

complete melting. For this reason, and others involving the measurements themselves, it is quite certain that the cell remained free of crystals.

Results and Discussion

The experimental values of the total resistance of the solution in the cell corrected to the melting point, and the freezing point lowering near absolute sulfuric acid, are plotted against the composition in Fig. 1 (data in Table I.) The maximum in resistance (minimum in electrical conductivity) can be taken as occurring at 99.996 ± 0.001 wt. % sulfuric acid if it is assumed that the 0.002 wt. % air present is inert with respect to electrical conductivity. Any future investigation should be made under such conditions that the samples in both the freezing point apparatus and conductivity cell can be kept free of air.

No attempt was made to determine the cell con-

stant, but the values of the resistance near the absolute acid (Fig. 1) are believed to be accurate, relative to each other, since the temperature coefficient corrections were very small. This is not true of the values near the monohydrate because the temperature correction was nearly as large as the differences themselves.

The minimum of electrical conductivity near the monohydrate was found to occur at 84.63 ± 0.05 wt. % H_2SO_4 (monohydrate is 84.48% H_2SO_4). It is of interest to note that the minimum near absolute acid is on the water side while the minimum near sulfuric acid monohydrate is on the sulfuric side.

Acknowledgment.—The authors thank Dr. J. C. Guffy for making the conductivity bridge and detecting apparatus available for this work.

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The Heat of Reaction of Graphite and Potassium

BY L. QUARTERMAN AND W. PRIMAK

The heat of reaction of graphite with an excess of potassium has been carefully redetermined, and it has been shown that the result given in the literature is considerably in error. The present determinations were made at several temperatures in the range 66–95°. For high density Acheson graphite, a mean value of 81 ± 2 cal./g. was obtained. There seemed to be a variation of about 5% in the heat of reaction of samples obtained from the same bar. The heat capacity of the calorimeter was found to have increased 0.25 ± 0.01 calorie for each gram of graphite introduced. Heats of reaction of some disordered forms of graphite were also determined and results some 15% lower than for Acheson graphite were indicated.

Introduction

Graphite-potassium compounds were studied by Fredenhagen and Cadenbach,¹ Fredenhagen and Suck² and Schleede and Wellman.³ The heat of reaction of graphite with potassium was determined by Fredenhagen and Cadenbach.¹ They reported that 1500 cal. ($\pm 5\%$) were released for each mole of carbon in the form of graphite introduced into an excess of potassium at a few degrees above its melting point. They also determined the heat of fusion of the potassium before and after introducing the graphite. From the ratio of this difference to the weight of graphite, they concluded the formula of the compound formed was close to KC_4 . The present paper describes a redetermination of the heat of reaction of graphite and potassium.

Experimental

Apparatus.—Refinements were introduced into the apparatus during the course of the successive determinations. The calorimeter described is that used in the final determinations. The essential parts of the calorimeter are shown in Fig. 1.

The calorimeter consisted of a conical platinum cup A, about 20 cc. capacity, standing in an evacuated Pyrex tube B, 48 mm. o.d., with tubulations for evacuation C, for introduction of leads D and E, for introduction of potassium F, and for introduction of samples G.

The apparatus was connected to a large diffusion pump with a large cock intervening. A side arm led to a reservoir from which helium, stored over potassium, could be ad-

mitted to permit a rapid equalization of the calorimeter with the bath temperature.

Graphite samples were delivered from a side tube placed at the top of the apparatus. A sample size was chosen which would give approximately a 2° temperature rise on reaction. Graphite samples which could be machined were turned to suitable diameter (3–4 mm.) on a lathe and cut to suitable length (about 12 mm.). Other samples were cut with a jeweler's saw and trimmed with a file. They were weighed and loaded into a magazine which was placed into the side tube at the top of the apparatus. A nickel wire was loaded into the magazine after the last sample. The samples could thus be moved by means of a magnet and introduced onto a gate at the top of the apparatus, one at a time. The temperature at the gate was determined with a thermometer strapped to the tube with its bulb and the gate wrapped in oil-saturated cotton. The gate was placed at the top of the apparatus after it was demonstrated that some reaction took place when the gate was just above the calorimeter cup. The magazine and side tube were made of silica when it was desired to bake out the graphite at high temperature (1000°). Several specially designed bends were placed in the sample delivery tube to decrease the speed of delivery and thereby prevent splashing of potassium.

