pressure as well as a similar isobar for P = 0.5 atm. showed this catalyst to have an indistinct minimum around −95° with relatively small adsorption and a small progressive change in amount over the range −126.5 to 302°, especially when compared to the BET value of V_m.

(e) **Nickel–Thoria.**—This catalyst was not so stable structurally as the others. During experimentation its surface area decreased from V_m = 29.8 to 25.8 cc. The one thousand-minute isobar indicates a minimum at −95° on the ascending temperature curve. There is a progressive spread between ascending and descending values most pronounced below 0°. This catalyst is, however, characterized by areas of surface which chemisorb hydrogen much more rapidly at −126.5° than does Nickel–Kieselguhr du Pont. From the surface areas one can conclude that the van der Waals adsorption on nickel–thoria at −126.5° cannot exceed 2 cc. Yet, after two minutes of adsorption on a clean surface at this temperature more than 16 cc. of gas was adsorbed. This points to areas of chemisorption with much lower energies of activation than are found on Nickel–Kieselguhr du Pont. The plots of the rate data in Fig. 4 contrast significantly with those in Fig. 2.

(f) **Nickel–Beryllia.**—The isobar for this catalyst with increasing temperature shows a flat minimum similar to that of nickel–chromia. The isobar for descending temperature shows a

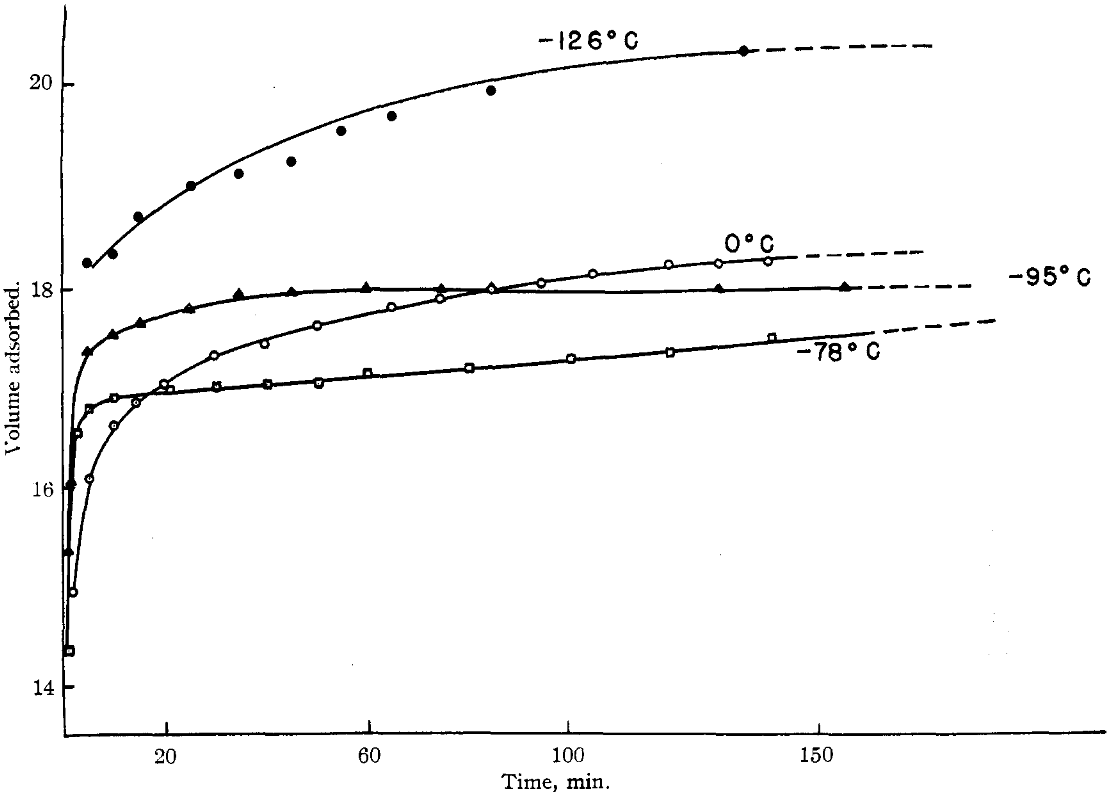

Fig. 4.—Rate of adsorption of hydrogen on clean surface of Ni-2% ThO$_2$, V_m = 29.82 cc.

progressively increasing divergence in values from those on the ascending curve down to −126.5°. The rates of adsorption on a clean surface were indicative of the presence of areas of surface which at one temperature were covered by chemisorbed gas while at a higher temperature they were bare, as was the case for chromium oxide gel discussed in detail in the earlier communications of Taylor and Liang.[1,2]

Extent of Chemisorption of Hydrogen at −195°.—An attempt was made to determine the actual amount of chemisorbed hydrogen at −195°. The adsorption of hydrogen on purified kieselguhr was measured at −195, −125.6, −78 and 0° on the assumption that only van der Waals adsorption would be involved. The BET surface area measurement was also made. It was found that there was a chemisorption of hydrogen especially marked at 0° which tended to vitiate the attempt. By making the assumption that the extent of van der Waals adsorption of hydrogen on the catalyst was the same as that of purified kieselguhr having equal surface or the same BET monolayer volume, the following data were computed for the adsorption on the Nickel–Kieselguhr du Pont.

