-1-

UNCLASSIFIED

UNITED STATES ATOMIC ENERGY COMMISSION

NYO-512

STUDIES ON FILTRATION OF MONODISPERSE AEROSOLS

By
Victor K. La Mer

March 31, 1951

Central Aerosol Laboratories
Columbia University

Technical Information Service, Oak Ridge, Tennessee

UNCLASSIFIED

[redacted]

DISCLAIMER

2

BIOLOGY

In the interest of economy, this report has been reproduced direct from copy as submitted to the Technical Information Service.

Work performed under
Contract No. AT(30-1)-651.

NYO-512

AEC, Oak Ridge, Tenn.-W20617

TABLE OF CONTENTS

4

STUDIES ON FILTRATION OF MONODISPERSE AEROSOLS

By Victor K. La Mer

ABSTRACT

SECTION I

The filter penetration characteristics of four filter papers - Chemical Corp. No. 5, A.E.C. No. 1 (Roll 13), Whatman Analytical No. 2, and some Glass Fiber filter pads - have been investigated as a function of the particle radius using three monodisperse (uniform particle size) aerosols; namely, dioctyl phthalate (DOP), oleic acid, and stearic acid, as representative liquid and semi-solid smokes (Section V).

The radii of the monodispersed aerosols ranged from 0.50 micron to as small as 0.02 micron in some cases.

The particle sizes were determined by light scattering methods and the extension of these methods to the smallest sizes was achieved by adapting the growth method developed by La Mer, Inn and Wilson, J. Colloid Science 5, 471 (October, 1950), for H_2SO_4 acid over master solutions of H_2SO_4-water to the systems DOP-Toluene and oleic acid-chloroform as the non-volatile aerosol solutes - miscible volatile growth producing solvents.

The reliability of the light scattering methods of determining filter penetrations was confirmed by a photographic method of counting the particles before and after filtration. By investigating the effect of varying the linear face velocity of passage of the aerosol through the filter over a tenfold range; 2.8 to 28 cm/sec, it is possible to allocate the relative contributions of the factors

(a) inertial deposition on fibers,
(b) direct interception by fibers,
(c) diffusional (Brownian movement) interception,

to filter efficiency and to correlate these effects with fiber diameter, fiber interspacing and other characteristics of the filter.

The importance of electrostatic effects and surface coatings of fibers merits further intensive study. A review of the factors influencing turbulent vs. laminar flow and pressure drop through porous media is given, and its bearing on the "pinhole theory" is discussed.

The maximum in the filter penetration vs. radius of aerosol particles predicted by Langmuir's theory of filtration (1941-2), which was in agreement in some special cases with early work at the Columbia (1941) and Toronto University Laboratories (1941-2), has never been observed in the present more extensive investigation with any of the liquid smokes, filters, particle radii or linear velocities employed in this investigation. (The maximum predicted has also never been observed in the extensive, independent and contemporary studies of Ramskill and Anderson of the Naval Research Laboratory (J. Colloid Science, in press, 1951)).

These findings that penetration always increases monotonically with decreasing radii down to 0.02 micron raise questions of the adequacy and reliability of the present standardized method of testing gas mask filters, employed by the Armed Services. All of these methods are based upon the use of a test smoke whose average radius corresponds to the postulated (but unconfirmed) maximum at a radius of 0.17 micron (so-called 29° on the polarization Owl). (Section VII).

The linear velocity studies lead to the conclusion that the Albrecht-Langmuir theory is qualitatively correct but quantitatively in error since this theory seriously underestimates the importance of inertial deposition at particle radii less than 0.5 microns (Section VII).

The importance of inertial deposition at the smaller particle radii overshadows completely the opposing diffusion effect and obliterates any possible maximum in the radius penetration curve.

Stearic acid aerosol consists of supercooled viscous liquid droplets which frequently crystallize in situ on contact with a filter fiber in complete contrast to liquid smokes like DOP and oleic acid which spread over the fiber. Pressure drop builds up very rapidly with stearic acid for this reason in contrast to DOP.

Alpha-web paper exhibits marked time variation in filtration and is unreliable for testing. The testing of alpha-web paper with stearic acid and other solid smokes has given unreliable results, which unfortunately have been carried over indiscriminately to liquid smokes leading to false conclusions and questionable methods of testing gas mask canisters and filters.

The reliability of the growth method for determining particle sizes in the sub-Tyndall region has been confirmed by an extensive series of measurements (Section IV).

The method is exact when correction is made for the influence of radius of curvature upon vapor pressure (Kelvin Effect, Appendix A, Section IV). The correction becomes of considerable importance below 0.1 micron when toluene or chloroform is the growth producing volatile solvent.

Conversely, these data may be considered as constituting the first convincing direct experimental verification of the validity of the Kelvin Equation. All previous attempts to verify this equation by direct measurement of the effect upon the vapor pressure have foundered on the rocks of experimental difficulties of detecting these minute vapor pressure differences.

The present method avoids these difficulties by equilibrating the droplet with the flat surface of the master solution. The resulting difference in composition of the equilibrated droplet and the flat master solution is measured by comparing the radii of the grown droplet measured by light scattering with the radius of the grown droplet predicted in the absence of a Kelvin effect.

Historical

The present investigation, although an immediate continuation of an investigation sponsored by the Office of Naval Research in 1948 at Columbia University and continued since 1949 by the Atomic Energy Commission, really represents a revival of a research initiated in September, 1940, by the Aerosol Section (W. H. Rodebush, Chairman) of the National Defense Research Committee of O.S.R.D. under Chemical Warfare Service Directive No. 1. An historical review of the subject is in order as informative and orienting to understand the need and importance of the present research.

At the close of World War I, Freundlich (Kapillar Chemie, Academische Verlagsges, 1922, p. 1085, given also in A. W. Thomas' COLLOID CHEMISTRY, McGraw Hill, 1934, p. 28) published some data showing that the sternutator (sneeze gas), diphenyl dichlor arsine, when dispersed as a solid aerosol by the (crude) method of detonation, showed a maximum penetration through the German Schnappdeckel mask for a particle size range of 0.1 to 0.2 micron. No details of the measurement of particle size are available.

The possibility that the Germans might use this sternutator to induce the removal of the gas mask preparatory to a second attack by a more lethal agent was imminent since the American gas mask at that time was inadequate to protect against this aerosol.

The Central Aerosol Laboratory at Columbia University was assigned the problem of devising a method for the accurate and rapid measurement of particle size of aerosols with a view to studying the effect of particle size on penetrability.

By the Spring of 1941, Dr. David Sinclair and the writer had developed for this purpose

(a) A monodisperse (uniform particle size) aerosol generator,

(b) The new optical method of Higher Order Tyndall Spectra combined with the older method of Polarization of Scattered Light to serve as a rapid and accurate method of determining particle radii by the use of the instrument known by the code name, "Owl" (Reference 6, p. 109), for the range 0.1 to 1 micron radius. A preliminary study of the filter penetration of alpha-web paper impregnated with carbon black by monodisperse stearic acid aerosol was reported using these methods.

The measurements were made by Sinclair using a Luckiesch Brightness meter to estimate the relative amounts of light scattered by filtered and unfiltered aerosol at 90° and by our newly developed Forward Angle Smoke Penetrometer (Ref. 5, Section V, and Ref. 6, p. 101). The principle employed in the latter instrument has since become the basis of the standard optical method used by the Chemical Warfare Service (MIT.E1R1), the Naval Research Laboratory (NRL E1 and E2) and N.D.R.C. (E1R2) penetrometers (Ref. 2 and Ref. 6, Chapter 10). These methods have been adequately described elsewhere[1,2,3,4] and need not be repeated here.

In their N.D.R.C. Report of July 14, 1941, La Mer and Sinclair presented data for a maximum in the filter penetration-radius curve at about 0.16 micron.

At the same time, Irving Langmuir[5] was conducting an important investigation of the theory of aerosol filtration. He predicted on theoretical grounds that a maximum should exist as the result of the opposing effects (in terms of radius of particle) of the factors,

(a) direct interception of particles by the fibers of a filter,

(b) capture by a fiber of particles subject to Brownian movement causing them to leave the normal streamlines of flow around the fiber,

(c) inertial deposition as developed earlier by Albrecht. Langmuir considered this factor entirely negligible below 0.5 micron. His view has been accepted by Rodebush[6].

However, La Mer and Sinclair (1941) using the experimental methods just described, found with the Canadian wool resin filter a *continuously increasing penetration with decreasing radii*; i.e., the curve exhibited no maximum and was of a form that would be consistent with a mechanism of purely inertial deposition. The curve resembles those shown in the figures of Section Vc of the present report.

This surprising finding, in the light of Freundlich's data and Langmuir's theory, was naturally looked upon with some suspicion at that time since the new light scattering methods developed by the Columbia University Laboratories had not as yet been tested by others.

Meanwhile, a group working under the direction of the late Professor Burton of the University of Toronto, was investigating filtration and particle size by other methods. They employed mainly a *polydisperse solid smoke* of methylene blue obtained by

---

[1] D. Sinclair and V.K. LaMer, Chem. Rev. *44*, 245 (1949).

[2] H.W. Knudsen and Locke White, Naval Research Laboratory Report P-2642, 14 Sept. 1945, and ref. 6, Chap. 10.

[3] V.K. La Mer, National Air Pollution Symposium, Pasadena, (1950).

[4] N.D.R.C.-O.S.R.D. Report of July 14, 1941.(La Mer and Sinclair).

[5] Report on Filtration of Aerosols and the Development of Filter Materials - W.H. Rodebush, Irving Langmuir and V.K. La Mer, O.S.R.D. No. 865 Serial No. 353 (Sept. 4, 1942) (Part IV).

[6] *Handbook on Aerosols*, Atomic Energy Commission, Washington, D.C. (1950), p. 120.

evaporating to dryness a spray of aqueous methylene blue. They measured carefully the size distribution and number of particles before and after filtration, using both visible light and electron microscope techniques for counting and measuring. Little criticism can be leveled against the methods of Burton's group for their immediate purpose. Their results as well as the previous work of La Mer and Sinclair and of Freundlich are summarized in Graph VIII of their report of February, 1942[7].

---

7. Report to National Research Council of Canada by Lorne T. Newman, Mrs. E.B. Deacon and J.H.L. Watson under direction of E.F. Burton, February, 1942.
   Also Graph I of C.E. Report 42, November, 1942, shows a maximum for A (cotton) and B (wool and asbestos) at a particle diameter of 0.45 microns, but no maximum for a wool-resin filter down to 0.1 micron diameter. This contrasting effect was tentatively ascribed to electrostatic as opposed to mechanical filtration.

This graph shows the predicted maximum in the filtration curve when using methylene blue aerosol on wool-asbestos filters. This curve is in remarkably close agreement in form of curve with La Mer and Sinclair's alpha-web-stearic acid data and Freundlich's older diphenyl arsine chloride-Schnappdeckel results. On the other hand, their curve for wool-resin (no maximum) was in agreement with that of La Mer and Sinclair.

In view of these apparent agreements, it is perhaps understandable that the Directors of the policy of the C.W.S.-N.D.R.C. program considered the fundamentals of the problem of filtration fully solved; i.e. the resin-wool filter was eliminated on the grounds that it operated by electrostatic action, and the other filters of immediate interest to the Armed Forces of the U.S.A. operated in a purely mechanical way in accordance with Langmuir's theory.

The filtration program at Columbia University was accordingly discontinued in the Spring of 1942; the Balanced Optical Photoelectric Penetrometer working on the Principle of the Forward Angle Tyndallometer, constructed by Dr. Seymore Hochberg as a more rapid and convenient method of prosecuting further studies on these discrepancies with existing theory, was ordered to be shipped to the new N.D.R.C. Testing Laboratories at Northwestern University before adequate tests of its reliability could be made by its builders[8].

---

8. O.S.R.D. No. 865, Part V, p. 1.

Further experimental work on filtration of aerosols was then concentrated at the Chemical Warfare Development Laboratory at the Massachusetts Institute of Technology and the N.D.R.C. Laboratory at Northwestern University.

As far as can be ascertained, all further fundamental experimental work involving the influence of particle size and the velocity of flow through the filter was discontinued except for some later work at the Naval Research Laboratory.

