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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY AND PALMER PHYSICS LABORATORY OF PRINCETON UNIVERSITY]

Low Angle X-Ray Diffraction of Colloidal Gold and Carbon Black[1a]

BY JOHN TURKEVICH AND HARRY HOPKINS HUBBELL[1b]

An apparatus for the determination of low-angle X-ray scattering of particles of colloid size has been described and applied to the determination of the particle size of monodisperse colloidal gold and of carbon black. The values of the particle size so obtained were found to agree satisfactorily with measurements using the electron microscope. The wave length dependence of the X-ray scattering was also determined and was found to agree with theoretical predictions. Experimental evidence is presented for the existence of a theoretically predicted maximum in the X-ray low angle scattering curve.

It has been known for some time that when a beam of monochromatic X-rays is passed through a finely-divided material consisting of particles of not more than a few hundred ångströms diameter, intense scattering occurs at angles within a degree or so of the undeviated beam.[2] In studying this phenomenon, Guinier[3a] adapted a calculation of Debye and Menke[3b] on the scattering of liquids and showed that the intensity (I) of X-rays scattered by a sample of uniform spherical particles of radius R was

$$I = KI_0 \left[\frac{3}{U_3}(\sin U - U \cos U)\right]^2$$

where

$$U = \frac{4\pi R \sin\theta}{\lambda} \doteq \frac{2\pi R\epsilon}{\lambda}$$

and

I_0 = intensity of original X-radiation
θ = Bragg angle
ϵ = scattering angle = 2θ
λ = wave length of X-ray
K = constant depending on the geometry of the apparatus

Guinier[3] showed, and the ideas have been developed much further by others,[4,5,6] that if the particles depart from spherical shape or have a distribution in size or shape, the simple scattering function just given is considerably modified. Because of the difficulty of preparing samples of known size and shape distributions, most workers have assumed the correctness of the theory and used it to determine particle sizes and distributions in unknown samples. Shull and Roess[6] obtained good indirect checks on sizes so determined by comparing them with those calculated from gas adsorption. The dependence of the intensity of scattered X-rays on the angle and particle size is also affected by the geometry of the apparatus. The original theory has been derived for X-ray beams collimated by pinholes of negligible area. Since it is customary to use slits instead of pinholes in order to obtain higher intensities of the scattered beam, numerous workers have studied the effect of such an experimental setup.[7,8,9]

The purpose of this investigation is to check the dependence of the scattering on the wave length of the X-rays used, to determine the shape of the scattering curve for a sample of uniform spherical particles and to correlate the size of the particles as determined with low angle X-ray scattering with that determined by the electron microscope.

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(1) (a) Preliminary results reported in *Phys. Rev.*, [2] **73**, 1250A (1948). Presented by Harry H. Hubbell in partial fulfillment of the requirements for a degree of Doctor of Philosophy at Princeton University in 1947. Presented at the 116th Meeting of the American Chemical Society at Atlantic City, New Jersey, September, 1949. (b) Physics Department, Middlebury College.

(2) American Society for X-Ray and Electron Diffraction, "Bibliography on X-Ray Small Angle Scattering," 1946.

(3) (a) A. Guinier, *Ann. de Phys.*, **12**, 161 (1939); Thesis, Univ. Paris, A 1854 (1938). (b) P. Debye and H. Menke, *Ergebnisse der technische, Röntgenkunde*, **2** (Fortschritte der Röntgenforschung, p. 1 (1931)).

(4) J. Biscoe and B. E. Warren, *J. Applied Phys.*, **13**, 364 (1942).

(5) M. H. Jellinek and I. Fankuchen, *Ind. Eng. Chem.*, **37**, 158 (1945).

(6) C. G. Shull and L. C. Roess, *J. Applied Phys.*, **18**, 295 (1947).

(7) M. H. Jellinek and I. Fankuchen, *Ind. Eng. Chem.*, **37**, 158 (1945).

(8) C. G. Shull and L. C. Roess, *J. Applied Phys.*, **18**, 295 (1947).

(9) R. Hoseman, *Z. Physik*, **114**, 133 (1939).

Experimental Method

The apparatus was built around a North American Phillips Type 4100 water-cooled X-ray diffraction unit. Chromium, iron, copper and molybdenum interchangeable tubes were used. One point-focus window of the tube was used with a crystal monochromater apparatus while the other point-focus window was used with a fluorescent ZnS screen and a photo-multiplier tube for continuous monitoring of the X-ray intensity. A line-focus window was used for the filtered radiation camera. The arrangement of the camera using monochromated radiation is given in Fig. 1. The design principle is to get the crystal close to the target so as to have as high an intensity as possible and then to count on the perfection of the crystal and the narrow range of angles permitted by the Bragg law to select the radiation and to collimate the beam.[10] Slits were used only to pick out the line wanted and to cut out scattered radiation. In order to check the choice of the desired X-ray line, the absorption coefficient of pure aluminum filters was determined and compared with that given in Compton and Allison.[11] A calcite crystal was used and X-ray voltage was kept as low as possible to avoid excitation of the harmonic X-radiation. The counter and the first stage amplifier were mounted in a lead-shielded can behind a scanning slit with lead jaws. This detecting device was attached to an aluminum plate which was screwed to the slide of a travelling microscope mount. In general the scattered intensity obtained with the monochromator camera was between one-tenth and one-hundredth of that obtained from the filtered radiation camera. The design of the latter is shown in Fig. 2. It consisted of a two-inch brass tube of $^1/_{32}$ inch wall thickness. The first collimating slit, covered with cellophane, was mounted at the end nearest the X-ray tube and the second was 30 cm. down the tube. The slits were mounted on $^3/_{16}$ and $^1/_4$ inch lead plugs. A third slit was located $1^3/_4$ inches beyond the second and was adjusted in width and length to catch any X-radiation scattered by the jaws of the other slit. It did not touch the main beam. Just beyond the third slit was a guide for a brass mount of the specimen holder. Sylphon bellows were so arranged that the rest of the tube, 70 cm. in length, could swing in an arc just in front of the specimen. The end of the tube was closed by a brass plug which held a guide for an envelope of photographic film, a lead strip to stop the main beam when photographic detection was used, and an adjustable slit with lead jaws to define the beam reaching the counter. There was a hole in the plug behind the slit and this was covered with cellophane to make it vacuum tight. The aluminum plate holding the counter was mounted in back of this hole on the same travelling microscope as used with the monochromator. All holes for inserting specimens and film were made vacuum tight with small aluminum sheets waxed over them. The tube was evacuated to less than a millimeter of mercury pressure. The slit arrangement gave a beam 1.5 inches long and 1 mm. wide.

