occurred, with evolution of heat and acid fumes, and only tarry products were obtained.

Summary

Organic amines form fluorine polyhalides, similar to those formed by the alkali metals, on adding a cold saturated solution of iodine trichloride to a cold saturated solution, slightly acidified, of the hydrofluoride of the amine, except in cases where the amine is chlorinated by the iodine trichloride.

The tetramethylammonium fluoride iodine trichloride is the most stable and the monomethylamine salt the least. The pyridine salt is next in stability to the quaternary amine salt and both of them compare favorably with the corresponding alkali metal polyhalides. The thermal decomposition is primarily dissociation as in the case of the alkali metal polyhalides.

All the organic fluoride polyhalides thus far prepared form orange-yellow tetragonal crystals.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY]

The Sorption of Oxygen by Nickel Catalysts[1]

BY W. WALKER RUSSELL AND LEONARD G. GHERING

In a recent investigation[2] it was found that catalytically active nickel strongly sorbed large amounts of oxygen at 0°. Because evidence of the true nature of a sorption process is probably best obtained by studying it at several temperatures, measurements in the present work have been extended below and somewhat above 0°. Furthermore, sorption measurements have been made on nickel catalysts in several states of activity, in an endeavor to throw further light upon the general problem of the correlation of sorptive behavior with catalytic activity.

Apparatus and Experimental Method

Apparatus.—Although the apparatus shown in Fig. 1 is almost self-explanatory, attention may be called to certain of its features. Catalyst bulb A allowed for successive reductions *in situ.* The manometer M could be used to measure pressures both in the catalyst system A, B, C, D and in the constant volume buret I, J. The by-pass G[3] facilitated the admission of oxygen to the catalyst. Mercury levels were adjusted at the fixed contacts D, E or F by means of a suitably connected radio loud speaker. These settings were reproducible to better than 0.02 mm., the sensitivity of the cathetometer used in the pressure measurements. A diffusion pump backed by a Sprengel pump allowed desorbed gases to be collected. The catalyst was protected by a liquid air trap

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(1) From a thesis submitted in May, 1933, by Leonard G. Ghering to the Graduate School in partial fulfilment of the requirements for the degree of Master of Science.

(2) Russell and Bacon, THIS JOURNAL, **54**, 54 (1932).

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

and trap B. The following baths were employed: ice, 0°; solid ammonia, −78 ± 0.3°; liquid air, −190 ± 3°. A copper–constantan thermocouple showed the constancy of the baths.

Preparation and Purification of Gases.—These operations were carried out as already described.[2]

Preparation of Catalysts.[2]—The pure nickel catalysts Ni II and VI which weighed 12.12 g. and 20.73 g., respectively, were reduced at 300°. The promoted nickel catalysts Ni III and VII which weighed 7.47 g. and 17.80 g. were reduced at 300 and 350°, respectively. Between measurements, irreversibly held oxygen was removed from Ni VI and VII by again reducing *in situ*, at 300° for the former and at 250° for the latter. Such oxygen was not removed from Ni II and III, but successive surfaces were "regenerated"[2] by heating *in vacuo* at 300° for four hours.

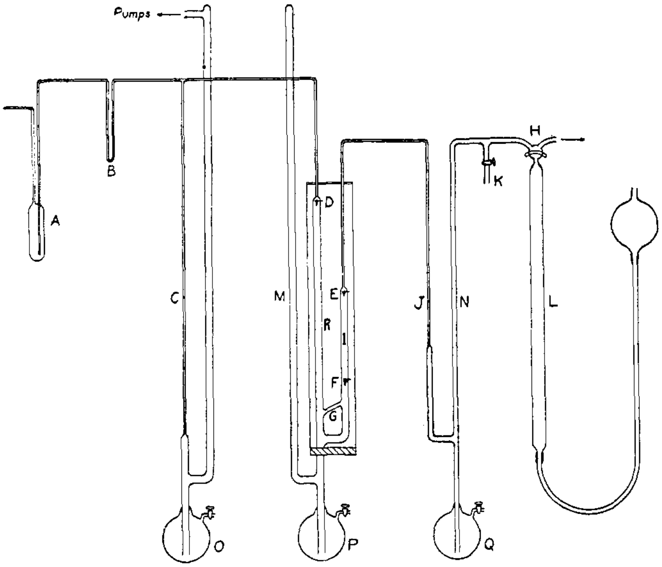

Fig. 1.—Apparatus.

