Br_3. Retreatment of the residue—which contained mainly polymeric oxide—with 4 g. of 47% HBr gave another 1.5 g. of crude n-$C_4H_9GeBr_3$, with a residue of 1 g. Fractional distillation of all the n-$C_4H_9GeBr_3$ (6.4 g. or 67% yield) furnished a 4 g. center fraction listed in Table I. Upon shaking with a large excess of water this n-$C_4H_9GeBr_3$ hydrolyzed easily to the polymeric oxide.

Discussion

Preparative Methods.—Gradual addition of deficiencies of $HgCl_2$, $HgBr_2$ or I_2 convert n-C_4H_9-GeH_3 or $(n$-$C_4H_9)_2GeH_2$ into the new partially substituted compounds of the $RGeH_2X$ or the R_2-$GeHX$ types, respectively. Table I lists six compounds, apparently the first examples of these types. This partial substitution is exactly like that of the alkylsilanes already demonstrated.[3-6] Although there are fewer known germanium compounds, 6 in all, of these types, several comparisons with the corresponding alkylhalosilanes are possible. First, the corresponding alkylgermanes are more reactive toward halogens or halides. Second, the alkylhalogermanes of the $RGeH_2X$ type are much less reactive toward water or aqueous NaOH. Efforts to change n-$C_4H_9GeH_2Cl$ into the analogous n-$C_4H_9GeH_2OGeH_2$-n-C_4H_9 either showed incomplete reaction or destruction of some of the Ge–H bonding in treatment with aqueous NaOH; the reaction with n-$C_4H_9SiH_2Cl$ and pure water proceeds satisfactorily.[6]

Molar Refractions.—Table I lists calculated molar refractions, based on the apparently reliable Ge–H bond refraction of 3.59[7] and some comparatively approximate bond refractions for Ge–Cl, Ge–Br and Ge–I.[8] The present paper merely follows the existing[8] values for the germanium to halogen bond, with intention to improve these values later.

[8] A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954); A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 531 (1952).

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Nitrogen Chemisorption at −195° on Reduced Iron and Cobalt Oxides

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Evidence has been presented for chemisorption of nitrogen at −195° on reduced iron and cobalt oxides. For iron the amount of nitrogen chemisorbed corresponds to 10 to 20% of V_m, as determined by the BET method; for cobalt this figure is 50 to 60%. These conclusions imply that nitrogen surface area determinations on metallic catalysts may be subject to large errors. If allowance is made for such errors it appears that carbon monoxide chemisorption on iron, cobalt and nickel is 1.1 to 1.2 times the correct V_m. value.

Although the validity of the formal theory of physical adsorption of gases on solid surfaces[1] has been questioned,[2] the now classic experiments of Emmett and Brunauer[3] provide ample evidence that physical adsorption provides a valid basis for the determination of surface area. Today, it is often forgotten that these investigators[1,3] clearly stated that this method is not valid when (a) the adsorbate is strongly, *i.e.*, chemically adsorbed and (b) when the pore structure of the adsorbent is such that all the surface is not accessible to the adsorbate. In these studies[3] it was found that for a wide variety of solids, nitrogen chemisorption at −195° was virtually non-existent; hence, nitrogen has become a preferred adsorbate for such measurements of surface area. In recent years, researches on evaporated metal films have shown that nitrogen chemisorption does occur on many transition metals between −195° and room temperature,[4-6] and this led Beeck[4] to question the validity of nitrogen surface areas on metals. At that time, however, evaporated metal films and catalysts prepared by reduction of oxides appeared to be different in many respects so that the low temperature nitrogen chemisorption on films was accepted as another difference between ultra-clean metals, *i.e.*, evaporated metal films, and metals prepared by reduction of oxides.

There seems to be a growing body of data which suggests that carefully reduced nickel oxides are, in fact, similar to the nickel films.[7] In particular, recent investigations[8,9] strongly suggest that reduced nickel oxides exhibit the same type of weak nitrogen chemisorption at −195° observed by Beeck[4] on evaporated nickel films. These results suggest that other transition metals prepared by reduction of the oxide also may show nitrogen chemisorption at −195°. If this be the case, it would not only provide additional evidence that results with reduced oxides are indeed comparable with those found for films but would also reemphasize the fact[3,4,8,9] that indiscriminate use of nitrogen for determinations of surface area can lead to large errors. In this paper we have examined reduced iron and cobalt oxides for nitrogen chemisorption.