About 12 g. of potassium was distilled into the cup from an auxiliary vacuum system in the manner described in a previous article.⁴ The analysis quoted there was for a sample used in the present work.

A copper-constantan thermocouple (#30 B & S gage wire) was welded to the platinum calorimeter cup. A piece of platinum sheet was placed over it and welded to the cup to prevent faulty temperature readings caused by heat conducted from the junction by the wires. The cold junction was attached to an aluminum shield surrounding the calorimeter tube and immersed in the thermostat. The couples were checked by placing one junction in an ice-bath while the other was in the thermostat. The couple was retained if the e.m.f. conformed within $1/2\%$ of the values given by Adams.⁵

(1) K. Fredenhagen and G. Cadenbach, *Z. angew. Chem.*, **158**, 249 (1926).

(2) K. Fredenhagen and K. Suck, *ibid.*, **178**, 353 (1929).

(3) A. Schleede and M. Wellman, *Z. physik. Chem.*, **B18**, 1 (1932).

(4) L. Quarterman and W. Primak, *THIS JOURNAL*, **72**, 3035 (1950).

(5) Adams, "Temperature," Reinhold Publishing Corp., New York, N. Y., 1941, p. 1306.

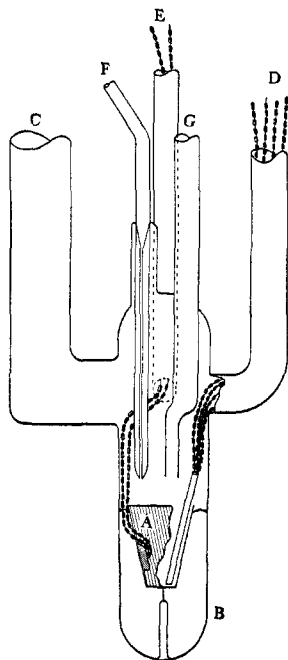


Fig. 1.—Calorimeter detail.

The electrical calibration heater was constructed like the flat calorimeter resistance thermometers described by Sligh.⁶ A bifilar winding of #32 Nichrome IV wire was made on a thin mica support. The four leads of #28 copper wire were silver-soldered directly to the nichrome. The winding was sandwiched between two thin sheets of mica and the whole was pressed flat in a platinum sheath. The heater was about 1.5 cm. wide and about 3 cm. long. In use, most of it was submerged in the liquid potassium. One-inch lengths of thin Pyrex capillary were used to insulate the leads within the evacuated apparatus. The leads were taken out of the apparatus through heavy wall capillary tubes filled with Apiezon "W" wax.

The calorimeter was set in a thermostated oil-bath whose temperature was controlled to several thousandths of a degree because greater fluctuations made the determination of the cooling curves difficult. The instruments used were the following: Leeds and Northrup K-2 Potentiometer; a recently calibrated standard cell; a rapid recording photoelectric potentiometer (GE-8CE 56J13); $\frac{1}{4}\%$ ammeters and voltmeters calibrated against the heater resistance with the aid of the potentiometer and a Leeds and Northrup 8063 Thermometer Bridge; synchronous electric timers operated by AC, whose frequency was controlled to $\frac{1}{4}\%$ or better.⁷ The application of the various instruments can be followed from the text.

Determination of Heat Equivalent of the Calorimeter.—The heat capacity of the calorimeter and its contents was determined several times at each temperature of operation, the determination being made before the samples reacted at that temperature and afterwards. The thermostat was set at the desired temperature and the calorimeter immersed in the thermostat. Helium was admitted to the calorimeter to hasten its approach to bath temperature. When the calorimeter was close to bath temperature, it was evacuated. After an interval of time, readings of the thermocouple were taken every $\frac{1}{4}$ minute with a K-2 potentiometer, thus establishing the lower rating curve. After two minutes, the electrical heater was turned on with a switch which simultaneously operated a $\frac{1}{10}$ second timer, and the current and voltage recorded. When the temperature of the calorimeter had risen the desired amount (usually about 2°), the heater was turned off and the time of heating recorded (usually about three minutes). Additional temperature readings were then taken at $\frac{1}{4}$ minute intervals for several minutes to establish the upper rating curve. The heat equivalent ($C + C_f$) could then be calculated from the formula

$$C + C_f = EIt/4.185(\Delta T + K'A) \quad (1)$$

The symbols are defined, and a typical set of values are enclosed in parentheses: C_f is the heat equivalent due to the added graphite; EIt is the electrical energy supplied to the cup (1.37 volts \times 0.130 amp. \times 210 sec.); ΔT is the temperature rise (2.203 deg.); and $K'A$ is the heat leak correction (0.284 deg.). E.m.f. readings were converted to temperatures by differentiating the formula⁸

(6) T. S. Sligh, Jr., Scientific Paper 407, U. S. National Bureau of Standards, Jan. 5, 1921.