General Procedure in Sorption Measurements.—The reduced catalyst was evacuated at the temperature of reduction continuously for twenty-four hours in order to remove sorbed hydrogen. About 2 mm. pressure of helium was then admitted to ensure temperature equilibrium. With the first increment of oxygen to show a persistent pressure, readings were extended over four hours or more and finally the pressure was built up to about 100 mm. Reversibly adsorbed oxygen was then pumped off in measured increments. Free space values were obtained with helium.

Experimental Results

A. Isotherms.—At liquid air temperature, even on the most inactive surfaces studied, at least 50% of the oxygen sorbed in four hours at a pressure of 80–100 mm. was taken up as fast as diffusion could occur in the apparatus, and with zero pressure, *i. e.*, less than 0.0001 mm. On very active surfaces at room temperature this figure was over 90%. After a persistent oxygen pressure appeared in the system, instantaneous sorption was always followed by a drift which was practically independent of the pressure above 10 mm., but which was larger the higher the temperature and the more active the surface. The forms of the drift curves were very similar to those obtained with hydrogen on zinc oxide in a higher temperature range by others.[4] While the rate of slow sorption on Ni VII during the fourth hour was only 0.05 cc. at −190°, it was twice as great at −78°, eight to nine times as large at 0° and amounted to 0.6 cc. at 24°. Therefore, although equilibrium could be closely approached in four hours at −19°, this was not true at the higher temperatures. However, in no case could oxygen which was slowly sorbed be pumped off at the temperature of sorption. Furthermore, it was found that an isotherm obtained at a given time coincided exactly with one obtained several hours later, if a correction was made for the drift which intervened. It is clear, therefore, that the experimental isotherms shown in Fig. 2 will not differ in shape from equilibrium isotherms but may lie below the latter. Because of the longer times of observation, *i. e.*, Curve 7 (twenty hours), Curve 8 (seven days), and the lesser activity of the surfaces, only Curves 2, 3 and 4 do not represent substantial equilibrium. While in the successive reductions the sorptive capacity of Ni VII could be reproduced to better than 0.5%, Ni VI