Experimental

Catalyst Preparation.—The procedure for the preparation of the iron catalyst was similar to that described by Emmett and Gray.[10] A 10% excess of ammonia was added to a solution of 200 g. of $Fe(NO_3)_3 \cdot 9H_2O$ in two liters of distilled water. The precipitate was coagulated by boiling the slurry

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[1] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[2] G. Halsey, *Discussions Faraday Soc.*, **8**, 54 (1950).

[3] P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 310, 1553 (1937).

[4] O. Beeck, *Adv. in Catalysis*, **II**, 151 (1950).

[5] E. Greenhalgh, M. Slack and B. M. W. Trapnell, *Trans. Faraday Soc.*, **52**, 865 (1956).

[6] J. Bagg and F. C. Tomkins, *ibid.*, **51**, 1071 (1955).

[7] *Cf.* G. C. A. Schuit and N. H. DeBoer, *Rec. Trav. Chim.*, **70**, 1067 (1951).

[8] R. J. Kokes and P. H. Emmett, THIS JOURNAL, **80**, 2082 (1958).

[9] R. J. Kokes and P. H. Emmett, *ibid.*, **82**, 1037 (1960).

[10] P. H. Emmett and J. B. Gray, *ibid.*, **66**, 1338 (1944).

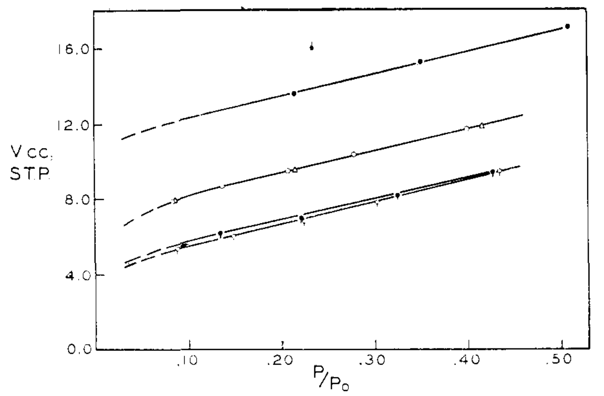

Fig. 1.—Adsorption on cobalt catalyst I, 14.6 g. as oxide: ○, N(T); △, N(P); ●, CO(T); ●̦, CO(P); ♀, N(OT).

for 1 hr., filtered, reslurried, washed until the filtrate was neutral to litmus and then dried at 130° for 48 hr. Prior to reduction, the iron oxide was degassed *in vacuo* at 300°.

A 15.8 g. sample of Fe_2O_3 was reduced with hydrogen purified by passage through a Deoxo unit and a trap filled with degassed charcoal cooled to −195° to remove water and traces of nitrogen. Reduction was started at 100° at a space velocity of 2000 to 3000 hr.$^{-1}$. The temperature was raised gradually to about 300–310° over a period of 4 hr. After 48 hr. of reduction the water in the effluent stream was less than 0.002%. The weight loss of the catalyst was 29.5% compared to a stoichiometric weight loss of 30.1%. At the conclusion of the adsorption experiments the catalyst was further reduced at 440°. A slight amount of additional reduction occurred; after 4 hr. the water in the effluent stream fell to ~0.01% and the over-all loss in catalyst weight changed from 29.5 to 29.7%. Thus, it would appear that the catalyst was effectively reduced completely at the lower temperature. Prior to the adsorption experiments the catalyst was evacuated about 1 hr. at the reduction temperature.

