In Fig. 9 this limiting value is nearly approached for $\bar{n} = 15$. Here in addition to the unimolecular layer one-third of the remaining 13 layers is adsorbed at saturation, giving a total of $v/v_m = 5.33$. That large capillaries according to the present theory are not completely filled up even near p_0 is probably due to the crude manner in which the fluctuations were calculated. We expect that one would get completely full capillaries at p_0 if the interaction of each molecule with its neighbors were to be taken into account in detail. For smaller capillaries with not too small g values the present theory predicts that the capillaries are practically full at p_0 and the above difficulty does not arise.

We believe that the present theory has two advantages over the capillary condensation theory. In the first place it is a unified theory that includes unimolecular adsorption, multimolecular adsorption on free surfaces, and the enhanced adsorption that takes place in capillaries; whereas the capillary condensation theory only deals with the last of these three phenomena. In the second place the present theory supplies an isotherm equation that can describe all the five different types of van der Waals adsorption isotherms and can be tested by experiment. The Kelvin equation, on the other hand, is not an isotherm equation; at best it allows only the calculation of one isotherm from another. A modified form of the capillary condensation theory, proposed by Patrick and McGavack,[17] although successful in many cases in fitting experimental data, is purely an empirical equation.

Summary

The isotherm equation derived in a previous paper for the multimolecular van der Waals adsorption of gases has been extended to cover two additional cases: (1) when the heat of adsorption in the first layer is smaller than the heat of liquefaction, (2) when the capillaries of the adsorbent are completely filled, the heat of adsorption in the last layer is greater than the heat of liquefaction. The new equation covers all the five types of adsorption isotherms found in the literature. Comparison is made with experimental data and with the capillary condensation theory.

(17) McGavack and Patrick, THIS JOURNAL, **42**, 946 (1920).

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Chemisorptions of Gases on Iron Synthetic Ammonia Catalysts[1]

BY STEPHEN BRUNAUER AND P. H. EMMETT[2]

Introduction

In several previous publications we reported the occurrence of chemisorptions[3] of carbon dioxide, oxygen, carbon monoxide,[4,5,6] hydrogen,[6,7] and nitrogen[8] on various promoted and unpromoted iron catalysts, and described a method[5,6] whereby the chemisorptions of carbon monoxide and carbon dioxide in connection with low temperature van der Waals adsorption measurements[9] can be utilized to determine the fraction of the surface covered by the aluminum oxide and the alkali promoter in singly and doubly promoted catalysts. The present experiments were undertaken to study further the concentration and distribution of the promoters on the surfaces of catalysts, to ascertain the nature of the binding of the chemisorbed gas to the surface, and in general to obtain additional information about the nature of the catalyst surface and the mechanism of promoter action.

Experimental

Most of the chemisorption experiments were performed on three iron synthetic ammonia catalysts: unpromoted catalyst 973 (containing 0.15% Al_2O_3 as impurity), singly promoted catalyst 954 (containing 10.2% Al_2O_3), and doubly promoted catalyst 931 (containing 1.59% K_2O and 1.3% Al_2O_3). Whenever in this paper we refer to the three catalyst types, or to the pure iron, singly promoted, or

(1) Not subject to copyright.

(2) Present address: Johns Hopkins University, Baltimore, Md.

(3) By "chemisorption" we refer to adsorptions that involve forces that are greater than those active in physical adsorption or in condensation, and approach in magnitude the forces active in chemical reactions (see reference 9). In this sense the term includes "activated adsorption" as well as chemical adsorptions that proceed so rapidly that no activation energies can be measured.

(4) Brunauer and Emmett, THIS JOURNAL, **57**, 1754 (1935).

(5) Emmett and Brunauer, *ibid.*, **59**, 310 (1937).

(6) Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

(7) Emmett and Harkness, *ibid.*, **57**, 1631 (1935).

(8) Emmett and Brunauer, *ibid.*, **56**, 35 (1934).

(9) Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

doubly promoted catalyst without specifying its number, we are referring to these three catalysts. We performed a few experiments on three other catalysts: catalyst 930 (containing 1.07% K_2O), singly promoted catalyst 424 (containing 1.03% Al_2O_3 and 0.19% ZrO_2), and doubly promoted catalyst 958 (containing 0.35% Al_2O_3 and 0.08% K_2O). Twenty-five cc. samples of each of the six catalysts were used; the mesh size of the granules was 8–14. The weights and reduction schedules of the six catalysts for the present work are given in Table I. The high pressure activities as determined previously on other samples of the same catalysts, following standard reduction and testing procedures, are shown in the last column.

TABLE I

Catalyst	Unreduced oxide, g.	Reduction schedule Time hr. Temp., °C.	Activity % NH_3 at 450°, 100 atm. and 5000 space velocity
424	68.1	48 at 350 to 450	Not detd.
		48 more at 450 to 500	
930	64.5	48 between 350 and 450	5.3
931	61.0	18 at 300 to 350	12.3
		65 more at 350 to 450	
		18 more at 450 to 530	
954	66.8	48 at 350 to 450	8.2
		48 more at 450 to 500	
958	71.9	36 at 350 to 450	10.4
		36 more at 450 to 500	
973-III	66.2	92 up to 400	3.3

The adsorption apparatus, the preparation and purification of the gases, the nature of the constant temperature baths, and experimental procedure have been described elsewhere.[5,6,8] The adsorption measurements were carried out in the usual manner; the dead space was determined by means of helium. To avoid the possibility of contamination of the catalyst surface by air diffusing into the apparatus overnight, the catalyst was reduced every morning for one hour in a stream of 500 cc. of hydrogen per minute. This reduction was followed by a one-hour evacuation of the catalyst at the same temperature with a mercury diffusion pump. Both reduction and evacuation were carried out at 400° for the unpromoted catalyst, and at 500° for the promoted catalysts. After evacuation the catalyst always was cooled in helium to the desired low temperature of the adsorption run; after temperature equilibrium was established the helium was removed by evacuation down to a pressure of 10^{-4} mm.

In calculating the adsorption correction was always made for the deviation from the ideal gas laws of the gas contained in the dead space around the catalyst, as previously described.[5]

Results

The experiments performed on each catalyst consisted of investigating the chemisorptions individually and, as far as possible, studying the effect of each chemisorption upon every other; the effects of a few combinations of two or three chemisorptions were also investigated. The results included in the following fifteen tables represent only a fraction of the experiments performed; practically every run was checked, some of them three or four times. Throughout all of the chemisorption experiments concurrent surface area measurements were made by means of the van der Waals adsorption of nitrogen at $-183°$.[4,6] The columns in the tables headed "nitrogen monolayer" represent the number of cubic centimeters of nitrogen necessary to cover the entire catalyst surface with a complete monomolecular adsorbed layer. The decrease in the value of the nitrogen monolayer on a given catalyst is due to gradual sintering.

Discussion

A study of the results obtained shows at once the extreme complexity of even the pure iron catalyst surface; correlation of all observations becomes difficult even on this catalyst. It goes without saying that the results on the singly promoted catalyst with both iron atoms and aluminum oxide molecules on its surface and the doubly promoted catalyst with iron atoms and possibly aluminum oxide, potassium oxide, and potassium aluminate surface molecules are even more difficult to interpret.

I. The Location of the Chemisorptions on the Catalyst Surface.—Tables II and III show respectively the extent of chemisorption of carbon monoxide and carbon dioxide on the various catalysts. The results are interpretable in terms of our previously expressed conclusion[6] that carbon dioxide is chemisorbed only by the alkali-containing surface molecules, whereas the carbon monoxide is held by the surface iron atoms. The chemisorption of carbon dioxide on the pure iron catalyst and the aluminum oxide promoted catalyst is probably due to undisclosed traces of alkali, since for catalyst 958 only 0.08% K_2O causes a coverage of about 27% of the surface with alkali. The fact that the ratio of chemisorbed carbon monoxide to physically adsorbed nitrogen is greater than unity on the pure iron catalyst is explained easily by the expected relative packing of the two molecules on the surface, one chemisorbed carbon monoxide molecule being held by each iron atom.[10]

The locations of chemisorbed carbon monoxide and carbon dioxide molecules could be inferred from the magnitude of their adsorptions compared to the total nitrogen monolayer. It is not

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[10] See discussion in section 4, also footnote on page 1561 in reference (6).

