[CONTRIBUTION FROM THE S. A. M. LABORATORIES OF THE MANHATTAN PROJECT]

The Viscosity of Gaseous Uranium Hexafluoride[1]

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A series of experiments was undertaken to investigate the reason for the large (10 to 20%) discrepancies between values for the viscosity of gaseous uranium hexafluoride reported by the Manhattan Project and corresponding workers in Great Britain. All investigators used the method of capillary flow to measure the ratio of the viscosity of uranium hexafluoride to air. It was found that with metal capillaries of small diameter the apparent value of this ratio may increase above the laminar value directly and linearly with Reynolds number from values of the latter as low as 10. Finally, accurate values are reported for the viscosity of gaseous uranium hexafluoride in the range 40 to 200°.

Introduction

The investigations described in this article were undertaken to resolve the discrepancies existing in 1944 among English and American data for the viscosity of gaseous uranium hexafluoride. The values obtained in England[3-5] were of the order of 10 to 20% lower than those determined in the United States,[6] throughout a temperature range of 85 to 200°. Because of the importance of the coefficient of viscosity in flow calculations of the U-235 diffusion process, it became desirable to ascertain the source of error and obtain accurate viscosity data from 40 to 200°.

In view of the highly corrosive nature of uranium hexafluoride and the fact that the method of capillary flow had been employed in all previous cases, it was decided that the viscosity determinations could be most expeditiously and appropriately made by the method of flow through a platinum capillary. Employing Poiseuille's and the perfect gas laws, the following equation can be applied to a gas flowing through a capillary of radius r, length L and temperature T_c into a constant pressure p_0.

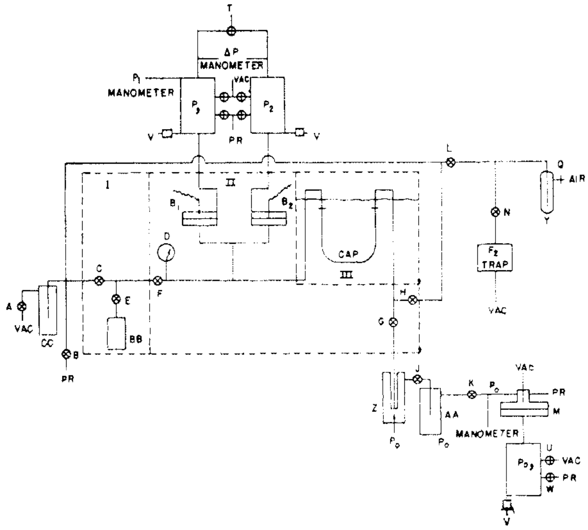

Fig. 1.—Apparatus for the determination of the viscosity of gaseous uranium hexafluoride.

Here t is the time required for the reservoir gas to drop from a pressure p_1 to p_2, and η is the coefficient of viscosity of the gas. It can be shown that

$$\frac{1}{2p_0}\ln\left[\frac{(p_2+p_0)(p_1-p_0)}{(p_2-p_0)(p_1+p_0)}\right] = \frac{\eta r^4 T v_0}{16 V_0 T_c L} \times \frac{t}{\eta} \qquad (1)$$

Hence for two gases, *e.g.*, uranium hexafluoride and dry air, allowed to flow successively in the same apparatus, under identical conditions of temperature and pressure

$$t_{UF_6}/\eta_{UF_6} = t_{air}/\eta_{air} \qquad (2)$$

Experimental

Apparatus.—A schematic diagram of the apparatus employed to apply the principles of equation (1) is shown in Fig. 1. Those parts of the apparatus which had to be maintained at a constant temperature were enclosed in a large (approximately 2′ × 5′ × 2′ in height), specially designed oven. Sections I and II were equipped with individual air circulatory systems and maintained at 60 and 70°, respectively. Section I contained the nickel reservoir of uranium hexafluoride, and two valves. These and all other valves designated by ⊗ were 100% nickel, Hoke No. 413 valves with silver soldered diaphragms. These eliminated contamination and leakage difficulties encountered with packed valves. Section II contained a vacuum Duragauge with a bronze Bourdon tube, and two Booth–Cromer[7] electrical pressure transmitters. The latter break contact between a nickel diaphragm and contact button when the known pressure on the air side of the diaphragm just exceeds that of the side open to the pressure to be measured. Such gages are admirably suited for pressure measurements of corrosive gases such as uranium hexafluoride and fluorine, since only nickel and copper surfaces are present on the system side.

