

the stoichiometric concentration and our experimental values of dissociation constants. The dotted line in Fig. 9 is the Debye-Hückel limiting slope, which is given by the following equation for 1-1 salts in diphenyl ether at 50°

$$-\log f = 33.8 \sqrt{c_i} \quad (7)$$

where c_i is total ionic concentration. Considering the large error in the experimental values of f , the results are not disappointing. The fact that we actually find a deviation of the right order of magnitude, which varies in the proper way with concentration, in a solvent of dielectric constant 3.53, is significant, if we recall that K is 2.7×10^{-11} . The highest ionic concentration in Fig. 9 is 6×10^{-7} .

Summary

1. The conductance of tetrabutylammonium picrate in diphenyl ether at 50° has been measured at 1000 cycles and low voltage and at 60 cycles under field strengths up to 15 KV/cm., over the approximate concentration range 10^{-3} to 10^{-6} normal.

2. Onsager's theory of the Wien effect is in good agreement with our data.

3. Deviations of activity coefficients from unity calculated by the limiting law of Debye and Hückel agree in order of magnitude with the experimental values obtained from the conductance curves.

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[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reduction of Carbon Dioxide by Graphite and Coke

BY MARTIN A. MAYERS

The rates of reaction of monolithic samples of artificial graphite with carbon dioxide and steam at atmospheric pressure and temperatures from 850° have been reported previously.¹ In that work the limiting effect of the diffusion field adjacent to the surface of the sample was eliminated and the measured reaction rates were considered to be true heterogeneous reaction rates and were referred to unit area of the surface exposed to the action of the gas. Later measurements of the reaction with carbon dioxide of artificial graphite and coke in granular form and of monoliths of both artificial and natural graphite have shown that in artificial graphite and in coke, the reaction rate measured depends not only on the surface exposed, but is the total of the contributions of elementary surfaces reached by the oxidizing gas by its perfusion throughout the body of these porous materials. This result suggests a possible explanation of part of the discrepancy between the measurements by this method and those made under high vacuum.²

Apparatus and Materials.—Carbon dioxide was withdrawn from a cylinder through a reducing valve, passed through a flowmeter and a purifying train consisting of a heated quartz tube containing reduced copper and copper oxide and a drying tower containing calcium chloride

followed by Anhydrone, and then into the furnace. Leaving the furnace the gas stream flowed through a cooling section, and then by way of a three-way stopcock, either direct to the analyzer, or into the large gasometer used in the tests reported before. The gas analyzer was the same one previously described, in which the carbon monoxide is oxidized by iodine pentoxide and its quantity determined by the titration of the iodine liberated which was collected in a condenser cooled by dry ice.

The furnace and sample holder differ from those used in the previous work and are shown in Fig. 1. The smaller diameter of the furnace tube permitted the attainment of high gas velocities without using extremely large volumes of gas. The mullite boat, used as a sample holder, permitted the use of either granular or monolithic samples of carbon. It was streamlined as shown in order to eliminate, as completely as possible, disturbances of the flow across the reacting surface.

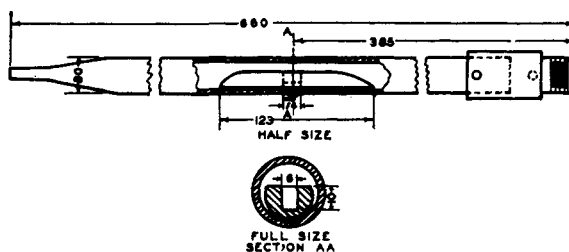


Fig. 1.—Reaction tube and sample boat. All dimensions in millimeters.

Granular samples were prepared for test by crushing coke in a small jaw crusher and by turning off heavy chips of graphite from cylindrical electrodes, and sieving the granular material between standard metal cloth sieves.

(1) M. A. Mayers, *THIS JOURNAL*, **56**, 70, 1879 (1934).

(2) H. Martin and L. Meyer, *Z. Elektrochem.*, **41**, 136 (1935); Lothar Meyer, *Trans. Faraday Soc.*, **34**, 1056-61 (1938).

The graphite electrodes were of Acheson graphite of spectroscopic grade, and were from the same lot as that used in the work reported previously. The cokes were experimental cokes made from a Pittsburgh Seam coal with controlled rates of heating to 1000°. Table I gives the details of the treatment of the various cokes tested. The boats were filled to the desired depth, shaken down, and uniformly compacted by pressing down the charge with a brass gage block of known dimensions which fitted the depression in the boat. The depth of the sample below the top surface of the boat was then determined by measuring the height of the top of the gage block above the top of the boat by the use of a vernier depth gage reading to 0.02 mm.