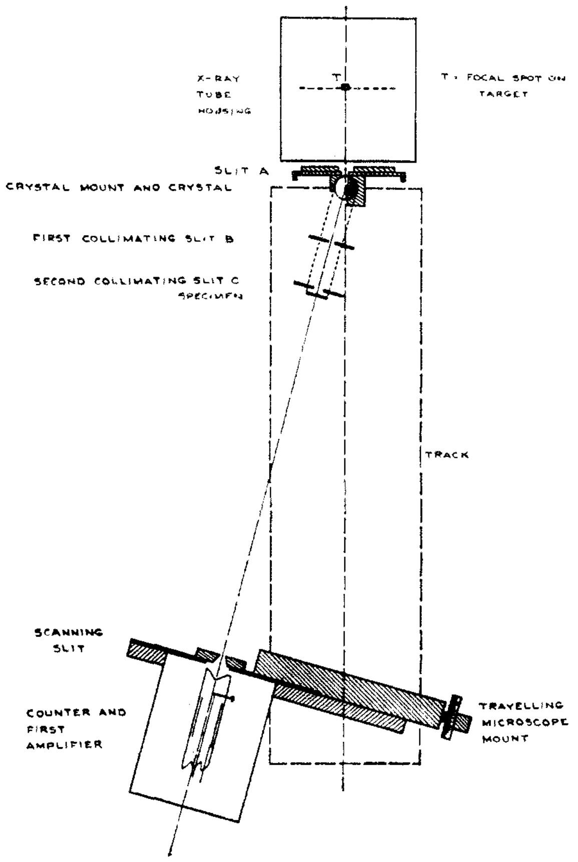

Fig. 1.—Low angle X-ray scattering apparatus using monochromatic radiation.

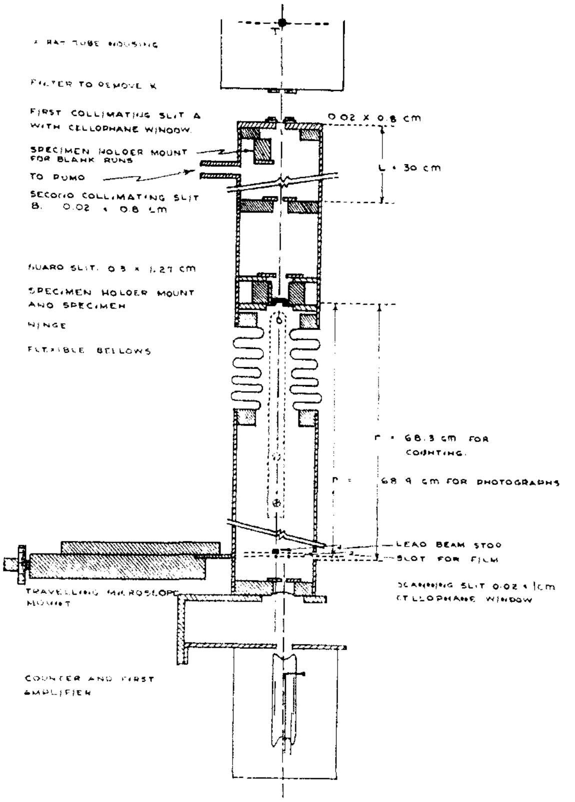

Fig. 2.—Low angle X-ray scattering apparatus using filtered radiation.

The X-ray intensities were measured by a GLB 20E Herbach and Rademan Company counter. The resolving time was about 10^{-4} second. The linearity of the detecting system was checked by using aluminum absorbing foils and determining to what extent the ratios of intensities before and after the insertion of each successive screen were the same. It was found that the absorption ratio for aluminum showed no trend with increasing counting rate and that the detecting system could be used with appropriate number of aluminum screens to measure X-ray intensities corresponding to 60,000 c./m. The second method of checking the linearity of the counter was to study the variation of the intensity with X-ray voltage using the relationship[12] $I = K(E - E_0)^{1.65}$ where I is the intensity of the characteristic radiation, E is the applied voltage, E_0 the appearance potential and K a constant. This relationship was found to hold to at least 20,000 c./m.

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[10] H. Lipson, J. B. Nelson and D. P. Riley, *J. Sci. Inst.*, **22**, 184 (1945).