The emphasis at the N.D.R.C. Northwestern and the C.W.S. Development Laboratories was apparently concentrated upon the objective of developing and testing a more efficient filter for mass scale production by (a) designing an aerosol generator (MIT-E1R7, ref. 6, p. 124), which would yield one constant size of the (supposed) maximum penetrability and presumably also reasonably monodisperse, (b) improvements in the precision and sensitivity of filtration measurements by refinements of the photoelectric techniques by electronic methods (ref. 6, p. 128).

The objective of producing a better filter for the gas mask canister was achieved, but at the expense of testing almost exclusively for one particle radius and at the one constant flow velocity of immediate practical importance.

In view of the possibilities inherent in Langmuir's brilliant theoretical reports when reviewed in the light of the results of the present investigation and the independent studies at the Naval Research Laboratory[9], it becomes evident that the decision to discontinue fundamental experimental studies on the mechanism of filtration was premature and unwarranted. The restriction of the testing program to one filter velocity and one particle size obscured an understanding of the available data which were incompatible with theory even in 1942.

In neither this investigation nor that of Ramskill and Anderson has a single example ever been found wherein a liquid smoke and a reproducible time independent filter have exhibited a maximum in the penetration-radius curve in accordance with Langmuir's theory.

Through the courtesy of Drs. Duncan MacRae and Saul Hormats, Chemical Center, Edgewood, Maryland, a generous sample of the original alpha-web paper was located and made available to us in February, 1951. Tests on this paper with the liquid smoke DOP (dioctyl phthalate) are reported in Figs. 18 and 19 of Section Vc. It will be noted that alpha-web paper shows time effects (noted also by La Mer and Sinclair in their report of July 14, 1941) which yield no maximum when compared after 15 seconds, but do exhibit an approach to a maximum when compared at 90 seconds. It seems a fair presumption at the present writing that when alpha web paper is tested with solid stearic acid smoke that the maximum observed in this special case may yet be duplicated experimentally.

The explanation of the maximum observed by Freundlich, by La Mer and Sinclair, and by Burton et. al., is not entirely clear as yet. It should be noted, however, that in all the cases exhibiting a maximum, the aerosol employed has been a solid - not a liquid - aerosol. Secondly, the filter papers used were not reproducible as compared to CC-5 paper, and furthermore exhibit a marked time dependency in percentage penetration and a clogging effect leading to increased pressure drop. Our tentative conclusion at this writing is that the maximum observed by Sinclair and La Mer is due to the fortuitous combination of a bad paper (alpha-web impregnated with carbon) which yields different results depending upon the time of passage of the aerosol -

---

[9] E.A. Ramskill and W.L. Anderson, J. Colloid Sci. (in press), 1951.

15 seconds, 90 seconds or longer - and a solid or semi-solid smoke of stearic acid which clogs the filters and raises the pressure drop unduly. All in all, stearic acid smoke is difficult to use because of its precipitation on the walls and bends of the tubing.

The importance of continuing these investigations in the light of Atomic Bomb tests, etc., are too obvious to require any detailed statement.

Plan of Work

The present investigation was planned to meet the following requirements:

(a) Rigid adherence to monodisperse aerosols of accurately known size controlled over a wide range and extended to as small a size as possible, viz. 0.02 micron to at least 0.5 micron.

(b) Variation of the linear velocity over a wide range - tenfold.

(c) Selection of declassified papers which exhibit as different types of fibers, fiber sizes and methods of preparation as possible.

(d) Improvement in the precision, accuracy and reproducibility of the measurements of particle size and filter penetration (Sections IV and V).

(e) Investigation of the theoretical aspects of turbulent and laminar flow as acquired in the construction of filter apparatus and the interpretation of the filtration results in terms of latent developments in the field of hydrodynamics (Section VI).

Source of Nuclei.

DOP (dioctyl phthalate), Oleic Acid and Stearic Acid aerosols were used in the present study of filtration. Sources of sodium chloride nuclei were obtained by melting and solidifying sodium chloride on a nichrome coil. These coils were used in most of the experiments since they provided a steady, easily controlled source of nuclei of sodium chloride. In most cases, a current of 3 amp. was passed through the wire, an increase of 0.1 amp. in the current causing approximately 0.2 micron decrease in radius of aerosol. Uniform emission was obtained in the 2.9 - 3.1 amp. range.

In a few experiments with DOP, the vapor of concentrated sulfuric acid was used as a source of nuclei as described by La Mer and Gordieyeff[1]. The DOP aerosol produced with sulfuric acid was very monodispersed, and for large particles all of the Higher Order Tyndall Spectra (H.O.T.S.) were sharp and could be easily measured with the Owl. The control by this nuclei source is difficult because of the effect of humidity on the vapor pressure of the sulfuric acid.

Flow Rate.

It was found experimentally that a total flow of 2 liters/min (half of this flow is sent through the nuclei source) is most appropriate for the production of monodisperse aerosol. With a total flow of 1 liter/min, condensation on the walls of the chimney takes place. A flow higher than 5 liters/min results in formation of polydisperse aerosol.

Control of Equilibrium Conditions.

It was essential in the present study of filtration to use a highly monodisperse aerosol of constant radius. To achieve this, the generator was in operation at least 6 hours before the beginning of an experiment. The equilibrium temperatures of the boiler and reheater were reached slowly. During the experiment a frequent check on the flow and temperatures was made. The thermoregulator in the boiler compartment provides a control of boiler temperature within ± 0.2°C of equilibrium temperature. If any deviation from equilibrium conditions occurs during an experiment, the thermoregulator and the nuclei source provide an easy means of restoring these conditions.

---

[1] La Mer, V.K. and Gordieyeff, V., Science 112, 20 (October 20, 1950).

Once equilibrium has been reached, the generator reacts quickly and is sensitive to changes in nuclei source and thermoregulator control. For example, a generator producing a monodisperse aerosol of 0.26 micron of DOP aerosol reacted <u>within 10 minutes</u> to a change from 3 amp. to 2.95 amp. in the current, through the nuclei source, and produced a highly monodisperse aerosol of 0.48 micron.

However, the variac settings and the flow rate should remain constant during the experiment as the generator reacts slowly to these changes, both of which affect the equilibrium temperature.

Reheater and Boiler Temperature Relation.

The relative temperatures of the reheater and boiler influence the monodispersity of the aerosol. The boiler temperature of the generator was allowed to come to equilibrium and the reheater temperature was set at a high value - say 20-30° higher than the boiler temperature. The reheater temperature was then lowered by slowly reducing the heat supplied. The boiler temperature remained constant. The aerosol was observed in the Owl at 5-minute intervals. The sharpness and the angular positions of the orders (H.O.T.S.) were noted. In general, a difference between reheater and boiler temperature of 3 - 10°C is the most appropriate for production of monodisperse aerosol with radii range between 0.3 - 0.6 microns and a difference of 15 - 25°C for particle radii smaller than 0.3 micron. A few experimental results are listed below:

	Radius microns	Boiler Temp. °C	Reheater* Temp. °C	Difference between Reheater and Boiler Temp
Oleic acid	0.39	103	112	9
	0.45	113	120	7
	0.50	116	123	7
Stearic acid	0.22	116	140	24

Flow rate - 2 liters/min.

*Temperatures noted are those at which sharpest orders were obtained.

It was observed that for aersols of large size, the orders remained sharp for a reheater temperature even slightly lower than the boiler temperature; also that the reheater temperature had almost no effect on the size of such particles.

These experiments were not very accurate as they were performed under thenon-equilibrium conditions of continuous lowering of the reheater temperature. The experiments were limited to particle radii larger than 0.2 micron as the growth method for determination of smaller particles could not be applied due to the above-mentioned reason.

The relation between reheater and boiler temperature might be of importance in improving the degree of monodispersity and merits further investigation. In future experiments, the reheater temperature should be allowed to reach its equilibrium value for a given variac setting before making a reading.

Concentration of Aerosol.

The concentration of aerosol was found to be of the order of 10^6 particles/cc for a nuclei source setting of 3 amp. A table of values obtained for DOP aerosol by the optical transmission method is given below:

Radius microns	Concentration × 10^{-6} particles/cc.
0.21	1.6
0.23	1.0
0.26	2.1
0.28	1.4
0.28	1.7

The concentration varies greatly with small changes in nuclei source.

A table listing the mass concentration for various DOP and Oleic Acid aerosol particle radii for 10^6 particles/cc is given below:

Particle radius in microns	Mass Concentration in micrograms/liter.	
	DOP	Oleic Acid
0.03	0.11	0.10
0.06	0.89	0.81
0.10	4.10	3.8
0.20	32.82	30.0
0.30	110.75	101.
0.40	262.53	240.
0.50	512.75	468.
0.60	886.	809.
0.70	1407.	1285.

The mass concentration in micrograms per liter (m_c) is calculated from the following formula:

$$m_c = 10^3 \cdot (4/3 \pi r^3) \cdot \rho \cdot n$$

where r is the particle radius

n, number of particles per cc (assumed to be = 10^6 part./cc)

ρ, the density of the substance (.9796 g/cc for DOP)
(.895 " " Oleic Acid).

Comparison of Aerosols.

DOP - Most of the experiments were performed with DOP aerosol. This aerosol is most appropriate for filtration studies for ranges of particle radii from 0.03 to 0.50 microns. Even aerosols of radius less than 1 micron give a scattered light beam of sufficient intensity for 90° Penetrometer measurements. The index of refraction of DOP is 1.49. DOP is a liquid aerosol and shows no clogging effect with filters like CC-5, A.E.C. No. 1 and W-2, which show no time effects within at least two hours. Master solutions of DOP and Toluene were used for the determination of small particle radii by the growth method. For a nuclei source current of 3 amp., a change in boiler temperature from 93° to 126°C produces an increase in particle radius from 0.03 to 0.3 microns (See Fig. 3.1). Particle radii from 0.3 to 0.5 microns are obtained for a boiler temperature of approximately 126°C and for different nuclei source current values ranging from 3A to 2.9A. (See Fig. 3.1) The reheater temperature cannot be raised above 130°C as decomposition appears at this temperature.

Oleic Acid - The filtration characteristics of this liquid aerosol were limited to the particle radii from 0.12 to 0.6 microns. The beam scattered from aerosols of particle size smaller than 0.12 is too weak for the filtration measurements with the 90° Penetrometer. Oleic acid aerosol like DOP does not clog the filters. Master solutions of Oleic Acid in Chloroform were used for the growth method. The flow rates used for the study of variation of penetration with particle radius were 2 liters/min and 1.5 liters/min respectively. The latter was used for study of penetration for small linear velocity (1.9 cm/sec for the filter holder of area≈to 13 cm^2). For a nuclei source current of 3 amp., a change of boiler temperature from 90°to 116°C produced an increase in particle radius from 0.12 to 0.36 microns approximately. Particle radii from 0.36 to 0.6 microns were obtained for nuclei source currents of 2.92 amp. and by gradual increase of the boiler temperature from 116 to 126°C. (See Fig. 3.1).

Stearic Acid - This is a semi-solid aerosol. By this term we mean that the aerosol exists as supercooled viscous liquid droplets which spontaneously crystallize after a lapse of time or on contact with the fibers of a filter. For a given particle radius, the penetration and the pressure drop are functions of time. (See Fig. 6, 7, 8, 9. Sec. Vc).