The Co_3O_4 was prepared following the procedure of Hofer and Peebles[11] by precipitating 1 *M* $Co(NO_3)_2 \cdot 9H_2O$ with a 10% excess of aqueous NH_3. The resulting precipitate was pink but after it was thoroughly washed and dried for 16 hr. at 130° it turned black. Prior to reduction the Co_3O_4 was degassed for 1 hr. at 300° *in vacuo*. Reduction of a 14.6 g. sample of this oxide was started at 200° with a hydrogen space velocity of about 2000 hr.$^{-1}$. (The purification train for the hydrogen was that described already.) The temperature was raised gradually to 300° over a period of 8 hr. and the reduction was continued for an additional 12 hr. at which time the exit hydrogen stream contained less than 0.005% water. (Metallic catalysts on reduction often shrink and coalesce to form a hard clump in the center of the tube and as a result channelling of the hydrogen will occur accompanied by a fall off in reduction rate. This was avoided by removing the catalyst tube and vigorously shaking it to break up the clump in the latter stages of the reduction.) The catalyst weight loss was 27.4% compared to the stoichiometric value of 26.6% for Co_3O_4. Prior to the adsorption experiment labeled I (Table I) the catalyst was evacuated 1.5 hr. at 300°. At the completion of adsorption experiments in set I, it was rereduced about 1 hr. at 300° and evacuated 1 hr. at the reduction temperature, then set II of the experiments was carried out.

Adsorption Experiments.—Argon and nitrogen used in these experiments were obtained in tanks from Mathieson Chemical Company. The argon was purified by slow passage over hot copper and fractionation at −195°; the prepurified nitrogen was simply fractionated at −195°. Carbon monoxide was prepared by fractionation at −195° of the gas produced by the addition of degassed formic acid to hot degassed concd. H_2SO_4.

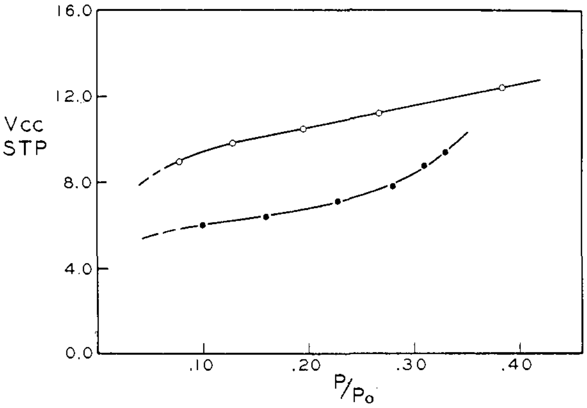

Fig. 2.—Adsorption on cobalt catalyst II, 14.6 g. as oxide: ○, N(T); ●, Ar(T).

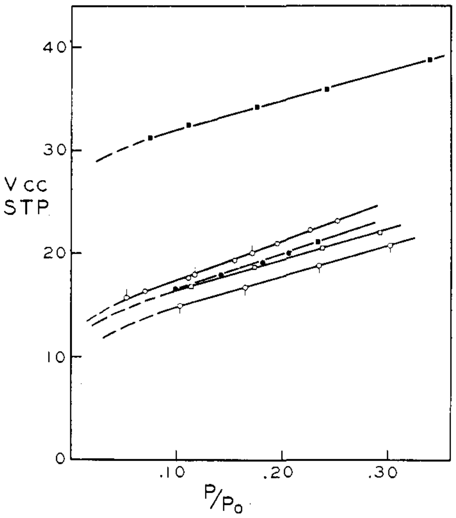

Fig. 3.—Adsorption on iron catalyst, 15.8 g. as oxide: ○, N(T); ό, N(P); ●, Ar(T); ■, CO(T); □, CO(P); ♀, N(OT).

In all the adsorption experiments (carried out in a standard BET apparatus), the sample was cooled to −195° in the presence of helium to assure thermal equilibrium. Corrections for departure from ideal gas behavior at −195° were made for all three gases. The value used for the saturation pressure of argon in the isotherm plots and V_m calculations was the extrapolated value for the liquid. It was assumed that the effective cross-sectional area of physically and chemically adsorbed carbon monoxide and nitrogen was 16.2 Å.^{2} whereas that for argon was 15.6 Å.^{2}.[12,13]

For the sake of brevity we will designate these isotherms, all obtained at −195°, by a series of abbreviations. N(T) refers to a nitrogen isotherm on a virgin catalyst; N(P) refers to an isotherm on a catalyst which had been exposed to nitrogen at −195° and evacuated for 1 hr. at −78°; N(OT) refers to an isotherm on a catalyst which had been exposed to carbon monoxide at −195° and evacuated for 1 hr. at −78°. The same symbols are used for the other gases, *mutatis mutandis*. The data and results for the iron and cobalt catalysts are summarized in Figures 1, 2 and 3 and in Table I.