[11] A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," D. Van Nostrand Co., New York, N. Y., 1935, p. 802.

[12] A. H. Compton and S. K. Allison, ref. 11, p. 81.

The third method of checking the linearity of the detecting device was to vary the X-ray current keeping the X-ray voltage constant. Deviations from linearity of the X-ray intensity with current were of the order of 5–10% in an intensity range of 1 to 18,000.

Materials.—The carbon black was "Super Spectra" brand of the Columbian Carbon Company. The material was compressed into a holder of the proper thickness of $1/\mu$. New specimens were made for each wave length because of the varying absorption coefficients (μ). Because of its intense scattering power this sample of carbon was very useful in studying the dependence of the scattering on the wave length.

Colloidal gold was prepared by treating a solution of gold chloride with sodium citrate at 100°.[13] The material was isolated from 0.01% solution by careful evaporation to dryness under reduced pressure collecting the coagulated gold and mounting it on collodion or formvar membranes.

Experimental Procedure

The experimental procedure using the monochromator was to determine the background with either the X-rays off or with a piece of lead in place of the specimen. Then a specimen of a thickness $1/\mu$ was mounted beyond the second collimating slit. Counts were taken at various intervals of the angle from a point where the counting rate was comparable to the background up over the main beam and down the other side of the beam into the scattered radiation region. Several runs were made on both sides of the beam. For high counting rates one or more pieces of aluminum were inserted in front of the scanning slit. The specimen was then removed and the run repeated at the same angles to determine the background scattering.

The experimental procedure for filtered characteristic radiation was similar, but aluminum absorption sheets were avoided because of the presence of short wave X-rays. Black runs were made with the specimen immediately behind the first collimating slit.

Comparison of Results Obtained with Monochromator and with Filters

Since the use of filters to remove the undesirable X-radiation is more convenient and results in radiation of higher intensity than the use of the monochromator, it was thought a comparison of the two methods would be of interest.

The results on carbon black are presented in Fig. 3 for filtered and monochromatic radiation. The $K\alpha$ lines of copper (1.54 Å.), iron (1.93 Å.), and chromium (2.28 Å.) were used. The data were plotted in terms of $(U/R)^{1/2}$ where

$$U/R = 2\pi X/\lambda r$$

with X equal to the distance from the center of the beam; r the distance from the specimen, and λ the wave length of the X-radiation. It was found that the square root plot gave a straight line for the carbon black specimen while the square plot did not. It is seen that the points for monochromated and filtered radiation fall on the same line except at very small angles. This is the type of deviation reported by Shull and Roess[8] and is to be expected since the continuous radiation of the short wave length will be scattered at the smaller angles. The deviations are, however, considerably smaller than those reported by Shull and Roess[8] who used a photographic method of detection. This may be due to the greater sensitivity of the photographic film to radiation of shorter wave length.

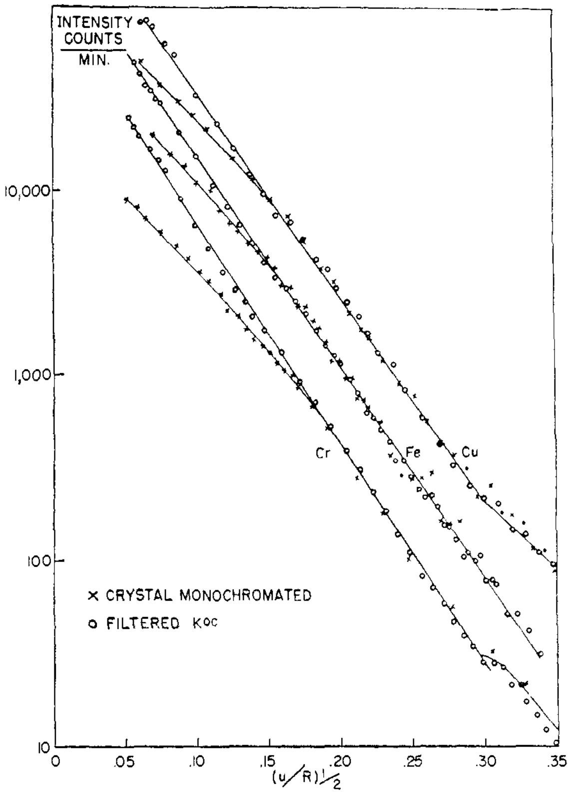

Fig. 3.—Comparison of the use of filtered and monochromatic radiation in the low angle diffraction of X-rays on carbon black. The lines from three radiations are displaced from one another to avoid confusion.

The data obtained on the citrate gold specimens with monochromatized and filtered radiation are given in Fig. 4. It is again seen that the data

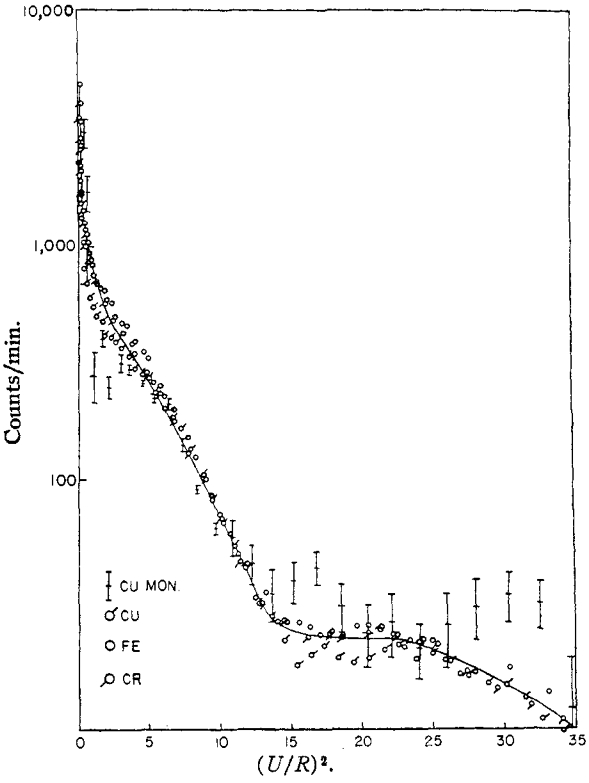

Fig. 4.—Low angle diffraction of X-rays on colloidal gold.