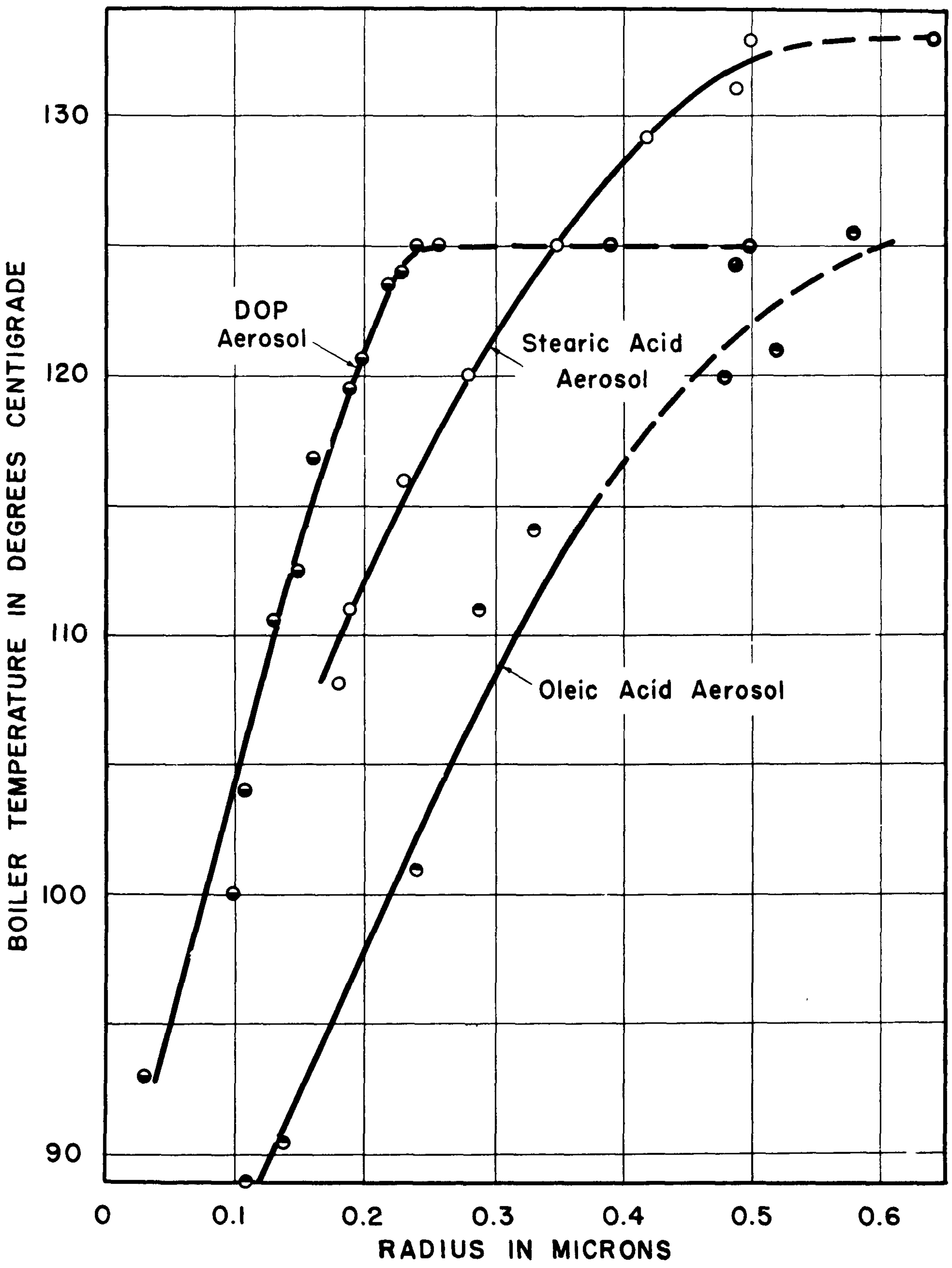
It is difficult to prevent losses of this aerosol as it precipitates readily on the inner walls of the rubber tubing and on constrictions of the aerosol circuit, becoming especially important for the larger particle sizes. The study of filtration characteristics of this aerosol was restricted to the radii ranging from 0.18 to 0.64 microns. The index of refraction of Stearic Acid is 1.43. For nuclei source current of 3 amp., a change in boiler temperature from 108 to 133°C produced an increase in particle radius from 0.18 to 0.50 microns. Larger particles are obtained with a boiler temperature of 133,and nuclei source current smaller than 3 amp.; 0.64 radius was obtained for nuclei source current of 2.92 amp. (See Fig. 3.1).

Fig. 3.1 shows the variation of particle radius with boiler temperature for a constant nuclei source current for DOP, Oleic Acid and Stearic Acid aerosols. These curves were obtained for a flow of 2 liters/min. For the region of 3 amp. nuclei source, the curves are practically straight lines of nearly the same slope (See solid portion of the curves in Fig. 3.1). Notice that in order to obtain a particle of given radius, the boiler temperature setting for DOP is higher than that for Stearic Acid and the latter higher than for Oleic Acid, as a result of the differences in vapor pressures of the three substances.

The large particle sizes were obtained by lowering the nuclei source current to values ranging from 2.90 to 2.99 amp., (See broken part of curves in Fig. 3.1), for a high boiler temperature instead of raising the temperature. A higher boiler temperature and a correspondingly high reheater temperature could cause decomposition of the substance.

For all the three types of aerosols, the reheater temperature was higher than the boiler temperature. The difference between these two temperatures was around 20°C for particle radius smaller than 0.3 microns and around 5°C for particle radius of approximately 0.5 microns.

The relation between boiler temperature and particle radius is affected by several factors; the curves in Fig. 3.1 give only approximate data. The individual nuclei sources differ among themselves and the same current sent through different sources will cause an emission of different numbers of nuclei per cc. Fluctuations of current in a given nuclei source affect the particle size. The flow rate changes and the time of usage of a given sample of substance for production of aerosol might also alter the boiler temperature vs. particle radius relation.



130
120
110
100
90
0
0.1
0.2
0.3
0.4
0.5
0.6
BOILER TEMPERATURE IN DEGREES CENTIGRADE
RADIUS IN MICRONS
DOP Aerosol
Stearic Acid Aerosol
Oleic Acid Aerosol

Fig. 3.1

15

1. INTRODUCTION

Until very recent times the smallest liquid aerosol particle which could be accurately measured by any of the various available methods was one of approximately 0.08 micron in radius. To overcome the limitations inherent in known methods of measurement, it was sought to develop a practicable, optical means of determining the size of particles whose radii were appreciably smaller than the value above stated. With this objective in view the so-called "growth" method was conceived by La Mer, Inn and Wilson (1,2) and its merits examined in this laboratory.

Since it is impossible to detect by direct optical techniques aerosol particles of radii smaller than 0.08 micron, it is necessary to "grow" smaller particles until their size is at least equal to this value. In order to accomplish this, aerosol droplets of a non-volatile substance, such as dioctyl phthalate (D.O.P.), having radii r_1, are exposed to the vapors of a "master solution," composed of a known amount of this non-volatile substance in a volatile solvent, such as toluene. The process for the D.O.P.-toluene case will be described with the understanding that the principle may be applied to <u>any</u> similar system. The spherical aerosol particles increase in size as toluene vapor diffuses to the droplets while liquid D.O.P. by the same process passes into the growing shells. Growth is complete when an equilibrium condition has been established; that is, when the partial pressure of each droplet is equal to that of the master solution. Since the vapor pressure of D.O.P. is negligible compared to that of toluene (v.p. of D.O.P. $\cong 10^{-7}$ mm.Hg; v.p. of toluene $\cong 33$ mm. Hg), the vapor pressure of the master solution is really the vapor pressure of the toluene component alone. The equilibrium state is reached almost instantaneously (See Appendix B). Since the initial D.O.P. droplet is surrounded by D.O.P. vapor, saturated with respect to the droplet and supersaturated with respect to the master solution, this D.O.P. vapor distills toward the solution. The composition of the master solution is not affected perceptibly by this process since the amount of D.O.P. going into solution is negligible because of its minute vapor pressure. As a first approximation, any effect of the radius of curvature upon the vapor pressure of the droplet will be neglected in this discussion. Since the composition of the droplet must be identical with that of the master solution at the equilibrium state, we may write r_{gk} kr_{ik} where r_{gk} is the radius of the particle grown k times, r_{ik} is the radius of the initial particle under consideration, and k is the growth factor used in the calculation.

---

1. La Mer, V.K., Inn, Edward C.Y., and Wilson, I., <u>Final Report</u> on Navy contract N6onr-27116, June 6, 1949.

2. La Mer, V.K., Inn, Edward C.Y., and Wilson, I., J. Coll. Sci., <u>5</u>, 471 (1950). (for sulfuric-acid-water systems).

The growth factor k may be expressed as

$$k = \left(\frac{v_1 + v_2}{v_2}\right)^{1/3}$$

where v_1 = volume of toluene in master solution
v_2 = volume of D.O.P. in master solution.

Thus, in order to grow four times an aerosol particle of radius 0.06 micron, a master solution of 63 parts toluene, 1 part D.O.P. is used and r_{gk} = 0.24 micron.

Once the droplet has increased in size beyond 0.08 micron, it may be measured by any of several standard methods, such as Polarization and Higher Order Tyndall Spectra (H.O.T.S.) (Ref. 2).

2. OBJECTIVES

The principal objective of this research was to investigate the reliability of the growth method for the measurement of very small aerosol particles. The particular aim of this investigation was the application of this method to D.O.P. and oleic acid aerosols and the extension of filtration measurements with these aerosols to regions of particle radius smaller than ever examined previously by the usual techniques.

3. SUMMARY AND CONCLUSIONS

The results and conclusions of the various aspects of this problem are listed below and any pertinent discussion included under the particular topic considered.

(a) Time Dependence of Radius (r_g) of Grown Aerosol Particle.

The time dependence of the radius (r_g) of the grown aerosol particle for a particular ungrown aerosol was investigated in 34 experiments, using a number of growth factors (See Fig. 1,a,b,c). It was found on examination of the position of the red orders of the H.O.T.S. with time that a steady state is reached almost instantaneously and that the angular position oscillates about this value for at least 15 minutes. In other words, the value of r_g is independent of time. It was also observed that the time and method of mixing does not affect r_g.

An Appendix (A) dealing with errors arising from the curvature of the droplet (Kelvin effect) and an Appendix (B) dealing with a possible time lag effect on growth due to diffusion in the liquid droplet during growth are attached.

(b) Oleic Acid vs. D.O.P. Aerosol.

These two aerosols behave identically when grown over their respective master solutions and proves that the growth method is not specific to a particular aerosol.

(c) Results of and Conclusions from the Growth Experiments, Surveying a Wide Range of Radii of Initial Aerosol.

The 139 experiments performed were distributed, with respect to the radius of the ungrown aerosol particle, as follows:

Range 1: 36 cases (35 D.O.P., 1 oleic acid)....$r_1 \leqslant 0.100$ microns

Range 2: 80 cases (72 D.O.P., 8 oleic acid)....$0.100 \text{ microns} < r_1 \leqslant 0.180$ microns

Range 3: 23 cases (13 D.O.P., 10 oleic acid)....$r_1 > 0.180$ microns

(1) Consistency of the Growth Method.

In order to investigate the consistency of this method, the various r_{1k} values, obtained for each initial ungrown aerosol, were examined for all 139 experiments and tested by the $\frac{\overline{\Delta r_{1k}}}{\overline{r_{1k}}} \cdot 100$ distribution, where $\overline{r_{1k}}$ is the mean of the r_{1k} values and $\overline{\Delta r_{1k}}$ is the average deviation from the $\overline{r_{1k}}$ for each original aerosol. This is illustrated in Fig. 2a for all sizes of r_1 used.

It may be noted that the curve has a very steep slope and that most of the cases lie within an interval of 10% average deviation. The ungrown aerosol as it comes from the generator has a 10% average deviation from the mean radius.

As another means of appraisal of the growth method, the maximum separation between any two r_{1k} values for a particular ungrown aerosol was tabulated for each of the 139 cases and the per cent maximum separation $\left\{\frac{(\Delta r_{1k})_{\max.}}{\overline{r_{1k}}}\right\}\cdot 100$ distribution made.

This curve (see Fig. 2b) also has a fairly steep slope and most of the cases lie within a 25% maximum separation. In other words, the growth method passes even this severe test. The results obtained from these two analyses indicate that the growth method offers an excellent means of measuring the size of small aerosol particles.

To estimate the value of this technique for various sizes of the original ungrown aerosol particle, these distributions were repeated, classifying the experiments according to the average size $(\overline{r_{1k}})$ of the ungrown particle. Three ranges were considered; namely, 0.03 micron $\leqslant \overline{r_{1k}} \leqslant$ 0.10 micron, 0.10 micron $< \overline{r_{1k}} \leqslant$ 0.18 micron, and 0.18 micron $< \overline{r_{1k}} <$ 0.30 micron. These distributions are shown in Figs. 3 and 4. The method seems to be excellent for all the sizes examined, but of the cases shown, it would seem best for the intermediate range, 0.10 micron $< \overline{r_{1k}} \leqslant$ 0.18 micron. Of course, this curve is the most reliable since the majority of experiments covered this particular range. In Figs. 3 and 4, the smallest initial size range would seem to yield the poorest results, but this is understandable since the monodispersity of the original ungrown aerosol becomes doubtful. Also corrections arising from Kelvin effect assume more importance as the size of the particle diminishes (Appendix A).

