[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE, AND CARBIDE AND CARBON CHEMICALS COMPANY]

The Adsorption of Chlorine Trifluoride on Porous Nickel Fluoride[1]

BY R. LYNN FARRAR, JR., AND HILTON A. SMITH

RECEIVED MARCH 3, 1955

A previous paper has shown that the product of the solid–gas reaction of nickel oxide with gaseous chlorine trifluoride is a porous nickel fluoride. The present paper describes some of the anomalous adsorption properties shown by this powder. After the initial rapid physical adsorption, the sample continued to sorb chlorine trifluoride with a rate which followed the parabolic law. Anomalous values of surface area were obtained as determined by the BET Method. An explanation is presented involving diffusion of the sorbate molecules down the micro-channels between the crystallites of the porous particles.

Introduction

In the preceding paper[2] the kinetics of the reaction of chlorine trifluoride with nickel oxide have been discussed. The product of this reaction was a very porous nickel fluoride powder which, from weight gain evidence, appeared to possess an unusual capacity for adsorption of the reactant gas, chlorine trifluoride. Therefore, a study of the adsorption of this gas on the solid nickel fluoride was made.

Experimental

Apparatus.—The apparatus used for these adsorption experiments was designed so that the amount of adsorption could be determined by pressure–volume relationships and also by weight increase. Materials of construction were nickel and copper. The powder was placed in a metal container which could be removed and weighed on an analytical balance. The temperature was carefully controlled at 28.2° with maximum fluctuation of the order of ±0.04°.

Nickel fluoride powder, prepared in the course of the kinetic studies described in the previous article was loaded into the sample container and evacuated to constant weight. A temperature of 125 to 150° was required to accomplish this in a reasonable time, even with the pressure over the powder maintained at less than 1×10^{-4} mm. After degassing, the container was weighed and then exposed to chlorine trifluoride. At frequent time intervals, the container was removed and weighed to determine the amount of gas which was sorbed by the powder sample. Each time the container was weighed, a section of the system was exposed to laboratory air. In order to ensure that no hydrogen fluoride was introduced to the sample by this procedure, the affected portion of the system was thoroughly dried by exposure to chlorine trifluoride followed by evacuation.

The chlorine trifluoride was purified by distillation and was known to have a purity of 99.8 mole per cent.

Results

The sample adsorbed chlorine trifluoride rapidly at first, and then slowly over a long period of time. Even after one hundred hours one was still not able to extrapolate to a saturation value. See Table I.

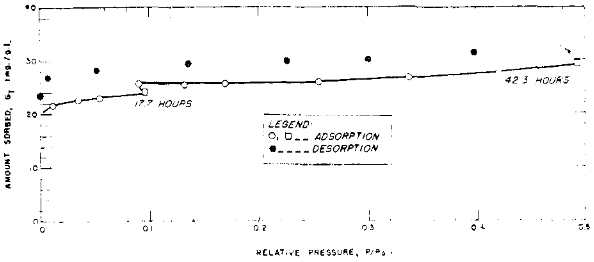

Fig. 1.—The sorption of chlorine trifluoride on nickel fluoride, uncorrected: $T = 28.2°$.

TABLE I

AMOUNT OF CHLORINE TRIFLUORIDE SORBED WITH TIME AT 28.2°

Total exposure time, hr.	Total amount sorbed, G_T, mg./g.	$y = G_T - 20.0$
0.4	15.9	
1.3	19.7	
2.8	20.1	$y_1 = 0.1$
19.6	22.1	2.1
27.0	22.7	2.7
48.6	23.7	3.7
67.6	24.6	4.6
92.5	25.1	5.1

It appears that this weight increase corresponds to a physical process. The sample and the container had previously been exposed to chlorine trifluoride until constant weights were obtained. Also, the sorbed material could be removed slowly by evacuation at room temperature or readily at elevated temperatures (125 to 150°). These reasons do not, of course, preclude the formation of a compound which is unstable and decomposes easily. The most likely possibilities for such a compound would be a nickel fluoride–chlorine trifluoride complex or nickel trifluoride. There is no evidence in the literature for the complex and it is not believed that conditions are suitable for the formation of the latter, whose existence is even in doubt. An X-ray diffraction pattern could not be obtained due to the great reactivity of the material. Further evidence that compound formation was not involved is that the equilibrium amount of chlorine trifluoride sorbed, varied with temperature.