TABLE II

CHEMISORPTION OF CARBON MONOXIDE

Catalyst	Nitrogen monolayer, cc. at S. T. P.	Carbon monoxide chemisorption, cc. at S. T. P.	Temp. of CO chemisorption, °C.	Ratio-$\frac{\text{CO chemisorption}}{\text{N}_2\text{ monolayer}}$
973	15.5	19.4	− 78	1.25
	15.5	17.1	−183	1.10
	13.2	17.2	− 78	1.30
	13.2	14.9	−183	1.13
	10.8	12.8	−183	1.18
	10.4	13.0	− 78	1.25
954	121	58	− 78	0.48
	121	50	−183	.41
	102	49.5	− 78	.49
	102	44	−183	.43
	83	41.7	− 78	.50
	83	36	−183	.43
424	104	68	−183	.65
931	30.0	15.2	− 78	.51
	30.0	13.3	−183	.44
	29.0	14.3	− 78	.49
	28.0	12.1	−183	.43
	27.4	13.4	− 78	.49
958	29.8	21.5	− 78	.72
	29.8	18.6	−183	.62

TABLE III

CHEMISORPTION OF CARBON DIOXIDE AT −78°

Catalyst	Nitrogen monolayer, cc. at S. T. P.	Carbon dioxide chemisorption, cc. at S. T. P.	Ratio $\frac{\text{CO}_2\text{ chemisorption}}{\text{N}_2\text{ monolayer}}$
973	13.2	1.7	0.13
954	108	5.0	.05
424	104	8.0	.08
930	5.7	4.2	.74
931[a]	32.7	21.5	.66
	30.7	19.4	.63
	30.2	17.6	.58
	29.8	16.6	.56
958	29.8	8.0	.27

[a] On catalyst 931 a CO_2 chemisorption run was performed at 0°. In this run the nitrogen monolayer was 30.7 cc., the CO_2 chemisorption 21.2 cc. and the ratio of CO_2/N_2 was 0.69.

so simple, however, for the two hydrogen,[11] the nitrogen and the oxygen chemisorptions. All of these, naturally, must take place on the surface iron atoms since they are found on the unpromoted catalyst. However, for the promoted catalysts one might ask whether these chemisorptions are located only on the iron atoms or also on the promoter molecules. We shall advance now some arguments showing that these four chemisorptions are located on the iron atoms *only*, and not on the promoter.

Oxygen appears to be located on the iron atoms, but not on the alkali promoter molecules, for, as shown in Tables XII and XIII, the oxygen chemisorption has no effect on the carbon dioxide chemisorption but a marked effect on the carbon monoxide chemisorption. Although we cannot advance a similar proof regarding the surface aluminum oxide, it seems to us safe to assume that aluminum oxide is no more capable of chemisorbing oxygen than are potassium oxide and $K_2Al_2O_4$.

Tables VII and VIII show that when the entire iron surface is covered with either chemisorbed carbon monoxide or oxygen on any of the three catalyst types, the Type A hydrogen adsorption is almost completely eliminated. Since oxygen and carbon monoxide are chemisorbed only on the iron atoms, this must be true of Type A hydrogen also.

The location of nitrogen and Type B hydrogen cannot be determined according to any of the above methods since these adsorptions take place at higher temperatures and consequently the effect of chemisorbed carbon monoxide, carbon dioxide or oxygen on them cannot be studied. However, one can study the reverse effects. Table VIII shows that the inhibiting effect of nitrogen on Type A hydrogen is roughly one to one. This indicates that the chemisorbed nitrogen is located on the same points of the surface as the Type A hydrogen adsorption, that is, on the iron atoms only. Furthermore, Tables X and XIII show that the effect of both Type A and Type B hydrogen adsorptions is probably zero on the carbon dioxide chemisorption after equilibrium is established, but is definitely inhibiting on the carbon monoxide chemisorption. The Type B hydrogen adsorption has roughly the same inhibiting effect as Type A on the carbon monoxide chemisorption on each of the three catalysts. Thus apparently Type B adsorption is also located only, or at least predominantly, on the surface iron atoms.

[11] Two types of activated adsorption of hydrogen have been found to exist on iron catalysts: one occurs rapidly at −78°, the other, at a comparable rate, at about 100°.[7] The former was designated Type A, the latter Type B adsorption. The −78° adsorption of hydrogen in the present work undoubtedly represents pure Type A; the 100° adsorption is predominantly, but not entirely, Type B. We do not know at present exactly what fraction of the 100° adsorption is Type A. For the sake of convenience we have called the 100° adsorption throughout the entire paper Type B. It should be noted also that in the runs where the effect of the chemisorption of hydrogen at 100° on other chemisorptions was studied the catalyst was necessarily evacuated with a Toepler pump down to a few mm. pressure; in all other runs the 100° hydrogen adsorption was measured at 760 mm. Since the heat of adsorption of Type A hydrogen is probably lower than that of Type B hydrogen, the 100° adsorption at low pressure probably contains a smaller fraction of Type A hydrogen than at atmospheric pressure.

TABLE IV

CHEMISORPTION OF HYDROGEN[a]

Catalyst	Nitrogen monolayer, cc. at S. T. P.	CO chemisorpt. at −78°, cc. at S. T. P.	Chemisorption of hydrogen		Volume ads., cc. at S. T. P. (at 1 atm.)	Ratio	
			Temp., °C.	Time		$\frac{H_2 \text{ Chemisorpt.}}{\text{CO Chemisorpt.}}$	$\frac{\text{Type A hydrogen}}{\text{Type B hydrogen}}$
973	15.5	19.4	−78	30 min.	7.33	0.38	0.98
	15.5	19.4	100	1 hr.	7.50	.39	
	12.8	16.7	−78	45 min.	6.65	.40	1.04
	12.8	16.7	100	1 hr.	6.40	.38	
	10.2	13.0	−78	1 hr.	5.53	.43	1.02
			−78	18 hr.	7.79	.60	
	10.2	13.0	100	3 min.	5.05	.39	
			100	2.5 hr.	5.54	.43	
		5.67	−78	2.5 hr.	3.20	.56	1.24
			−78	20 hr.	3.67	.65	1.24
	..	5.56	100	1 hr.	2.57	.46	
			100	18.5 hr.	2.95	.53	
	3.1	..	−78	1.5 hr.	2.25		1.43
			−78	20 hr.	2.75		1.62
	3.1	..	100	1 hr.	1.57		
			100	18.25 hr.	1.70		
954	102	49.5	−78	1 hr.	25.6	.52	0.88
	102	49.5	100	1 hr.	29.2	.59	
	83	41.6	−78	3 min.	21.7	.52	1.18
			−78	30 min.	25.0	.60	1.00
			−78	1 hr.	25.2	.61	0.92
			−78	20.25 hr.	25.8	.62	.67
	83	41.6	100	3 min.	18.3	.44	
			100	30 min.	25.0	.60	
			100	1 hr.	27.4	.66	
			100	18 hr.	38.4	.92	
931	30.7	15.9	−78	1 hr.	15.0	.94	.99
	30.7	15.9	100	2 hr.	15.2	.96	
	26.3	14.0	100	1 hr.	12.3	.88	1.07
			100	18 hr.	13.9	.99	0.99
	26.3	14.0	−78	1 hr.	13.2	.94	
			−78	20 hr.	13.8	.99	
958	29.8	21.5	−78	1 hr.	10.7	.50	

[a] In the table we have listed only the runs performed at −78° and 100°. The −78° adsorption represents pure Type A hydrogen; the 100° adsorption is, for simplicity, called Type B, although it contains some Type A hydrogen.

Several runs were performed in which the amount of the total hydrogen chemisorption (Type A plus Type B) was investigated. The maximum amount of mixed adsorption that we obtained on Catalyst 954 was 68.4 cc., the CO chemisorption at −78° was 58 cc., the ratio of total hydrogen to CO was 1.18. The maximum mixed adsorption on Catalyst 931 was 19.4 cc., the CO chemisorption at −78° was 13.6 cc., the ratio of hydrogen to CO was 1.42.