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[13] J. Turkevich and P. C. Stevenson, in press.

with the monochromatic X-rays agree fairly well with those obtained with filtered radiation except in the region of high angles. In the latter region the intensity of the scattered monochromatic radiation was very small and the probable error was large. It is therefore concluded that the intensity results obtained with filtered characteristic radiation are the same as those obtained with a crystal monochromator for angles greater than $U = 0.016R$. Below this value the filtered radiation will give a higher intensity of scattered radiation because of the presence of shorter wave lengths.

Effect of Wave Length on Small Angle Scattering.—One of the objects of this study was to determine the variation of the small angle scattering with the wave length of the X-ray. It was pointed out earlier that the argument of the scattering function should be

$$U = \frac{4\pi R \sin\theta}{\lambda} \doteq \frac{2\pi R\epsilon}{\lambda}$$

Hence if we plot intensity as a function of U or U/R or of any power of U/R, the curves for all wave lengths should coincide. This relationship has been experimentally verified in the case of carbon black for seven monochromatic radiations with wave lengths from 0.71 to 2.28 Å., as shown in Fig. 5. Figure 6 shows the data obtained with the same specimen using filtered characteristic K radiation of copper, chromium and iron. Again the agreement with theory is excellent.

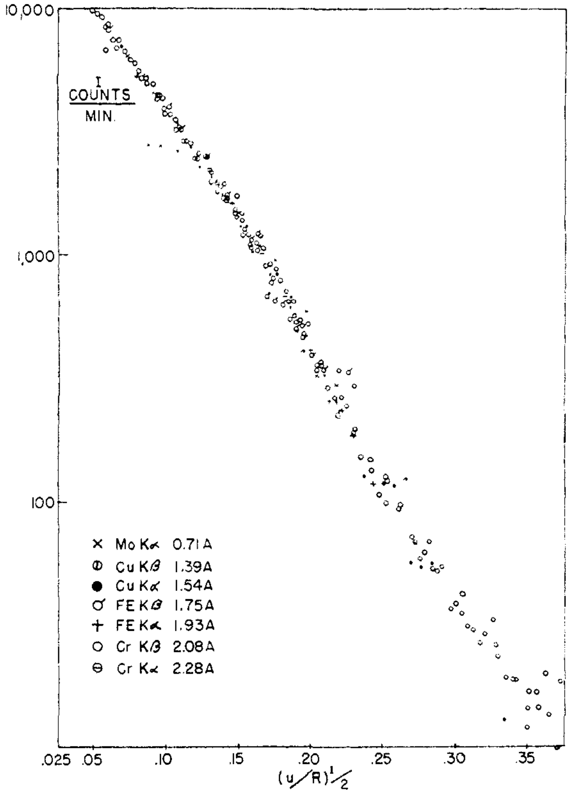

Fig. 5.—Effect of wave length of monochromatic X-rays on the low angle diffraction of carbon black.

The Angular Dependence of Small Angle X-ray Scattering.—The angular dependence of the scattering of X-rays was studied for the case of uniform gold particles of 200 Å. diameter, and carbon black.

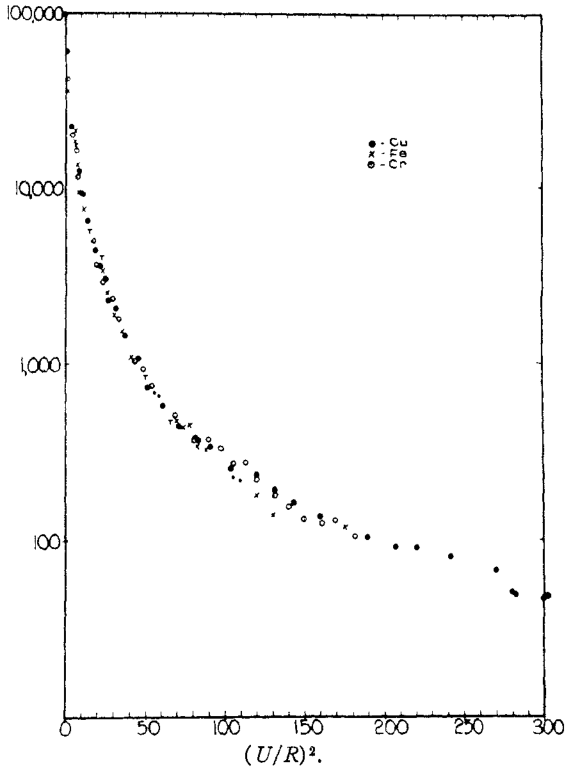

Fig. 6.—Effect of wave length of filtered X-rays on the low angle diffraction of carbon black.