TABLE I
LABORATORY COKES MADE FROM PITTSBURGH SEAM COAL
(EDENBORN MINE)

Designation	Maximum temp., °C.	Rate of heating, °C./min.
W 85	1000	1.4
W 88	1000	1.4
W 92	1000	21.8
W 93	1000	21.8

Monolithic samples of different thicknesses were cut out of portions of artificial graphite electrode, and from a single mass of foliated Ceylon graphite, to fit the depression in the boat. They were cut out with a sharp knife and finished with a steel file, and then were cemented into the boats so that their top surfaces were not more than 0.5 mm. above the top of the boat. A commercial cement with a sodium silicate base (Insa-lute) was used to seal the samples into the boat. Great care was taken to prevent the cement from coming in contact with the top surface of the sample, and the cement was carefully finished off, after partial drying, to give a smooth contour rising from the boat surface to the surface of the sample.

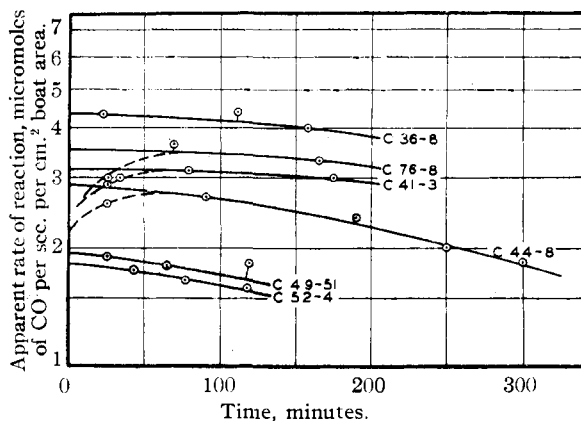


Fig. 2.—Reaction in micromoles of carbon monoxide per second per sq. cm. at various times for several samples of granular graphite.

Procedure and Calculations.—When a boat had been filled as described above, it was introduced into the furnace, and advanced in about fifteen minutes to the center. During this time the furnace was maintained at the

temperature at which runs were to be made, and carbon dioxide was passed through the furnace but was not collected. The slow advance of the boat was necessary to prevent breakage of the boat or the mullite furnace tube by thermal shock. Immediately after introducing the boat, and at thirty-five to forty-five-minute intervals thereafter, runs were made in which the gas leaving the furnace was collected and analyzed, the duration of each run being two to three minutes. During the runs, the temperature, the rate of gas flow, and the gas pressure at the inlet and outlet of the furnace were read every minute. Three to six runs were made on each sample.

The rates of reaction measured in several groups of runs at 1000° are plotted in Fig. 2 against the time after the boat was inserted in the furnace. It will be observed that the reaction rates rise to a maximum and then fall off. Since the quantity and approximate condition of the graphite are known only at the time the sample was inserted into the furnace, it is necessary to refer the reaction rate to that time. In performing this extrapolation, the rapidly rising initial portion of the curve is neglected. This is believed to be justified on the ground that this portion of the curve represents a transient condition, while the normal concentration gradients through the body of the sample are being set up. Such an assumption is supported by the fact that this portion of the curve was less pronounced in the measurements on granular samples, when the normal gradient might be expected to be attained more rapidly, than it was in measurements on monolithic samples. The differences in the intercepts at zero time in Fig. 2 are due to differences in the thicknesses of the samples tested, the thickest sample producing the largest reaction.

Theoretical.—In order to interpret these results it is necessary to analyze the conditions under which the reaction takes place. Let the concentration of carbon dioxide in the porous bed be p_1 and that of carbon monoxide be p_2 . Since the reaction takes place under a constant total pressure, and these are the only gases present

$$p_1 + p_2 = P \quad (1)$$

where P is the constant total pressure, atmospheric. Then, if D is the diffusion coefficient, a the void volume in the bed, v the gas velocity in the bed caused by the expansion due to the reaction, μ the reaction rate per unit of carbon crystallite surface, and s the surface of carbon crystallites per unit volume of bed, and if a steady state is reached, p_1 and p_2 must obey the differential equations