Section III consisted of the oil-bath in which the platinum capillary (shown as CAP) was immersed. The bath was controlled to ± 0.05° by means of a thermosensitive nickel resistance coil, galvanometer and photoelectric cell. The temperature was read with a Type K potentiometer and a five-junction copper–constantan thermocouple.

All lines carrying uranium hexafluoride were constructed of nickel wherever possible; and otherwise, of copper. Any tubing and valves containing the corrosive gases and external to the oven were heated by asbestos-wrapped nichrome wire and controlled by Variacs. Critical temperatures were followed by means of numerous strategically located thermocouples.

The pressures p_1 and p_2 of the air side of the B–C gages, each of which was connected to a 20-liter ballast tank (P_1 and P_2) were set as desired by means of the valves on the VAC and PR lines of P_1 and P_2. An absolute mercury manometer (P_1 manometer) was used with P_1 and a differential butyl sebacate manometer (P manometer) between P_1 and P_2. Fine pressure settings were made by means of variable volumes V, consisting of adjustable sylphons. All valves on this part of the system were rubber seated and bonneted Kerotests and are designated by ⊕.

The constant downstream pressure, P_0, was maintained through traps Z and AA (cooled by Dry Ice) to the capillary by means of a Moore 1:1 pneumatic pressure transmitter,[8] M. This instrument is normally used to maintain and re-

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(1) Rewritten from the declassified report MDDC-494 of the USAEC.

(2) Present address: The Franklin Institute Laboratories for Research and Development, Phila., Pa.

(3) D. R. Llewellyn and G. Swaine, Directorate of Tube Alloys, B-100 (1942).

(4) D. R. Llewellyn, Oxford Research Note, 12 BR-427 (1944).

(5) L. E. J. Roberts, Oxford Research Note, 14BR-468 (1944).

(6) R. D. Fowler, NDRC. OEMSR, 271, A-1398 (1942).

(7) SAM, AEC Drawing P-1353.

(8) SAM, AEC Drawing P-1375.

cord the pressure on one side of a nickel diaphragm equal to the unknown pressure on the other side. In the present experiments, the pressure, p_{0x}, of the Moore transmitter and the ballast P_{0x} was set at such a value that the automatically maintained pressure of nitrogen in the downstream side of the capillary was of the desired magnitude p_0. The latter pressure was determined by an absolute mercury manometer which, like the P_1 manometer, was read with a Gaertner cathetometer.

Trap Z was specially constructed to permit external heating of inlet tubing which extended to within a few cm. of the bottom of the trap. An immersion heater was fitted into a well surrounding this tubing, thereby preventing the hexafluoride issuing from the capillary from freezing until it reached the bottom of the trap, with the consequent freedom from plugging.

Procedure.—In determining t_{UF_6}/t_{air} under given temperature and pressure conditions, the system was first evacuated to a micron or less (as read on a McLeod gage) through valve A and Dry Ice trap CC, with valves E, G, N and B and stopcock Q closed and valves C, F, H and L open. After closing A, F and H, the system was filled with air to approximately one atmosphere pressure, through Q. The air was purified and dried by passage through a train of drierite, liquid oxygen, ascarite drierite, phosphorus pentoxide and a flowmeter, and was obtained from a cylinder under a pressure of 1200 to 1800 pounds per square inch.

Valve F was carefully opened until the pressure in the reservoir of constant volume V_0 (F to the upstream side of capillary) was greater than both p_1 and p_2, the previously set pressures on the air side of the B–C gages. The higher pressure of the system side was indicated by pilot lights connected to the B–C contacts. On opening valve G, air flowed through the capillary into the downstream section maintained at p_0. When the pressure in the reservoir had dropped to p_1, an electric timer was actuated by the breaking of the contact of B_1. The timer was stopped by B_2 when the pressure had reached p_2. This operation was repeated to obtain three or more consistent values for t. Valves G and L were then closed; F and H were opened and the system was evacuated through A.

