bromomesaconic acid obtained. The procedure involved treatment of DL-*threo*-α,β-dibromomethylsuccinic acid with concentrated alkali and, while this indubitably afforded the desired compound, several competing reactions (substitution of Br by OH, simultaneous loss of Br$^-$ and CO_2 etc.) interfered materially.

Consequently, dehydrobromination of the dimethyl ester of DL-*threo*-α,β-bromomethylsuccinic acid by pyridine was attempted. The results were most gratifying, yields as high as 93% being obtained. Saponification of the resulting ester readily afforded 86% of the desired acid.

Experimental[13]

DL-*erythro*-α,β-Dibromomethylsuccinic Acid.[14]—A mixture of 11.9 g. (0.86 mole) of mesaconic acid and 200 ml. of water was heated to boiling and 47.2 ml. (0.92 mole) of bromine was added over 45 minutes. The heating was continued for one-half hour, and the water was then removed by heating on a steam-bath under reduced pressure. The residue was slurried with water, filtered and washed with a little water; yield 83.3 g. (33.4%); m.p. 190–191° dec. On crystallization from chlorobenzene the product underwent some decomposition giving 55.1 g.; m.p. 187–188° dec. Nitromethane was later found to be an excellent solvent giving material which after a single crystallization melted at 196.5–197.5° dec. on slow heating (previously reported,[8] 193–194° on slow heating; 204° on rapid heating).

DL-*threo*-α,β-Dibromomethylsuccinic Acid (A).[8]—Two solutions, one of 57.00 g, (0.438 mole) of citraconic acid in 115 ml. of sodium-dried ether and 200 ml. of alcohol-free chloroform, and the other of 24.85 ml. (0.48 mole) of bromine and a few iodine crystals in 50 ml. of chloroform were mixed in a darkroom by the light of a small luminous flame. The reaction flask was stoppered and kept at room temperature in total darkness during the 17 hours required for complete disappearance of color. A considerable quantity of hydrogen bromide was observed when the flask was opened. The solution was evaporated in an air stream, and the residue was dried for 24 hours (*in vacuo*) over phosphorus pentoxide; yield 120.6 g. The oily residue was pressed on filter paper and washed with 150 ml. of benzene; 78.8 g. (62.0%); m.p. 148–149°. The product crystallized with 81% recovery from nitromethane in rectangular prisms; m.p. 153–153.5° (previously reported, 150–151°[8]).

(B).—A few iodine crystals were added to a solution of 6.72 ml. (0.131 mole) of bromine in 14.607 g. (0.1303 mole) of citraconic anhydride and the homogeneous solution was kept stoppered in total darkness for 7 days and then exposed to light for another 10 days. A precipitate began to accumulate gradually after 4 days. To the resulting dark mixture there was added 2.35 ml. (0.130 mole) of water. The crystalline mass, which formed rapidly with considerable evolution of heat, was not worked up for 2 months; but then the crude product (35.68 g.) was crystallized once from nitromethane; yield 26.82 g. (71.0%); m.p. 149–151°.

Methyl DL-*threo*-α,β-Dibromomethylsuccinate.—An ethereal diazomethane solution was added to 50.0 g. (0.172 mole) of DL-*threo*-α,β-dibromomethylsuccinic acid until the yellow diazomethane color persisted. The solution was then washed with a little 5% hydrochloric acid, water, 5% aqueous sodium bicarbonate, water, and then was dried over anhydrous calcium sulfate. After evaporation of the ether in a slow nitrogen stream the residue was vacuum distilled under nitrogen. A total of 53.114 g. (96.9%) boiling at 94–96° (1.8 mm.) was collected. Of this amount, 30.371 g. distilled at a constant temperature of 94.9° (1.8 mm.); n^{25}_{D} 1.4959.

Anal.[15] Calcd. for $C_7H_{10}Br_2O_4$: C, 26.44; H, 3.17; Br, 50.27. Found: C, 26.68; H, 3.26; Br, 50.05.

The product is a very pale yellow, fragrant, sweet-tasting liquid which is stable to hot aqueous alcoholic silver nitrate solution.