Discussion

Criteria for Chemisorption.—Results of adsorption studies with reduced nickel oxide indicated that nitrogen chemisorption was very weak; in fact, it was concluded[8,9] that about half of the chemisorbed nitrogen was pumped out at −78°. (This latter observation is consistent with the data of Beeck[4] which indicate that the initial heat of nitrogen chemisorption is only 10–12 kcal.) Now,

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(11) L. J. E. Hofer and W. C. Peebles, THIS JOURNAL, **69**, 893 (1947).

(12) P. H. Emmett and M. Cines, *J. Phys. and Colloid Chem.* **51** 1248 (1947).

(13) H. K. Livingston, *J. Coll. Sci.*, **4**, 447 (1949).

TABLE I

SUMMARY OF ADSORPTION RESULTS ON REDUCED IRON AND COBALT CATALYSTS

Isotherm	V_m, cc.	Surface area, m.^{2}/g.[a]
	Fe_2O_3(15.8 g.)	
N(T)	18.2	5.05
N(P)	18.2	5.05
Ar(T)[b]	16.5	4.40
CO(P)	16.3	4.50
N(OT)	15.3	4.22
	Co_3O_4(14.6 g.)	
	I	
N(T)	7.68	2.29
N(P)	7.68	2.29
CO(P)	5.74	1.72
N(OT)	5.68	1.70
	II	
N(T)	8.55	2.56
Ar(T)[b]	5.62	1.62

Catalyst	$\frac{CO(T) - N(OT)}{V_m N(OT)}$	$\frac{N(T) - N(OT)}{V_m N(OT)}$
Fe	1.11 ± 0.01	0.21 ± 0.02
Co	1.18 ± 0.01	0.48 ± 0.02

[a] Expressed per gram of degassed but unreduced catalyst.
[b] The cross-sectional area of an argon atom was assumed to be 15.6 Å^2. If we assume A has the same cross-sectional area as assigned the N_2 (16.2 Å^2.), the calculated argon areas for Fe and Co become 4.57 m.^{2}/g. and 1.68 m.^{2}/g., respectively.

the traditional interpretation of the (T) and (P) isotherms (*cf.* Figs. 1 and 3) would be that the former includes both chemically and physically adsorbed gases; the latter includes only physically adsorbed gases; and the difference represents the amount of chemisorbed gas. This simple interpretation, however, breaks down when the chemisorption is so weak[14] that the second isotherm includes chemisorption. Then, the above estimate yields a minimum value which for very weak chemisorptions could approach zero. Thus, the agreement of N(T) and N(P) isotherms does not rule out the possibility of weak nitrogen chemisorption; alternative procedures must be designed for a conclusive test.

With nickel catalyst other procedures were used to estimate the total amount of nitrogen chemisorption. In one such procedure (a) the N(T) isotherm was compared to the Ar(T) isotherm. Since the latter gas could not chemisorb, the difference between N(T) and Ar(T), adjusted for differences in the cross sectional areas, should represent the amount of chemisorbed nitrogen. The other procedure (b) involved the assumption that the CO(P) isotherm must include all of the physically adsorbed carbon monoxide; hence, if carbon monoxide has a similar cross-section to nitrogen, the CO(P) isotherm should provide a maximum value for the amount of physically adsorbed gas. If this lies below the N(T) isotherm the difference (which would be too low if CO(P) included some chemisorption) must be attributed to nitrogen chemisorption. In the last procedure (c) it was assumed that a layer of chemisorbed carbon monoxide prohibited chemisorption of nitrogen but did not change the amount of physically adsorbed nitrogen. Thus, the N(OT) isotherm represents still another estimate of the amount of physically adsorbed nitrogen. All three methods are subject to criticism. For example, methods a and b suffer from the fact that the cross-sectional areas of argon and carbon monoxide are subject to some uncertainty; method c is vitiated by observations that chemisorption of carbon monoxide on copper has a profound effects on subsequent physical adsorption of krypton.[15,16] Thus, no one of these methods constitutes an unequivocal test for nitrogen chemisorption, but if all three methods combine to give consistent evidence for nitrogen chemisorption, it seems clear that it exists. This will be especially true when the effects are large since the effective cross sectional areas of physically adsorbed carbon monoxide and argon are probably known within ±10%.