(2) The Investigation of r_{1k} vs. k.

A slight tendency for r_{1k} to decrease with increasing k was observed, but in the majority of experiments this decrease fell within the limit of precision of the apparatus (0.02 micron for the "Owl"), and can be corrected at least in major part by consideration of the Kelvin effect.

(3) Comparison of Calculated $\overline{r_{1k}}$ with the Radius of the Initial Ungrown Aerosol Particle, As Measured Directly.

To test the validity of the mean radius $(\overline{r_{1k}})$ of the initial ungrown aerosol particle, calculated for different growths, the $\overline{r_{1k}}$ values within the proper size limits were compared with those r_1 values, obtained directly by the polarization or H.O.T.S. techniques. In Fig. 5 the variation of $\overline{r_{1k}}$, obtained by the growth method, from the r_1, observed directly by H.O.T.S. vs. the radius r_1, is plotted. Most of the variations lie between zero and 0.020 micron, the latter being the limit of precision of the "Owl." (Ref. 3,4). There is excellent agreement between the results of the two methods.

A similar plot is made for the comparison of the growth and polarization techniques (3), (see Fig. 6). Precisely the same conclusions as before may be drawn here; namely, the two methods agree within the limits of precision of the instruments involved.

(d) Test of Value of First Red Order of H.O.T.S. as Measure of Radius of an Aerosol Particle.

In each of the 139 experiments performed, the r_{1k} values, obtained from a use of the first red order of the H.O.T.S. alone, were compared with those obtained from an average of the results from all the red orders. The maximum separation between any two r_{1k} values was found and with this as a criterion it was concluded that the first red order is not as reliable as the entire red spectrum for use in the determination of the radius of an aerosol particle.

---

3. Sinclair, D. and La Mer, V.K., Chem. Rev. 44, 245 (1949).

4. Johnson, F. and La Mer, V.K., J. Am. Chem. Soc. 69, 1184 (1947).

4. PROPOSED PROGRAM FOR FUTURE WORK

There are several phases of this part of the investigation which warrant further study. This list, by no means complete or final, represents the most obvious aspects to be considered:

(a). The lowest size range of the initial aerosol ($r_i < 0.1$ micron) should be investigated further since it is felt that an insufficient number of cases in this category was chosen. By far the largest percentage of the initial aerosols possessed radii in the 0.11 - 0.18 micron range. The boiler-reheater temperature ratio in the generator should be carefully regulated for optimum operating conditions.

(b). The growth factor, k, as a function of temperature should be studied for the D.O.P.-toluene and oleic acid-chloroform systems. This relation was explored only for the case of sulfuric acid and water. (Ref. 1).

(c). Experiments, emphasizing the Kelvin effect, should be performed in the region of very small radii where large growth factors are mandatory. This would lend better experimental confirmation of the theoretical considerations.

(d). The grown aerosol particles should be observed in the differential settling apparatus to make use of an independent method for their size determination and to investigate any inhomogeneities which may be present, and perhaps also by a direct photographic method of observing aerosols which is being developed presently in this laboratory under an Air Force contract.

5. EXPERIMENTAL DETAILS

The general procedure employed in the growth method will be described below, whereas a description of the experimental apparatus will be included in a separate section to follow.

Notation

1.	k	growth factor
2.	r_1	radius of the initial ungrown aerosol particle produced in the generator.
3.	r_g	radius of the grown particle
4.	r_{gk}	radius of the particle grown k-fold (over a master solution of k growth factor)
5.	r_{1k}	radius of the ungrown particle calculated from the k-fold grown particle ($r_{1k} = r_{gk}/k$)
6.	$\overline{r_{1k}}$	the arithmetic mean of all the r_{1k} for different k.
7.	$\overline{\Delta r_{1k}}$	the average deviation of r_{1k} from the $\overline{r_{1k}}$ ($\overline{\Delta r_{1k}} = \frac{\sum_k \lvert d_j \rvert_k}{N}$. N is the number of growth master solutions used).
8.	$\frac{\overline{\Delta r_{1k}}}{\overline{r_{1k}}}$	$\cdot 100$ is the percentage average deviation.
9.	$(\Delta r_{1k})_{max}$	is the maximum separation between two r_{1k} for the same initial ungrown particle r_1.
10.	$\frac{(\Delta r_{1k})_{max}}{\overline{r_{1k}}}$	$\cdot 100$ is the percentage maximum separation.

D.O.P. or oleic acid aerosols of uniform size are prepared in the LaMer-Sinclair uniform particle size generator (5) in the usual way. A stream of aerosol is passed through a 100 cc. Erlenmeyer flask, containing about 15 cc of a master solution of known composition of solute in volatile solvent (for example, D.O.P. in toluene). The flask is stoppered and contents swirled. It is important that care be taken not to shake the flask and thereby produce a spray. The aerosol particles grow to their final size almost instantaneously in the vapor atmosphere. The flask is then placed in a modified "Owl" to measure the angular positions of the

---

5. La Mer, V.K., Proc. First National Air Pollution Symposium, 5 (1949).

red orders of the H.O.T.S., exhibited by the grown particles. The radius of the grown particle is then determined from the θ vs. r curves (1,2,3,4,5) and the results averaged over all the values obtained from the various angular positions. This average value is defined as the radius (r_{gk}) of the grown particle for one particular growth factor, k. The radius (r_{1k}) of the original ungrown aerosol particle is then calculated by dividing the radius of the grown aerosol particle by the growth factor.

The initial aerosol is exposed to the vapors of master solutions of D.O.P. in toluene, yielding 2-, 3-, 4-, 5-, and 7-fold growth in radius. The exact growth factors used are determined by the requirement that the value of r_{gk} lie in the 0.18 - 0.70 micron range for observation of H.O.T.S. In other words, the growth factor, $k = r_g/r_1$, where r_g and r_1 represent the radii of the grown and initial aerosol particles, respectively, is fixed by the ultimate size of the grown particle necessary for determination by the method of H.O.T.S. Thus an original aerosol particle, having a radius of 0.06 micron must be grown at least 3-fold. The same approach is followed for the oleic acid aerosol. Here chloroform is a convenient volatile solvent. The values of r_{1k} found for the various growth factors are then compared by the usual statistical methods.

In some cases it is possible to compare the average value radius ($\overline{r_{1k}}$) of the initial particle, calculated in this fashion, with the r_1 from polarization measurements (2), (0.12 micron $< r <$ 0.16 micron), or from observation of the H.O.T.S. ($r >$ 0.18 micron) on the initial aerosol.

In this study 139 experiments were performed, in which aerosol particles of initial radii 0.030 to 0.30 micron were grown 2-, 3-, 4-, 5-, and 7-fold. Of these cases 19 were made with oleic acid aerosol grown over master solutions of oleic acid in chloroform while 120 were carried out on the D.O.P.-toluene system. These experiments were conducted with no intentional emphasis on a particular size but rather as a survey of the normal working range; however, a large proportion of the r_1 lay in the 0.110 - 0.180 micron range for filtration studies.

Table I lists representative data obtained in this analysis and shows:

1. Growth of particles with various initial radii,
2. Experiments with different growth factors on a given ungrown aerosol to investigate consistency of method,
3. Type of analysis made on data obtained,
4. Comparison of results with those by other methods (H.O.T.S. and Polarization),
5. Comparison of results obtained with D.O.P. and oleic acid aerosols.

In this compilation values of the calculated radius of the initial particle are tabulated although it is the radius of the grown particle which is actually observed. The value of k is known from the composition of the master solution.

The values of r_{1k} obtained by using different growth factors for a given ungrown aerosol are averaged. This mean value is called $\overline{r_{1k}}$. The average deviation (a.d. = $\frac{\sum_k |d_j|_k}{N}$ where k = growth factor and N = number of growth experiments of each r_{1k} from the mean $\overline{r_{1k}}$) is calculated and then the percentage error $\frac{\overline{\Delta r_{1k}}}{\overline{r_{1k}}} \cdot 100$ found. A frequency distribution of the percentage average deviation for all 139 cases is made and the results plotted in the error curves, shown in Fig. 2a. The distribution for three ranges of $\overline{r_{1k}}$ appears in Figs. 3 and 4. The maximum separation $(\Delta r_{1k})_{max}$ between any two r_{1k} values for a given ungrown aerosol are tabulated for each of the 139 cases and the distribution of the percentage maximum separation $\frac{(\Delta r_{1k})_{max}}{r_{1k}} \cdot 100$ examined (see Fig. 2b and 4). In Fig. 5 a comparison of the values of $\overline{r_{1k}}$ and the r_1 from direct H.O.T.S. observation is made. A similar analysis appears in Fig. 6 for the growth method vs. direct measurement by the polarization technique.

For a particular aerosol grown by a given amount, the reliability of the r_{1k}, calculated by using the angular position of the first red order of the H.O.T.S., is tested against that found by averaging the values of the radius obtained from <u>all</u> the red orders.

The following procedure was used to investigate the time dependence of the angular positions of the red orders of the higher order Tyndall spectra of the grown D.O.P. aerosol:

> D.O.P. aerosols were produced which showed no H.O.T.S. but rather a bluish cast, indicating a particle size just above the Rayleigh region. These aerosols were exposed to the vapors of master solutions of D.O.P. in toluene, each flask swirled and the position of each red order of the H.O.T.S. observed simultaneously for a period of 7 minutes, at 30 second intervals, as a rule.

In Figs. 1a and 1b, the time average mean angular position vs. time (in minutes) is plotted for the first order for the case of two and three growth respectively, with a 20 second swirling time. Fig. 1c shows the results of third order observations for 5-fold growth. In Fig. 1c a 30 second swirling time was employed. These represent typical results obtained out of the 34 such experiments performed. The fluctuations of the readings about the average were found to lie within ± 3°.

The first reading, recorded by the operator, deviated most from the average and in some cases had to be discarded entirely. The time elapsed between agitation and observation did not affect this result, indicating that the naked eye requires a finite time to adapt itself to its measuring task and is inaccurate for the first observation.

Laboratory Apparatus Used in Connection with Growth Method for the Measurement of Aerosol Particle Size.

1. Generator.

The monodisperse aerosol is produced in the La Mer-Sinclair generator (3).

2. Electronic Photometer.

An electronic photometer (Model No. 512 produced by the Photovolt Corporation) and a set of optical filters (Corning No. 2-61 and 1-57) were used to measure the angular position of the red orders of the H.O.T.S. The particular filters were chosen to isolate a narrow band around 6290A°. This apparatus was tested in an effort to find a device to eliminate the error introduced by using the naked eye to observe the red spectrum. This model of the photometer proved of little value for the purpose at hand since the photocurrent decreased gradually with increasing angle with no maximum at the position of a red order. In other words, it was sensitive only to a decrease in light intensity without detecting the position of any red order. This decrease in intensity is so acute that a variation of 10° in angle covers the full scale of the meter, which means that the approximate position of the red band had to be located with the naked eye. The intensity effect of the incoming light is so great that the positions of the second and third orders are completely masked. It is not possible to record their angles even with a maximum sensitivity of the photometer. A light intensity ratio meter, which measures the ratio of red to green light, is needed to eliminate this intensity effect.

3. The "Owl".

For a complete description of this optical device, see (6).

---

6. Handbook on Aerosols, Atomic Energy Commission, 1950, p. 106.

6. DISCUSSION OF ERRORS

The sources of errors will be classified in three groups: those originating in the production of aerosol in the generator, those introduced in the growth of the aerosol particles, and those arising in the determination of the particle radii.

1. Errors in Original Aerosol.

Since a moderately polydisperse aerosol exhibits broad and diffuse Higher Order Tyndall Spectra, making difficult the recording of their angular positions, it was deemed necessary to investigate the matter of polydispersity in the generator and its effect on the growth method as far as we could with presently available techniques.