The rapid initial uptake, complete in about two hours, was due to physical adsorption. The complications due to the "slow sorption" process are indicated by the hysteresis illustrated in Fig. 1. From the data of Table I, the amount of physical adsorption is very close to 20 mg./g. The quantity $y = G_T - 20.0$ is, therefore, a good estimate of the amount of material taken up by the slow sorption process. An equation of the type

$$y_n^2 - y_1^2 = k(t_n - t_1) \qquad (1)$$

gave the best fit of the data. A plot of $(y_n^2 - y_1^2)$ *vs.* $(t_n - t_1)$ was linear and from the slope, one calculates the constant, k, to be 0.34 (mg./g.)^2 hr.$^{-1}$.

Using this equation for the slow sorption process, one can correct the data at 28.2° and obtain esti-

---

[1] This document is based on work performed for the Government by Union Carbide and Carbon Corporation at Oak Ridge, Tennessee.

[2] R. L. Farrar, Jr., and H. A. Smith, *J. Phys. Chem.*, **59**, 763 (1955).

mates of the amount of physical adsorption. These data are shown in Table II where G_T is the total amount of material taken up, G_R is the correction term representing that amount which was taken up due to the slow process, and finally the desired quantity G_S is the estimate of the amount physically adsorbed. The units of G throughout are milligrams of chlorine trifluoride per gram of nickel fluoride.

TABLE II

ADSORPTION OF CHLORINE TRIFLUORIDE ON 4.66 G. OF NICKEL FLUORIDE AT 28.2°

Exposure time, hr.	Pressure, mm.	Rel. pressure $x = p/p_0$	Total ClF_3 in reactor, mg.	G_T, mg./g.	G_R, mg./g.	G_S, mg./g.
1.0	16	0.011	103.8	21.7		21.7
2.3	49	.034	113.4	22.7		22.7
3.3	79	.054	119.6	23.1		23.1
21.0	131	.090	139.9	25.7	2.5	23.2
22.1	192	.132	149.2	25.7	2.5	23.2
23.3	246	.169	158.0	25.8	2.6	23.2
24.5	372	.255	179.8	26.2	2.7	23.3
91.5	329	.226	190.0	29.9	5.5	24.4
93.5	198	.136	167.8	29.5	5.5	24.0
97.8	74	.051	143.8	28.4	5.6	22.8
		Evacuated to constant weight				
0.3	11	0.0075	78.7	16.5		16.5
1.5	35	.025	104.1	21.2		21.2

The value of G_T, which was calculated from the weight increase of the sample container when exposed to chlorine trifluoride, has been corrected for the amount of chlorine trifluoride in the gas phase including the small amount of association which is known to be present.[3] The data are plotted in Fig. 2 by the BET and Langmuir equations which are, respectively

$$\left(\frac{x}{1-x}\right)\frac{1}{V} = \frac{1}{cV_m} + \left(\frac{c-1}{c}\right)\frac{x}{V_m} \tag{2}$$

$$\frac{X}{V} = \frac{1}{cV_m} + \frac{x}{V_m} \tag{3}$$

where x, c and V_m have their usual significance. In practice V and V_m which are volumes of gas are replaced by G and G_m which are weights of gas, both per gram of adsorbent.

It is easily seen that the Langmuir equation represents the data over a larger range of relative pressures and indicates that monolayer adsorption predominates at least over the pressure range of the experiments. From the slope of the line, the value of G_m is found to be 23.6 mg./g.

The equation of Brunauer,[4] which assumes closest packing of the molecules for the area covered by each molecule is

$$A = (4)\,0.866\left[\frac{M}{4\sqrt{2}N_A d_l}\right]^{2/3} \tag{4}$$

where M is the molecular weight, N_A is Avogadro's number and d_l is the liquid density. Based on the density of 1.798 g./cm.^{3} at 28.2° from the data of Banks and Rudge,[5] the chlorine trifluoride surface area of the nickel fluoride is 32 sq. m./g. as compared to the nitrogen values of 26 to 36 sq. m./g.

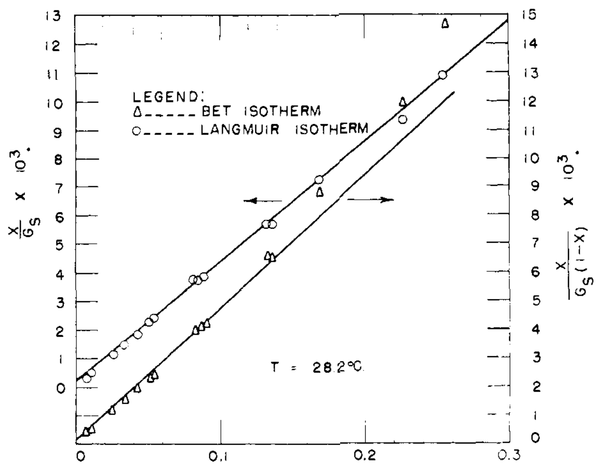

Fig. 2.—Correlation of adsorption data.