II. The Nature of the Adsorbed Particles.—One question of great interest is whether chemisorbed particles remain molecules or dissociate into atoms on the catalyst surface. We believe that the results of our experiments answer this question quite definitely for all six chemisorptions investigated, and show that in the temperature ranges studied the chemisorptions of carbon monoxide and carbon dioxide are molecular, whereas the chemisorptions of both types of hydrogen as well as nitrogen and oxygen are atomic.

The existence of carbon monoxide as a molecular rather than a dissociated form on an iron surface would be expected because of the known readiness of formation of iron–carbon monoxide bonds in iron pentacarbonyl. It will suffice, therefore, to point out very briefly four definite additional indications that the adsorption of carbon monoxide on iron is molecular. (1) The volume of carbon monoxide adsorbed (Table II) is consistent with its being molecular rather than atomic (see footnote, page 1561 in reference (6)). (2) When an iron catalyst on which carbon monoxide is chemisorbed is slowly heated, a mirror forms on the glass adsorption bulb indicating that the chemisorbed carbon monoxide molecules react

TABLE V

CHEMISORPTION OF NITROGEN

Catalyst	Nitrogen monolayer, cc. at S. T. P.	CO chemisorpt. at −78°, cc. at S. T. P.	Chemisorption of nitrogen[a]			Ratio	
			Volume ads., cc. at S. T. P. (at 1 atm.)	Temp., °C.	Time	N_2 Chemisorpt. / CO Chemisorpt.	N_2 Chemisorpt. / N_2 Monolayer
973	12.8	16.7	3.6	395	30 min.	0.22	0.28
		14.6	3.6	395	30 min.	.25	
	10.2	13.0	3.2	395	1 hr.	.25	.31
	7.2		2.4	392	1 hr.		.33
	4.2		2.1	393	1 hr.		.50
954	102	49.5	12.8	440	34 min.	.26	.13
	83	41.7	14.3	391	1 hr.	.34	.17
931	31.2	16.4	8.1	392	34 min.	.49	.26
	30.2	15.4	7.6	391	34 min.	.49	.25
	26.3	14.0	7.2	391	1 hr.	.51	.27

[a] When the catalyst is cooled down from the temperature of the run to room temperature a slight additional adsorption takes place: the adsorption rises from 3.6 to 3.9 cc. for the unpromoted, 14.3 to 14.6 cc. for the singly promoted, and 7.6 to 7.8 cc. for the doubly promoted catalyst.

with the surface iron atoms to form iron pentacarbonyl. (3) A layer of chemisorbed carbon monoxide almost completely eliminates Type A hydrogen (Table VII). At −183° such a chemisorbed carbon monoxide layer reduces the oxygen sorption by more than 90% (Table XIV). (4) Carbon monoxide, though adsorbed only on iron atoms, is able to inhibit carbon dioxide adsorption on adjoining promoter molecules (Table XVI). The large carbon monoxide molecules overlap from the iron atoms to the neighboring alkali molecules, thereby inhibiting the chemisorption of carbon dioxide. No such inhibition would be expected if the chemisorbed particles were small, that is, atoms.

The expected molecular rather than dissociative chemisorption of carbon dioxide on the alkali promoter molecules is confirmed by two types of evidence. (1) Any products of dissociation of carbon dioxide would be held strongly by iron atoms, yet the chemisorption of carbon dioxide decreases with increasing ratios of iron atoms to alkali promoter molecules (Table III). (2) Carbon dioxide chemisorbed on the promoter molecules inhibits chemisorption of carbon monoxide (Table XV) and slows down the rate of Type A hydrogen adsorption (Table VII) on the adjoining iron atoms. Such overlapping effects can be expected only from chemisorbed molecules and not from atoms, as pointed out before.

The atomic nature of nitrogen adsorption and of Types A and B hydrogen adsorption appears established by their comparatively small inhibitive effects on the chemisorption of carbon monoxide at −183 and −78° as shown in Tables X and XI. If either a nitrogen or hydrogen mole-

TABLE VI

CHEMISORPTION OF OXYGEN[a]

Catalyst	Nitrogen monolayer, cc. at S. T. P.	CO chemisorption at −78°, cc. at S. T. P.	Chemisorpt. of oxygen		Ratio	
			Cc. at S. T. P.	Temp., °C.	O_2 Chemisorpt. / CO Chemisorpt.	O_2 Chemisorpt. / N_2 Monolayer
973	5.5	6.0	25	−183	4.2	4.5
	5.5	6.0	46	− 78	7.7	8.4
954	96	46	519	− 78	11.3	5.4
	94	44.5	376	− 78	8.5	4.0
	92	43.5	318	− 78	7.3	3.5
	83	41.7	242	− 78	5.8	2.9
	83	41.7	322	− 78	7.7	3.9
931	29.6	14.9	104.5	− 78	7.0	3.5
	28.0	13.8	94.7	− 78	6.9	3.4
	27.4	13.4	48.3	−183	3.6	1.8
			54.3	−183	4.1	2.0
	25.6	12.3	94.9	− 78	7.7	3.7
			89.5	− 78	7.3	3.5

[a] The ratios in the last two columns indicate that the adsorption here is not monomolecular; several of the top layers are oxidized. The word "chemisorption," therefore, is not strictly applicable here.

TABLE VII

EFFECT OF THE CHEMISORPTIONS OF CARBON MONOXIDE AND CARBON DIOXIDE ON TYPE A HYDROGEN ADSORPTION

Catalyst	Nitrogen monolayer, cc. at S. T. P.	Type A hydrogen adsorption on pure surface Cc. at S. T. P.	Time	Inhibiting chemisorption, cc. at S. T. P.	Type A hydrogen adsorption on top of inhibitor Cc. at S. T. P.	Time
973	14.4	7.19[a]	3 min.	18.3 CO[a]	0.0	3 min.
		7.33	30 min.		.0	30 min.
954	102	25.6	1 hr.	52 CO	.4	3 min.
					.5	23 min.
931		12.6	30 min.	14.7 CO	.0	30 min.
		12.6	30 min.	4.7 CO	7.9	30 min.
		13.1	1 hr.	13.4 CO	.0	32 min.
					.2	18.5 hr.
931	30.7	12.2	3 min.	21.2 CO_2[b]	.2	3 min.
		15.0	1 hr.		.6	30 min.
					.9	55 min.
					8.8	17.5 hr.
931	30.7	12.2	3 min.	19.0 CO_2	0.8	3 min.
		15.0	1 hr.		2.6	30 min.
					3.8	50 min.
					12.2	16 hr.
958	29.8	10.5	12 min.	8.0 CO_2	6.5	12 min.
		10.7	52 min.		8.9	52 min.
					9.6	18 hr.

[a] Type A hydrogen and carbon monoxide was adsorbed always at −78°. [b] Carbon dioxide was adsorbed on the catalysts at −78°, except the 21.2 cc. which was adsorbed at 0°.