TABLE III

ESTIMATED VAN DER WAALS AND CHEMISORPTION OF HYDROGEN ON NICKEL-KIESELGUHR DU PONT AT 1-ATM. PRESSURE

Temp., °C.	Cc.$_{\text{ads.}}$/g.[a]	Van der Waals, cc./g.	Chemisorption, cc./g.
−195	(a) 8.17	7.70	0.47
	(d) 14.21	7.70	6.52
−126.5	(a) 5.65	0.46	5.19
	(d) 7.57	0.46	7.11
− 95	(a) 6.15	.23	5.92
	(d) 7.50	.23	7.27
− 78	(a) 6.35	.17	6.18
	(d) 7.34	.17	7.17
0	(a) 5.84	.11	5.73
	(d) 6.60	.11	6.59

[a] (a) Signifies ascending temperature, (d) signifies descending temperature.

If the assumption be made that the van der Waals adsorption of hydrogen at −195° on the several other catalysts here investigated is determined by their respective surface areas in the amount governing the adsorption of hydrogen per unit area on kieselguhr at −195°, it is possible to estimate what is the amount of van der Waals adsorption and chemisorption of hydrogen on these catalysts. The assumption is, at best, only approximate but it should serve to give an order of magnitude of the two types of adsorption. In this manner the data in Table IV were obtained.

TABLE IV

COMPUTED VAN DER WAALS ADSORPTION AND CHEMISORPTION OF HYDROGEN AT −195° AND 1 ATMOSPHERE PRESSURE

Catalyst	Cc.$_{\text{ads.}}$/g.	van der Waals, cc./g.	Chemisorption, cc./g.
Ni–Cr_2O_3	4.30	2.37	1.93
Ni–ThO_2	1.06	0.55	0.51
Ni–BeO	6.08	6.06	0.02

An alternative essay to estimate the extent of chemisorption of hydrogen at −195° was attempted by comparison of hydrogen isotherms at −195° with nitrogen isotherms at −78° on the same catalyst. In all the cases examined, Nickel-Kieselguhr du Pont, Nickel–Thoria, Nickel-Beryllia and Catalyst No. 6545, when the data were so plotted on scales adjusted to give the same plot at 0 and 760 mm. pressure the hydrogen isotherm always lay to the left of the nitrogen isotherm in the direction of greater adsorption of hydrogen at −195° at a given pressure than of nitrogen at −78° at the same pressure. Since such a comparison is favorable rather to nitrogen than hydrogen based on the critical data for these gases, one is forced to conclude that there is already chemisorption of hydrogen on these nickel catalysts at −195°. Figure 5, which shows the comparison for nickel–thoria, indicates marked chemisorption of hydrogen at −195°.

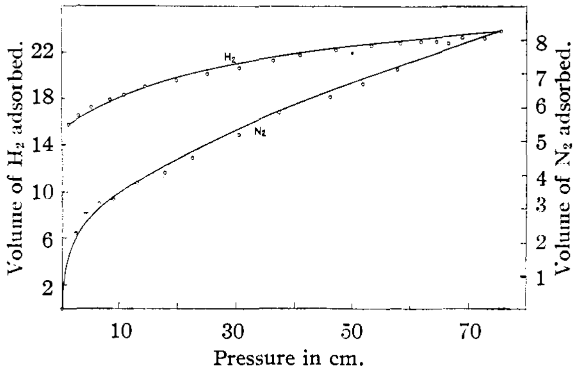

Fig. 5.—Adsorption isotherms of hydrogen (at −195°) and of nitrogen (at −78°) on Ni-2% ThO_2.

Hydrogen–Deuterium Exchange Reaction.—Two catalysts, nickel–chromia and nickel–thoria, were selected by reason of the data just cited to study their efficiency in the hydrogen–deuterium exchange reaction at low temperatures. A mixture containing 1.165% deuterium was allowed to flow over samples of the catalysts at the total hydrogen–deuterium flow rates of 1.435, 2.15, 2.51 and 2.87 liters per hour in the temperature range of room temperature to −78° in the case of nickel–thoria and from room temperature to −195° in the case of nickel–chromia. The mixed gases were passed through two successive traps maintained at −78° to ensure removal of traces of water prior to passage over the catalyst.