The data obtained with colloidal gold are presented in Fig. 4. The number of counts on a logarithmic scale are given as ordinates and the abscissa are $(U/R)^2$. The curve can be divided into four sections: a steep drop A; a linear portion B; a flat portion C; and finally a section D decreasing gradually with angle at large angles. The steep drop A close to zero angle is difficult to evaluate because of the interaction of the main beam with scattered beam. At best it represents scattering by particles of diameter greater than 200 Å. Since the electron microscope reveals that these do not exist as homogeneous bodies, the high scattering observed in this region must be ascribed to either clumps of gold particles, to X-rays of short wave length, or to an insufficiently refined collimation. This region is worthy of further study to reveal whether the small angle scattering can detect and measure clumping.

The linear portion B is of particular interest in this investigation. It is of some significance that this portion is almost a straight line. Previous investigations of small angle scattering showed as a rule a concave upward curve for the scattering data presented in this way. Guinier[8] obtained linear portions in his investigations of ovalbumin and nickel. However in his investigation on these specimens no direct correlation was made with particle size and shape as determined by other methods. Numerous attempts have been made to determine the size of the particle from the slope of the ln I/I_0 *vs.* $(U/R)^2$ curve. Guinier[3] suggests that the curve of the scattered intensity as a function of angle should be a bell-shaped curve approximated by an error-type function

$$I = I_0 N^2 e^{\frac{-4\pi^2 R^{*2}\epsilon^2}{3\lambda^2}}$$

where R^* is the radius of gyration. The slope of the curve when ln I/I_0 is plotted against $(U/R)^2$ will be $-R^{*2}/3$ and if we set for the radius of gyration R^* the value of $3/5\ R$, the slope becomes $0.2\ R^2$. The value for the radius of the gold soln. becomes 114 Å. Biscoe and Warren[4] proposed that the slope be equal to $0.221\ R^2$. This gives a radius of 108 Å., Fig. 7. The size distribution curve as determined by the electron microscope is given in Figs. 8 and 9. The average radius as determined from this curve is 100 Å. In both of the above formulas for the slope of the X-ray scattering curve an assumption is made that the beam is defined by a pinhole. In practice, however, one uses a slit of finite height. Jellinek and Fankuchen[5] have assumed that the above formulas were valid, broke the slit up into a series of pinholes and integrated the effect. The functional nature of the scattering curve so obtained for a slit was found to be the same as that for a pinhole, and the over-all intensity was changed by a constant factor independent of U. One of us (H. H. H.) has calculated the effect of replacing a pinhole by a slit using Guinier's more exact function for spherical particles. The calculation was carried through by numerical integration and the results obtained for spherical particles of radius 100 Å. are presented in Fig. 10 for various values of H

$$H = 200\pi Rh/r$$

where h is the measured height of the slit, λ is the wave length, R is the radius of the particle taken equal to 100 Å., r is the distance between the specimen and detector. The H can be interpreted as the angle subtended by the slit at the detector divided by λ/R. It is seen that there is a significant difference between these calculated curves and the type suggested by Jellinek and Fankuchen.[5] In particular it is shown that as one increased the value of H the maximum as predicted by Guinier[3] is displaced to smaller angles and the minimum tends to be filled up. The effect on the "linear" portion of the scattering curve is very slight. It might be pointed out

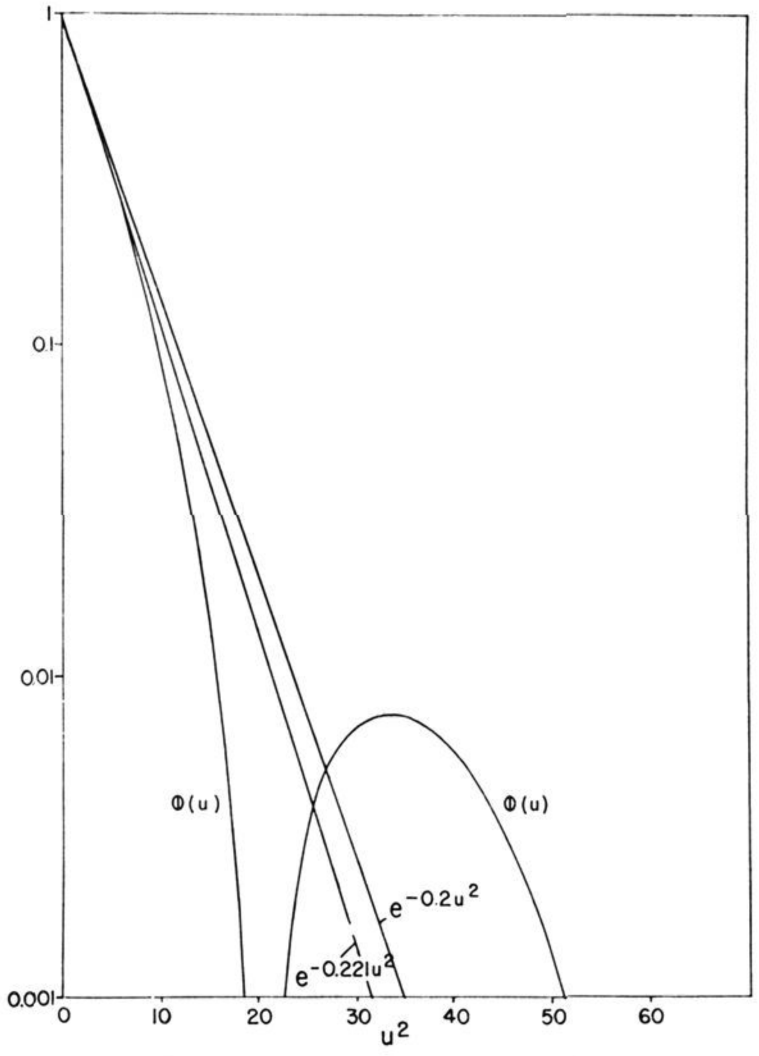

Fig. 7.—Various types of scattering functions proposed for low angle X-ray diffraction.