TABLE VIII

EFFECT OF THE CHEMISORPTIONS OF OXYGEN AND NITROGEN ON TYPE A HYDROGEN

Catalyst	Nitrogen monolayer, cc. at S. T. P.	Type A hydrogen adsorption[a] on pure surface Cc. at S. T. P.	Time	Inhibiting[b] chemisorpt., cc. at S. T. P.	Type A hydrogen on top of inhibitor Cc. at S. T. P.	Time	Ratio[c]: Decrease / N_2 Chemisorpt.
973	5.5	3.4	30 min.	42 O_2	0.17	30 min.	
954	99	21.5	3 min.	519 O_2	1.0	8 min.	
		26.2	20 min.		1.3	30 min.	
		26.9	1.25 hr.		2.5	18 hr.	
931		12.2	30 min.	31.8 O_2	4.8	30 min.	
931	29.8	11.0	3 min.	100.6 O_2	0.2	3 min.	
		14.1	1 hr.		0.3	1 hr.	
973	12.8	6.65	45 min.	3.9 N_2	2.34	48 min.	1.10
973	4.2	3.0	2 hr.	2.1 N_2	0.4	1 hr.	
		3.1	3 hr.		0.9	3 hr.	1.05
954	99	21.5	3 min.	13.5 N_2	6.8	3 min.	1.09
		26.2	20 min.		14.2	33 min.	0.91
		26.9	1.25 hr.		14.7	1 hr.	.90
954	83	21.7	3 min.	14.6 N_2	5.8	3 min.	1.09
		25.0	30 min.		11.5	31 min.	0.93
		25.2	1 hr.		11.9	1.25 hr.	.91
		25.9	21.25 hr.		13.2	20.75 hr.	.87
931	31.2	12.2	3 min.	8.1 N_2	1.8	3 min.	1.28
		15.0	1 hr.		5.3	1 hr.	1.20
					5.7	5 hr.	
931	26.3	11.8	3 min.	7.4 N_2	2.9	3 min.	1.20
		13.3	1 hr.		4.4	1 hr.	1.20
		13.8	20 hr.		5.0	20 hr.	1.19

[a] All Type A hydrogen runs were performed at −78°. [b] Oxygen was adsorbed on the catalysts at −78°, except the 31.8 cc. which was adsorbed at −183°. Nitrogen was adsorbed at 392–395°, except the 13.5 cc. which was adsorbed at 439°. [c] This column gives the ratio of the decrease in the number of cc. of Type A hydrogen adsorption (caused by the nitrogen chemisorption) to the number of cc. of nitrogen chemisorption put on the surface.

TABLE IX

EFFECT OF THE CHEMISORPTION OF NITROGEN ON TYPE B HYDROGEN ADSORPTION

Catalyst	Nitrogen monolayer, cc. at S. T. P.	Type B hydrogen adsorption[a] on pure surface		Inhibiting N_2[b] chemisorpt., cc. at S. T. P.	Type B hydrogen on top of inhibitor		Ratio[c]: $\frac{\text{Decrease}}{N_2\text{ Chemisorpt.}}$
		Cc. at S. T. P.	Time		Cc. at S. T. P.	Time	
973	12.8	6.26	30 min.	3.9	3.95	30 min.	0.59
		6.40	1 hr.		4.3	1 hr.	.54
973	10.2	4.7	3 min.	3.45	1.4	3 min.	.96
		5.5	1 hr.		4.2	1 hr.	.38
		7.8	18 hr.		5.5	16 hr.	.67
973	7.2	3.0	3 min.	2.5	1.3	3 min.	.68
		3.5	1 hr.		2.5	1 hr.	.40
		4.6	17 hr.		3.3	16.5 hr.	.52
954	83	25.8	1 hr.	14.7	26.5	1 hr.	− .05
		27.1	1.5 hr.		29.3	1.5 hr.	− .15
		37.2	19 hr.		44.8	21.5 hr.	− .52
954	83	24.1	30 min.	14.5	23.2	30 min.	.06
		26.5	1 hr.		27.0	1 hr.	− .03
		37.0	18 hr.		41.5	18 hr.	− .31
954	83	18.3	3 min.	13.6	10.9	3 min.	.54
		25.1	30 min.		23.8	31 min.	.10
		27.4	1 hr.		28.9	1.25 hr.	− .11
		38.4	18 hr.		42.1	18 hr.	− .27
931	31.2	12.7	3 min.	8.0	4.1	3 min.	1.07
		14.2	30 min.		7.2	30 min.	0.88
		14.7	1 hr.		7.9	1 hr.	.85
931	26.3	10.7	3 min.	7.5	3.4	3 min.	.97
		12.3	1 hr.		6.2	1 hr.	.80
		13.9	18 hr.		8.4	20 hr.	.73

[a] All hydrogen runs were performed at 100°; it was assumed that at this temperature all adsorption is Type B. [b] The inhibiting nitrogen was chemisorbed at 391–395°. [c] This column gives the ratio of the decrease in the number of cc. of Type B adsorption (caused by the nitrogen chemisorption), to the number of cc. of nitrogen put on the surface as inhibitor. The negative ratios for the singly promoted catalyst show that there was in this case an *increase* in the Type B adsorption caused by the nitrogen, instead of a decrease. The two other catalysts show strong inhibition.

cule were adsorbed as such on an iron atom, it would be physically impossible for carbon monoxide to be adsorbed on the same iron atom. There simply would not be room for both the nitrogen molecule and the carbon monoxide molecule. Corroborative evidence of the atomic nature of chemisorbed hydrogen and nitrogen is to be found in the absence of any appreciable inhibitive effect by them on the chemisorption of carbon dioxide (Table XIII), in marked contrast with the strong inhibiting effect of the molecular carbon monoxide chemisorption.

The last chemisorption to be considered is that of oxygen (Table VI). If the number of carbon monoxide molecules chemisorbed is approximately equal to the number of iron atoms on the surface, then the number of oxygen atoms sorbed at −78° is about 15 times as great. Clearly, we cannot speak here strictly about chemisorption; actually at least the outer 7 or 8 layers of the catalyst are oxidized in the sorption process. Further evidence for this is found in the very high heat evolution (about 110 kilocalories per mole of oxygen), found by Dr. R. A. Beebe (unpublished), that was obtained when oxygen was admitted at −183° to catalyst 973 or 931 in sufficient quantities to oxidize several layers of iron to FeO. Oxygen that thus penetrates several layers deep into the iron lattice instantly at −183° obviously cannot be held as molecules; it must be in the atomic or, more probably, the ionic form. Table XIII shows that the inhibiting effect of oxygen on carbon dioxide is zero, quite in line with the idea that the former is not molecular on the iron catalysts.

The effect of oxygen on the carbon monoxide chemisorption, given in Table XII, deserves a close scrutiny. While the inhibiting effects of chemisorbed nitrogen and hydrogen on carbon monoxide are either slight or zero, the inhibiting effect of oxygen on carbon monoxide is very strong. Thus on the oxygen covered surface of the singly promoted catalyst at −78° after four minutes only one-third as much carbon monoxide

TABLE X

EFFECT OF TYPE A AND TYPE B HYDROGEN ON THE CARBON MONOXIDE CHEMISORPTION

Catalyst	Chemisorption of CO on pure surface		Inhibiting chemisorption,[b] cc. at S. T. P.	CO Chemisorption on top of inhibitor, cc. at S. T. P.	Decrease in CO chemisorpt., cc. at S. T. P.	Decrease per hydrogen atom[c]
	Cc. at S. T. P.	Temp., °C.[a]				
973	17.7	−78	6.3 Type A	16.5	1.2	1/10.5
	14.8	−183	6.8 Type A	12.3	2.5	1/5.4
	4.9	−183	3.0 Type A	3.9	1.0	1/6.0
	4.6	−183	1.3 Type B	4.3	0.3	1/8.7
954	44.0	−183	26.0 Type A	39.5	4.5	1/11.5
	49.5	−78	40.0 Mixed[d]	42.5	7.0	1/11.4[d]
	41.7	−78	21.1 Type A	39.3	2.4	1/17.6
	41.7	−78	26.5 Type B	38.7	3.0	1/17.7
	36.0	−183	20.8 Type A	32.5	3.5	1/11.9
	36.0	−183	26.8 Type B	32.0	4.0	1/13.4
931	14.4	−183	14.0 Type A	11.5	2.9	1/9.7
	14.4	−183	21.8 Mixed	10.1	4.3	1/10.1
	13.5	−78	10.8 Type A	13.0	0.5	1/43.2
	11.2	−183	11.5 Type A	9.1	2.1	1/11.0
	12.4	−78	14.9 Mixed	11.1	1.3	1/22.9

[a] These temperatures also refer to the CO chemisorption runs on top of the hydrogen adsorptions. [b] The Type A hydrogen was adsorbed at −78°, the Type B hydrogen at 100°. Where "mixed" hydrogen is indicated first the Type B hydrogen was adsorbed at some higher temperature, then the temperature was lowered to −78° and the catalyst was allowed to come to equilibrium with the hydrogen. [c] This column gives the decrease in the CO chemisorption per hydrogen *atom;* thus the fraction 1/10.5 means, for example, that one chemisorbed CO molecule is eliminated per 10.5 chemisorbed hydrogen atoms. [d] We performed on the singly promoted catalyst a run testing the combined inhibitory effect of nitrogen, Type A and Type B hydrogen on the CO chemisorption. It was performed immediately after the run in which 40 cc. of Type A and Type B hydrogen was used as inhibitor. First 12.4 cc. of nitrogen was put on the catalyst at 440°, then 37.9 cc. of mixed Type A and Type B hydrogen in the usual manner; thus altogether 50.3 cc. of inhibiting gas was adsorbed on the surface. The decrease in CO chemisorption at −78° was 9.0 cc., which corresponds to the elimination of one CO molecule per 11.2 adsorbed atoms, hydrogen or nitrogen.