Bromocitraconic Anhydride.[16]—A mixture of 50 g. (0.172 mole) of DL-*erythro*-α,β-dibromomethylsuccinic acid and 25 g. of phosphorus pentoxide was heated slowly until the evolution of hydrogen bromide moderated. The semi-solid mass was then distilled to dryness at atmospheric pressure. The product distilled at 215–235° and rapidly solidified in the receiver; yield 30.8 g. (93%). The product was treated with Norit in carbon disulfide, and on concentration of the filtrate, 19.9 g. was obtained in five crops. A single recrystallization (from *ca.* 250 ml. of carbon disulfide) gave 15.2 g.; m.p. 100–101° (previously reported 100–101°[17]). The oily residues were not worked up even though a considerable amount of product remained in them.

Methyl Bromomesaconate.—A solution of 7.950 g. (0.0250 mole) of methyl DL-*threo*-α,β-dibromomethylsuccinate and 3.958 g. (0.050 mole) of pyridine was heated in an oil-bath at 120° for 10 minutes. The solution, which deposited crystals after 3 minutes and became very dark after 5 minutes, was cooled and extracted with water. The aqueous extract was acidified with 0.025 mole of nitric acid and titrated with silver nitrate and potassium thiocyanate showing that 51.2% of the bromine had been removed as bromide ion. The ester was dissolved in ether and the ethereal solution was dried over anhydrous sodium sulfate. Following the removal of the ether in a nitrogen stream, the ester was vacuum-distilled under nitrogen. Four clear, colorless fractions were collected over the range 85.9–89.0° (2 mm.); yield 4.604 g. (77.7%). The four fractions had refractive indices showing a spread of only 0.0006 unit, and no forerun and almost no residue were obtained. The second fraction was collected at 85.9–86.0° (2 mm.); b.p. 238° (734 mm.); n^{25}_{D} 1.4862.

Anal.[15] Calcd. for $C_7H_9BrO_4$: C, 35.46; H, 3.83; Br, 33.71. Found: C, 35.66; H, 3.94; Br, 33.49.

The reaction is exothermic, and when run on a 0.133 molar scale sufficient heat is developed, once the reaction starts, to afford an 81.2% yield without external heating. However, the yield was raised to 93.3% by increasing the heating period to 25 minutes, acidifying the cooled reaction mixture with sulfuric acid and extracting the ester with ether.

Bromomesaconic Acid.—A mixture of 0.790 g. (0.00333 mole) of methyl bromomesaconate and 0.40 g. (0.010 mole) of sodium hydroxide dissolved in 3 ml. of water was warmed on a steam-bath with stirring until the two layers became miscible (*ca.* 15 minutes). The solution was then cooled and extracted with ether. The dried ethereal extract on evaporation left no residue. The aqueous solution was acidified with 0.915 g. (0.010 mole) of concentrated nitric acid (sp. gr. 1.42), extracted with ether, and tested for bromide ion with silver nitrate with a negative result. The latter ethereal extract was dried over anhydrous calcium sulfate and evaporated leaving 0.597 g. (85.7%) of product; m.p. 197–216°. A single crystallization from nitromethane yielded 0.408 g.; m.p. 222.5–223° (previously reported[12] 220° after recrystallization of the zinc salt). A second crop of 0.040 g. was obtained on concentration of the filtrate after treatment with Norit.

---

[13] Melting points are corrected to ±0.5°.

[14] *Cf.* preparation of mesodibromosuccinic acid by H. S. Rhinesmith in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 177.

[15] Clark Microanalytical Laboratory, Urbana, Illinois.

[16] *Cf.* preparation of bromomaleic anhydride by P. Walden, *Ber.*, **30**, 2883 (1897).

[17] A. Angeli and G. Ciamician, *ibid.*, **24**, 74 (1891).

ANN ARBOR, MICHIGAN RECEIVED MAY 3, 1951

A Method for Obtaining Approximate Pore Size Distribution Curves from Nitrogen Desorption Isotherms

BY LOWELL G. WAYNE

Barrett, Joyner and Halenda[1] have recently devised a numerical method for the approximate solution of Wheeler's integral equation[2] to give

---

[1] E. P. Barrett, L. G. Joyner and P. P. Halenda, THIS JOURNAL, **73**, 373 (1951).