(3) Wm. B. Warren, *Ind. Eng. Chem.*, **27**, 72-77 (1935).

$$aD \frac{d^2 p_1}{dx^2} + a \frac{d}{dx} (p_1 v) - \mu s p_1 = 0 \tag{2}$$

$$aD \frac{d^2 p_2}{dx^2} + a \frac{d}{dx} (p_2 v) + 2 \mu s p_1 = 0$$

with the boundary conditions

$$\begin{aligned} dp_1/dx = dp_2/dx &= 0 & x = c; \\ v = 0, x = c; \text{ and } p_1 &= P_1, x = l \end{aligned} \tag{3}$$

where x is the distance below the top of the boat, l is the level of top of the sample, and c is the level of its bottom. Combining (1) and (2), it is found that v satisfies

$$\frac{dv}{dx} = - \frac{\mu s}{a} \frac{p_1}{P} \tag{4}$$

Eliminating p_1 between (4) and the first of (2), the non-linear equation

$$\frac{d^2 v}{dx^2} + \frac{1}{D} v \frac{dv}{dx} - \frac{\mu s}{aD} v = 0 \tag{5}$$

is obtained, whose solution, by the use of (4), could be used to calculate the total reaction per unit of sample surface by means of the integral

$$R = \int_c^l 2 \mu s p_1 dx = 2aPv(l)$$

A general solution to equation (5) has not been found, but a series expansion can be set up⁴ for small values of $\mu s/aD(c - l)^2$ in the form

$$R \sim 2 \mu s (c - l) \left\{ 1 - \frac{2}{3} \frac{\mu s}{aD} (c - l)^2 + \frac{2}{3} \left[\frac{\mu s}{aD} (c - l)^2 \right]^2 - \dots \right\} \tag{6}$$

which, however, converges very slowly. If the coefficient of p_1 in the second of equations (2) were μs instead of $2\mu s$, v would vanish and a simple analytic solution is possible in the form

$$R = 2 \sqrt{\mu s a D} \tanh \sqrt{\frac{\mu s}{aD}} (c - l) \sim 2 \mu s (c - l) \left\{ 1 - \frac{1}{3} \frac{\mu s}{aD} (c - l)^2 + \dots \right\} \tag{7}$$

Hence, it seems probable that the effect of the non-linearity of equation (5) is merely to change the rate of convergence of R in the neighborhood of $(c - l) = 0$; the similarity between (6) and (7) suggests that near $(c - l) = 0$ there will be a linear relation between $R/(c - l)$ and $(c - l)^2$, and that the value of $2\mu s$, the true rate of formation of carbon monoxide per unit volume of sample, will be given by the intercept of the line at $(c - l)^2 = 0$.

Results

The tests on granular samples of artificial graphite were made on beds of such thickness that

(4) H. G. Landau, to be published.

this method of plotting gave straight lines, as shown in Fig. 3, in which the reaction rates per unit area at zero time determined from the curves of Fig. 2, divided by the sample thickness, are plotted against the square of the sample thickness. The fact that the experimental results appear to fit straight lines on this plot indicates that the analysis given above may apply to the experimental condition, while the departures from the lines at values of $(c - l)^2$ greater than about 0.4 show that the higher order terms begin to be of influence above the corresponding value of $\mu s/aD(c - l)^2$. The intercepts of these lines, representing the rate of formation of carbon monoxide at 1 atmosphere pressure per unit volume of the bed of granules, can then be plotted as the triangles in Fig. 5, to the coördinates of the Arrhenius equation, showing that the reaction rate has a temperature coefficient corresponding to the heat of activation of 52.3 kcal. The departure of the points from the line corresponds to a probable error of a single determination of about 17%.

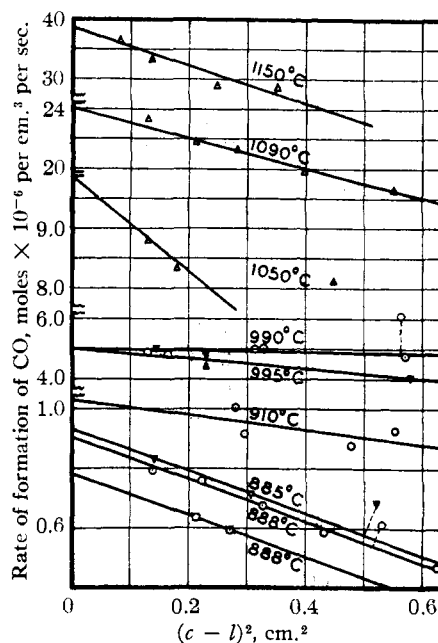


Fig. 3.—Determination of reaction rate per unit volume for granular graphite passing no. 16 and on no. 20 U. S. std. mesh sieves: Δ , gas velocity 1.9 l./min.; \circ , gas velocity 2.5 l./min.; ∇ , gas velocity 3.4 l./min.