The generator produces under normal operating conditions a highly monodisperse aerosol with only a 10% average deviation from the mean radius (See ref. (4), and ref. (6), p. 77).

If this distribution were preserved in the growth process, the width of the red orders should increase with increasing growth factor until no H.O.T.S. can be seen. For example, an original aerosol, having an r_i of 0.120 ± 0.012 microns should yield a grown aerosol of radius 0.240 ± 0.024 microns for $k = 2$; for $k = 3$; $r_g = 0.360 \pm 0.036$ microns, etc.

Although it is recognized that the intensity of scattered light increases with increasing particle size, inhomogeneities in radius present in the original aerosol did not affect the grown particles to the point where their H.O.T.S. could not be seen.

2. Errors in the Growth Process.

Since the growth factor, k, is such a vital quantity in the calculation of particle radius by the growth method, it is most important that its accurate value be known, which is determined directly from a knowledge of the composition of the master solution. It is possible for the master solution to change in composition if the proper precautions are not taken. Passage of aerosol over the master solution for a long period of time causes an increase in solute concentration as some aerosol passes into solution and a decrease in solvent concentration with the sweeping out of vapor by the aerosol stream. Similarly, a frequent or lengthy exposure of the flask containing the master solution may result in loss of the more volatile component. If the master solution is replaced often by a fresh sample, all of these errors can be avoided.

The errors in k, attributed to the Kelvin effect, will be discussed in the Appendix (A).

The effect of temperature variations is important in this case as in all processes dealing with aerosol particles. It is necessary that the temperatures of the flask, containing the master solution, and of the generator outlet be equal and constant to prevent changes in the initial aerosol radius. Care should also be taken that the flask, containing the grown aerosol and the master solution, and the measuring instruments or study of this aerosol be at the same constant temperature to maintain constant grown particle radii. This is particularly important for the sulfuric acid-water system (2). For this case, the sensitivity of the grown aerosol to temperature variations increases with increasing growth factor. The mere precaution of keeping the flask at room temperature is sufficient to reduce the errors due to temperature gradients. Theoretical calculations for the D.O.P.-toluene system show that the heat, liberated in the condensation of solvent on the solute aerosol particle in the growth process does not raise the temperature of the droplet by more than 0.02°C and cannot be observed.

3. Method of Observation of Aerosol.

(a) Errors in H.O.T.S.

The angular positions of the red orders of the grown aerosol, as estimated by the naked eye, are precise to within ±2°, due to the operator's location of the "red" band and to its finite width. This uncertainty in angle introduces an error of about ±0.02 micron in the determination of radius from the "r vs. θ" curves of the Mie theory. This error in the measurement of the red orders could be reduced by using a Photoelectric Ratio Intensity Meter (8) for detecting the angular positions of the red orders by measuring the red/green intensity of scattered light.

The value of the grown particle radius is also affected by the limit of precision of the "r vs θ" curves and their use for master solutions of varying indices of refraction. For example, these curves for an index of refraction, m, of 1.5 were applied to the following cases: D.O.P. with $m = 1.4859$ and toluene with $m = 1.4978$; the oleic acid-chloroform system the indices of refraction of which are 1.463 and 1.498, respectively.

It was found that the value of a particle radius as averaged from those of all the red orders is certainly more reliable than the radius, estimated from the first order alone. The maximum separation between any two r_{ik} was larger for those calculated with the first order exclusively.

(b) Errors in Polarization Method.

A two per cent average error is introduced in the estimation of the extinction angle in the determination of the ungrown particle radius by polarization method.

---

8. Progress Report No. 3, Air Force Contract AF-19(122)-164, This Laboratory, Columbia University, August 31, 1950, p. 15).

TABLE I

Characteristic Data of Some Representative Experiments On D.O.P.-Toluene Aerosols Obtained by the Growth Method. Radii in microns.

r_{12}	r_{13}	r_{14}	r_{15}	$\overline{r_{1k}}$	$\frac{\overline{\Delta r_{1k}}}{\overline{r_{1k}}} \cdot 100$ %	r Polarization H.O.T.S. (P) (H)
0.260	0.250			0.255	2.0	0.280 (H)
	.230*	0.210*		.220*	4.6	.220 (H)
	.220*	.220*		.220*	0	.220 (H)
.215	.210			.212	2.4	.210 (H)
.200	.200			.200	0	.200 (H)
.178	.173			.176	1.1	.180 (H)
.185*	.157*			.171*	8.2	
.185	.195	.165	0.140	.171	10.6	
.185	.170	.150		.168	7.1	.160 (P)
.165	.168	.167		.167	0.7	
.158	.158	.158		.158	0	
.150	.170	.150		.157	4.5	.160 (P)
.162	.153	.150		.155	2.6	.157 (P)
.158	.147	.141		.149	4.0	.158 (P)
.140*	.140*	.120*	.140*	.135*	5.9	
.150	.140	.110		.133	12.1	
.140	.125	.133		.133	3.8	.146 (P)
.150*	.130*	.120*		.133*	8.9	
.130	.130	.130		.130	0	
.115	.110	.119		.115	2.6	
.105	.110	.105		.108	1.8	
.090	.080	.070		.080	8.8	
.085	.083	.080	.080	.082	2.4	
.075	.070	.070	.064	.070	4.3	
.073	.068	.060		.067	7.5	
	.063	.060	.053	.058	6.9	
	.050	.052	.052	.051	2.0	
		.040	.046 r_{17}= .042	.043	7.0	
		.030	.030 r_{17}= .030	.030	0.0	

---

* refers to oleic acid-chloroform system.

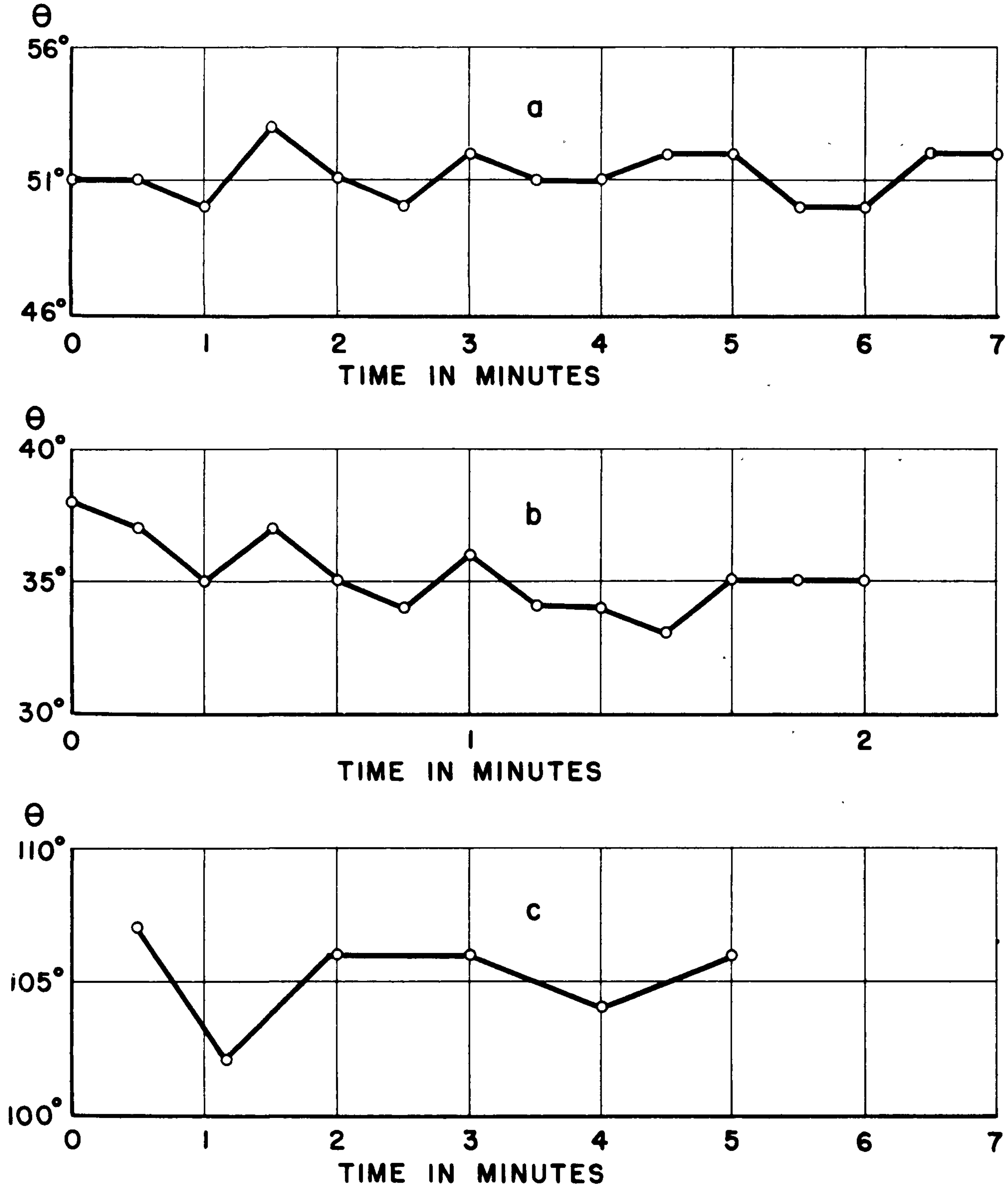

θ
56°
51°
46°
a
0
1
2
3
4
5
6
7
TIME IN MINUTES
θ
40°
35°
30°
b
0
1
2
TIME IN MINUTES
θ
110°
105°
100°
c
0
1
2
3
4
5
6
7
TIME IN MINUTES