[2] A. Wheeler, Presentations at Catalysis Symposia, Gibson Island A. A. A. S. Conferences, June 1945 and June 1946; reported in ref. (1).

a "pore size distribution" function of a porous material from its nitrogen desorption isotherm. They applied this method to the analysis of a wide variety of porous materials, obtaining results which were in reasonable agreement with those derived from measurements with the high-pressure mercury porosimeter, and which yielded values for the internal surface areas consistent with the areas derived from nitrogen adsorption isotherms by the BET theory.[3]

Since the method that they propose is inconveniently elaborate and time-consuming for some purposes, it seemed useful to devise and evaluate some more rapid, if less refined, methods for obtaining approximate pore size distributions. The procedure described below permits a rapid approximate determination of the main features of the BJH distribution function; furthermore, subject to certain restrictions, this approximate result can be easily corrected to give close quantitative agreement with the BJH function in a substantial portion of the pore size range.

Like the BJH method, the rapid approximations here proposed are based on Wheeler's theory of simultaneous capillary condensation and multilayer adsorption. Assuming that the void space of a porous material exists principally in pores of circular cross section and that the actual radius of a pore, r_p, is greater than its "Kelvin radius," r_k,[4] by the thickness, t, of an adsorbed multilayer, Wheeler deduced the equation

$$V_s - V = \pi \int_{r_p}^{\infty} (r - t)^2 L(r) \mathrm{d}r \qquad (1)$$

which relates the volume, V, of adsorbate contained in a gram of porous material, to the multilayer thickness, t, and the maximum radius, r_p, of pores containing condensate, at any given relative pressure; $L(r)\mathrm{d}r$ is the total length of pores whose radii are between r and $r + \mathrm{d}r$. For a system conforming exactly to Wheeler's assumptions, the void volume in pores of radius not greater than r_p would be $\int_0^{r_p} \pi r^2 L(r) \mathrm{d}r$. The argument of this integral is the function approximated by the BJH "pore size distribution" function; in what follows, it will be called the "Wheeler distribution" function.

The basis of the present method is a rapid graphical approximation of the Wheeler distribution function, obtained by plotting the adsorbate volume, from data of the desorption isotherm, in terms of the variable r_p rather than the relative pressure,[5] and differentiating the transformed isotherm graphically or otherwise. The resulting curve gives the derivative $\mathrm{d}V/\mathrm{d}r_p$ as a function of r_p, and this derivative, as shown below, constitutes a useful first approximation to the Wheeler distribution function. From this curve a second approximation is readily obtained simply by multiplying the ordinates by appropriate values of the factor r_p^2/r_k^2; this factor is also a function of the relative pressure, and, except for very small radii, corresponds closely to the factor listed as R in the BJH tables.[1]

In Figs. 1 and 2, curves W1 and W2, respectively, represent the approximate distribution curves obtained by the two methods proposed above; for purposes of comparison the BJH curves are included, and also (curve K) the distribution based on the uncorrected Kelvin equation,[6] *i.e.*, $\mathrm{d}V/\mathrm{d}r_k$.

Figure 1 presents such curves for a small-pore silica gel produced by hydrolysis of ethyl orthosilicate. The single very prominent maximum is shown by all the curves, but in curve K it is found at a radius value 7 Å. less than in the others. In the vicinity of the peak and to the right of it, curve W2 shows excellent quantitative agreement with the BJH curve, while to the left of the peak W1 approximates the BJH curve more closely than does W2.

Figure 2 presents curves for a bone char of wide pore-size range. Here all the curves exhibit a maximum and a minimum separated by about 20 Å.; these features in curve K are displaced to the left relatively to the other curves. In addition, the BJH curve displays a maximum at about 30 Å. which is not evident in any of the other curves, but is apparently reflected as a slight shoulder in W1. Curve W2 gives the best quantitative approximation to the BJH curve for the radius range above 60 Å., but is poorest for radii below 40 Å., while W1 seems to be more satisfactory if the entire range of measurement is considered.

It may be concluded that the second approximation represented by curves W2 in these graphs will, in general, be most useful if the distribution (as obtained by the first approximation) shows a single narrow peak, with little volume in pores of larger radius, as in Fig. 1. In other cases, as illustrated by Fig. 2, the delineation of the main features of the distribution function by the first approximation should be sufficiently rewarding.