Cobalt Catalysts.—The N(T) and N(P) isotherms (Fig. 1) for the reduced cobalt catalyst agree within experimental error; hence, nitrogen chemisorption is either very weak or non-existent. Since the CO(P) and N(OT) isotherms are far below N(T) and N(P), it would appear that the nitrogen chemisorption while weak is extensive. Further evidence for this is given in Fig. 2, wherein it may be seen that Ar(T) is much lower than N(T) on the rereduced catalyst. [Direct comparison of N(T) and Ar(T) is permissible since the difference in cross-sectional areas is only about 5%.] An estimate of the extent of this chemisorption can be made by taking the difference between the N(T) isotherm and that for physical adsorption. If we assume that N(OT) or CO(P) represents a true measure of the physical adsorption, we find that the nitrogen chemisorption is about 48% of V_m. [Estimates from run II in which Ar(T), corrected for cross-sectional area, represents the physical adsorption yields a value of 56%.] Similar estimates for nickel catalysts yield values of 57%.[9]

Cobalt catalysts prepared in a similar manner to that used here have been studied by Anderson, Hall and Hofer.[20] The lower value found by them for the V_m of the N(T) isotherm (0.73 compared to 2.29 cc./g.) is to be expected since their catalyst was reduced at 360–400° whereas ours were reduced at 300°. In spite of the difference in surface area, however, the ratio of CO(T) to N(T) at the pressure corresponding to the V_m value for the latter

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[14] For a discussion of such complications in CO chemisorption studies, see J. T. Kummer and P. H. Emmett, THIS JOURNAL, **73**, 2886 (1951).

[15] F. S. Stone and P. F. Tiley, *Nature*, **167**, 654 (1951).

[16] Much of the work on iron and cobalt was done on promoted catalysts and, consequently, is rather difficult to interpret. It has been found that a layer of chemisorbed carbon monoxide on synthetic ammonia catalysts (does not[17]) does[18] decrease subsequent nitrogen adsorption to 90% of that on a clean surface. Similar inhibitions have been reported for promoted cobalt catalysts.[19] Although this inhibition may result from the effect of a chemisorbed layer on physically adsorbed nitrogen, it could also result from the blocking out of weak nitrogen chemisorption by chemisorbed carbon monoxide in line with method C. The effect of a chemisorbed gas on physical adsorption can be deduced from such experiments only when the physically adsorbed gas is incapable of chemisorption, *e.g.*, an inert gas.

[17] A. S. Joy and T. A. Dorling, *Nature*, **168**, 433 (1951).

[18] H. H. Podgurski and P. H. Emmett, private communication.

[19] M. V. C. Sastri, T. S. Viswanathan and T. S. Nagarjunan, *J. Phys. Chem.*, **63**, 518 (1959).

[20] R. B. Anderson, W. K. Hall and L. J. E. Hofer, THIS JOURNAL, **70**, 2465 (1948).

is 1.65 for their catalyst and 1.57 for ours; hence, the surface structures of these catalysts appear to be similar. On the basis of these experiments, Anderson, Hall and Hofer[20] concluded that the ratio of chemisorbed carbon monoxide to V_m was 0.65 and that this factor combined with carbon monoxide adsorption studies could be used to estimate what fraction of the surface of promoted catalyst was metallic cobalt. In view of the existence of nitrogen chemisorption, it would appear that CO(T) − N(OT) affords a better measure of the chemisorbed carbon monoxide; similarly, V_m N(OT) offers a better measure of the surface area. The factor thus calculated (Table I) yields a value more similar to those reported for iron[21] and nickel.[8] It is difficult to state definitely what effect this will have on interpretation of the carbon monoxide chemisorption studies designed to determine the amount of metallic cobalt on different promoted catalysts.[20] Nitrogen chemisorption appears to be negligibly small on Raney nickel catalysts[22] which function much like promoted catalysts. If nitrogen chemisorption is also trivial for promoted cobalt catalysts this would mean that the studies of Anderson and co-workers[20] are quantitatively correct except for a scale factor. In any case, it seems most likely that the results of this study would, at worst, render their conclusions qualitative rather than quantitative.