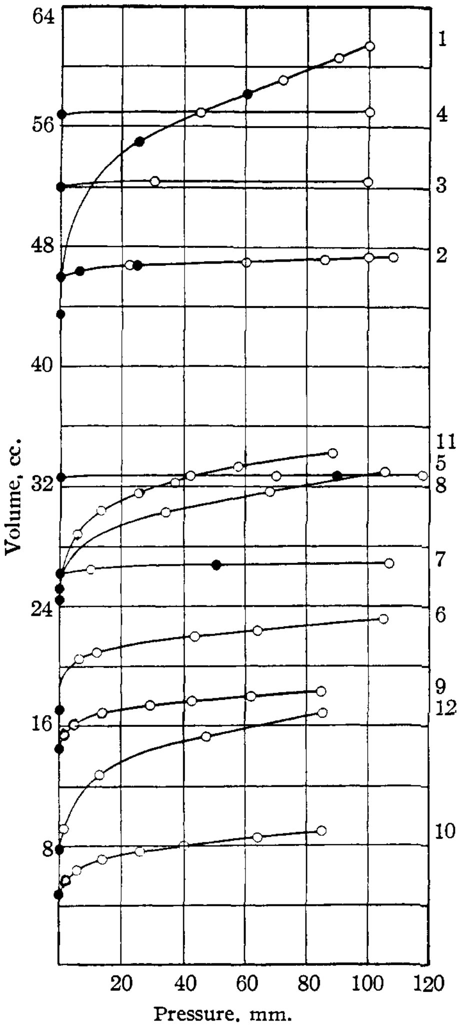

Fig. 2.—Total sorption isotherms. Ni VII: Curve 1, −190°; Curve 2, −78°; Curve 3, 0°; Curve 4, 24°. Ni VI: Curve 5, −190°; Curve 6, −190°, sintered; Curve 7, −78°; Curve 8, 0°. Ni II: Curve 9, −190°; Curve 10, −190°, first regenerated surface. Ni III: Curve 11, −190°; Curve 12, −190°, first regenerated surface. Curves 2, 3 and 4 do not represent equilibrium. Other curves are very near to equilibrium.

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(4) Taylor and Sickman, THIS JOURNAL, 54, 610 (1932).

was sintered at first rapidly and then at a slow linear rate. Because of this sintering, it was considered that isotherms obtained on the original surface would best illustrate the behavior of Ni VI, *i. e.*, pure active nickel, even though at −78° and above, oxygen sorbed at lower temperatures was present. For like reasons Curves 5 to 12, inclusive, were obtained in this unusual manner which, as will be shown later, has the effect of displacing these isotherms somewhat upward. The reversibility of the sorption depending upon pressure is evidenced by the fact that the open circles (sorption) and the black circles (desorption) lie on the same smooth curves. While at −190° none of the isotherms appear to approach saturation, at 0° and above total sorption becomes almost entirely independent of pressure. A comparison of Curves 1, 2 and 3 with 5, 7 and 8, and also 11 with 9 brings out the function of the promoter in increasing the extent of surface, and, due to the relatively smaller weights of the promoted catalysts, such a comparison is conservative. The larger weights of Ni VI and VII should also be kept in mind. The effect of the first regeneration of Ni III and II was to displace Curves 11 and 9 without distortion downward to new positions as Curves 12 and 10. Sintering Ni VI for 124 hours at 300° has caused the decrease in total sorption shown by the relative positions of Curves 5 and 6.

B. **Isobars.**—The isobars for sorptions at 100 mm. pressure at the end of four hours, shown in Fig. 3, serve to emphasize certain characteristics of sorptive behavior. Because of the short time allowed, it is clear that the points at the higher temperatures do not represent equilibrium. Some idea of the difference which this makes can be had by comparing Curves 5 and 6, since the latter is an equilibrium curve. The isobars for Ni VI are unusual in the sense already discussed under isotherms. While the total sorption, in general, at first decreased with rising temperature, passing through a minimum near −78° and then increasing, that on the regenerated surfaces showed the initial decrease, but little change above −78°. Unlike sintering, regenerating a surface caused no change in its reversible adsorption. On all surfaces the reversible adsorption decreased sharply above −190° and became very small near 0°. As a result the irreversible adsorption, except on the regenerated surfaces, increased with temperature, and at an accelerating rate. The term reversible adsorption as used here designates oxygen which can be desorbed by pumping at the temperature of sorption. By irreversible adsorption is meant the difference between the experimentally determined total and reversible adsorptions.

Because of the unusual method of obtaining the isobars for Ni II, III and VI, the effects of heating a surface carrying sorbed oxygen could be directly observed. When a surface initially saturated with oxygen at −190 or −78° was heated to −78 or 0°, some of the reversibly adsorbed oxygen was desorbed. Only if the surface was relatively inactive, *e. g.*, regenerated, or if it was evacuated prior to heating, was irreversibly adsorbed oxygen observed to be appreciably desorbed. Due to the rapid drift setting in near 0°, desorption amounted to less than 0.5 cc. on Ni VII, and a permanent decrease in irreversible adsorption was found only on the regenerated surfaces.