is chemisorbed as corresponds to the equilibrium adsorption on the pure surface; even after twenty-three hours the adsorption is only about half of that equilibrium value. The most reasonable explanation that occurs to us is that oxygen here is in the ionic rather than atomic form. This is suggested by the fact that the oxides of iron are ionic structures, the nitrides non-ionic. Apparently the nitrogen and hydrogen atoms do not alter markedly the activity of the surface iron atoms, but oxygen ions bring about a profound alteration. The small carbon monoxide chemisorption that actually does take place is probably due to inward migration of the surface oxygen. In the half hour that is necessary to evacuate the oxygen from the gas phase, about one-third of the oxygen ions seems to migrate inward, leaving one-third of the surface of the singly promoted catalyst free to chemisorb carbon monoxide; in the next twenty-three hours some further inward migration takes place, resulting in further adsorption of carbon monoxide. The observed increase in oxygen chemisorption at −78° overnight is approximately equivalent to this slow increase in carbon monoxide chemisorption. At −183° the inward migration of oxygen ions is much slower; consequently, we find that only 7% of the surface iron atoms is capable of chemisorbing carbon monoxide on the doubly promoted catalyst after two hours.

III. Concentration and Distribution of the Promoters on the Catalyst Surface.—It has been pointed out in previous publications[5,6] that the chemisorptions of carbon monoxide and carbon dioxide can be utilized to determine the promoter concentration on the catalyst surface. Carbon monoxide is chemisorbed on the iron atoms only, not on the promoter molecules; carbon dioxide is adsorbed on the alkali promoter only, not on the iron atoms, nor on the aluminum oxide molecules. These facts enable us to estimate the percentage covering of the surface with promoter molecules.

The data obtained in the present work afford added confirmation of this picture and also throw some light on the distribution of the promoters on the catalyst surface.

For the singly promoted catalysts 954 and 424 the data in Table II confirm our previously expressed conclusion[6] that about 55% of the sur-

TABLE XI

EFFECT OF THE CHEMISORPTION OF NITROGEN ON THE CHEMISORPTION OF CARBON MONOXIDE

Catalyst	Inhibiting N$_2$[a] chemisorption, cc. at S. T. P.	Total CO adsorption, cc. at S. T. P.[b] On pure surface	On top of nitrogen	Temp.,[b] °C.	Pressure[b] of CO, mm.	Decrease in total CO adsorption,[c] cc. at S. T. P.
973	3.6	25.8 (Run 1)	24.4 (Run 2)	−183	200	0.8
		24.6 (Run 3)		−183	200	
973	3.6	24.6 (Run 3)	24.4 (Run 2)	−183	200	0.6
			23.5 (Run 4)	−183	200	
954	13.3	54.2	54.2	− 78	56	0
		63.2	62.2	− 78	296	1.0
954	13.0	142.0	142.0	−183	80	0
		163.0	163.0	−183	231	0
931	8.3	45.8	45.8	−183	70	0
		52.1	52.1	−183	256	0
		55.8	55.8	−183	364	0
931	7.4	20.2	19.6	− 78	302	0.6
		22.4	22.0	− 78	581	0.4

[a] The nitrogen was chemisorbed on catalysts 973 and 931 at 391 to 395°, on catalyst 954 at 439°. [b] These columns represent the total adsorption of CO, not the chemisorption alone. Since in the case of the pure iron catalyst the surface decreased in each consecutive run, the order in which the runs were performed is also indicated. The temperature and pressure refer to the CO adsorption on both the pure and "poisoned" surface. [c] Since this column gives the decrease in the total adsorption (including van der Waals), obviously the decrease in the chemisorption of CO is either equal to or less than this quantity. One can, therefore, safely conclude that the chemisorbed nitrogen has practically no influence on the CO chemisorption either at −78 or −183° on any of the three types of catalysts.

face of 954 and 35% of 424 is covered with aluminum oxide promoter molecules. When one takes into consideration the fact that the packing of chemisorbed carbon monoxide is denser by about 25% than that of physically adsorbed nitrogen and that at −183°, and perhaps even at −78°, a small part of the iron surface may still be free of carbon monoxide, it seems probable that the coverage of 954 by aluminum oxide is 55 ± 5%, and of 424, 35 ± 5%, even though chemical analysis gives only 10.2% zirconium oxide for catalyst 954, and 1.03% zirconium oxide and 0.19% zirconium oxide for catalyst 424.

The fact that potassium oxide evaporates much more readily from catalysts containing no aluminum oxide than from doubly promoted catalysts (see footnote, page 314 of reference (2)) indicates that the potassium oxide is combined with aluminum oxide on the doubly promoted catalyst surface. Evidence furnished by Tables II and III is consistent with this. If free potassium oxide and free aluminum oxide existed on the surface of catalyst 931 (containing 1.3% aluminum oxide and 1.6% potassium oxide), the sum of the carbon monoxide chemisorbed by iron atoms and the carbon dioxide chemisorbed by the alkali promoter molecules would be smaller than the volume of physically adsorbed nitrogen required for a monolayer since aluminum oxide molecules do not chemisorb either carbon monoxide or carbon dioxide. Actually 17.6 cc. of carbon dioxide (Table III) and 15.2 cc. of carbon monoxide are chemisorbed compared to 30.0 cc. of nitrogen for a monolayer. Hence no large concentration of free aluminum oxide appears to be present, the potassium oxide and aluminum oxide promoters being, presumably, combined on the surface. For catalyst 958 the ratio of aluminum oxide to potassium oxide in the solid phase is four to one. One may possibly, therefore, expect an excess of aluminum oxide on the catalyst surface. There are indications that this is really the case. Table II shows that the carbon monoxide chemisorption at −78° is 21.5 cc., and if we assume that the density of packing of chemisorbed carbon monoxide is 25% greater than that of van der Waals nitrogen, as we found for the pure iron catalyst, the iron part of the surface could be covered by 17.2 cc. of nitrogen. The nitrogen monolayer is 29.8 cc., which leaves for the promoter part 12.6 cc. Actually only 8.0 cc. of carbon dioxide is chemisorbed (Table III), which means that 4.6 cc. of the nitrogen covers free aluminum oxide. This represents about 15% of the total surface. Since the catalyst contains only 0.35% aluminum oxide, we find in this case a strong concentration of both promoters on the surface.

The inhibiting effects of carbon dioxide on carbon monoxide and Type A hydrogen and the

TABLE XII

EFFECT OF THE CHEMISORPTION OF OXYGEN ON THE CHEMISORPTION OF CARBON MONOXIDE[a]

Catalyst	CO Chemisorpt. on pure surface, cc. at S. T. P.	Temp. of[b] CO chemisorpt., °C.	Inhibiting O_2[c] chemisorpt., cc. at S. T. P.	CO Chemisorpt.[d] on top of oxygen, cc. at S. T. P.	Decrease in[e] CO chemisorpt., cc. at S. T. P.	Time of adsorption of CO[d] on O_2 covered surface
954	45	− 78	519	17	28	1.5 hr.
954	44.5	− 78	376	17.1	27.4	30 min.
				18.2	26.3	1 hr.
954	44	− 78	721	14.1	29.9	4 min.
				17.3	26.7	2 hr.
				18.8	25.2	4.25 hr.
				23.0	21.0	23 hr.
954	36.0	−183	323	6.0	30.0	2 hr.
931	14.3	− 78	105.7	7.4	6.9	1.25 hr.
				7.8	6.5	2.25 hr.
				9.0	5.3	5.5 hr.
				12.3	2.0	23.5 hr.
931	12.1	−183	97.0	1.0	11.1	2 hr.