Fig. 4.1

NYO-512

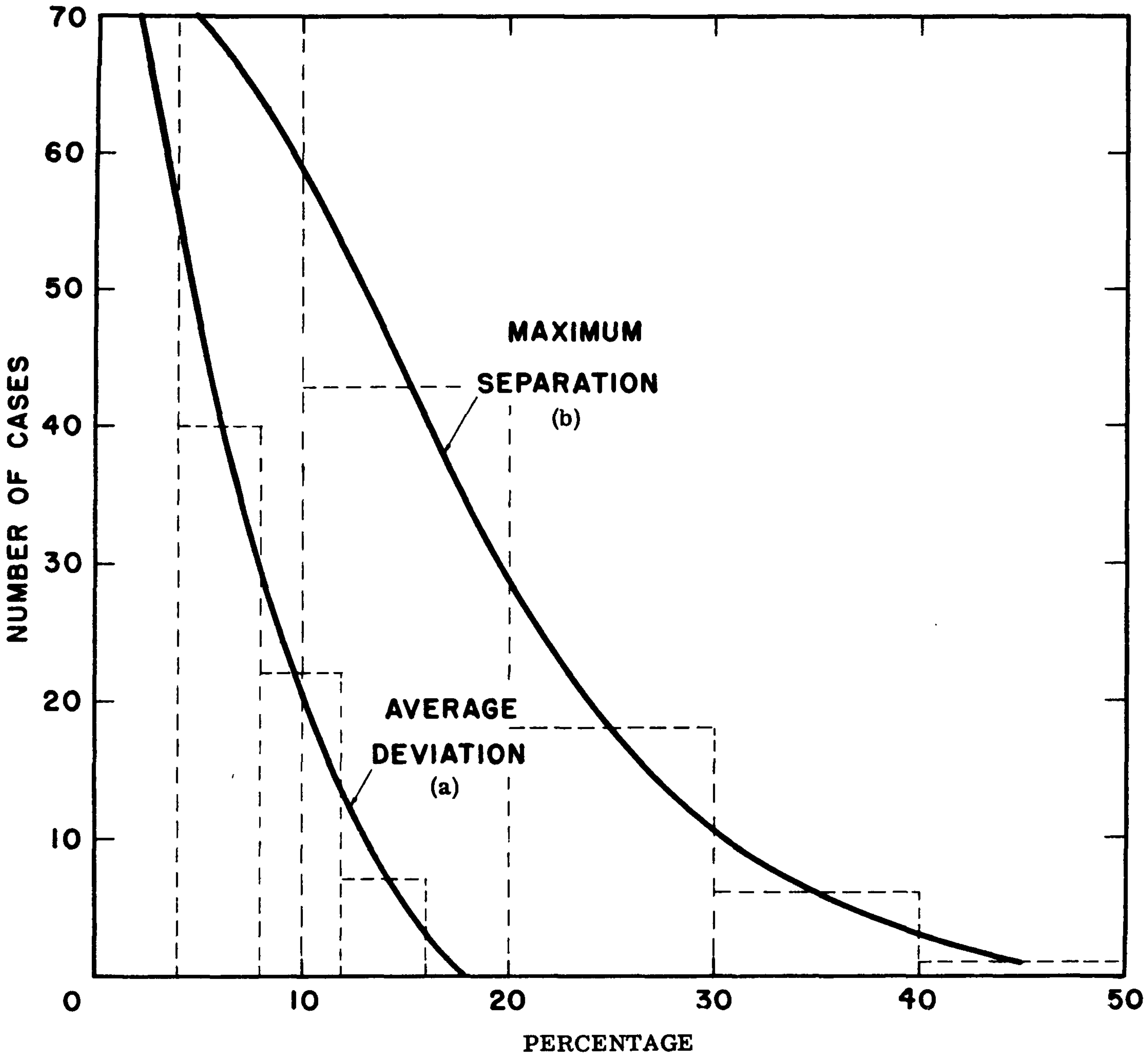


Fig. 4.2

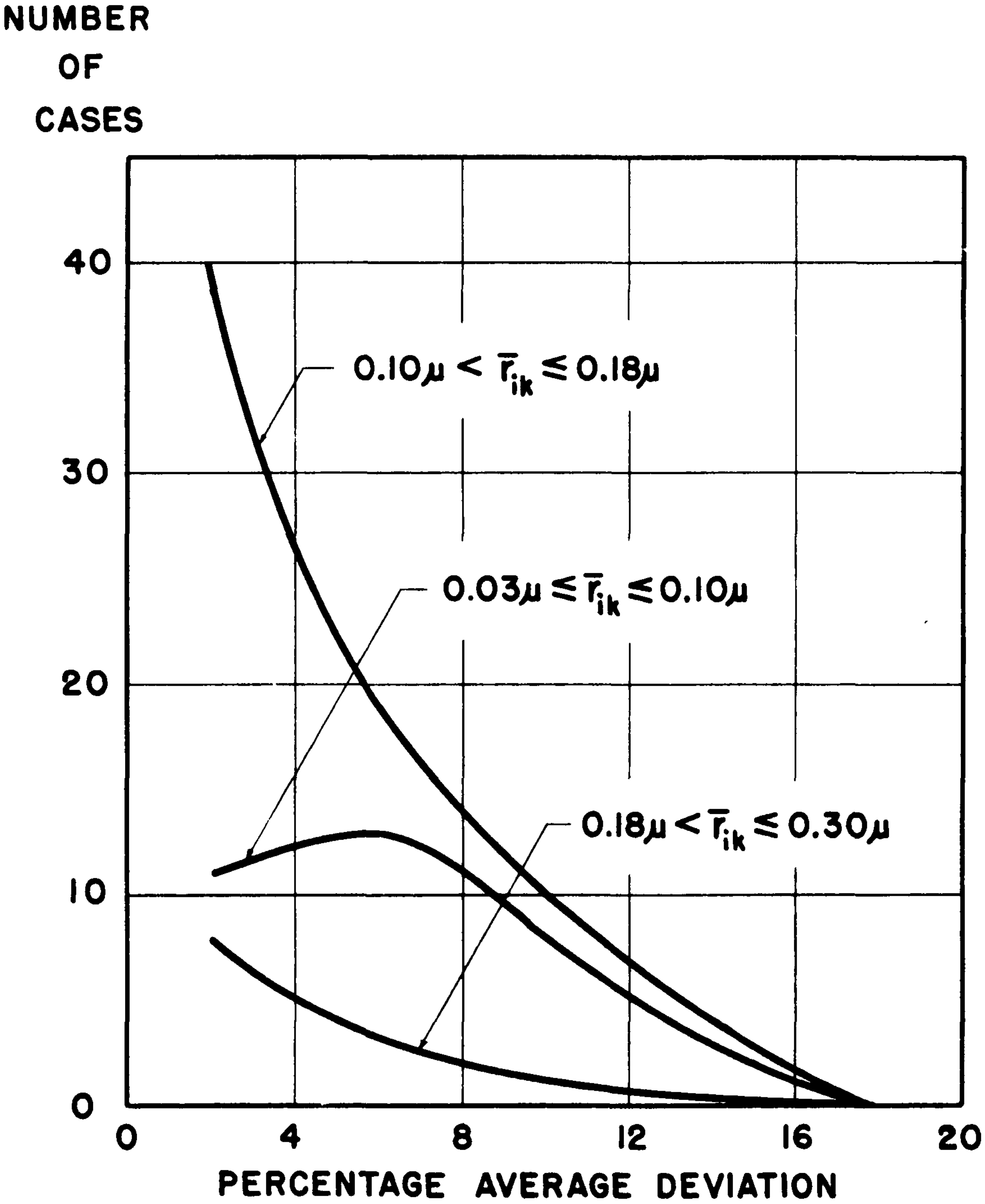

NUMBER OF CASES
40
30
20
10
0
0
4
8
12
16
20
PERCENTAGE AVERAGE DEVIATION
$0.10\mu < \bar{r}_{ik} \leq 0.18\mu$
$0.03\mu \leq \bar{r}_{ik} \leq 0.10\mu$
$0.18\mu < \bar{r}_{ik} \leq 0.30\mu$

Fig. 4.3

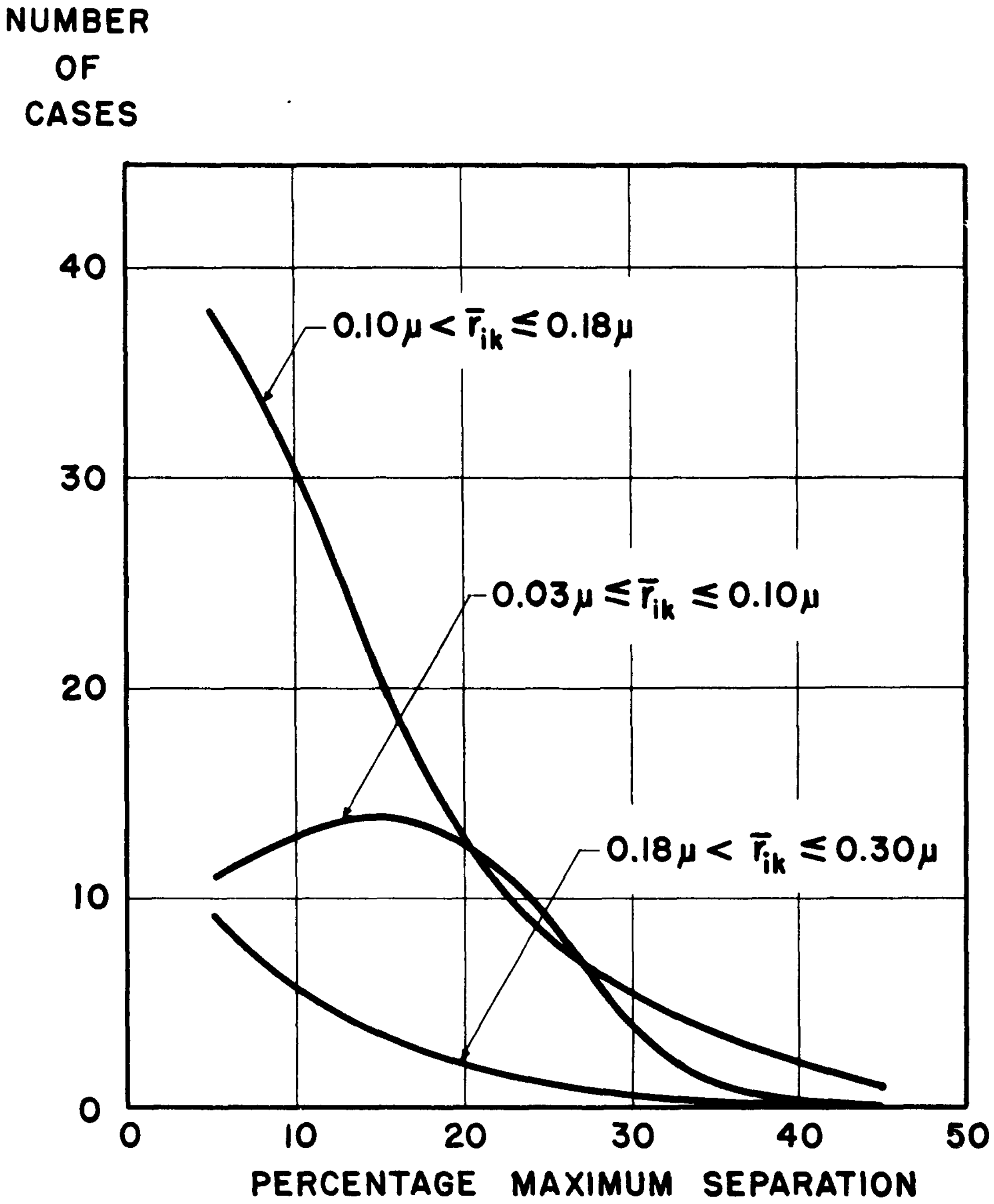

NUMBER OF CASES
0
10
20
30
40
0
10
20
30
40
50
PERCENTAGE MAXIMUM SEPARATION
$0.10\mu < \bar{r}_{ik} \leq 0.18\mu$
$0.03\mu \leq \bar{r}_{ik} \leq 0.10\mu$
$0.18\mu < \bar{r}_{ik} \leq 0.30\mu$

Fig. 4.4

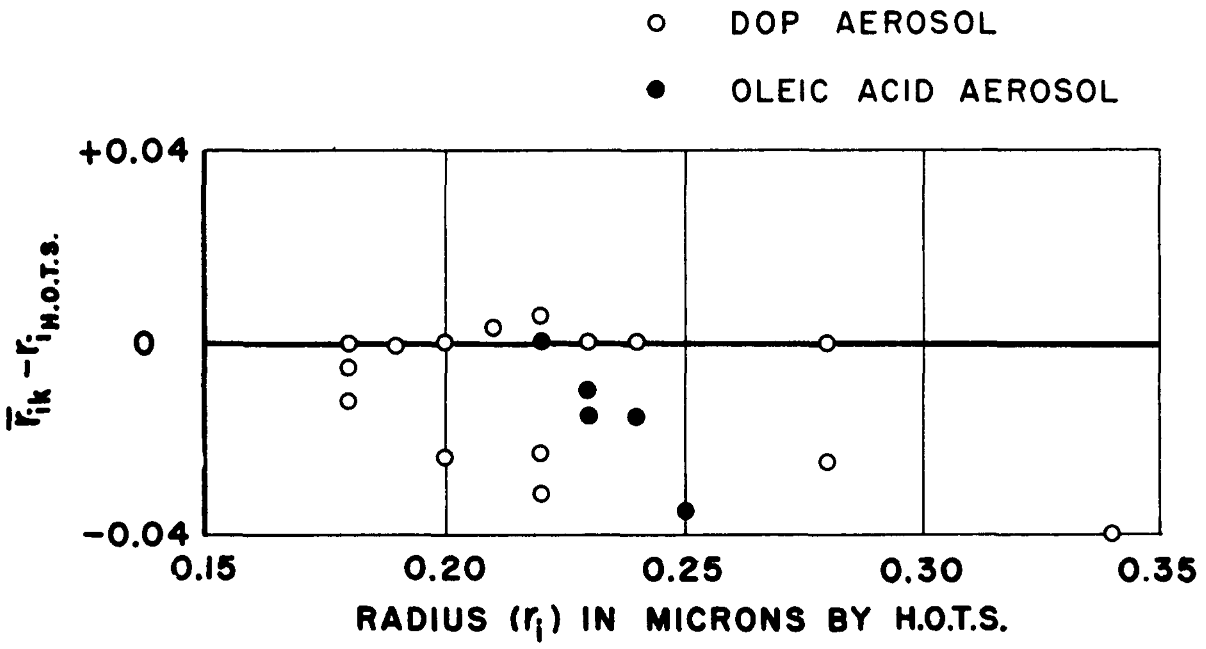

○ DOP AEROSOL
● OLEIC ACID AEROSOL
+0.04
0
−0.04
$\bar{r}_{ik} - r_{i_{H.O.T.S.}}$
0.15
0.20
0.25
0.30
0.35
RADIUS (r_i) IN MICRONS BY H.O.T.S.