When the pressure read a micron or less, valves A, C, F and H were closed and E opened. The time t was then determined for uranium hexafluoride by first carefully opening valve E until the pressure in the reservoir was greater than p_1. After opening G, the procedure was identical with that followed for air. The hexafluoride was then removed from the system by freezing the vapor into trap CC, and t_{air} redetermined to ascertain the constancy of the B–C zero points, etc. The results from the two air runs were averaged so that

$$t_{UF_6}/t_{air} = 2t_{UF_6}/(t_{1air} + t_{2air})$$

All parts of the system which were in contact with uranium hexafluoride at any time were maintained in a state considered stable to that compound by conditioning, at intervals, with equal parts of fluorine and nitrogen, and by the exclusion of moisture. Both platinum capillaries were first rinsed with acetone, and then treated for an hour at 220° with the fluorinating mixture, which was frequently flushed through the capillary.

The major source of error in these experiments was the Booth–Cromer gages. These instruments exhibited a fluctuation of zero points, usually less than the equivalent of 2 mm. of butyl sebacate, during consecutive timings at a given pressure setting. The probable error incurred in obtaining a mean value of t from such a set of consecutive values was of the order of a few tenths of a per cent. This gage variation infrequently increased to as high as 4 mm. of butyl sebacate after evacuation and subsequent increase of pressure. However, through the use of pressure differentials as large as practicable, the maximum error introduced by even this latter rarely occurring deviation was kept reasonably small. Thus in the case of the final viscosity values given in Table I, it can be shown from consideration of equation (1) that the evacuation effect would introduce a maximum error of ±1.3%. Actually the initial and final air runs of a given determination only rarely exhibited a discrepancy of this order of magnitude.

Other sources of error were relatively unimportant. The pressures p_1, p_2 and p_0 were controlled to within ± 0.1 mm. without difficulty, generally introducing errors no greater than ± 0.1%. The temperature of the nickel reservoir was maintained within ± 0.4°, with a consequent error of ±0.15%, while the capillary bath was controlled to within ±0.05°. Hence, ±1.5% represents the maximum but rather improbable error, and ± 0.6% the probable error, of the final viscosity–temperature curve, on which no point is actually more than 0.1% removed from the straight line of $\log \eta$–$\log T$ with the exception of the point at 200° which exhibits a deviation of −1%.

Since the accuracy of all viscosity data obtained in these experiments is dependent on the use of the correct values for air, an exhaustive literature search and statistical analysis were made of all available data for the viscosity of air at 0, 23, 100 and 191°. Ninety papers were consulted and the values judiciously weighted and averaged as fully described in the original report.[1] The four final values obtained were 171.65, 182.73, 220.38 and 255.63 micropoises, respectively.

As a check on the validity of the air standard and the accuracy of the apparatus, determinations were made of the viscosities of argon and methane. Values in micropoises of 269.3 at 79.8°, and 137.1 at 99.8° were obtained for argon and methane, respectively. The average of five literature values for argon, ranging from 268.1 to 271.5, is 269.5, and of two for methane (135.1 and 136.2), 135.7.

Discussion of Results

The viscosity values available at the inception of the present work are summarized in Fig. 2, which also shows the final data of this paper. In seeking an explanation for the significant differences between the English and U.S. data, it was noted that the higher values had been obtained at pressures greater than 760 mm. whereas all English experiments were performed at comparatively low pressures (*i.e.*, less than 50 mm.). Since gaseous viscosity is essentially independent of pressure in this range, whereas the onset of turbulence is determined by the Reynolds number (*Re*) which is a direct function of the pressure, it seemed possible that the high values represented varying degrees of non-laminar flow. This inference necessitated further investigation, since all the high U.S. values had been obtained at Reynolds numbers of less than 400, normally considered safe for viscous flow. Although it is true that for pipes and glass capillaries the critical value for *Re* is 2000, Ruckes[9]

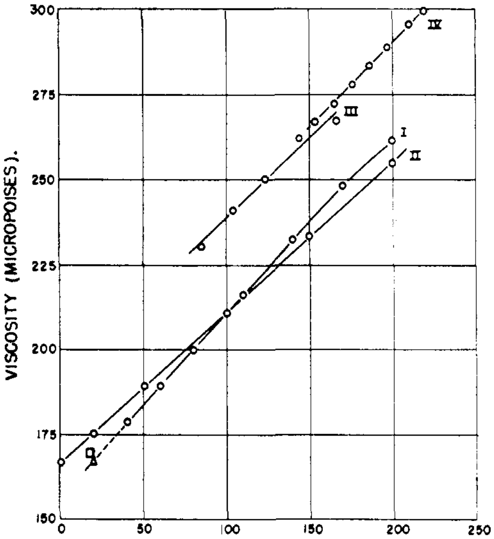

Fig. 2.—Summary of data on the viscosity of gaseous UF_6 as a function of temperature: I, Myerson and Eicher; II, ref. 3; □, ref. 4 and 5; Δ, Fleischman, ref. 11; III, IV, ref. 6.