Iron Catalysts.—Results with iron catalysts are shown in Fig. 3 and Table I.[23] The value of V_m for N(T) on this catalyst (5.05 m.^{2}/g.) is quite a bit higher than that found by Emmett and Gray[10] (1.1 m.^{2}/g.) but their catalyst was reduced at 360 to 405° whereas ours was reduced at 300°. Nitrogen chemisorption on this catalyst, if it occurs at all, is smaller than that noted for cobalt. Calculations in which N(OT) is accepted as true physical adsorption (Table I) suggest that the nitrogen chemisorption may be as high as 21% of V_m. On the other hand, if we base the calculations on CO(P) or Ar(T), we would obtain values of 9.3 and 13%, respectively. These calculated chemisorptions represent small differences in isotherms. Thus, the evidence for nitrogen chemisorption on iron at −195° is not as definite as with cobalt. Nonetheless, the conclusions reached by the three procedures are consistent and, at least, suggest that there is such weak chemisorption on iron catalysts.

If we accept completely these conclusions regarding nitrogen chemisorption, we find the carbon monoxide chemisorption on all three of these metals is roughly 15% greater than V_m. Furthermore, surface areas determined by nitrogen adsorption on virgin nickel and cobalt should be too high by 50 to 55%. This is reminiscent of the observation of Beeck[4] that for iron films such surface areas are 55% greater than those determined with non-chemisorbed gases.

There are several aspects of these and earlier[7,8] investigations which require comment.

1. The fact that the nitrogen chemisorption is half that required for a monolayer of physically adsorbed nitrogen (at least for cobalt and nickel) makes it tempting to assume the adsorption may be atomic. It is, however, highly unlikely that the nitrogen–nitrogen bond is split to yield extensive chemisorption which is also very weak at all coverages. It is more likely that the adsorption is molecular. Partial surface coverage by chemisorbed nitrogen is common on evaporated films of transition metals.[5]

2. On nickel catalysts, for which nitrogen chemisorption is stronger, the difference between N(T) and N(P) isotherms per unit surface decreases when the surface area is reduced by sintering. Since the nitrogen metal bond becomes weaker with treatment equivalent to annealing, this might mean that the stronger nitrogen chemisorption occurs at surface faults and defects.

3. High temperature (~300°) adsorption of nitrogen on nickel blocked out substantial portions of the low temperature nitrogen adsorption.[8] It is well known[24] that traces of nitrogen in the hydrogen used to reduce iron catalysts will yield a catalyst partially covered with chemisorbed nitrogen. For this reason the purification train for the hydrogen included a charcoal trap at −195°. It might be that with iron, which chemisorbs nitrogen more strongly at high temperatures than cobalt or nickel, the treatment is inadequate. Then, the presence of nitrogen chemisorbed during reduction could lead to low values for the chemisorption at −195°.

4. The estimated values of nitrogen chemisorption on iron catalysts are so small that the results are indicative of rather than conclusive evidence for nitrogen chemisorption at −195°.

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(21) S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1940).

(22) R. J. Kokes and P. H. Emmett, unpublished data.

(23) It should be recalled that iron synthetic ammonia catalysts are generally made by reduction of Fe_3O_4; this catalyst was made by reduction of Fe_2O_3. For this reason comparison of these results to those with reduced Fe_3O_4 may be invalid. We chose to study reduced Fe_2O_3 because its preparation was similar to the cobalt and nickel preparations.

(24) J. T. Kummer and P. H. Emmett, *J. Phys. and Colloid Chem.*, **55** 337 (1951).