Fig. 4.5

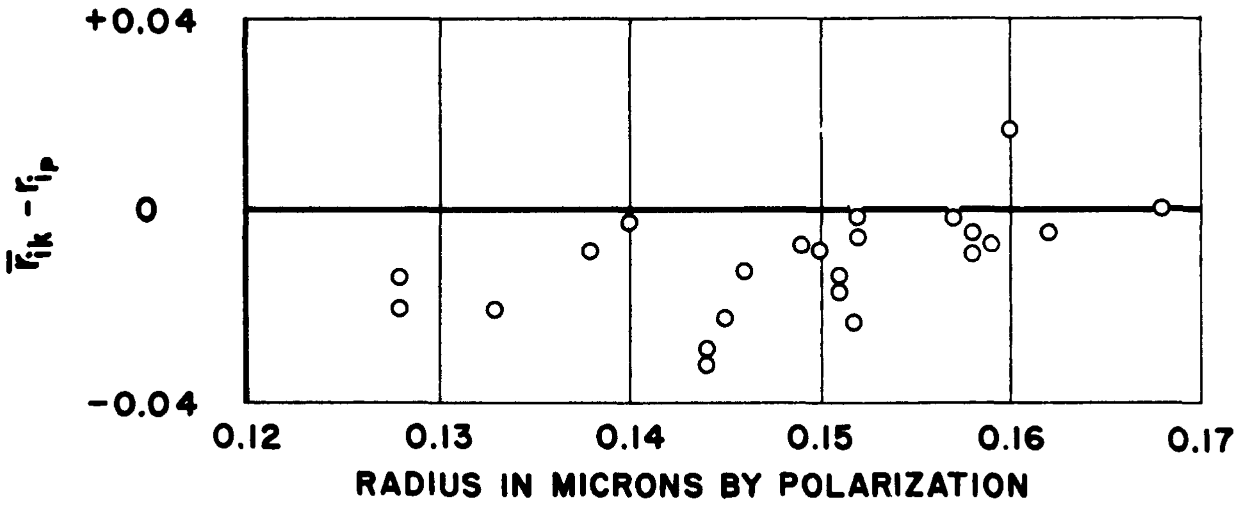

+0.04
0
−0.04
$\bar{r}_{ik} - r_{i_p}$
0.12
0.13
0.14
0.15
0.16
0.17
RADIUS IN MICRONS BY POLARIZATION

Fig. 4.6

APPENDIX A

Correction to Growth Factor Arising from Curvature of Small Droplets

Kelvin Effect

by

Victor K. La Mer and Ruth Gruen

Whenever equilibrium is established between an aerosol droplet and its master solution, the vapor pressures of the volatile component of the droplet and of the master solution must always be exactly equal; otherwise, the droplet will continue to grow (or contract) until this condition is met.

Since p_2, the vapor pressure of the solute, is negligible in the case of DOP ($p_2^\circ \cong 10^{-7}$ mm Hg) as compared to that of the volatile component Toluene ($p_1^\circ \sim 30$ mm Hg at room temperature), the total vapor pressure of the droplet $p_{(r)}$ is sensibly that of the volatile component $p_{1(r)}$.

In the main report, we have also assumed that the composition of the grown droplet and the master solution are identical at equilibrium. This assumption, while very convenient and satisfactory for a first approximation calculation, is no longer valid when the droplets become small enough that the increase in vapor pressure arising from the curvature of the droplet as compared to that of the flat surface of the master solution can no longer be ignored. It is the purpose of Appendix A to investigate the magnitude of this effect.

For a one component system, W. Thomson (Lord Kelvin) (1871 - not 1881 as referenced by Freundlich, G. W. Lewis and others - this mistake of a decade is significant as Willard Gibbs offered a superior derivation in 1876-79), developed the following equation for the relative increase of vapor pressure arising from curvature (1/r) as

$$p_r/p_\infty = \exp \frac{2\gamma V}{RT} \cdot \frac{1}{r} = \exp(y/r) \qquad (1)$$

Here p_r is the vapor pressure of the droplet of radius r; p_∞ the vapor pressure of the flat surface of infinite radius of curvature; γ is the surface tension and V the molecular volume of the pure liquid.

Although this equation forms the fundamental basis of much of colloid science and in particular, is involved in the rate equations of the Volmer-Becker-Doering theories of aerosol formation, it has never been verified by direct experimental tests.

Bikerman[1] states "The pressure differences predicted by W. Thomson's theory are so small that a direct experimental confirmation has not yet been carried out in a convincing manner."

The direct proofs attempted by Shereshevsky[2] and by Woodland and Mack[3] yielded results which deviated considerably from the theoretical predictions and are not considered valid tests by their authors.

Indirect tests have been made by Lyakilov[4] and by K.V. Chmutov[5].

The general acceptance which Eq. (1) enjoys really rests on the cogency of the Gibbs-Poynting thermodynamic derivation[6], and the success of further theories based upon it.

As a by-product of the present development, it will appear later that we have obtained for the first time a direct quantitative confirmation of Eq. (1).

No one appears to have extended Eq. (1) to a binary system composed of two volatile liquids, but in the present case of interest where one of the components is sensibly non-volatile, it is obvious from the derivation just cited, that V in Eq. (1) should be replaced by the partial molal volume of the volatile component in the liquid state and that γ is the surface tension of the mixture.

In Table I, we give some preliminary measurements by Miss Joan Kruger of the surface tensions of DOP-Toluene mixtures using the capillary rise method. Apparently, γ is practically independent of the DOP-Toluene composition and equal to about 27.5 dynes/cm.

---

1. J.J. Bikerman, SURFACE CHEMISTRY, Academic Press, 1947, (p. 581).
2. J.L. Shereshevsky, J. Am. Chem. Soc. <u>50</u>, 2966, 2980 (1928).
3. D. Woodland and Ed. Mack, ibid. <u>55</u>, 3149 (1933).
4. K.S. Lyalikov, Acta. Physicochem. U.R.S.S. <u>12</u>, 48 (1940).
5. K.V. Chmutov, Kolloid Thur. <u>11</u>, 44 (1949); c.a. <u>43</u>, 6882.
6. E.A. Guggenheim, THERMODYNAMICS, AN ADVANCED TREATMENT FOR CHEMISTS AND PHYSICISTS, Interscience (1949), p. 44-5, p. 166.

<u>Footnote</u>: No one appears to have extended Eq. (1) etc. except for a brief statement by Volmer - Kinetik der Phasenbildung, p. 89.

Table I

Mole fraction DOP	Density	h(cm)	γ (dynes/cm)
1	0.980	2.2 ± .05	26.4
.04	.880	2.55	27.5
.01	.870	2.62	28.0
.004	.868	2.6	27.7
0	.866	2.6	27.6

No appreciable error should be introduced if we set the partial molal volume of toluene as equal to its molal volume in the present system. Accordingly, $y = 2\gamma V/RT = 2.42 \cdot 10^{-7}$, a value considerably greater than that for water; namely, $y = 1.05 \cdot 10^{-7}$. A plot of p_r/p_∞ as a function of r for the liquids of interest in this research are plotted in Fig. 47.

The calculation of the effect of curvature upon the composition of the droplet in equilibrium with the flat surface follows:

At equilibrium,

$$p_{rg} \equiv p_{1(\text{droplet})} = p_{1(\text{master})} = \alpha_1 N_1 p_1^\circ \qquad (2)$$

Here N_1 is the mol fraction of the volatile component (1) in the master solution and α_1 is the rational activity coefficient correcting for all deviations from Raoult's Law. The effect of curvature is to produce an increase in vapor pressure of the volatile component equal to $(p_r - p_\infty)$, so that mol fraction of this component in the droplet must be reduced from N_1, its value in the master solution, to an actual lower value N_1' in order to conserve equilibrium.

Thus for the grown droplet designated by the subscript g

$$p_{rg} = \alpha_1' N_1' p_1^\circ + (p_{rg} - p_{\infty g}), \qquad (3)$$

where $p_{\infty g}$ is the vapor pressure of a flat surface whose composition is equal to the composition of the droplet. The primes refer to values corrected for curvature.

Solving Eq. (2) and (3) for p_{rg} and $p_{\infty g}$ respectively and substituting in (1), we obtain

$$N_1 / N_1' = \exp (y/r_g) \qquad (4)$$

when we recognize that the ratio α'/α is almost exactly unity for these small differences in composition regardless of the character of the solution.

For the system DOP-toluene

$$\mathrm{Exp}\ (y/r_g) = \mathrm{Exp}\ \left(\frac{.00242}{r_g} \right) \qquad (5)$$

when r_g is expressed in microns.

When $r_g = .05$ microns, $y/r_g = 0.048$ or 4.8%; hence, Exp (γ/r_g) can be replaced by $1 + y/r_g$ without significant error, yielding the working equation

$$y/r_g = N_1 / N_1' - 1 . \qquad (6)$$

To express k', the actual radius growth factor in terms of the corrected mol fractions, we proceed as follows:

$$k' \equiv (r_g/r_1') = \left(\frac{v_1' + v_2}{v_2} \right)^{1/3} \qquad (7)$$

$$N_2' \equiv \frac{n_2}{n_1' + n_2} = \frac{v_2}{v_2 + \dfrac{V_2^\circ\ v_1'}{V_1^\circ}} , \qquad (8)$$

where v_1', n_1' are the volume and the number of molecules of toluene, respectively, in the droplet. v_2, n_2 are the volume and the number of molecules of DOP, respectively, in the droplet.

Combining (7) and (8) we get

$$k' \equiv r_g / r_1' = \left(1 + \frac{V_1^\circ}{V_2^\circ} \quad \frac{N_1'}{N_2'} \right)^{1/3} \qquad (9)$$

and similarly

$$k = \left(1 + \frac{V_1^\circ}{V_2^\circ} \quad \frac{N_1}{N_2} \right)^{1/3} \qquad (10)$$

For Toluene: V_1° = 106.84 cc.

DOP: V_1° = 398.40 cc.

Table II gives a set of values for the mol fraction of toluene (N_1) for various growth factors.

Table II

k	2	3	4	5	6	8	10
N_1	0.9631	.9902	.9958	.9978	.9988	.9995	.99973

Table III contains values of (y/r_g) for r_g the observed radius of the grown droplet in microns.

Table III

r_g	0.06	.08	.10	.16	.20	.30	.40	.60
y/r_g	0.040	.030	.024	.015	.012	.008	.006	.004

In Table IV are given some typical calculations for growth factors of 2 and 10 respectively. The last column gives $100(r'_{1k} - r_{1k})/r_{1k}$, or the percentage correction to r_{1k}, the radius of the initial droplet calculated from $r_{1k} = \frac{r_g}{k}$, arising from the effect of curvature. It is apparent that the correction is of considerable magnitude for large growth factors and cannot be neglected even for $k = 2$ at the smaller sizes.

Table IV for $k = 2$

r_g	N_1'	k'	$\frac{(r'_{1k} - r_{1k})}{r_{1k}} \cdot 100$
0.10	.940	1.73	15.6
.20	.951	1.84	8.7
.40	.957	1.91	4.7
.60	.959	1.94	3.1

for $k = 10$

r_g	N_1'	k'	$\frac{(r'_{1k} - r_{1k})}{r_{1k}} \cdot 100$
.20	.988	2.85	251.
.30	.992	3.25	208.
.40	.994	3.57	180.
.50	.995	3.79	164.
.60	.996	4.08	145.
.70	.997	4.32	132.

Table V

System DOP-Toluene. Values of k', the actual radius growth factor corrected for Kelvin effect to be employed in calculating initial radii (in microns) for various values of the final measured radius r_g when equilibrated against master solutions yielding a calculated growth factor k valid asymptotically for sufficiently large droplets.

r_g	$k/2$	3	4	5	7	10
0.08	1.67	1.95				
.16	1.81	2.25	2.46			
.20	1.84	2.35	2.60	2.71	2.77	2.85
.30	1.88	2.50	2.85	3.02	3.13	3.25
.40	1.91	2.59	3.02	3.25	3.39	3.57
.50	1.92	2.65	3.13	3.39	3.57	3.79
.60	1.94	2.71	3.25	3.57	3.79	4.08
.70	1.95	2.77	3.40	3.79	4.08	4.32

The results for Table V are plotted in Figure 4.8.