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(9) W. Ruckes, *Ann. Physik*, [4] **25**, 983 (1908).

reported critical numbers as low as 400 for iron capillaries of inside diameter 0.04 cm. and length 150 cm. Hence, for shorter capillaries of smaller diameter and uncertain surface properties, it was conceivable that even smaller critical Reynolds numbers existed.

The present study began with a series of measurements of t_{UF_6}/t_{air} at 80°, over a mean pressure $(= (p_1 + p_2 + 2p_0)/4)$ range of 50 to 760 mm. A platinum capillary (A) of i.d. 0.02 cm. and length 50 cm. was employed. Results obtained at higher pressures with this capillary were essentially in agreement with the high viscosity data, while the lower English values were observed at the lower end of the pressure range. A plot showing the variation of time ratio with Reynolds number was then in order.

All Reynolds numbers were calculated for the upstream side of the capillary (where the number is highest) at both the beginning and ending of timing. Thus, initially

$$Re_i = \frac{2\rho vr}{\eta} = Mr^3\frac{(p_1 + p_0)(p_1 - p_0)}{8LRT\eta^2} = K_{Re}(p_1 + p_0)(p_1 - p_0) \qquad (2)$$

where ρ = density, v = linear velocity, M = molecular weight and R is the gas constant. Finally, $Re_f = K_{Re}(p_2 + p_0)(p_2 - p_0)$, and the mean $Re = Re_m = (Re_i + Re_f)/2$. When Re_m was plotted against the time ratios for the data taken over the pressure range previously mentioned, an excellent linear relationship resulted as shown in curve I of Fig. 3. At low values of Re_m (< 10), the ratio t_{UF_6}/t_{air}, is in good agreement with the English figure for η_{UF_6}/η_{air}.

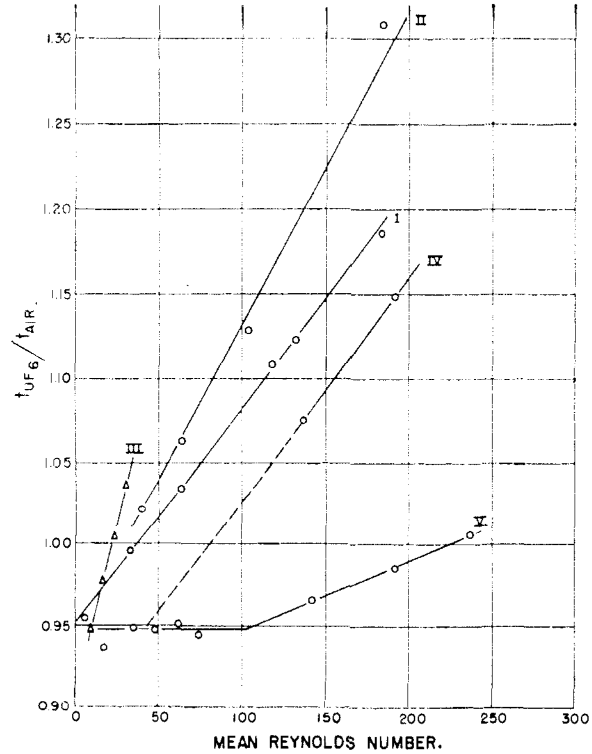

Fig. 3.—Variation, at constant temperature, of the UF_6/air time ratio with the mean Reynolds number: I, at varying mean pressures; II, III, mean pressure 755 and 135 mm., respectively; IV, calculated from data of ref. 6; V; capillary B, mean pressure = 130 to 180 mm.