[a] Since the oxygen chemisorption injures the surface of pure iron catalysts, this effect was studied only on the promoted catalysts. [b] These temperatures refer to the chemisorption of CO both on the pure and the oxygen covered surface. [c] The oxygen was adsorbed on the catalysts at −78°, except the 721 cc., which was adsorbed between −78 and 100°. [d] The CO chemisorption values on top of oxygen were determined after the lapse of time indicated in the last column. It is uncertain whether at −78° even the adsorption values after 23 hours represent final equilibrium values. [e] The decrease in CO chemisorption given in this column represents the difference between the CO chemisorption values in the second and fifth column. These values do not correspond to equal times of adsorption.

TABLE XIII

EFFECT OF NITROGEN, OXYGEN, AND TYPE A AND TYPE B HYDROGEN ADSORPTIONS ON THE CHEMISORPTION OF CARBON DIOXIDE

Catalyst	Inhibiting[a] chemisorption, cc. at S. T. P.	CO_2 adsorption at −78°[b] On pure surface, cc. at S. T. P.	CO_2 adsorption at −78°[b] On top of inhibitor, cc. at S. T. P.	Pressure, mm.	Decrease in[c] CO_2 adsorption, cc. at S. T. P.
931	13.7 Mixed H_2	53.4(T)	52.6(T)	200	0.8(T)
		56.8	56.2	300	.6
		59.1	58.7	400	.4
		61.9	61.6	500	.3
931	11.5 Type A H_2	18.0(C)	17.4(C)	200	.6(C)
			17.7	500	.3
931	18.6 Mixed H_2	17.5(C)	16.3(C)	200	1.2(C)
			17.5	500	0
931	7.8 N_2	17.0(C)	15.8(C)	200	1.2(C)
			16.1	474	0.9
931	7.8 N_2	17.0(C)	15.6(C)	200	1.4(C)
			15.9	478	1.1
931	104.3 O_2	42.8(T)	42.8(T)	200	0 (T)

[a] The Type A hydrogen was put on the surface at −78°, the "mixed" hydrogen at some higher temperature first and then at −78°. The nitrogen was put on at 391–392°, and the oxygen at −78°. [b] The CO_2 adsorption values represent in some cases total adsorption (sum of van der Waals and chemisorption), in other cases merely the chemisorption value. The former are indicated with (T), the latter with (C). [c] The decrease in CO_2 adsorption also refers in some cases to the decrease in total adsorption (T), in other cases to the decrease in the chemisorption alone (C). It will be seen that the decrease is slight always, whether caused by hydrogen, nitrogen or oxygen.

effect of carbon monoxide on carbon dioxide lead to the conclusion that the iron atoms and alkali promoter molecules are not distributed over the catalyst surface in larger patches alternating with each other, but are mixed so thoroughly that practically every promoter molecule has an iron atom for its neighbor, and *vice versa*. Let us consider first the inhibiting effect of carbon dioxide on carbon monoxide chemisorbed on catalyst 931 at −183°, given in Table XV. After 17.7 cc. of carbon dioxide is chemisorbed, the carbon monoxide chemisorption on top of it becomes 3.7 cc., instead of the 13.8 cc. that takes place on a pure surface. The 10.1 cc. decrease is apparently due to the overlapping of the carbon dioxide molecules from the alkali to the iron atoms; it

TABLE XIV

EFFECT OF THE CARBON MONOXIDE CHEMISORPTION ON THE OXYGEN CHEMISORPTION

Catalyst	Inhibiting CO[a] chemisorption, cc. at S. T. P.	Oxygen sorption, On pure surface		cc. at S. T. P. On top of CO	Temp. of O_2 sorpt., °C.	Pressure[c] of oxygen, mm.	Time of adsorpt.	Decrease[b] in O_2 sorpt., cc. at S. T. P.
954	44.5	376	260	308	− 78	0	18 hr.	uncertain
954	43.5	302	322	300	− 78	340	2 hr.	12 ± 8
931	13.9	48.3	54.3	4.5	−183	0	2.5 hr.	47 ± 3
931	13.3	81.6	78.5	65.4	− 78	670	2 hr.	14 ± 2
	13.3	94.9	89.5	79.0	− 78	0	20 hr.	13 ± 3

[a] The carbon monoxide was always chemisorbed at −78°. [b] Because the oxygen sorption changed strongly from run to run, it was determined on the pure catalyst surface both before and after the run performed on the carbon monoxide poisoned surface. The average of these two runs was then taken, and the decrease reported in the last column was computed from the average. [c] This column gives the pressure at which the oxygen sorption was measured both on the pure and CO covered surface. Where zero pressure is indicated the catalyst was evacuated with a Toepler pump to a pressure that could not be read on a manometer, and the residual adsorption was determined.

represents the number of surface iron atoms that have alkali molecules for neighbors. The other 3.7 cc. of carbon monoxide chemisorption (27% of the total) then represents the number of iron atoms that have no alkali molecules as neighbors. One would expect that when the same effect is measured at −78° the initial decrease should be the same, and indeed the decrease in carbon monoxide chemisorption is 9.9 cc. after six minutes. Later at this higher temperature some surface rearrangement takes place that leaves room for further carbon monoxide chemisorption, so that after two and one-half hours the decrease is only 8.8 cc. If these views are correct, then the reverse effect of carbon monoxide chemisorption on carbon dioxide chemisorption at −78° should be also 10 cc. initially, and Table XVI shows that this is apparently the case. Unfortunately, the carbon dioxide adsorption was not measured in the first few minutes, but the decrease after one hour was 8.8 cc., after three and one-half hours 8.2 cc., so the initial decrease must have been close to the expected 10 cc. It seems therefore that about three-fourths of the iron atoms of the surface have alkali molecules for neighbors on the surface of catalyst 931. The surface of this catalyst consists roughly of 40% iron atoms and 60% potassium aluminate molecules. In the case of catalyst 958 only about one-fourth of the surface is covered with alkali. One would expect, therefore, that every alkali molecule has an iron atom for its neighbor. This is indeed so. Table XV shows that 9.2 cc. of chemisorbed carbon dioxide causes an initial decrease of 11.3 cc. in the carbon monoxide chemisorption at −78°, indicating possibly that some carbon dioxide molecules overlap to two neighboring iron atoms. After twenty-two hours the decrease becomes 7.3 cc., showing that surface migration and rearrangement enabled some further adsorption of carbon monoxide.

The effect of carbon dioxide chemisorption on Type A hydrogen, given in Table VII, further confirms the above expressed views. When carbon dioxide is chemisorbed on catalyst 931 about three-fourths of the iron atoms are put out of commission, as we have seen above. Under such circumstances one would expect that the number of free iron atom pairs available for the adsorption and dissociation of hydrogen would be rather small, and indeed when the surface is loaded with carbon dioxide at −78° the initial Type A hydrogen adsorption is only 0.8 cc. after three minutes. Later, surface rearrangement enables further hydrogen adsorption to take place, so that when final equilibrium is reached the decrease may be slight, or even zero. The situation is quite different with catalyst 958, three-fourths of the surface of which consists of iron atoms. In this instance, after the chemisorption of carbon dioxide, there are still a large number of iron atom pairs available for the hydrogen adsorption and, consequently, the initial adsorption on this catalyst is much greater than on catalyst 931.

IV. The Heterogeneous Nature of the Iron Surface.—Many of the data contained in Tables II to XVI can be explained if we assume that the iron crystals expose on their surfaces a variety of developed faces. These faces may be divided into two groups for the sake of convenience. The first group presents a closed structure, as exemplified in the (110) plane (Fig. 1), the plane of densest packing in a body-centered cubic crystal. The second group, exemplified by planes (100), (111), (211), etc., has an open structure; the iron atoms are loosely packed and expose a lower lying layer

TABLE XV

EFFECT OF CARBON DIOXIDE CHEMISORPTION ON THE CARBON MONOXIDE CHEMISORPTION

Catalyst	Inhibiting CO_2[a] chemisorption, cc. at S. T. P.	Chemisorption of CO, cc. at S. T. P. On pure surface	On top of CO_2	Temp. of CO chemisorpt., °C.	Time of CO adsorpt.	Decrease in CO chemisorption, cc. at S. T. P.
958	9.2	21.6	10.3	− 78	3 min.	11.3
			11.9		1.5 hr.	9.7
			12.3		4.75 hr.	9.3
			14.3		22 hr.	7.3
931	18.3	15.7	5.8	− 78	6 min.	9.9
			6.6		1 hr.	9.1
			6.9		2.5 hr.	8.8
931	17.7	13.8	3.7	−183	1 hr.	10.1
			3.7		2.5 hr.	10.1

[a] The CO_2 chemisorption was put on catalyst 958 at 0°, on catalyst 931 at −78°.