Besides relative ease of calculation, the method here presented has one further advantage over the full BJH procedure: it does not require tabulation of volume values for fixed radius intervals, hence it is more flexible than the BJH procedure and can be applied to desorption data without interpolation. For the same reason, it eliminates the necessity of unwarranted smoothing of isotherms which may show irregular, but real, fine detail. An example of this sort is illustrated in Fig. 3, where the BJH function (calculated using 5 Å. fixed intervals) for a treated silica gel is compared with the curve found by the simple approximation method (W1) from the desorption isotherm in the upper part of the figure, where the size of the circles indicates approximately the accuracy of the data. It is clear that the detail readily indicated in curve W1 would be largely missed in any BJH calculation based on intervals larger than 1 Å.

---

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

(4) $r_k = -2\sigma v/RT \ln (p/p_s)$, where σ represents the surface tension, v the molar volume of the adsorbate, R the gas constant, T the absolute temperature, and p/p_s the relative pressure; r_k, then, is the radius of curvature of a meniscus in equilibrium with vapor at the given relative pressure, and in a cylindrical capillary, $r_k = r_p - t$.

(5) Values of t as a function of relative pressure may be taken from the data of C. G. Shull, THIS JOURNAL, **70**, 1405 (1948); values of r_p as a function of p/p_s are then obtained by adding the corresponding values of r_k calculated from the Kelvin equation.

(6) A. G. Foster, *Trans. Faraday Soc.*, **28**, 645 (1932).

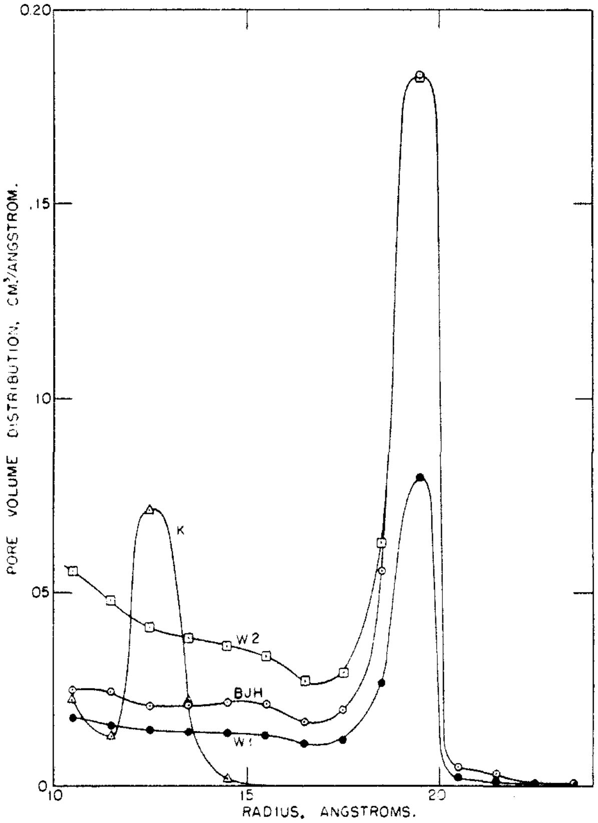

Fig. 1.—Approximate pore size distribution functions for a small-pore silica gel.