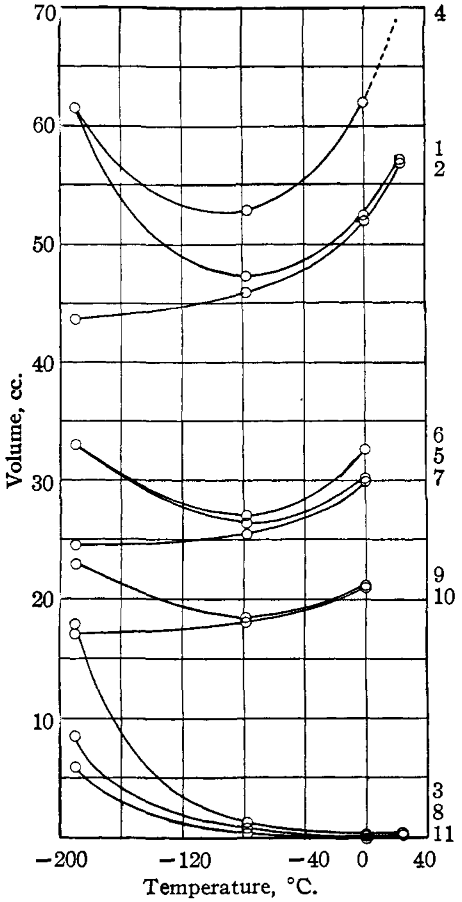

Fig. 3.—Isobars, at 100 mm., for amounts sorbed in four hours. Abbreviations: T. S., total sorption; I. A., irreversible adsorption; R. A., reversible adsorption. Ni VII: Curve 1, T. S.; Curve 2, I. A.; Curve 3, R. A. Each remaining curve, 4–11, involves successive sorption without intermediate removal of strongly sorbed oxygen. Ni VII: Curve 4, T. S. Ni VI: Curve 5, T. S.; Curve 6 (equilibrium) T. S.; Curve 7, I. A.; Curve 8, R. A. Ni VI (sintered): Curve 9, T. S.; Curve 10, I. A.; Curve 11, R. A.

Comparing Curves 1 and 4 in Fig. 3, for total sorption on Ni VII, since they represent the usual, and the unusual, method (already mentioned) of obtaining isobars, it is apparent that the procedure used in obtaining Curve 4 has resulted in an increased total sorption of 9.8 cc. at 0°, which when corrected for the 2.5 cc. of slow sorption which occurred at the lower temperatures gives a net increase of 7.3 cc. to be accounted for. Similar instances of this effect were also exhibited by Ni VI. In an endeavor to learn more about the effect of temperature sequence upon sorption, Ni VII was evacuated after the completion of Isobar 4 and sorption again started at −190°. The initial reversible adsorption of 20 cc. was again found, also an irreversible adsorption of 8.6 cc. which, however, was immediately desorbed upon heating to 0°. This experiment indicates that the oxygen first sorbed at −190° underwent a change in configuration upon heating to 0° and an unsaturation of surface was created, even though the irreversible adsorption had increased over 40% while at −78 and 0°. In another instance, the sorption measurements begun at 24°, on a freshly reduced surface of Ni VII, to determine the last point on Curve 1, Fig. 3, were continued at −190°, after evacuating the catalyst, and an increase of 12.55 cc. irreversible adsorption was found. This amount was immediately desorbed upon raising the temperature back to 24°. Since an extrapolation of Curve 4 to 24° would cause it to lie some 12 to 13 cc. above Curve 1, it seems very probable that had sorption been started at −190° this increment would not have been wholly desorbed but would have appeared in part as enhanced sorption. At all events it is clear that enhanced sorption such as was obtained at 0° by starting at −190°, was not obtained when sorption at −190° took place on a surface previously saturated at 24°.