(7) Private communication, Load Dispatcher, Commonwealth Edison Co., Chicago, Ill.

(8) Obtained by fitting Adams' table to a polynomial using tetragamma functions (H. J. David, "Tables of the Higher Mathematical Functions," Vol. II, Principia Press, Bloomington, Ind., 1935).

$$\text{e.m.f.} = 3.3561 + 0.4523 \left(\frac{T}{10} - 8 \right) + 0.00381 \left(\frac{T}{10} - 8 \right)^2 - 0.000028 \left(\frac{T}{10} - 8 \right)^3$$

and using a factor obtained by substituting a temperature near the midpoint of the range of the determination. The temperature rise, ΔT , was taken as the difference in temperature between a convenient point on the upper rating curve and a convenient point on the lower rating curve. The slopes of all the rating curves for the heat equivalent determinations and for all the heat of reaction determinations (see later) were plotted as a function of the temperature at their midpoint of a two-minute rating period.⁹ No order depending on the temperature of the calorimeter could be observed. The slopes were extrapolated to zero slope and this (-0.55 deg.) was taken as the mean difference between equilibrium temperature and bath temperature. The thermal leak modulus, K' , (0.0323/min.) was determined from the upper rating curve and the mean equilibrium temperature according to the formula

$$K' = \frac{T_1 - T_2}{\tau} \frac{2}{T_1 + T_2 - 2T_0}$$

where $(T_1 - T_2)/\tau$ is the slope of the rating curve (0.178 deg. \div 2 min.); T_0 is the equilibrium temperature and $(T_1 + T_2 - 2T_0)$ is twice the average temperature (5.52 deg.) over the rating period τ (2 min.). The quantity A was obtained graphically: the calorimeter temperature T was plotted as a function of the time; the area bounded by the curve between the points chosen to compute the difference ΔT and by $T = T_0$ was determined with a planimeter; and the area so obtained was reduced to proper units. The heat equivalents obtained using the foregoing procedures are plotted in Fig. 2.

A line was fitted to the points in Fig. 2 by the method of least squares.¹⁰ The equation

$$C + C_f = 3.361 + 0.2487 g \quad (2)$$

was obtained, where g is the weight of graphite introduced into the cup. Since these results include those obtained at a number of different temperatures, it is necessary to consider the temperature dependence of the results. When the results were corrected to 80° using temperature coefficients of heat capacity found in the literature, it was found that the maximum correction occurred in the results obtained at 66° and this was only 5–9 parts in 3500, far beyond the precision of the calorimetry. At all other temperatures the correction was less than $\frac{1}{700}$. The value 3.361 could therefore be taken as the heat equivalent of the calorimeter before any graphite was introduced and the equation used to compute the proper heat equivalent after each addition of graphite.

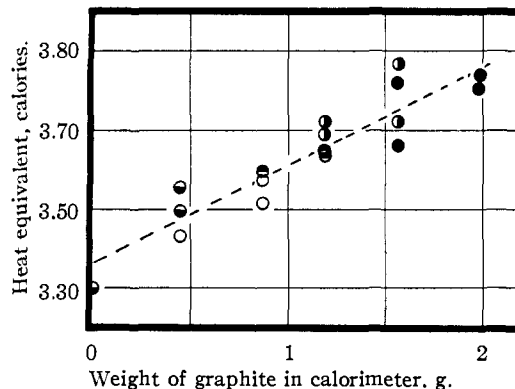


Fig. 2.—Heat equivalent of calorimeter as a function of the weight of graphite introduced into the calorimeter cup: O, 66.5° ; ●, 74.5° ; ●, 80.3° ; ●, 87.4° ; ●, 94.6° ; ---, least squares fit.

(9) Cf. P. E. Klopsteg, *J. Opt. Soc. Am. and Rev. Sci. Instruments*, **13**, 589 (1926).