The reaction was followed by mass-spectrometric analysis and the figures cited in the succeeding tables refer to the percentage of HD in the gas mixture after it had attained flow equilibrium. The gases were allowed to flow for at least one hour before a sample was taken for analysis. By plotting the percentage HD formed against the absolute temperature one can interpolate the temperatures at which half the equilibrium percentage of HD was obtained at a given rate of flow. The activation energy of the exchange reaction could then be calculated from a plot of the logarithm of the flow rate against the reciprocal of the absolute temperature corresponding to half-equilibrium. The data thus obtained are summarized in Tables V and VI.

TABLE V

HYDROGEN–DEUTERIUM EXCHANGE ON NICKEL–THORIA

Flow rate, l./hr.	% HD in exit gas at t°C. = 25	0	−21	−40	−60	−78	T, °K., 1/2 eqm.
1.435	2.25	2.30	2.25	2.02	1.67	1.11	194
2.151	2.24	2.22	2.22	1.89	1.38	0.82	202
2.509	2.17	2.16	2.14	1.71	1.30	0.60	207.5
2.870	2.22	2.26	2.14	1.50	0.86	0.53	221.5

TABLE VI

HYDROGEN–DEUTERIUM EXCHANGE ON NICKEL–CHROMIA

Flow rate, l./hr.	% HD in exit gas at t°C. −78	−95	−126	−183	−195	T, °K., 1/2 eqm.
1.435	2.24	2.25	2.14	1.10	0.81	88
2.151	2.26	2.17	1.75	0.85	.64	104
2.509	2.24	2.18	1.72	0.70	.57	113
2.870	2.20	2.15	1.71	0.60	.45	117

The activation energies calculated from the tabulated data yielded for nickel–thoria, E = *ca.* 2 kcal. and for nickel–chromia, E = 0.45 kcal. The tables indicate that equilibrium at the several flow rates is attained at much lower temperatures in the case of nickel–chromia with the lower activation energy. The energy of desorption is equal to the sum of the energy of activation plus the heat of adsorption. Hence, it is very probable that these low values of the activation energy of reaction of hydrogen and deuterium are actually apparent activation energies. The smallness of the values would then be ascribable to the heterogeneous effects revealed by the adsorption–readsorption phenomena discussed in the preceding pages which would, in the respective temperature ranges involved, cause marked variations with temperature in the fraction of the total surface available for reaction. This variation would enter into the calculation of the value of the measured activation energy. The data represent results with nickel catalysts in the temperature range 0 to −195° parallel to those obtained by Smith and Taylor[9] on zinc oxide catalyst in the temperature interval 132–157°.[10]

General Discussion

The adsorption isobars as well as the contrast in results from the exchange reaction on the two catalysts studied indicate abundantly the qualitative differences between the chemisorption of hydrogen on the several surfaces. They reveal that the temperature interval in which chemisorption of hydrogen occurs is a function of the preparation of the catalyst and determined by the particular distribution of active centers over the catalyst surfaces. Sintering the catalyst as revealed by the Nickel–Kieselguhr du Pont can redistribute the active centers and raise the temperature at which chemisorption begins to be significant when this is approached from low temperatures but not on the descending curve when the necessary activation energy to fill sites is available.

We have examined the suggestion that the desorption–readsorption phenomena revealed in this study and earlier studies with oxide catalysts might be due to a penetration of the gas into the interior of the preparations as the temperature is progressively raised. We believe that we can discount immediately the view that such penetration is solution in the interior of the metal crystals. There are excellent data of Sieverts[11] on the solubility of hydrogen in nickel, which decreases with decreasing temperature and is no larger than 0.18 volume per volume of nickel at 200°. Such quantities are at least one or two orders of magnitude lower than the quantities of hydrogen involved in the desorption–readsorption phenomena here presented. That desorption should be followed by readsorption on less accessible areas of the surface under the influence of increased temperature is scarcely more credible to us when we observed that the areas occupied by the hydrogen even in the most favorable circumstances are less than those freely accessible to nitrogen in the surface area determinations at −195°. We believe that our interpretation, based on a distribution of active centers, analogous to that deduced by Eucken and Hunsmann[5] from their technique of study, including measurements of both heats of adsorption and rates of desorption, is more satisfactory.

We have attempted to interpret our data with the aid of a concept developed by Beeck, Ritchie and Wheeler[12] to explain similar observations by them on evaporated nickel films. As in our experiments, these workers find an increasing adsorption isobar with temperature rise followed by decreased adsorption at higher temperatures. Similarly the isobar adsorptions with decreasing temperatures lie above the isobar for increasing temperatures. In Beeck's experiments, however, the difference between the two values on the ascending and descending isobars is apparently independent of the surface area as measured by low-pressure adsorption of hydrogen, or by BET values using krypton. This suggests to Beeck that the difference between the two values observed at a given temperature is to be ascribed to an en-

---

[9] Smith and Taylor, THIS JOURNAL, **60**, 362 (1938).