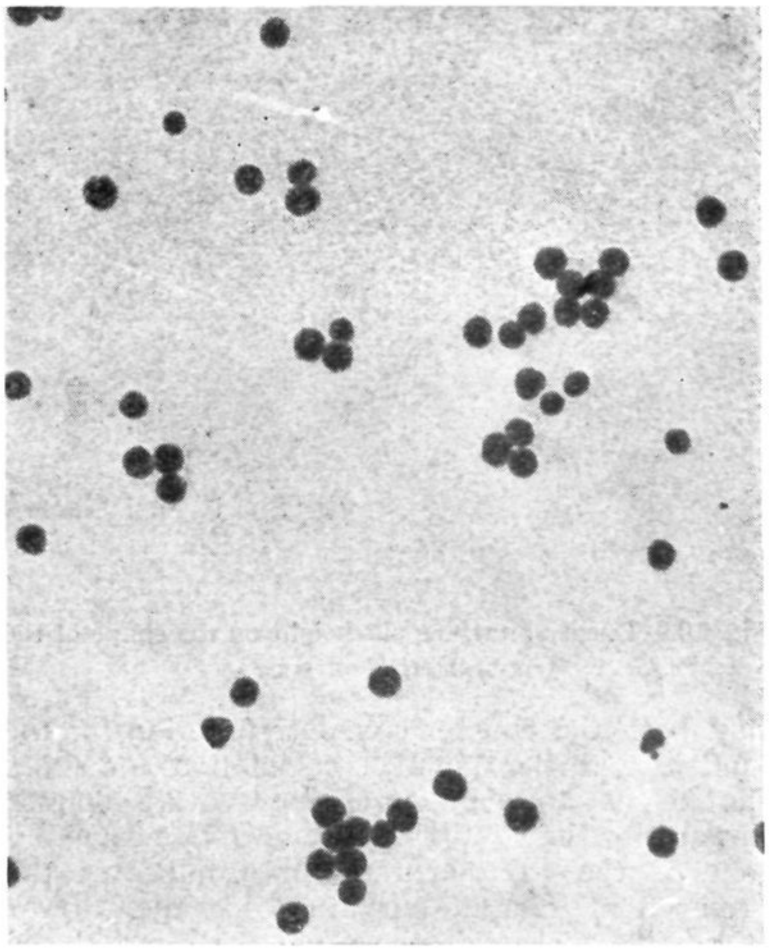

Fig. 8.—Electron micrograph of "citrate" gold sol 100,000×.

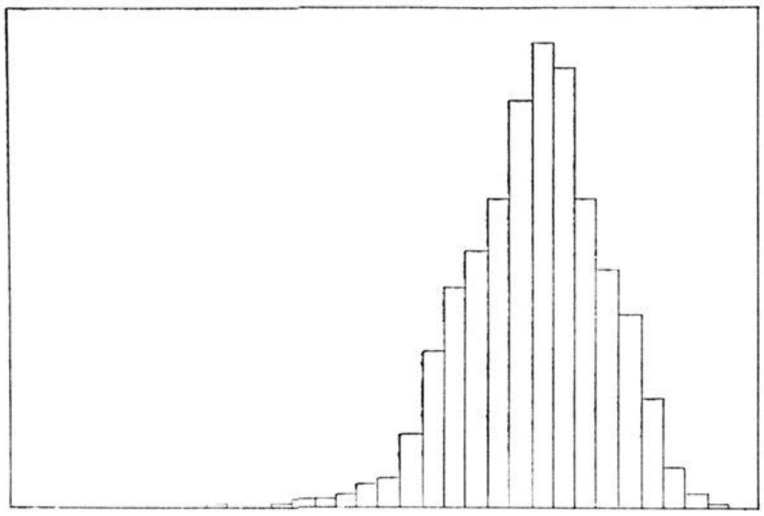

Fig. 9.—Particle size distribution of "citrate" gold sol, d = diameter in Å.

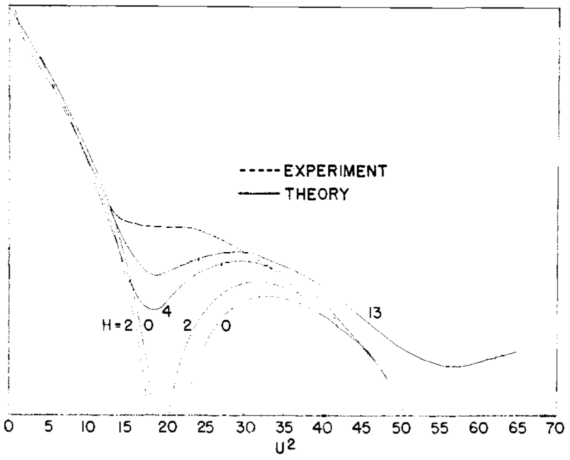

Fig. 10.—Effect of varying slit height on the shape of the scattering curve.

that both the Guinier complete function for the pinhole and the Hubbell calculation for finite slit height both indicate a curvature convex upward for the "linear" portion. Close examination of the experimental curve indicates the presence of such a curvature for the "linear section." If, therefore, we use the slope of the first part of our "linear region" as being the more valid for substitution in the Biscoe–Warren and Guinier–Jellinek–Fankuchen formulas rather than the average slope of the complete "linear region" we get values of R of 103 and 98 Å. which are to be compared with the value of 100 Å. obtained from the electron microscope.