By means of the Langmuir plot, Fig. 2, one can get a better view of the effect of the slow sorption process. Here, the uncorrected quantity G_T is used and since G_R changes only slightly over a few hours, the plot has the effect of showing the apparent decrease in slope of the line with time. This may be converted into apparent G_m values which change with time and extrapolated to $t = 0$ to obtain the best estimate of the true G_m.

The results of the adsorption of chlorine trifluoride on nickel fluoride at elevated temperatures have been correlated by the Langmuir equation in the form

$$\frac{p}{G} = \frac{p_0}{cG_m} + \frac{p}{G_m} \tag{5}$$

where p is the pressure at which G mg./g. of chlorine trifluoride was adsorbed at a given temperature. G_m and G have the same significance as before. The equation is expressed in this form rather than the relative pressure form (equation 3) because the vapor pressure, p_0, has not been determined above 30° and extrapolation of the available data to the experimental temperatures would be susceptible to rather large errors. Furthermore the critical temperature of chlorine trifluoride has been estimated to be 174 ± 5°[6] by the method of Smith, Greenbaum and Rutledge[7] and the density of Banks and Rudge.[5] The calculation of the value p_0 at the highest temperature, 180°, would of course be meaningless. In equation 5 the uncertain quantity p_0, is lumped with other constants which occur as the intercept of the Langmuir plot.

The weight factor per monolayer is of course readily obtained from the slope of the Langmuir plots and is independent of the vapor pressure value. The constantly increasing slope of the Langmuir plots as the temperature increases produces a constantly decreasing value of G_m as shown in Fig. 3. G_m decreases faster than one would expect from the density change and application of

---

[3] G. Schmitz and H. J. Schumacher, *Z. Naturforsch.*, **2a**, 362 (1947).

[4] S. Brunauer, "The Adsorption of Gases and Vapors," Vol. I, Princeton University Press, Princeton, N. J., 1944, p. 287.

[5] A. A. Banks and A. J. Rudge, *J. Chem. Soc.*, 191 (1950).

[6] G. P. Rutledge, private communication.

[7] W. T. Smith, S. Greenbaum and G. P. Rutledge, *J. Phys. Chem.*, **58**, 443 (1954).

equation 5; however, this effect has been observed by others.[8]

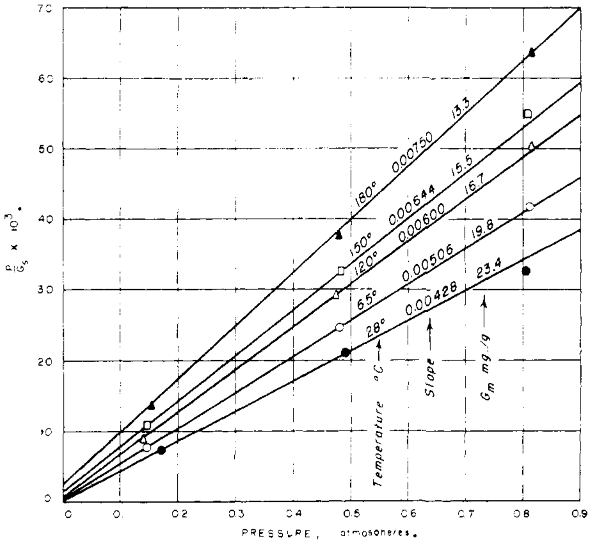

Fig. 3.—Langmuir plots, elevated temperatures.

The curves of Fig. 4, which have been taken from the straight lines of the Langmuir plots summarize the data. The units on the abscissa at the left are in terms of mg./g. of the sample having a surface area of approximately 30 sq. m./g. The units on the right are expressed as micromoles per square meter of surface area which is a more general unit.

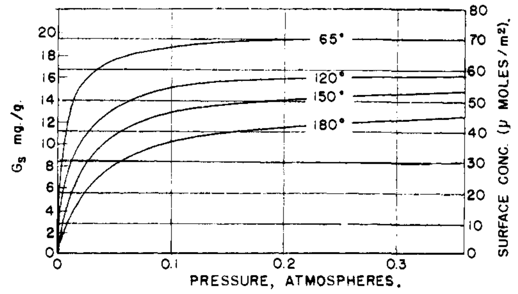

Fig. 4.—Adsorption at elevated temperatures.