(10) J. W. Mellor, "Higher Mathematics for Students of Physics and Chemistry," 4th Ed., Dover Publications, New York, N. Y., p. 326

Determination of the Heat of Reaction of Graphite and Potassium.—The procedure used to determine the heat of reaction was the following one. A sample was transferred to the gate by manipulating the nickel wire behind the samples with an external permanent magnet. The calorimeter was brought close to the bath temperature by admitting helium. It was then evacuated, and a rating curve obtained exactly in the manner described for the determination of the heat equivalent.

At a precisely determined time, the gate was opened by means of a solenoid and the recording potentiometer (now connected to the thermocouple) started. Within a fraction of a second the start of the temperature rise appeared. The initial part of the temperature rise was usually so rapid that the recording mechanism could not follow it and the whole heat rise was completed in a few tenths of a second. At 50 seconds the thermocouple was switched to the K-2 potentiometer and a rating curve determined. The recording potentiometer could not be read with the precision required for the determination of the temperature rise. This was taken as the difference between two convenient points on the respective upper and lower rating curves, as was done previously in determining the heat equivalents. The heat leak correction was a small part (<10%) of the total heat and therefore it was not necessary to know it as precisely as the temperature rise. The heat leak correction was obtained by planimetry of the recording potentiometer charts and multiplying the area by K' obtained in the manner described for the calibrations. The calculation of the heat of reaction, H_r , was made as follows

$$H_r = [C_p \delta T + (C + \Sigma C_f)(\Delta T + K'A)]/g \quad (3)$$

The symbols are defined and a typical set of values are enclosed in parentheses: δT is the difference between gate temperature and initial calorimeter temperature (2.173 deg.); C_p is the average heat capacity of the sample¹¹ over this range (0.0203 cal./deg. g.); g is the weight of the sample (0.1075 g.); $(C + \Sigma C_f)$ is the heat capacity given by formula (2) and includes the sample just dropped (3.544); $(\Delta T + K'A)$ (2.173 + 0.0823 deg.) has the meaning given in connection with equation (1).

The results obtained at a number of different temperatures for a number of high density, high purity Acheson graphite samples are given in Table I. These samples were baked

TABLE I
HEAT OF REACTION OF GRAPHITE AND POTASSIUM AT VARIOUS TEMPERATURES

Temp., °C.	Heat of reaction, cal./g.
66.5	83.8, 84.3, 82.8
74.5	83.7, 82.9, 84.0
80.3	83.9, 82.0, 83.8
87.4	81.6, 83.6, 83.3
94.6	81.4, 81.6, 81.6

out in high vacuum at 1000° for three hours prior to the determinations. It is believed the relative results are good to $\pm 1\%$. A serious systematic error was introduced into the determination by the use of #28 copper wires as current and potential leads in the heater. The potential leads were fastened within the sheath.

From the heat capacity of the heater and its temperature lag, it was estimated that the interior was about 2° above the

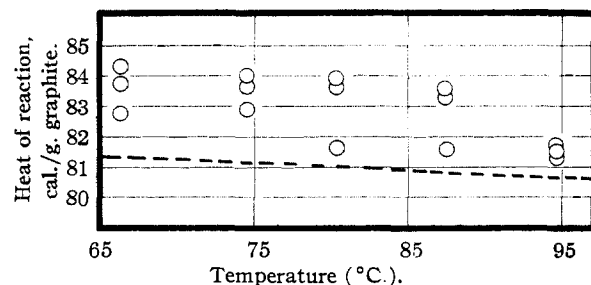


Fig. 3.—Heat of reaction as a function of temperature: --- Kirchoff's law.

(11) A. Magnus, *Ann. Physik*, **70**, 303 (1923).

calorimeter temperature and that the heat conducted by the heater wires represented a 2% correction in the heat input. The results represented by Equation (2) should therefore be decreased by 2%. The results obtained for another series of determinations in which smaller copper wire (#32) was used for current leads and for which the potential leads were fastened outside the heater sheath were: 81.4, 83.6, 78.5, 81.3 cal./g. This variation was observed for this set of samples despite the fact that the results obtained with 19 other graphite samples (not reported here) indicated a precision of $\pm 1\%$. The samples with which the high precision was obtained were contiguous samples in a graphite bar. The samples reported here were obtained at random from a 30-cm. piece of bar. It is therefore believed that the heat of reaction of samples in this bar may vary at least as much as 5%.

Before the present precision had been achieved, the heat of reaction of a number of different kinds of carbon was determined. The relative results are probably good to $\pm 5\%$, while the absolute values should probably be adjusted to make the heat of reaction for the high purity, high density graphite 81 cal./g. The results are given in Table II.