When the data for monolithic samples are plotted as in Fig. 4 it is observed that the points do not fall on a straight line, but appear to approach

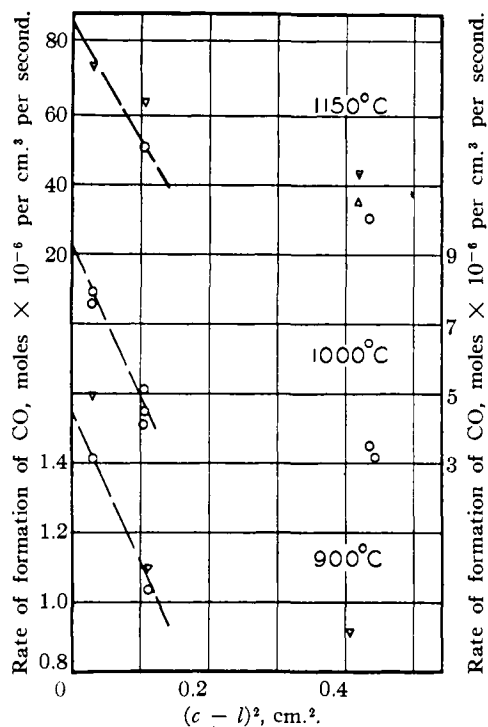


Fig. 4.—Determination of reaction rate per unit volume for monolithic graphite.

a hyperbolic form. This might be taken to indicate that the monolithic samples have a true surface reaction with carbon dioxide, whose value might be obtained by plotting R against $(c - l)$ and reading the intercept at zero thickness. It must be observed, however, that the quantity $\mu s/aD(c - l)^2$ is a function of the porosity, or the void volume of the sample. Comparing samples of the same material packed to different densities, it will be observed that $\mu s/aD$ varies as $(1 - a)/a$. Since the volume of voids of the monolithic samples, determined by comparing their true density determined with helium⁵ as the displacing fluid with their apparent densities as shown in Table II, is about 29%, while that for the granular samples may be expected to be about 50%, the value of $\mu s/aD$ for the monolithic sample would be nearly three times that for the granular sample at the same temperature. Since the results for the granular samples departed from the straight line at values of $(c - l)^2$ of about 0.4, those for the monolithic samples may be expected to do so at about 0.13. Because of the difficulty of cutting out thin samples of graphite, there are only two points at each temperature at values

(5) H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, **28**, 1082 (1924).

of $(c - l)^2$ less than 0.13, but passing straight lines through these points permits making an estimate of the value of $2\mu s$ for the monolithic samples. These values have been plotted on Fig. 5 as circles. The line passing through them corresponds to a heat of activation of about 50.6 kcal. The difference between the heats of activation of the reaction on monolithic and on granular samples indicates the order of the precision of the determination of this quantity, or about ± 1.7 kcal. The ratio between the rates of reaction in the two kinds of samples, which is almost constant at a value of 1.58, indicates that the volume of voids in the granular sample is about 55%, corresponding to particles packed to a density of 64%.

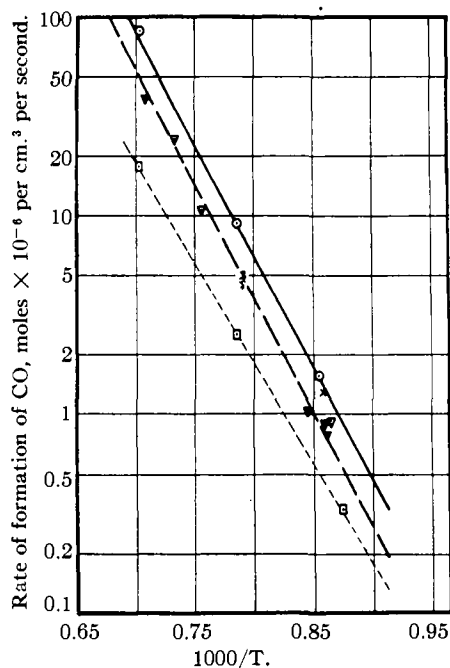


Fig. 5.—Reaction rates per unit volume at various temperatures: \circ , monolithic samples of artificial graphite; ∇ , artificial graphite -16 +20 mesh; \square , natural graphite—read scale in moles $\times 10^{-6}$ per sq. cm. per sec. Laboratory cokes: \times , W 85; $+$, W 88; \odot , W 92; \oslash , W 93.