The flat portion C of the experimental curve has not been observed by previous workers. It shows the same wave length dependence as the linear portion. The error-type formulas do not predict the existence of such a flat portion. If one assumes that these formulas correctly describe the X-ray scattering phenomenon, one might interpret the flat portion of the curve as due to very small particles. The more accurate Guinier formula predicts the existence of a series of secondary minima and maxima as one increases the scattering angle. Its experimental verification involves two difficulties. In the first place, Guinier's prediction was based on a point source of X-radiation. Calculations made by H. H. H. referred to above indicate that as the slit gets "longer" the minima and maxima disappear. In the second place, the particles scattering the X-ray must be of uniform size and shape, otherwise the maxima will superimpose. Such uniform particles were difficult to obtain. We were fortunate in having gold particles of 100 Å. radius synthesized by one of us (J. T.). An electron micrograph of these particles is presented in Fig. 8 and the particle size distribution in Fig. 9. The results of a calculation made by H. H. H. on the effect of particle size inhomogeneity on the maxima and minima for a long slit are presented in Fig. 11. It is seen that with a 10% mean deviation the minimum has disappeared. Electron microscopic measurements indicate a mean deviation of 12%. It must be realized that the resolution of the microscope was about 20 Å. and this resolution error would increase the mean deviation of the particles. Other evidence based on studies of graded gold sols indicates that the actual mean deviation is about 8%. Our experimental data obtained on gold particles of uniform 100 Å. radius definitely confirm the existence of such maxima. The agreement of the theoretical curve with the experimental is not as good as could be desired in that the inflection point occurs at too small an angle, in that the intensity in the flat region is too great and in that it falls off too rapidly in approaching the possible second minimum at larger angles. Recently Lund and Vineyard[14] have pointed out the possibility of clumping as a cause of a flattening in this portion of the curve.

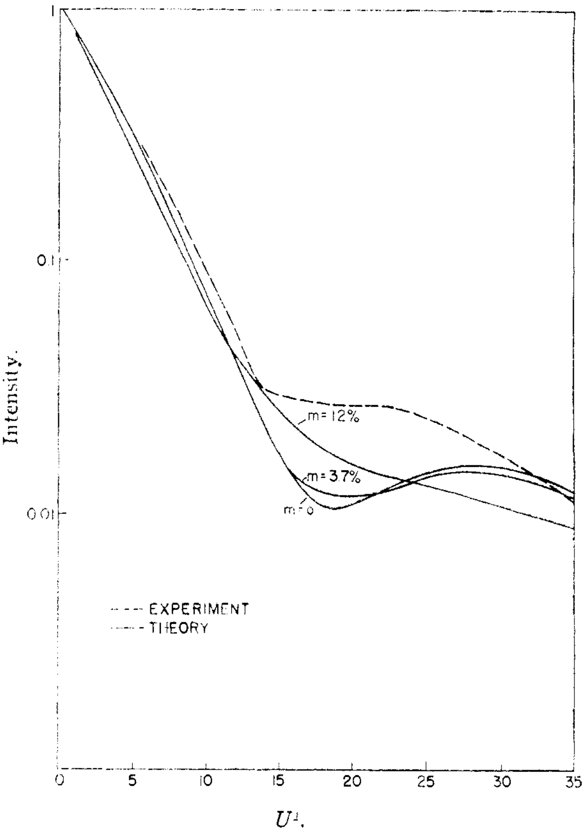

Fig. 11.—Effect of particle size inhomogeneity on the scattering curve.

The results obtained on the Super Spectra carbon black presented using the conventional logarithm of intensity *vs.* angle square plot do not yield a straight line. If one treats the data according to the method of Jellinek, Solomon and Fankuchen[15] one obtains the following particle size distribution.

Radius, Å.	Wt. %
18.8	69.7
21.2	20.0
31.1	7.1

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[14] L. H. Lund and G. H. Vineyard, *J. Applied Phys.*, **20**, 592 (1949).

[15] M. H. Jellinek, E. Solomon, and I. Fankuchen *Ind. Eng. Chem., Anal. Ed.*, **18**, 172 (1946).

38.2	2.7
74.6	0.4
229	.02

The method of graphical resolution is not very accurate and the distinction between a radius of 21.2 and 18.8 Å. cannot be considered as significant. It thus appears that about 90% by weight of the material consists of particles of radius 18.8 to 21.2 Å. Electron micrograph studies have revealed this carbon black to be particles of about 20 Å. radius clumped to form aggregates of about 120 Å. Surface and measurements carried out by gas adsorption indicate a particle size of 19 Å. radius.

Acknowledgment.—We wish to thank Dr. James Hillier of the R. C. A. Laboratory for the electron micrographs of colloidal gold and carbon black.