[10] Note added in proof, Jan. 31, 1950: The low activation energies involved are interpretable, as pointed out by Rideal and Trapuell (Lyons Conference on Adsorption and Heterogeneous Kinetics, September, 1949), as the difference between the differential heats of adsorption of hydrogen at one atmosphere pressure at the two temperatures.

[11] Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).

[12] Beeck, Ritchie and Wheeler, *J. Colloid Sci.*, **3**, 505 (1948).

trance of hydrogen into the lattice structure of nickel by an exothermic reaction process or to "sorption of hydrogen into the interfaces between the crystallites." The exothermic nature of the process distinguishes it from the endothermic solubility already considered.

Our data with Nickel-Kieselguhr du Pont which we have obtained with a single sample both unsintered and subsequently sintered do not accord with Beeck's observations. At −126.5° the difference between the values on the isobars for increasing and decreasing temperatures amounts to 4.9 cc. with the unsintered material and to 8.35 cc. with the sintered material. On each of these surfaces the van der Waals adsorption at this temperature cannot exceed 1.5 cc. If one subtracts this value from the values received from the descending isobars, the amount of hydrogen chemisorbed, *plus* that taken up into the interior or interfaces (on Beeck's postulate), amounts to 17.8 cc. for the unsintered and 9.75 cc. for the sintered sample. By neither method of calculation do we obtain the identity of divergence between the two isobars that Beeck and his co-workers observe. The differences which we observe are straightforwardly interpretable on the basis of surface areas with different activation energies. The data for rates of chemisorption at single temperatures support this view. The kinetic data for the hydrogen–deuterium exchange are additional confirmation. Indeed, all our experiments with these metal catalysts are parallel to those previously recorded with oxide catalysts, the only difference being the temperature range in which the phenomena, desorption–readsorption, or measurable rates of adsorption are observed. With our nickel catalysts the principal temperature range is −126.5 to −78°. With zinc oxide it is in the range +110° upward. The Beeck interpretation could not be generalized for all our observations since that would require that hydrogen (and indeed other gases such as carbon monoxide and nitrogen) enter oxide or metal lattices or interfaces.

Acknowledgment.—One of us (H. S.) wishes to express his appreciation to the Government of Egypt for a fellowship which enabled him to carry out these investigations in fulfillment of the thesis requirements for the Ph.D. degree at Princeton University during 1947 and 1948.

Summary

1. The heterogeneity of the surfaces of six different nickel catalyst preparations has been confirmed, using the technique devised by Taylor and Liang and hydrogen as the adsorbate.
2. The adsorptions at −195° have been analyzed to determine the relative amounts of van der Waals adsorption and chemisorption of hydrogen and to show that different preparations adsorb different relative amounts of the two types.
3. The velocity of the hydrogen–deuterium exchange reaction on nickel–chromia and nickel–thoria has been studied to support these findings. There are marked differences in rates with activation energies of 0.45 and 2 kcal., respectively.
4. Our data do not support an interpretation based either on solubility of hydrogen in the lattice or an exothermic entry of hydrogen into the nickel lattice at temperatures between −195 and −78°.

PRINCETON, NEW JERSEY RECEIVED APRIL 12, 1949

[CONTRIBUTION FROM THE ATLANTIC REFINING COMPANY]

Nitrous Oxide as a Constituent of the Atmosphere

BY R. L. SLOBOD AND M. E. KROGH

The presence of nitrous oxide in soil gas samples has previously been established by the mass spectrometer as shown by R. A. Brown, *et al.*[1] Consideration of these findings by the present authors suggested nitrous oxide as a possible constituent of the atmosphere which, although previously suspected,[2,3] had not been isolated and confirmed, in part at least, because of the difficult analytical problem presented by this relatively inert gas. Because of the unequivocal nature of its findings, the mass spectrometer was chosen in this case to establish the presence of nitrous oxide in the atmosphere. A nitrous oxide concentrate obtained by fractional condensation of atmospheric samples improves the precision of the mass spectrometer analyses, making possible quantitative determinations.

Results.—Ten samples of air from six locations including five in Texas (two in Dallas, two in East Texas, and one in Irving) and one in Wyoming have been analyzed using the methods and apparatus described below. The significant data on each run including location, amount of gas sampled, amount of condensed gas after purification in high vacuum system, amount of nitrous oxide, per cent. of nitrous oxide in original sample, and finally, the deviation of each value from the mean are given in Table I. An appreciable variation in nitrous oxide content was observed, the extremes being 0.000025% and 0.000067%.

---

(1) Brown, *et al.*, *Anal. Chem.*, **20**, 396–401 (1948).

(2) Adel, *Astrophys. J.*, **90**, 627 (1939); **93**, 509 (1941); *Science*, **103**, 280 (1946).

(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, 1931, p. 12.