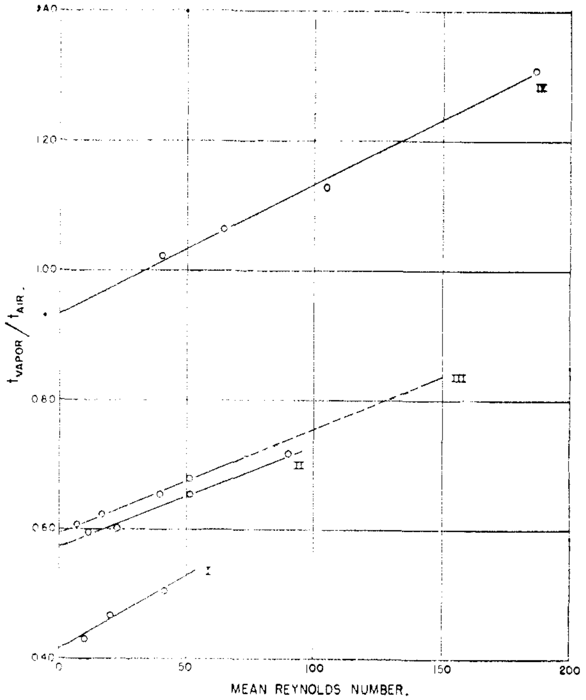

Fig. 4.—Variation of the time ratio (air standard) with mean Reynolds number for four vapors, at 80°: I, benzene; II, C_8F_{16}; III, CCl_2F-CF_2Cl; IV, UF_6.

Curves II and III represent data taken at constant temperature (80°) and mean pressures (p_m) of 755 mm. and 135 mm., respectively, in contrast to the varying p_m of curve I. Again, linear variation of time ratios with Re_m is noted, and extrapolations to low values of Re_m fall in the same region. Thus, in the turbulent region at constant mean pressure, t_{UF_6}/t_{air} can be considered a linear function of one variable, Re_m, which essentially becomes a measure of the degree of turbulence. Similar phenomena were observed with the same apparatus for various vapors such as benzene, CCl_2F-CF_2Cl, and C_8F_{16}, of molecular weights 78, 187.5 and 400, respectively. As seen in Fig. 4, the slopes of the time ratio *vs.* Re_m lines are approximately the same for these gases and UF_6 (mol. wt. 352). At sufficiently low Reynolds number (*i.e.*, when the critical Re or Re_c is reached), the time ratio becomes independent of the Reynolds number and equal to the viscosity ratio. Then, employing the value of η_{UF_6}/η_{air} eventually found to be correct (0.946), Re_c for capillary A must have been less than 10 as indicated by the value of Re at the points at which curves I, II and III of Fig. 2 approach this time–viscosity ratio. However, a critical Reynolds number of 10 is low even for a capillary of this size. This abnormally low value of Re_c was accounted for by the poor physical condition of the capillary as noted on its removal from the oil-bath. It was bent badly (though not actually kinked), and partially constricted at one end. Curve IV, which is based on two points calculated from data of reference 6, and extrapolated (dotted line) to low Reynolds number, shows that the critical Re for the capillary used must have been sufficiently low to have necessitated measurements in the turbulent region at the pressures used.

All final data were obtained with a second platinum capillary (B) of length 75 cm. and i.d. 0.03 cm. Both ends were carefully smoothed and extreme care taken in mounting to avoid constrictions and sharp bends. The critical Re_m for this capillary at p_m = 13 to 18 cm., was found to be approximately 100 at 80° as seen from the data plotted as curve *V* of Fig. 3. Below $Re_m = 100$, the observed values for t_{UF_6}/t_{air} are constant to ±0.5% which are within the limits of experimental error at this low Reynolds number.

Values were then obtained, with this capillary, for $t_{UF_6}/t_{air} = \eta_{UF_6}/\eta_{air}$ in regions of experimentally established non-turbulent flow over a temperature range of 40 to 200° presented in Table I. The viscosity η is given in poises and both the small slip and kinetic energy corrections[10] have been applied

$$\eta_{cor.} = \eta\left(1 + \frac{4}{r}\zeta\right) - \frac{m}{8L\pi}\left(1.12 + \ln\frac{p}{p_0}\right)$$

where ξ is the path and m = flow in g./sec. The slip correction was always less than 0.5% and the kinetic energy correction less than 0.2%.