TABLE XVI

EFFECT OF THE CARBON MONOXIDE CHEMISORPTION ON THE CARBON DIOXIDE CHEMISORPTION

Catalyst	Inhibiting CO chemisorption,[a] cc. at S. T. P.	Chemisorption of CO_2, cc. at S. T. P. On pure surface	On top of CO	Temp. of CO_2 chemisorpt., °C.	Time of CO_2 adsorpt.	Decrease in CO_2 chemisorption, cc. at S. T. P.
931	16.9	16.8	8.0	−78	1 hr.	8.8
			8.6		3.5 hr.	8.2
931	13.6	16.8	9.7	−78	1 hr.	7.1
			9.9		2 hr.	6.9

[a] The 16.9 cc. was chemisorbed at −78°, the 13.6 cc. at −183°.

of iron atoms, as in plane (100), or even two lower lying layers of atoms, as in plane (111). The atoms marked "A" lie in the outermost plane of the crystal, those marked "B" lie in the plane below. It is assumed as a working hypothesis that on each "A" type iron atom one atom of Type A hydrogen or one atom of nitrogen, and on each "B" type iron atom one atom of Type B hydrogen can be chemisorbed. (It is also possible that in planes like the (111) the iron atoms marked "C" can also chemisorb Type B hydrogen.) The chemisorbed carbon monoxide molecules are assumed to be located in all instances on the "A" type iron atoms. The manner in which these assumptions help to explain the experimental observations of the present work can be illustrated by the following correlations.

(1) Chemisorbed nitrogen decreases Type A hydrogen adsorption in the ratio 1:1 as is evident from Table VIII. This agrees with the postulated adsorption of nitrogen on the same group of iron atoms on which Type A hydrogen is adsorbed.

(2) The ratio of Type A hydrogen to Type B hydrogen increases for the unpromoted iron catalyst as sintering takes place (Table IV, last column). This trend is consistent with a preferential disappearance during sintering of faces having open structures in comparison with the (110) planes. The (111) plane is the one of loosest packing for the body-centered iron crystal; it is also probably the plane of greatest energy and catalytic activity (judged by ethylene hydrogenation), as the work of Beeck, Wheeler and Smith[12] seems to indicate. The (110) plane is the plane of densest packing, and probably of least energy and maximum stability. The increase of the ratio of Type A to Type B hydrogen with sintering is therefore in accord with the gradual transformation of various faces to those consisting of (110) planes.

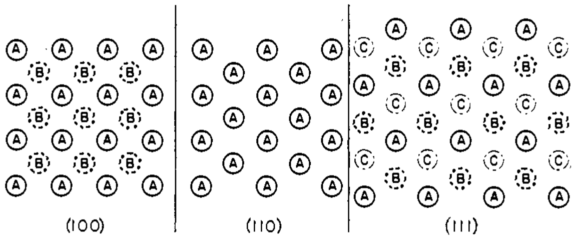

Fig. 1.—Arrangement of iron atoms in the (100), (110), and (111) planes. The distances between the centers of the iron atoms are drawn to scale, a_0 being taken as 2.86 Å. The circles are not intended to represent the sizes of the iron atoms.

(3) The ratio of Type A hydrogen to carbon monoxide chemisorbed at −78° increases on sintering the pure iron catalyst (Table IV, column 7). Because of the very dense packing of iron atoms in the (110) plane, it is necessary to assume that two iron atoms are required for the chemi-

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[12] Beeck, Wheeler and Smith, *Phys. Rev.*, **55**, 601 (1939).

sorption of a carbon monoxide molecule, whereas one iron atom is sufficient in the (100), (111), or (211) planes.[6] The limiting ratio of Type A hydrogen to carbon monoxide chemisorption on this basis is 1.0 for plane (110), and 0.50 for the other planes. Thus, the increase in ratio is consistent with the preferential increase in (110) planes on sintering. The ratio of Type B hydrogen to carbon monoxide also increases on sintering to some extent. This is probably due to the fact that the 100° adsorption of hydrogen is not purely Type B; if as much as 20% or so of the adsorption is Type A the increased ratio can be accounted for easily.

(4) The ratio of chemisorbed nitrogen to the volume of physically adsorbed nitrogen required to form a monolayer also increases with sintering of the unpromoted catalyst (Table V, last column). Since the iron atoms in the (110) plane can chemisorb more nitrogen per unit surface than any of the planes of open structure, this is an added indication of the preferential increase in (110) planes on sintering.

(5) The ratio of the volume of carbon monoxide chemisorbed at −78° to the volume of physically adsorbed nitrogen required to form a monolayer is 1.25 for the pure iron catalyst (Table II, last column). This ratio is reasonable, since if 13.7 sq. Å. be taken as the area occupied by a physically adsorbed nitrogen molecule,[6] the value of this ratio would be 1.68 if all of the developed faces were (100) planes; 0.97, if (111) planes; 1.35, if (211) planes; and 1.19, if (110) planes and, in this last instance, two iron atoms were required for each chemisorbed carbon monoxide molecule.

(6) In a previous work[13] the conversion of ortho to para hydrogen at −183° was found to be decreased 85% by a given volume of hydrogen adsorbed at 100°, compared to 15% by the same volume adsorbed at −78°. This must mean, if the present postulates are correct, that Type B iron atoms in Fig. 1 are much more active in the magnetic conversion of ortho to para hydrogen than are Type A iron atoms and that hydrogen adsorption at 100° occurs predominantly on the "B" type iron atoms. Since the magnetic conversion depends upon the non-homogeneous nature of the magnetic field with which the hydrogen molecule comes in contact, it is entirely reasonable that hydrogen molecules in passing between Type A iron atoms to Type B iron atoms would be subjected to greater magnetic perturbation than if they were adsorbed directly on the Type A iron atoms.

The explanation given above for the experimental data mentioned under items 1 to 6 appears to us fairly satisfactory. We fully realize the speculative nature of the considerations about the developed crystal faces on a catalyst surface; yet, we believe that these chemisorption experiments suggest some interesting new possibilities for the investigation of the surface structure of catalysts.

V. Penetration of Adsorbed Atoms below the Surface.—All of our results obtained for the chemisorptions of carbon monoxide and carbon dioxide are consistent with the idea that these take place only on the surfaces of the catalysts. Indeed, one would not expect that large particles like carbon monoxide and carbon dioxide molecules could penetrate into the crystal lattices of the catalysts. The four other chemisorptions, however, are atomic. Offhand it does not seem impossible that these small particles may be able to diffuse some distance below the surface layer. In this section we shall consider the evidence relative to the penetration of oxygen, hydrogen, and nitrogen atoms below the surface.

There can be no doubt that oxygen penetrates to lower layers. If we take the carbon monoxide chemisorption at −78° as the measure of the number of iron atoms on the surface, then Table VI shows that at −78° roughly fifteen times as many oxygen atoms are sorbed by all three catalyst types as there are iron atoms on the surface. Undoubtedly here an oxidation of the upper layers of the iron crystallites takes place even at −183°. The oxygen in the lattice is probably in the form of ions, just as it exists in the oxides of iron.