PRINCETON, N. J. RECEIVED NOVEMBER 25, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Chemistry of Scandium.[1] I

BY LEWIS POKRAS AND PETER M. BERNAYS[1a]

A new insoluble, non-volatile compound of scandium, $Sc(C_9H_6ON)_3 \cdot C_9H_7ON$, has been prepared by the reaction of 8-hydroxyquinoline (oxine) with an aqueous solution of $Sc(ClO_4)_3$ at *p*H 7.5. This lemon-yellow compound is unstable on prolonged heating. However, no indication of the formation of $Sc(C_9H_6ON)_3$ has been found. It is suggested that the extra molecule of oxine is held by molecular forces. A similarity in chemical behavior between thorium and scandium is suggested.

A rigorous classification of scandium ($Z = 21$) has never been given in the literature. Hopkins[2] includes scandium in the general term "rare earths," elements closely related chemically, which are placed in Division A of Group III. Yost[3] does not include scandium in the term rare earth, which he defines as a group of chemically similar elements, occurring between barium (Group II) and hafnium (Group IV). In the course of an investigation to determine the chemical nature of scandium ions in solution, it became necessary to devise a quantitative method having a small gravimetric factor, for the determination of scandium. (The analytical aspects of this problem will be described elsewhere.) In this connection an attempt was made to use 8-hydroxyquinoline (oxine) as a precipitant, since this compound had previously been used for several trivalent elements, including aluminum, gallium and indium.[4] The most frequently found compounds of oxine with transition elements are those in which each oxine satisfies one covalent and one coördination bond, *i. e.*, $Al(On)_3$ (HOn will be used as symbol for the free oxine, and On^- for the oxinate anion). In a few cases, an additional molecule of oxine may enter the compound, *i. e.*, $Th(On)_4 \cdot HOn$.[5]

Experimental

Materials.—All materials used herein were C. P. grade, and unless otherwise stated were used as commercially available with no further purification.

Scandium Perchlorate.—Scandium oxide purchased from the Var-Lac-Oid Corp., 116 Broad Street, New York, was dissolved in concd. $HClO_4$, and purified to remove rare earths and calcium by the buffered pyridine,[6] followed by the basic tartrate[7] method. A weighed amount of the purified oxide was then dissolved in a minimum of 0.5 *N* $HClO_4$ and diluted to volume.

Preparation of $ScOn_3 \cdot HOn$.—10.0 ml. of 0.02471 *N* $Sc(ClO_4)_3$ solution was diluted to 110 ml., 5 drops of 0.005% aerosol in water was added, and the solution was heated to 75°. Ten ml. of HOn in 2 *N* NH_4OAc was added, followed by the addition with stirring of 45 ml. of a buffer made by mixing 30 ml. of 2 *N* NH_4OAc with 15 ml. of 2 *N* NH_4OH. After standing, with occasional stirring, for 2 hours, the lemon-yellow precipitate was filtered through a sintered-glass crucible, washed with a minimum quantity of distilled water at room temperature, and heated to constant weight at 110° to remove free HOn which is always associated with the compound. When thus prepared the melting point is 195–197°.

Anal.[8] Calcd. for $Sc(C_9H_6NO)_3(C_9H_7NO)$: C, 69.43; H, 4.05; N, 9.00; Sc_2O_3 as ash, 11.09. Found: C, 69.47; H, 4.30; N, 8.74; Sc_2O_3 as ash, 11.36.

In order to establish the thermal stability of the new compound, a freshly prepared sample contaminated with excess HOn was heated at various temperatures up to 165° for a total of 898 hours. At intervals throughout this period the mass of the sample was determined. Results are indicated in Table I and in Fig. 1.

The solubility of the new compound $Sc(On)_3 \cdot HOn$ in H_2O is extremely low. This can be shown by testing for residual Sc^{+++} ions in solution after precipitation of $Sc(On)_3 \cdot HOn$ as described above. Using cochineal,[9] a reagent known to be sensitive to 1 part in 50,000, no Sc^{+++} ions could be found in the combined mother liquors of six precipitations, even on concentration of the filtrates to *ca.* 25 ml.

The non-volatility of scandium oxinate and its insolubility in water was proven as follows: $Sc(On)_3 \cdot HOn$ was prepared as described above, utilizing a known quantity of Sc_2O_3. The scandium content of the oxinate was then determined using the basic tartrate method[7]: taken as Sc_2O_3, 0.0684 g.; found as Sc_2O_3, 0.0687 g. Since the amount of scandium oxide recovered is equal to that taken,

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[1] Part of a paper presented at the Detroit Meeting of the American Chemical Society, April 18, 1950.

[1a] Southwestern Louisiana Institute, Lafayette, La.

[2] B. S. Hopkins, "Chapters in the Chemistry of the Less Familiar Elements," Stipes Publishing Co., Champaign, Ill., 1938, Chapter 6, p. 2.

[3] D. M. Yost, H. Russell, Jr., and C. S. Garner, "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1.

[4] R. Berg, "Die analytische Verwendung von *o*-Oxychinolin (Oxin) und Seiner Derivate," 2nd revised edition, F. Enke, Stuttgart, 1938, p. 3.

[5] F. J. Frere, THIS JOURNAL, **55**, 4362 (1933).

[6] E. A. Ostroumov, *Zhur. Anal. Khim.*, **3**, 153 (1948). See also *C. A.*, **42**, 7655e (1948).

[7] R. Fresenius and G. Jander, "Handbuch der Analytischen Chemie," Springer, Berlin, 1940–1942, Part III, p. 734.

[8] Performed by the Micro-Tech Laboratory, Skokie, Illinois.

[9] P. E. Wenger and R. Duckert, *Helv. Chim. Acta*, **28**, 872 (1945).