The data on cokes were analyzed by the same methods as described above, and the results are shown by various symbols in Fig. 5. Measurements on natural graphite were made on samples of different orientations with respect to the grain of the sample. The results of these measurements were very erratic, being greatly affected by the quantity of ash exposed, the ash being distributed

irregularly through the foliated mass from which samples were cut. The results on this material were so erratic as to obscure any differences of reaction rate with orientation of the face or with thickness of the sample that may have been present. The order of magnitude of the reaction rate with this material was, however, the same as that of the monolithic samples, considered as a reaction rate per unit area. These values are also shown in Fig. 5.

Discussion

While the precision of the results is not high, it is great enough to make it certain that the results obtained in this work differ from those previously reported on the same material. The hypothesis that the monoliths of artificial graphite were actually porous, required to correlate the results, was checked by comparing the true density determined by displacement with helium with the apparent density of several samples as shown in Table II. It may be noted that the results of these experiments agree with those previously reported if the correction for volume reaction is not made. Thus it must be concluded that the earlier work is in error because of failure to take account of the perfusion process.

TABLE II
TRUE DENSITIES OF VARIOUS GRAPHITES

Sample, Acheson graphite	True density in g./cc.
Monolith	2.07
Monolith, heat treated at about 2200°	2.08
-16 +20 mesh	2.08
-140 mesh	2.11

APPARENT DENSITIES OF VARIOUS MONOLITHIC SAMPLES
OF ACHESON GRAPHITE

Sample	Apparent density in g./cc.
25	1.47
26	1.50
27	1.48
Apparent volume of voids	29%

This result suggests the explanation for some of the discrepancies that exist in the literature concerning this reaction. The present value of the temperature coefficient for the reaction of carbon dioxide with artificial graphite is in approximate agreement with the value that may be calculated from the work of Blakeley and Cobb.⁶ It also suggests an explanation of the peculiar temperature coefficient of the reaction

rate of artificial graphite with oxygen calculated by Davis and Hottel⁷ from their experiments on the burning of carbons in oxygen under conditions in which the diffusion path was fixed and known. From this work both the diffusion coefficient and the specific reaction rate could, theoretically, be calculated, if the reaction took place on a geometrical surface at the end of the diffusion path. However, the reaction rates calculated on this assumption had abnormal temperature coefficients that did not follow the Arrhenius equation, and the reaction rates for different forms of carbon crossed in a peculiar fashion. Davis and Hottel were unable to give an explanation for this behavior; it is suggested, in the light of the results reported here, that the reason for the apparently abnormal behavior may be sought in the perfusion phenomena accompanying the reaction, since the samples used in that work also were porous. The differences in the behavior of the two kinds of carbon for which data are reported probably arise from their having both different porosities and different reactivities, which easily could lead to the change in order of apparent reaction rate that was observed with changes in temperature.

Finally, this work suggests the possibility of partly reconciling the discrepancies observed between determinations of the reaction rates at normal pressures, and those determined in high vacuum.² The reaction rates observed at normal pressures, when referred to unit area of the carbon used, are of the order of thousands of times as great as those determined under vacuum. Since, however, the samples tested in the vacuum work⁸ had uniform solid surfaces of deposited graphite whose basal planes were parallel to the geometrical surface, the discrepancy must arise in part from the porous nature of the carbons used in the experiments at normal pressures, in almost all of which a large internal surface, which easily could be a thousand times the exposed geometrical surface, was available for reaction. This hypothesis fails to explain, however the large difference in temperature coefficient, which in the vacuum experiments² corresponds to a heat of activation of the order of 90 kcal. This extraordinarily high value may be due to the fact that, in the vacuum experiments, only the graphite filament was heated, while the gas was cold.

(6) T. H. Blakeley and J. W. Cobb, *Gas World*, **101**, 452, 498, 612 (1934); *Gas J.*, **308**, 351, 526, 748 (1934).