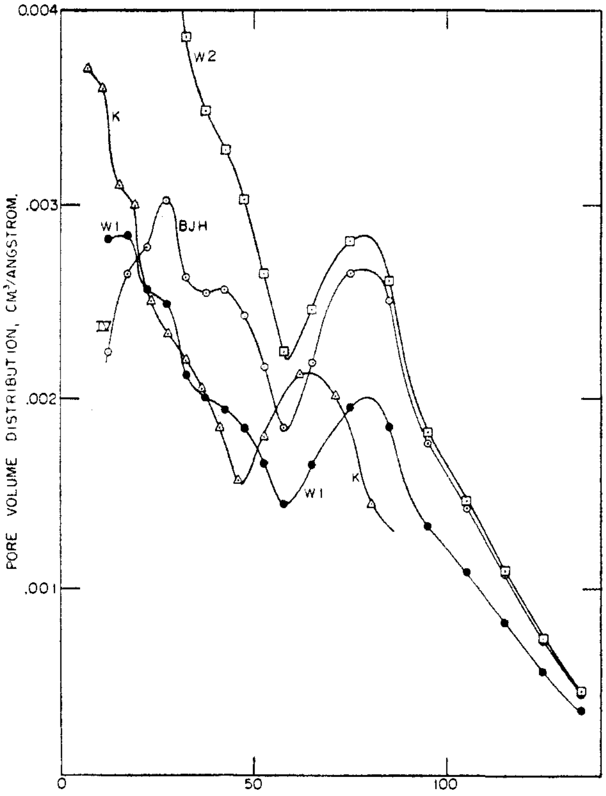

Fig. 2.—Approximate pore size distribution functions for a bone char.

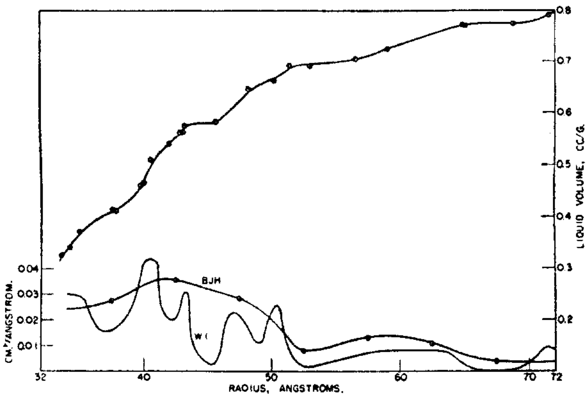

Fig. 3.—Transformed nitrogen desorption isotherm and approximate pore size distribution functions for a treated silica gel.

Mathematical Considerations.—To show the comparison between the W1 approximation function, $\mathrm{d}V/\mathrm{d}r_p$, and the Wheeler distribution function, $\pi r_p^2 L(r_p)$, equation (1) may be differentiated analytically

$$\mathrm{d}V/\mathrm{d}r_p = \pi(r_p - t)^2 L(r_p) + 2\pi(\mathrm{d}t/\mathrm{d}r_p)\int_{r_p}^{\infty} (r - t)L(r)\mathrm{d}r \quad (2)$$

Considering $\mathrm{d}V/\mathrm{d}r_p$ as a measure of the variation of adsorbate volume with change in the maximum radius of pores containing condensate, one sees that the first term on the right of equation (2) corresponds to liquid removal by evaporation of condensate, while the second term corresponds to multilayer thinning. The first term is always smaller than $\pi r_p^2 L(r_p)$; the second is always positive and therefore represents a correction toward the value sought. Its magnitude is negligible at higher relative pressures (here $L(r_p)$ is small); however, the identity

$$\pi \int_0^{\infty} r_p^2\, L(r_p)\mathrm{d}r_p = V_s = \int_0^{\infty} (\mathrm{d}V/\mathrm{d}r_p)\mathrm{d}r_p \quad (3)$$

shows that the total area under curve W1 must be equal to the total area under the Wheeler distribution function; hence at sufficiently small relative pressures the second term of (2) must represent an over-correction, giving curve W1 greater ordinates than the Wheeler function. In Fig. 2, curve W1 exhibits this relation to the BJH curve, which must be considered the best available approximation to the Wheeler distribution function. Physically, this relation indicates that at high relative pressures the amount of adsorbate left behind during the evaporation of condensate from large capillaries will not be compensated by an equivalent loss of gas by multilayer thinning from pores previously emptied of condensate, whereas at low relative pressures, where only a small amount of condensate remains, it will be overcompensated. (In Figs. 1 and 3, this over-compensation is not manifest even at the lowest pressures for which data were available.)