TABLE I

T	p_m	Re_i	Re_m	t_{UF_6}/t_{air}	$\eta_{UF_6} \times 10^6$
40.0	125.3	82.5	56.8	0.933	178.7
60.0	125.3	71.2	49.0	.937	189.0
80.0	132.7	99	74.3	.944	199.9
110.0	125.3	46	31.6	.955	216.1
140.0	134.9	56	38.4	.970	231.9
170.0	134.9	46	31.5	.991	248.0
200.0	134.9	40	27.4	1.004	261.1

As seen in Fig. 2, the short extrapolation of these data to 20° essentially passes through the only viscosity value available that was obtained by a method other than capillary flow. This value was determined by R. Fleischmann using the swinging disk method, and represented captured German data.[11] Further confirmation of the accuracy of these values has resulted from unpublished determinations of thermal conductivity data by the Manhattan Project, and brought to the authors' attention through personal communication.

PHILADELPHIA, PENNSYLVANIA

[10] F. W. G. Kohlrausch, "Praktische Physik," M. Rosenberg Book Co., New York, N. Y., 1947, Vol. 1, p. 95.

[11] R. D. Present, S. A. M. Laboratories Report USAEC M-2511 (1945).

[CONTRIBUTION FROM THE GENERAL RESEARCH DIVISION, OWENS-ILLINOIS GLASS COMPANY,* AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN†]

Properties and Structures of Vitreous and Crystalline Boron Oxide[1]

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(1) A foundation is given for the understanding of the "anomalies" of boron-containing glasses. The consideration of the properties of boron oxide and its analogs is based on the assumption of electric forces acting between more or less strongly polarized ions with the electronic configurations O^{2-}, Be^{2+}, B^{3+}, Al^{3+}, etc. (2) A coördinative three-dimensional network, or a two-dimensional network (layer structure) are not compatible with the relatively low melting point and molar refraction of boron oxide. (3) The character of the temperature dependence of thermal expansibility, surface tension and viscosity, in the range up to 1400°, proves that, in the crystalline state and in the vitreous state below about 300°, boron oxide consists of units held together by "weak" forces and that with increasing temperature this structure changes gradually toward a "strong" one. (4) The occurrence in crystalline boron oxide of two types of forces of widely different strength follows from the fact that its heat capacity shows much larger deviations from a single Debye function than that of coördinative Al_2O_3 and BeO. The available data suggest that at very low temperatures the heat capacity of boron oxide may be due mainly to vibrations of B_4O_6 molecules held within the crystal by weak intermolecular forces. If so, boron oxide conforms to the parallelism found between the melting points of crystals consisting of symmetrical molecules and the force constants of the intermolecular vibrations.

Introduction

The current views[2] concerning the arrangement of atoms in vitreous boron oxide originated in Zachariasen's[3] general theory of the structure of oxide glasses. Warren, Krutter and Morningstar[4] interpreted the results of their X-ray diffraction study to be "in complete agreement with Zachariasen's predictions" of a "three dimensional random network" in which each boron is "at the center of a triangle of three oxygens, each oxygen bonded to two borons, with the two bonds presumably roughly diametrically opposite."

The discovery of a crystalline form of boron oxide[5] was supported by X-ray diffraction data from which, however, no structure has been derived. The view is usually held[3,2b] that the planar BO_3 groups are common to both crystal and glass, which are supposed to differ merely in the regularity of the mutual orientation of these groups.

The main characteristic of these structures for boron oxide is that they are supposed to be continuous networks. Such networks composed of planar

[1] Presented in part at the Cleveland Meeting of the American Chemical Society on April 10, 1951, Symposium on Physical Chemistry of Glass, and before the Section of Physical and Inorganic Chemistry at the XIIth International Congress for Pure and Applied Chemistry in New York, N. Y., on September 12, 1951.

[2] (a) W. A. Weyl, *The Glass Industry*, **29**, March–Nov. 1948, especially Part II, p. 200. (b) S. Glasstone, "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 520 ff.

[3] W. H. Zachariasen, THIS JOURNAL, **54**, 3841 (1932); fig. 1b.

[4] B. E. Warren, H. Krutter and O. Morningstar, *J. Am. Ceram. Soc.*, **19**, 202 (1936).

[5] L. McCulloch, THIS JOURNAL, **59**, 2650 (1937). See also S. S. Cole and N. W. Taylor, *J. Am. Ceram. Soc.*, **18**, 55 (1935).