Discussion of Results

This powder has previously[2] been shown to be porous and to possess a microcrystalline structure. Between these crystallites are grain boundaries or micro-pores whose diameters are larger than the interatomic distances in the solid and probably of the same order of magnitude as the dimensions of the chlorine trifluoride molecule itself. One would postulate then that the initial rapid adsorption corresponded to sorption on the surface whereas the slow rate process would correspond to a diffusion down the micro-pores or grain boundaries toward the cenof the particle.

The phenomenon of intercrystalline sorption, the specific type of persorption under discussion, has been observed by several previous workers. Tompkins[9] observed a slow prolonged sorption down grain boundaries in the case of the adsorption of ammonia on sodium chloride. Sulfur dioxide on sodium chloride[10] and hydrogen chloride[9] on potassium chloride also have shown these effects. Tompkins found that the rate process in the adsorption of ammonia followed a parabolic equation which he expressed as

$$S = 2A(Dt/\pi)^{1/2} \qquad (6)$$

where S is the amount of material sorbed by the grain boundaries on micro-pores, A is the material which is physically adsorbed on the surface, D is the diffusion coefficient for the migration process and t is the time.

Barrer[11] has derived the expressions for the kinetics of intercrystalline sorption, for the case of spherical particles.

$$Q_t = 8\pi a^2 C_0 \sqrt{Dt/\pi} \qquad (7)$$

where C_0 is the sorbate concentration just inside the surface or the concentration in the solid at saturation, Q_t is the total amount sorbed at time t and a is the particle radius.

Nitrogen Surface Area Anomalies.—The surface area of several samples of oxide and of fluoride have been determined by low temperature (−195°) nitrogen adsorption using the BET method. The "apparent area" of the fluoride was strongly dependent on the degassing treatment which the sample received while the area of the oxide was independent of the degassing treatment, behaving in a normal manner. Two series of determinations may be considered.

In each run, the oxide had been converted completely to the fluoride as evidenced by the fact that there was no longer any increase in weight with time upon exposure to a chlorine trifluoride atmosphere.[2] Each sample increased in weight more than the theoretical amount for the conversion of oxide to fluoride but the sample was then evacuated until the weight slowly approached the theoretical weight. The samples were then exposed to normal laboratory air for about one week prior to determination of nitrogen surface area. All evacuations were carried out at a pressure of 1×10^{-5} mm. or less.

Typical results of the surface area determination of samples of fluoride powder are shown in Table III. The starting oxide had a surface area of 6.5

TABLE III

APPARENT SURFACE AREA OF THE FLUORIDE POWDER FROM RUN 5

Degassing treatment	Apparent surface area, sq. m./g.
Sample No. 1 (1 wk. exposure to normal lab. air)	
1. 16 hr. evacuation at room temp.	25.8
2. 16 hr. at room temp. + 2 hr. at 150°	34.2
3. 16 hr. at room temp. + 2 hr. at 200°	36.8
4. 16 hr. at room temp. + 2 hr. at 230°	36.9
Sample No. 2 (1 wk. exposure to normal lab. air)	
1. 16 hr. at room temp. + 2 hr. at 150°	33.0
2. Exposed to normal lab. air for 2.5 days, followed by 16 hr. evacn. at room temp.	28.9

---

(8) J. W. McBain and G. T. Britton, THIS JOURNAL, **52**, 2198 (1930).

(9) F. C. Tompkins, *Trans. Faraday Soc.*, **34**, 1460 (1938).

(10) R. M. Barrer, "Diffusion in and through Solids," Second Edition, University Press, Cambridge, 1951, p. 115.

(11) R. M. Barrer, *Trans. Faraday Soc.*, **45**, 358 (1949).

sq. m./g. These observations show that (1) increasing the degassing temperature increases the apparent nitrogen surface area, and (2) the surface of a sample was lowered upon exposure to normal laboratory air after it had previously been degassed sufficiently to produce a high surface area.

The behavior of the nitrogen surface areas may be interpreted on the basis of the persorption mechanism described previously. When a sample of nickel fluoride, which has been completely converted from nickel oxide and from which the excess chlorine trifluoride has been carefully evacuated, is exposed to normal laboratory air, the sample increases in weight over a long period of time. This sorbed material, believed to be water vapor from the air, may also be removed on evacuation. It may be assumed here that the initial rapid uptake is due to surface adsorption, and the slow sorption process due to persorption which was noted previously with chlorine trifluoride. Before determining the amount of nitrogen which the sample would adsorb, it was first evacuated under various conditions as previously shown in Table III. The 16-hour evacuation at room temperature apparently removed the water vapor from the surface but only very little from the internal structure. The nitrogen was then adsorbed over the surface, while the water molecules blocked the pore structure. Increasing the temperature removed increasing amounts of water from the pores and allowed more nitrogen to enter giving a higher apparent surface area.