TABLE II
HEAT OF REACTION OF VARIOUS CARBON SAMPLES
(Heats of reaction should be adjusted to make the high purity, high density graphite 81 cal./g.)

Sample	Heat of reaction (cal./g. graphite)	Average
High purity, high density graphite	89, 85, 89, 84	Av. 87
Pitch bonded natural graphite	89, 85, 81	85
Pitch bonded lampblack	85, 74, 75	78
Pitch bonded petroleum coke	88, 81, 80	83
Natural Ceylon graphite	90, 80	85

The variation in the heats of reaction of some of these materials is greater than the experimental error. The extreme variation in the second and third samples of carbon is attributed to the extreme difference between the binder (graphitized pitch) and the base (natural graphite and lampblack in the second and third cases, respectively). The fourth sample had not been completely graphitized, having been heated to only 2400° in manufacture. The last sample was cut from a lump of Ceylon graphite and one of the specimens may have contained inclusions of impurities.

Discussion

The Effect of Temperature on the Heat of Reaction.—The heat of reaction at different temperatures as given in Table II is graphed in Fig. 3. If the compound is assumed to be KC_4 ,¹² and the heat capacity of potassium¹³ and carbon¹¹ are taken as given in the literature, one can use equation (2) to calculate the heat capacity of the compound. This is found to be 0.228 cal./g. The dependence of the heat of reaction on temperature according to Kirchoff's law is that shown by the dotted line in Fig. 3 if the heat of reaction at 80° is taken to be 81 cal./g. of carbon. The upper points seem to fall on a line of about this slope and the lower points on another line of about this slope. The results are taken to be a further indication of inhomogeneous reacting material.

Comparison with Previous Results.—The only results previously reported are those of Fredenhagen and Cadenbach¹ previously referred to, 125 cal./g. of carbon. It would seem that their results are reported from a single experiment. It is not possible that their high result was caused

(12) A redetermination by the freezing curve method of Fredenhagen and Cadenbach¹ gave the C/K ratio as 3.8 ± 0.3 . The precision was low because only a small fraction of the potassium had reacted. The freezing point found was in agreement with that given by Carpenter and Steward¹⁴ and an analysis of the freezing curve by the method of White indicated less than 0.014 mole per cent. of impurities.

(13) L. Carpenter and C. Steward, *Phil. Mag.*, **27**, 560 (1939).

by either their use of a different graphite, or a differently treated graphite, or a different calorimeter temperature, since the effect caused by all these was tested in the present experiments and found to produce only minor variations. They did not describe their calorimeter in detail, but from their description it is evident that their calorimeter was not adequately isolated from its surroundings and that their calibration heater was isolated from their calorimeter to some extent. It is apparent that their thermocouple, therefore, was not located in the same position relative to the heat flow during calibration and during reaction. The location was such that a high final result would be expected.

The results reported here were derived from a series of experiments performed in calorimeters

which were successively refined to eliminate variable heat losses, and the heat losses were then measured or (in the case of small ones) estimated. Experiments were performed with a variety of graphite samples some of which were outgassed at 1000° in high vacuum. All the results obtained were in the range 72–90 cal./g. carbon. From the most refined experiments the value 81 cal./g. was chosen as best representing the value for Acheson graphite, and the value seems to vary from sample to sample in the manner previously described.

Acknowledgment.—We are indebted to T. J. Neubert and S. Gordon for suggesting this problem and for guiding the work in its early stages.

CHICAGO 80, ILLINOIS

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[CONTRIBUTION FROM THE UNIVERSITY OF ILLINOIS AND WESTERN RESERVE UNIVERSITY]

Synthesis and Fluorination of Phosphorus(III) β -Chloroethoxy Dichloride¹

BY DONALD RAY MARTIN,² W. DOUGLAS COOPER, DWIGHT R. SPESSARD AND HAROLD SIMMONS BOOTH³

Phosphorus(III) β -chloroethoxy dichloride has been synthesized by a new procedure in which ethylene chlorohydrin is allowed to react with phosphorus(III) chloride. Phosphorus(III) β -chloroethoxy dichloride has been fluorinated by means of the Swarts reaction to give phosphorus(III) β -chloroethoxy difluoride. The above compounds have been purified and characterized by the determination of their molecular weights, percentage compositions, freezing points, vapor pressures, boiling points, heats of vaporization, Trouton's constants and liquid densities. The solubilities of the above compounds in seven solvents have been noted. Certain chemical properties, including hydrolytic reactions and the corrosion of steel, have been observed.