Discussion

The peculiarities which differentiate the observed sorptive behavior of oxygen from that of a gas like hydrogen on catalytically active metals for example are mainly the former's large zero pressure adsorption, and the impossibility of removing such adsorption even at high temperatures, which, incidentally, necessitated the somewhat unusual experimental method of attack. It has been found that the magnitude and the type of oxygen sorption depend not only upon the activity and temperature of the nickel surface, but also upon the temperature sequence followed. The rate curves, and, except for the peculiarities above noted, the isotherms and isobars for oxygen, are not abnormal. Because of the ease with which the large irreversible oxygen adsorption found at all temperatures could be completely removed with hydrogen, *i. e.*, below 100° if not first heated to convert it to oxide, it is believed that true oxide formation does not have any considerable part here. Neither is dissolved oxygen indicated because at 0° and above where solution should have become more marked, it was increasingly easy to pump off reversibly adsorbed oxygen which in no case involved gas taken up by slow sorption. Since the irreversible adsorption has the characteristics of activated adsorption[5] one must assume that the latter can occur instantaneously, at least on the most active portions of the nickel even at −190°, its rate finally falling to a value which is greater the higher the temperature. The reversible adsorption at −190° must be largely capillary condensation and, at higher temperatures, molecular adsorption. The evidence already presented indicating that oxygen sorbed at a lower temperature is transformed to a different type of sorption complex at a higher temperature, namely, the desorption of oxygen irreversibly held on the less active surfaces by heating, and its readsorption; the unsaturation at −190° produced by heating to 0° a surface already saturated at −190°, may well demand the presence of more than one type of activated adsorption as would also the enhanced sorption obtained at 0° by starting sorption at −190°.

[5] Taylor, THIS JOURNAL, **53**, 578 (1931); Taylor and Williamson, *ibid.*, **53**, 2168 (1931); Taylor, *Chem. Rev.*, **9**, 29 (1931); Taylor and Sickman, THIS JOURNAL, **54**, 602 (1932); Taylor, *Trans. Faraday Soc.*, **28**, 131 (1932); Taylor and Sherman, *ibid.*, **28**, 247 (1932); Benton and White, THIS JOURNAL, **54**, 1373 (1932).

Summary

1. Large amounts of oxygen have been found to be instantaneously and irreversibly adsorbed by catalytically active nickel even at −190°. The amount of such low temperature sorption is greater the more active the surface. In general the amount of irreversible adsorption increases with the temperature.

2. Large amounts of reversibly adsorbed oxygen occur only at −190°.

3. Sintered and regenerated nickel surfaces possess certain like and different sorptive characteristics.

4. The rates of slow sorption are small at −190°, but increase with the temperature, and at a given temperature are greater the more active the surface.

5. The interpretation of the various phenomena observed makes it most probable that activated adsorption occurs even at −190° and is the major fraction of the oxygen sorbed at 0°.

PROVIDENCE, R. I.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE CARNEGIE INSTITUTE OF TECHNOLOGY AND THE CARNEGIE HIGH SCHOOL]

The Ternary System Diphenyl–Diphenylamine–Benzophenone

BY H. HOWARD LEE AND J. C. WARNER

Diagrams for the binary systems of diphenyl, diphenylamine and benzophenone were reported in a previous paper.[1] In the present investigation the freezing point–composition diagram for the *ternary* system of these components has been determined. The method of purification and the experimental procedure have been the same as in the previous investigation.

With most samples the initial crystallization temperature was checked by determining the temperature at which the solid phase disappeared. To accomplish this, a large number of solidified samples were placed in a thermostat set at a suitable temperature. After a period of from eight to ten hours, a record was made of samples which were completely liquid at the thermostat temperature. The temperature of the thermostat was then increased by from 0.1 to 1.0° depending upon the appearance of the remaining samples. After eight to ten hours, another record was made. The samples were freshly solidified each time the temperature of the thermostat was changed. This procedure for determining the temperature at which the solid phase disappeared was referred to as "thermostating" in a previous paper.[1]

Experimental Results.—The distribution of the samples used is indicated by the circles in Fig. 1. The experimentally determined initial

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[1] Lee and Warner, THIS JOURNAL, **55**, 209 (1933).