Curve W2 is given by the equation

$$[r_p^2/(r_p - t)^2]\, \mathrm{d}V/\mathrm{d}r_p = \pi r_p^2 L(r_p) + 2\pi[r_p^2/(r_p - t)^2]\mathrm{d}t/\mathrm{d}r_p \int_{r_p}^{\infty} r_p(r - t)L(r)\mathrm{d}r \quad (4)$$

Obviously, this curve will always lie above the Wheeler function, inasmuch as the last term on the right of equation (4) is always positive. It will furnish a close approximation to the Wheeler function for radii large enough so that this term is negligible; however, since it always exceeds the W1 function, and most drastically so for small radii, for which the W1 function is necessarily too high, its usefulness will be clearly limited to the range of relatively large pores. This behavior is illustrated in Figs. 1 and 2.

Acknowledgment.—The author wishes to thank Dr. L. G. Joyner and Dr. E. P. Barrett for permitting study of their paper prior to its publication. Thanks are also due to Dr. Joyner and Mr. W. B. Spencer for furnishing data used

in preparing the above figures, and to Dr. P. H. Emmett for his helpful comments and suggestions.

CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP
OF GULF RESEARCH AND DEVELOPMENT COMPANY
MELLON INSTITUTE
PITTSBURGH, PENNA. RECEIVED JUNE 9, 1951

The Preparation and Properties of Tetrakistribromophosphine Nickel and Tetrakistrifluorophosphine Nickel

BY GEOFFREY WILKINSON[1]

In 1936, the suggestion was made by A. A. Blanchard of this Institute that phosphorus trichloride might form a compound with nickel analogous to nickel carbonyl. The preparation of the crystalline non-volatile yellow compound, tetrakistrichlorophosphine nickel, $Ni(PCl_3)_4$, together with some of its properties, has been described in a previous paper.[2] It was also reported there that although phosphorus tribromide reacts with nickel carbonyl in the liquid phase with loss of carbon monoxide and formation of an orange solution, no compound of nickel with phosphorus tribromide could be isolated, presumably due to the ready decomposition of some intermediate replacement compound. Tetrakistribromophosphine nickel has now been made by the action of phosphorus tribromide on tetrakistrichlorophosphine nickel.

That phosphorus trifluoride might form a compound analogous to nickel carbonyl by the action of phosphorus trifluoride on nickel carbonyl was suggested by Chatt[3] following his preparation of phosphorus trifluoride complexes of divalent platinum chloride. The similarity of phosphorus trifluoride to carbon monoxide in its ability to form covalent complexes has been further demonstrated by the formation of an unstable ferrohemoglobin complex,[4] $HbPF_3$. The compound $Ni(PF_3)_4$, tetrakistriflucrophosphine nickel, has now been prepared both by direct fluorination of tetrakistrichlorophosphine nickel and by the action of phosphorus trifluoride on $Ni(PCl_3)_4$ and $Ni(PBr_3)_4$.

Tetrakistribromophosphine Nickel, $Ni(PBr_3)_4$.—The compound $Ni(PBr_3)_4$ is made by treating $Ni(PCl_3)_4$ with excess phosphorus tribromide. On warming the mixture to about 70°, the $Ni(PCl_3)_4$ dissolves and a deep orange-red color appears. Phosphorus trichloride is pumped off in a vacuum system, after which the residual solution is cooled to a temperature, just above the melting point of phosphorus tribromide (−38°). Small orange-red crystals separate; these are removed and recrystallized from phosphorus tribromide after which excess phosphorus tribromide is removed by washing with cold pentane. The solid is dried by aspiration of dry nitrogen, or by pumping in a vacuum system at room temperature. The yield of $Ni(PBr_3)_4$ is about 60% of the theoretical yield. Attempts to grow large crystals by slow cooling of the solutions have failed. The crystals are thermochroic like those of $Ni(PCl_3)_4$. The color changes from deep orange-red at room temperature to very pale yellow at −38°.

Qualitative analysis after removal of bromide by the persulfate or permanganate–acetone methods[5] showed the absence of chloride in the compound. Quantitative analysis of the compound after decomposition with sodium hydroxide was made as in the case[2] of $Ni(PCl_3)_4$ and gave Ni, 5.2 (calcd. 5.14); P, 10.7 (calcd. 10.84); Br, 83.5 (calcd. 83.9), confirming the formula $Ni(PBr_3)_4$.

The compound is notably less stable than $Ni(PCl_3)_4$. It begins to decompose thermally at about 80° to yield metallic nickel, phosphorus tribromide, and some nickel bromide. It is reasonably stable in a dry atmosphere and can be kept thus for several days.