If the water molecules were chemisorbed on the surface, the adsorption of nitrogen should proceed just as readily over the occupied chemisorbed sites as over the uncovered surface. This was the conclusion of Brunauer and Emmett[12] who investigated the adsorption of nitrogen on an iron catalyst with and without chemisorbed oxygen.

[12] S. Brunauer and P. H. Emmett, This Journal, **62**, 1732 (1940).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Rhenium(IV) Compounds: Synthesis and Properties

BY CHARLES L. RULFS AND ROBERT J. MEYER[1]

RECEIVED MARCH 25, 1955

Hypophosphorous acid has been used, in place of iodide, for the reduction of perrhenate in an improved synthesis of several hexahalorhenates(IV). Solubility measurements and spectrophotometric absorption data are presented for a number of rhenium(IV) complex salts. The hydrolysis of hexachlororhenate(IV) ion has been studied conductimetrically, and the existence of the species $[Re(OH)_3(H_2O)_3]^+$ is postulated as the final intermediate prior to precipitation of the dioxide.

Aqueous solutions of the four halides, K_2ReX_6, hydrolyze to varying degrees, depending on the halogen in the complex. The most general method used for the preparation of these salts involves iodide reduction of potassium perrhenate in the presence of a large excess of the appropriate halogen acid.[2] The iodine product and large excesses of potassium halide must be removed in the purification. The only accurate solubility data recorded on these salts are measurements by the Noddacks[3] on two hexachloride salts in rather strong hydrochloric and sulfuric acid. The only well characterized absorption spectrum is that of the chloride in the visible region.[4,5] Little is known concerning the hydrolysis products of the hexahalorhenates. Maun and Davidson[5] have shown that there are several varieties of yellow-brown rhenium(IV) complexes. They postulate that the several varieties might be accounted for by a series of complexes of the type $[ReCl_{6-n}(OH)_n]^{-2}$.

Syntheses

Hydrazine dihydrochloride has been found to reduce small amounts of perrhenate quantitatively.[6] For the macro synthesis of hexahalorhenates, however, neither hydrazine, formaldehyde nor sulfur dioxide proved suitable. Controlled quantities of hypophosphorous acid gave good yields of the chloride and bromide salts. In the case of the fluoride a black precipitate, similar to that obtained with the bromide when too much reducing agent is used, was obtained. With the iodide, the hydriodic acid reduced the perrhenate in preference to the hypophosphorous acid.

Reagents.—Distilled water and C.P. or reagent-grade chemicals were employed throughout this investigation, as were University of Tennessee 99.8% grade potassium perrhenate, and Mallinckrodt 50% hypophosphorous acid in the modified synthesis.

Procedure.—Approximately 3 g. of potassium perrhenate and a stoichiometric amount of potassium chloride (0.77 g.) are added to 100 ml. of hydrochloric acid in a 250-ml. beaker. Twenty milliliters of 50% hypophosphorous acid is added and the beaker is covered with a watch glass. The solution is kept just below boiling until it becomes a clear light green; it will turn brown first, then dark green and finally light green. The hydrochloric acid lost by evaporation is replaced periodically to keep the salt from precipitating. The hot solution is filtered to remove any rhenium dioxide or rhenium metal which has formed. The solution is evaporated down to 20 ml., preferably by a heat lamp to prevent spattering, and placed in an ice-bath. The bright green salt is filtered onto a sintered glass filter and suction dried. The salt is washed twice with small volumes of ice-cold dilute hydrochloric acid and then, twice each, with ethyl alcohol and diethyl ether. The salt is air-dried by drawing air through the filter by means of suction, and is finally dried in an oven at 110° for one hour.

The preparation of the bromide differs only in that 5 ml. of hypophosphorous acid is used for the same amount of potassium perrhenate, and all chloride reagents are replaced by bromide reagents.

The reactions for the preparation of both the chloride and the bromide require approximately three hours up to the isolation of impure product. If a recrystallization is added,

---

[1] Abstracted from a dissertation submitted by R. J. M. in partial fulfillment of the requirements for the Ph.D. degree.

[2] L. C. Hurd and V. A. Reinders in H. S. Booth (ed.), "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, pp. 178-180.

[3] I. and W. Noddack, *Z. anorg. allgem. Chem.*, **215**, 129 (1933).

[4] H. Schmid, *ibid.*, **212**, 187 (1933).

[5] E. K. Maun and N. Davidson, This Journal, **72**, 2254 (1950).

[6] R. J. Meyer and C. L. Rulfs, *Anal. Chem.*, in press.