This investigation is a continuation of a study of the effects of the substitution of an alkoxy radical for a halogen atom in phosphorus(III)⁴ and boron⁵ halides. In this study, it was of particular interest to observe the effect of the Swarts reaction on the chlorine atoms in phosphorus(III) β -chloroethoxy dichloride.

Experimental

Preparation and Purification of Phosphorus(III) β -Chloroethoxy Dichloride.—Kabachnik and Rossiiskaya⁶ have prepared phosphorus(III) β -chloroethoxy dichloride by allowing ethylene oxide to react with phosphorus(III) chloride. In this investigation phosphorus(III) β -chloroethoxydichloride was prepared by a new procedure which is a modification of the method of Menschutkin.⁷ One mole of purified anhydrous ethylene chlorohydrin was added dropwise to one mole of phosphorus(III) chloride with vigorous stirring at a reaction temperature of 0°. The ethylene chlorohydrin was added at a rate of about 80 g. per hour. The reactor was a three-necked flask fitted with a glass stirrer with a mercury seal, a water-cooled condenser which was attached to a drying tube containing barium oxide, and a dropping funnel. Agitation was continued while the reaction mixture was allowed to warm slowly to room temperature to facilitate the evolution of hydrogen chloride. The remaining mixture of reaction products was distilled under a pressure of 40 mm. The residual liquid in the still pot at about 100° was regarded as impure phosphorus(III) β -chloroethoxy dichloride (yield about 77% based on ethylene chlorohydrin). The product was distilled under a pressure which varied from 5–10 mm. in a

fractionating column packed with glass helices.⁸ The vapor of the purified product condensed at 70° (5 mm.) and 75° (10 mm.) as a colorless liquid (yield of about 72%).

Fluorination of Phosphorus(III) β -Chloroethoxy Dichloride.—The method and apparatus used for the fluorination by the Swarts reaction were the same as described earlier,⁴ except no catalyst was required. The fluorination was begun at room temperature, but during the course of the reaction the generator became warm, attaining a maximum temperature of 60°. The pressure within the generator was approximately 50 mm.

The products of fluorination were fractionally distilled in a modified Dufton column.⁹ The column was operated at approximately atmospheric pressure until the fractions with very low boiling points were removed. The desired product distilled at about 14° ca. 40 mm.

Analyses.—The samples were collected and weighed in glass ampoules of approximately one-milliliter capacity. These samples were hydrolyzed in a slight excess of dilute (ca. 0.5 *N*) solution of sodium hydroxide. The concentration of caustic was maintained as low as possible as a precaution against obtaining silica in the solution, which would interfere with the analysis for phosphorus.

Chlorine was determined by the Volhard procedure, the necessary precautions being exercised to prevent the phosphite ion from reducing the silver ion.¹⁰ Phosphorus was determined gravimetrically as magnesium pyrophosphate after oxidation of the phosphite ion to the phosphate ion with bromine and nitric acid.⁴ Carbon and hydrogen were determined by means of the standard methods of microanalysis. A summary of the analyses is contained in Table I.

Determination of the Physical Constants (see Table I).—Phosphorus(III) β -chloroethoxy dichloride and phosphorus(III) β -chloroethoxy difluoride are colorless in the vapor and liquid states. Upon freezing, these compounds

(1) Presented at the XII International Congress of Pure and Applied Chemistry, New York, N. Y., September 10–13, 1951.

(2) Naval Research Laboratory, Washington, D. C.

(3) Deceased.

(4) D. R. Martin and P. J. Pizzolato, *THIS JOURNAL*, **72**, 4584 (1950).

(5) D. R. Martin and Leona S. Mako, *ibid.*, **73**, 2674 (1951).

(6) M. I. Kabachnik and P. A. Rossiiskaya, *Izvest. Akad. Nauk S. S. R., Otdel Khim. Nauk*, 295 (1946).

(7) N. Menschutkin, *Ann.*, **139**, 343 (1866).

(8) H. S. Booth, D. R. Martin and F. E. Kendall, *THIS JOURNAL*, **70**, 2523 (1948).

(9) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(10) H. S. Booth and A. R. Bozarth, *THIS JOURNAL*, **61**, 2927 (1939).