(7) H. Davis and H. C. Hottel, *Ind. Eng. Chem.*, **26**, 889 (1934).

(8) Lothar Meyer, *Z. physik. Chem.*, **B17**, 385-404 (1932).

Conclusions

Measurements of the rates of reaction of carbon dioxide with both artificial and natural graphite and with several high temperature cokes of known history have been reported. The results have been calculated to give the reaction rates per unit volume of coke or graphite and have been corrected for the perfusion of the reacting gas throughout the body of the porous samples. Because of this manipulation, the results are not particularly precise, errors of the order of 20% being possible.

It is shown that artificial graphites and cokes behave, in reaction, like porous bodies whose internal surface contributes to the reaction rate. The reaction of carbon dioxide with artificial graphite has a temperature coefficient corresponding to a heat of activation of about 52 kcal. That of the reaction with natural graphite is more uncertain because of the marked effect of the mineral impurities which the sample contained, but it appears to be of the order of 44 kcal.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Colorimetric Determination of Palladium with *p*-Nitrosodiphenylamine¹

BY JOHN H. YOE AND LYLE G. OVERHOLSER

The colorimetric methods available for the determination of palladium have been developed in connection with platinum analysis,^{2,3} and while they do provide rapid and accurate methods for the determination of quantities of palladium of the order of 0.1 mg., no colorimetric method has been reported that will yield reasonably accurate results with quantities of the order of a few γ . Studies have been made on reagents for the detection and approximate estimation of minute quantities of palladium. *p*-Dimethylaminobenzylidene rhodanine⁴ has been used for the detection of palladium, but no application of this reagent for the quantitative determination of the metal has been reported. This reagent is extremely sensitive for palladium but not so nearly specific as *p*-nitrosodiphenylamine. Feigl and Fränkel⁵ report that as little as 0.0025 γ of palladium per ml. (1:400,000,000) can be detected by the catalytic effect of palladium on the reduction of nickel salts by sodium hypophosphite. Pierson⁶ utilized the reducing action of mercurous chloride for the de-

tection and approximate estimation of minute quantities of the metal by observing the shades of color produced by the adsorbed metal. But there is need of a method that may be used for the determination of minute quantities of palladium and that is not rendered useless by the presence of the other metals frequently accompanying palladium.

p-Nitrosodiphenylamine has been found to react with palladous chloride in neutral and weakly acid solution to give either a deep red colored solution or a purplish-brown precipitate, depending on the concentration of the metal. The reaction is extremely sensitive, permitting the detection of 0.005 γ of palladium by the spot-plate technique, and compares favorably with *p*-dimethylaminobenzylidene rhodanine. The reagent is practically specific for palladium, in the sense that the only other metals forming colored compounds are gold and silver. The sensitivity for gold and silver, however, is much less than for palladium. Oxidizing agents interfere by giving colored solutions; cyanides and iodides prevent the formation of the colored compound. The sensitivity is affected by the *p*H of the solution and the concentration of salts present, but these can be controlled easily.

If the reagent is added in excess to a weakly acidic palladous chloride solution, the palladium is quantitatively precipitated. On the other hand, if a sodium acetate-hydrochloric acid buffer of the proper *p*H and salt concentration is used, a deep red colored solution results which may

(1) This investigation was partly supported by a grant-in-aid from the Carnegie Corporation. It is the first of a projected series based upon studies of inorganic reagents in organic analysis. These studies are being conducted as a cooperative effort in which eight Virginia institutions are participating under the direction of John H. Yoe. Those cooperating with the University of Virginia are: Hampden-Sydney, Mary Baldwin, Randolph-Macon (Ashland), Virginia Military Institute, Virginia Polytechnic Institute, Washington and Lee, and William and Mary.

(2) O. E. Zvyagintzev, *Ann. inst. platine*, 364 (1926).

(3) F. C. Robinson, *Bull. Am. Inst. Mining Met.*, No. 260 (1926).

(4) F. Feigl, P. Krumholz and E. Rajmann, *Mikrochemie*, 9, 165 (1931); H. Holzer, *ibid.*, 8, 271 (1930).

(5) F. Feigl and E. Fränkel, *Ber.*, 65B, 539 (1932).

(6) G. C. Pierson, *Ind. Eng. Chem., Anal. Ed.*, 6, 437 (1934); *ibid.*, 11, 86 (1939).