It is much more difficult to decide whether the hydrogen and nitrogen atoms penetrate to lower lying layers. If the surface of a catalyst consists of faces of open structure, such as (100), (111), or (211) planes, then the maximum Type A hydrogen adsorption that can take place on the surface is equal to one-half of the maximum carbon monoxide chemisorption. If on the surface we find (110) faces also, the ratio of Type A hydrogen to carbon monoxide chemisorption will be greater than 0.50, since it is assumed from molecular size considerations that at least two iron atoms will be needed to chemisorb one carbon monoxide mole-

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[13] Emmett and Harkness, THIS JOURNAL, **57**, 1624 (1935).

cule but only one iron atom for each hydrogen atom. It was also pointed out in the previous section that sintering increases the relative number of (110) faces. Table IV shows that on a sintered pure iron catalyst the ratio of Type A hydrogen to carbon monoxide was 0.65, and on a singly promoted catalyst, 0.62. These ratios indicate that on the pure iron or the singly promoted catalyst, Type A hydrogen adsorption takes place on the surface only, and the hydrogen atoms do not penetrate to lower lying layers. For the doubly promoted catalyst, however, the ratio 0.99 was obtained, definitely indicating that all the hydrogen could not be located on the surface iron atoms. Either some of the hydrogen atoms must have penetrated to lower lying layers, or they must have migrated to iron atoms lying immediately below the surface promoter molecules.

We have assumed that the chemisorption of nitrogen takes place on the same iron atoms that are capable of chemisorbing Type A hydrogen. Table V shows that for the pure iron catalyst that is not strongly sintered the ratio of nitrogen to carbon monoxide chemisorption is 0.25, suggesting that only every other "A" type iron atom on the surface can chemisorb a nitrogen atom. The solid phase iron nitride of highest nitrogen content is Fe_2N, and here we seem to deal with a surface whose apparent composition is Fe_2N. Obviously in this case there is no evidence of penetration below the surface. With the two promoted catalysts, however, higher ratios are obtained: 0.34 for the singly promoted and 0.50 for the doubly promoted catalyst. It is possible that the promoter enables every iron atom of the surface to chemisorb nitrogen, and that the surface composition approaches FeN instead of Fe_2N. On the other hand, nitrogen may migrate to the iron atoms lying directly under the promoter molecules, or penetrate further within the lattice as dissolved nitrogen. Since the high ratios occur on the promoted catalysts and not on the pure iron, we are inclined to favor the view that the excess nitrogen atoms are also located under the surface promoter molecules.

The Type B hydrogen adsorption presents an even more complex problem. The reason for this is that the open structure faces vary with respect to capability of adsorbing Type B hydrogen. If, for example, the atoms marked "C" in the (111) plane (Fig. 1) can also chemisorb Type B hydrogen atoms, then faces crystallized in the (111) plane are able to adsorb twice as much Type B hydrogen as those in the (100) or (211) planes. Thus, if the surface would consist of (111) planes only, the maximum ratio of the Type B hydrogen to the carbon monoxide chemisorption would be 1.0, and the maximum ratio of the mixed hydrogen to carbon monoxide would be 1.5. The Type B to carbon monoxide ratios found for the pure iron catalyst indicate no penetration to lower layers. The maximum Type B to carbon monoxide ratio found for the singly promoted catalyst was 0.92, for the doubly promoted catalyst 0.99; the maximum mixed hydrogen to carbon monoxide ratio was 1.18 for the singly promoted and 1.42 for the doubly promoted catalyst (Table IV). Since from the foregoing discussion it is clear that the surfaces of the promoted catalysts cannot consist solely of (111) faces, we may safely conclude that the high ratios obtained indicate migration of the Type B hydrogen atoms to iron atoms lying under the surface promoter molecules.

VI. **Chemical Effects of Promoters.**—Several investigators[14,15,16] have shown by indirect methods that one function of the aluminum oxide promoter was to provide and maintain a large surface. We have confirmed this by direct surface measurements[6] and found that the singly promoted catalyst 954 had five times as large surface after reduction at 450° as the pure iron catalyst 973 reduced with utmost care at 350°. Sintering up to 500° had very little effect on the aluminum oxide promoted catalyst, but decreased the surface of the unpromoted catalyst to one-fourth of its value. Thus, the physical action of aluminum oxide is unquestionably established. However, until now, no positive evidence has been presented of a specific chemical action of the promoter aluminum oxide for iron synthetic ammonia catalysts.

A very interesting evidence for a chemical effect of aluminum oxide is found in the effect of nitrogen chemisorption on Type B hydrogen adsorption on catalyst 954 (Table IX). In the study of seventeen different effects of chemisorptions upon each other in the present work we have found that in only this one instance does a chemisorption increase rather than decrease the chemisorption of another gas. The ratio of the decrease in Type B adsorption per unit amount of

[14] Wyckoff and Crittenden, This Journal, **47**, 2866 (1925).

[15] Brill, *Z. Elektrochem.*, **38**, 669 (1932).

[16] Mittasch and Keunecke, *ibid.*, **38**, 666 (1932).

chemisorbed nitrogen is 0.97 after three minutes and 0.73 after twenty hours for the doubly promoted catalyst 931; 0.68 after three minutes and 0.52 after sixteen and one-half hours for the pure iron catalyst. In contrast to this, for the singly promoted catalyst the initial decrease in the Type B adsorption is followed by a rapid pick up of hydrogen at 100° that amounts after twenty hours to an increase of 0.5 volume of hydrogen per volume of chemisorbed nitrogen.

This enhancement of hydrogen adsorption at 100° by chemisorbed nitrogen is apparently to be attributed to the catalytic action of aluminum oxide on the formation of NH or NH_2 complexes between hydrogen and the chemisorbed nitrogen. Such complex formation appears from the data of Table IX to be slow at 100° on pure iron, even slower on doubly promoted catalyst 931, and relatively fast on singly promoted catalyst 954. Since ammonia is known to inhibit ammonia synthesis, it is possible that the tendency of aluminum oxide to catalyze and of potassium oxide-aluminum oxide to inhibit the formation of a poisoning NH or NH_2 complex on the iron may be a factor in explaining the well-known superiority at high pressures of the doubly promoted catalyst over the singly promoted. The fact that nitrogen causes any initial retardation of the Type B hydrogen adsorption appears at first to be inconsistent with the allocation of chemisorbed nitrogen to "A" type iron atoms (Fig. 1) and Type B hydrogen to "B" type iron atoms. When it is remembered, however, that Type B hydrogen is adsorbed much more slowly than Type A and may possibly result from an activated migration of hydrogen atoms from the A position to the B, the inhibitive effect of chemisorbed nitrogen atoms on Type B hydrogen adsorption is easily understood.

In conclusion it should be pointed out that the volume of chemisorbed nitrogen per unit surface area of iron atoms is greater on the doubly promoted catalyst than on either the pure iron or the singly promoted catalyst (Table V, column 7). Whether the excess nitrogen adsorption takes place on the surface iron atoms or on iron atoms located immediately below the surface alkali molecules, this may be a factor in accounting for the greater catalytic activity of doubly promoted catalysts over singly promoted catalysts at high pressures.

Summary

The chemisorptions of oxygen and carbon monoxide at −183 and −78°, carbon dioxide at −78 and 0°, nitrogen at 400–450°, Type A hydrogen at −78° and Type B hydrogen at 100° were studied on an unpromoted, a potassium oxide promoted, two aluminum oxide promoted, and two potassium oxide plus aluminum oxide promoted iron synthetic ammonia catalysts. From the investigation of these adsorptions individually and from their mutual inhibitory effects the following conclusions can be drawn:

1. The carbon dioxide chemisorption is located on the surface alkali molecules, the five other chemisorptions on the surface iron atoms.
2. Carbon monoxide and carbon dioxide are chemisorbed as molecules; nitrogen, Type A, and Type B hydrogen as atoms; oxygen probably as ions.
3. Both the aluminum oxide and potassium oxide promoters are strongly concentrated on the surfaces of singly and doubly promoted catalysts. The alkali promoter is very intimately mixed with iron atoms on the surface.
4. The iron surface is heterogeneous, the heterogeneity probably being due to different developed crystal faces.
5. The molecular carbon monoxide and carbon dioxide chemisorptions are purely surface adsorptions; oxygen ions penetrate several layers below the surface; nitrogen and hydrogen atoms probably do not penetrate below the surface but migrate to iron atoms located under surface promoter molecules.
6. Both the potassium oxide and aluminum oxide promoters give evidences of specific chemical effects.

WASHINGTON, D. C.

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