Tetrakistribromophosphine nickel dissolves in inert organic solvents such as benzene, carbon tetrachloride, cyclohexane and xylene but decomposition rapidly follows with the disappearance of the characteristic orange color and with the slow formation of pale yellow or white flocculent precipitates of undetermined composition. In hot solutions blackening occurs at once. The solid is sparingly soluble in pentane and since at low temperatures decomposition is very slow, this solvent can be used for washing the solid free from phosphorus tribromide during its preparation. With the oxygenated solvents diethyl ether, ethyl acetate, ethanol and acetone, solution of the compound is accompanied by rapid decomposition.

The compound is, like $Ni(PCl_3)_4$, surprisingly stable toward water and dilute acids at room temperature, and even with 8 *N* nitric acid in the cold, the decomposition reaction takes several hours to accomplish. Sodium hydroxide solutions react readily to give a brown precipitate of undetermined composition and a solution of phosphorus acid; traces of phosphine also are liberated.

Tetrakistrifluorophosphine Nickel, $Ni(PF_3)_4$.—The preparation of $Ni(PF_3)_4$ has been attempted in several ways. The direct interaction of nickel carbonyl and phosphorus trifluoride under pressure appears to give replacement of no more than two or three molecules of carbon monoxide, presumably because of a reversible equilibrium; this observation has also been made by Chatt.[6] The interaction of metallic nickel and phosphorus trifluoride at pressures up to 150 atm. and temperatures of 200° gave none of the desired product. Success was achieved by the direct fluorination of $Ni(PCl_3)_4$ suspended in a fluorinated hydrocarbon (Fluorolube FS, b.p. ~160°) with antimony trifluoride, using a trace of antimony pentachloride as a catalyst; small quantities of a volatile liquid, b.p. ~70°, were produced.

The most effective method of preparation yet found is the reaction of $Ni(PCl_3)_4$ or $Ni(PBr_3)_4$ with phosphorus trifluoride at 50 to 100 atm. pressure and at about 100°. Sealed tubes containing $Ni(PCl_3)_4$ and excess phosphorus trifluoride were heated in steam for about 24 hours; the tubes were then cooled in liquid nitrogen, opened, and the volatile components transferred to a high vacuum system. The excess phosphorus trifluoride was removed by distillation from a bath at −115°. On allowing the residue to warm up to 0°, the liquid separated into two phases which were mechanically separated. The upper phase is phosphorus trichloride and the lower $Ni(PF_3)_4$. The $Ni(PF_3)_4$ was purified from traces of phosphorus trichloride by fluorination with antimony trifluoride (and antimony pentachloride catalyst) and by fractionation in high vacuum. The yield of $Ni(PF_3)_4$ produced from $Ni(PCl_3)_4$ in the reaction is about 50% of the theoretical yield; the only other products are metallic nickel and phosphorus trichloride.

Samples of the compound were condensed into a weighed tube with a constriction joined to the vacuum system by a ground glass joint; the sample was sealed off, both parts of the tube reweighed, and the bulb of $Ni(PF_3)_4$ then broken under 6 *M* sodium hydroxide in a closed system. After complete absorption of the compound, the solution was made just acid and diluted to a known volume, and aliquots were taken for analysis. Nickel was determined by precipitation with dimethylglyoxime.[7] For determination of phosphorus, the phosphorous acid formed in hydrolysis of the compound was oxidized by boiling nitric acid to phosphoric acid which was then determined by the standard ammonium

---

[1] Department of Chemistry, Harvard University, Cambridge, Mass.

[2] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

[3] J. Chatt, *Nature*, **165**, 637 (1950).

[4] G. Wilkinson, *ibid.*, 1951, in press.

[5] R. K. McAlpine and B. A. Soule, "Prescott and Johnson's Qualitative Chemical Analysis," D. Van Nostrand, New York, N. Y., 1933.

[6] J. Chatt, private communication, December, 1950.

[7] N. H. Furman, Editor, "Scott's Standard Methods of Chemical Analysis," 5th Edition, Vol. I, D. Van Nostrand, New York, N. Y., 1939.