In Table VI are given the results of two sets of experiments. In column 1, r_{gk} is the radius of aerosols grown over master solutions of the growth factor k of column 2, measured by light scattering methods. The calculated initial radii r_{ik} of column 3 show a progressive decrease with increasing values of k. On the other hand, the values of r_{ik} of column 5, the initial radii calculated by using k' (column 4), the growth factor corrected for Kelvin effect is remarkably constant and well within the limit of experimental error of the measured values of r_g.

The correct initial radii of the aerosols are therefore 0.099 and 0.161 microns respectively. The data are plotted in Fig. 4.9.

Table VI

Aerosol No. 1

r_{gk} (observed)	k	r_{ik} (calc.)	k'	r'_{ik} (corrected)
0.18	2	0.090	1.81	.099
.24	3	.080	2.42	.099
.28	4	.070	2.80	.100

Aerosol No. 2

r_{gk} (observed)	k	r_{ik} (calc.)	k'	r'_{ik} (corrected)
0.30	2	0.150	1.88	.160
.42	3	.140	2.59	.162
.52	4	.130	3.17	.164
.55	5	.110	3.50	.157

Although we have presented these data to illustrate (a) how a reliable value of the radius of a given aerosol can be computed by averaging the results obtained when this aerosol is grown simultaneously over master solutions of different compositions (growth factors) and, (b) the constancy of the results when corrected for curvature of the final grown droplets, it would be equally logical to reverse the procedure. In other words, assume the validity of the growth method since it depends only upon the well-established principle that at equilibrium the partial pressures of the droplet and master solution must be equal and to consider that bringing the decreasing values of r_{ik} with increasing k to a constant value r'_{ik} by employing the Kelvin correction as shown in Table VI and Fig. 4.9, is a direct experimental verification of Kelvin's equation.

A statistical analysis of all of the 115 growth experiments which were of varying degrees of precision of measurement, shows that in 57 of the 115 experiments, introduction of the Kelvin correction improved the constancy of r_{1k} as compared to r_{1k}, by reducing the corresponding a.d. values by a factor of two and often considerably more. In some cases, the a.d. of r'_{1k} was greater than that of r_{1k} values. However, we believe these results should be disregarded as the experiments were made at a time when the technique of measurement had not been adequately developed. The data in Table VI were especially planned for the purpose and merit the most weight.

The previous attempts to confirm the Kelvin equation have foundered on the difficult problem of measuring the minute variation in vapor pressure with radius. The present approach circumvents this difficult experimental task by making the significant experimental measurement one of measuring the radii of the grown droplets by the newer optical methods - a much easier task since equilibrium is relatively easy to achieve.

We believe these data furnish for the first time a convincing experimental test of the validity of Kelvin's equation.

The method merits further investigation particularly with solvents of large molecular volumes ($V > 200$ cc), and if possible larger surface tensions, whereby the magnitude of the correction is increased over the customary small values encountered with water ($V = 18$). If possible, the method should be extended to still smaller radii to investigate the moot question of the constancy of the surface tension with decreasing radius. See discussion by V.K. La Mer and G.M. Pound, J. Chem. Phys. 17, 1337 (1949) and F.P. Buff and J.G. Kirkwood, ibid. 18, 991 (1950).

A second objective for further investigation would be to ascertain the effect of impurities by surface film action in reducing the rate of attainment of equilibrium in the growth process. In particular, how rapidly does a grown aerosol whose droplet surfaces have been contaminated by an added impurity, decrease in size when transferred to a master solution of lower k value.

Finally, it should be emphasized that the agreement with Kelvin equation which we now present rests upon starting with a monodisperse aerosol. If the ungrown aerosol is polydisperse, the differential growth resulting from the Kelvin effect will indirectly tend to increase the polydispersity and thereby render measurement of the radius of the grown particle ambiguous.

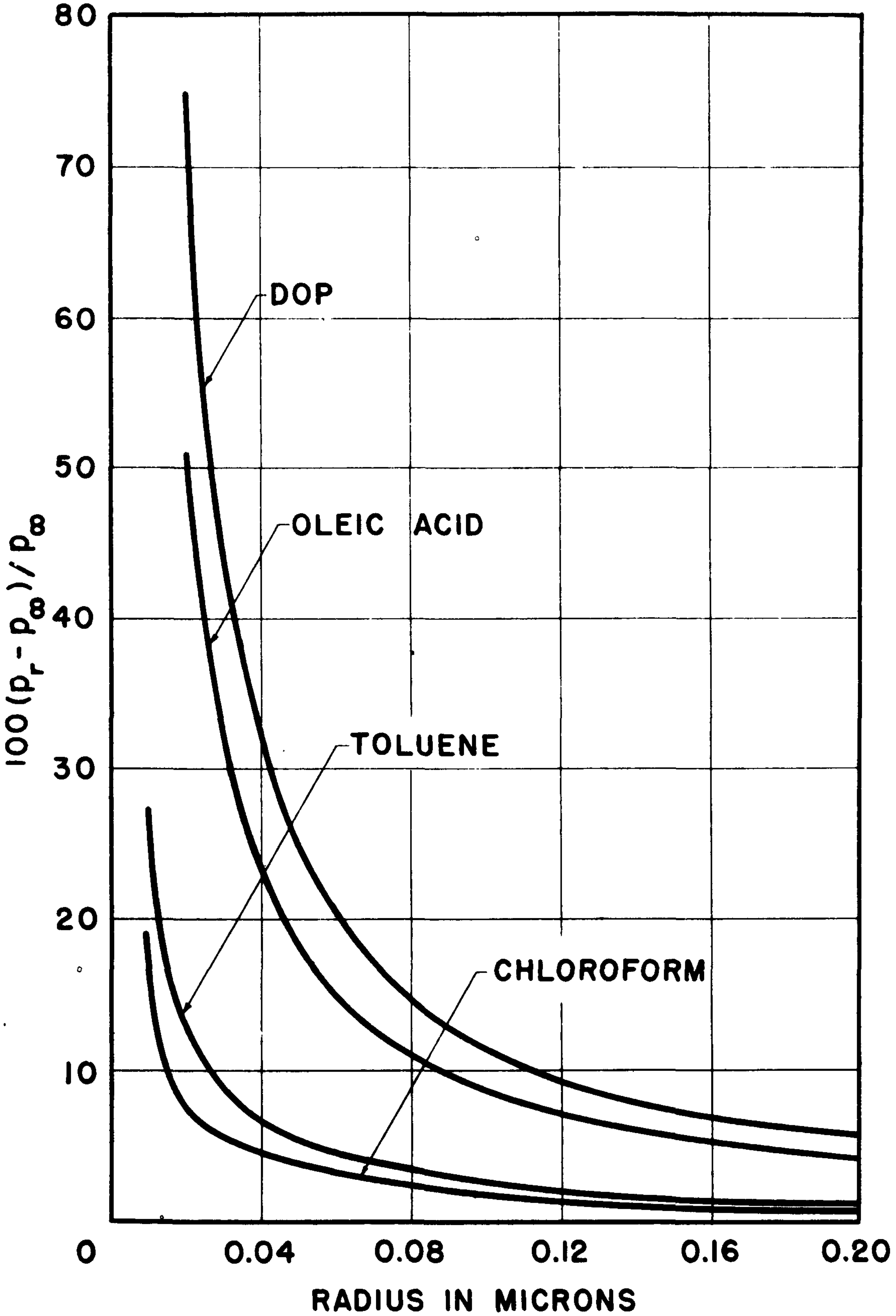

80
70
60
50
40
30
20
10
0
0.04
0.08
0.12
0.16
0.20
$100(p_r - p_\infty)/p_\infty$
RADIUS IN MICRONS
DOP
OLEIC ACID
TOLUENE
CHLOROFORM

Fig. 4.7

42-A

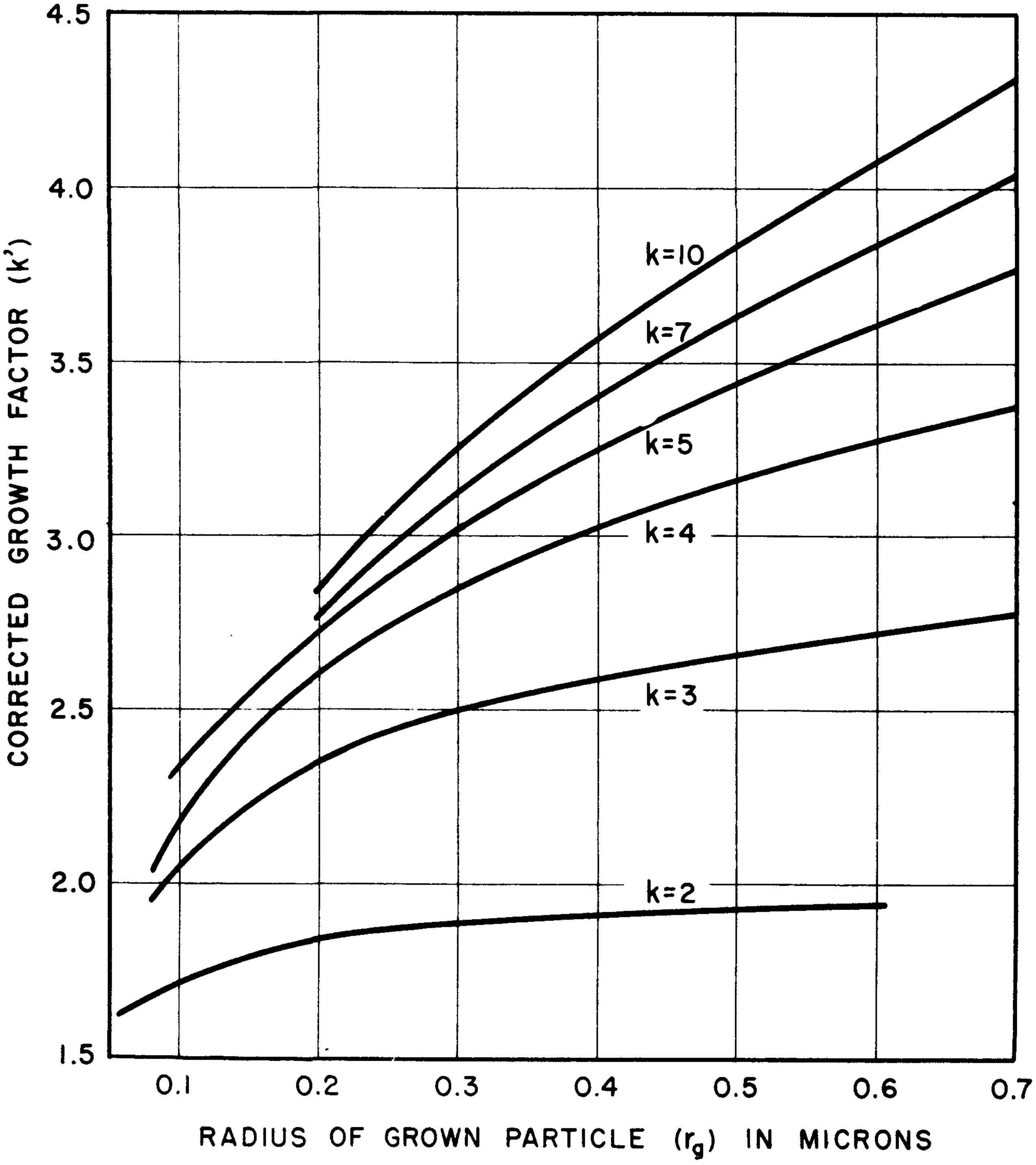

4.5
4.0
3.5
3.0
2.5
2.0
1.5
CORRECTED GROWTH FACTOR (k')
k=10
k=7
k=5
k=4
k=3
k=2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
RADIUS OF GROWN PARTICLE (r_g) IN MICRONS

Fig. 4.8

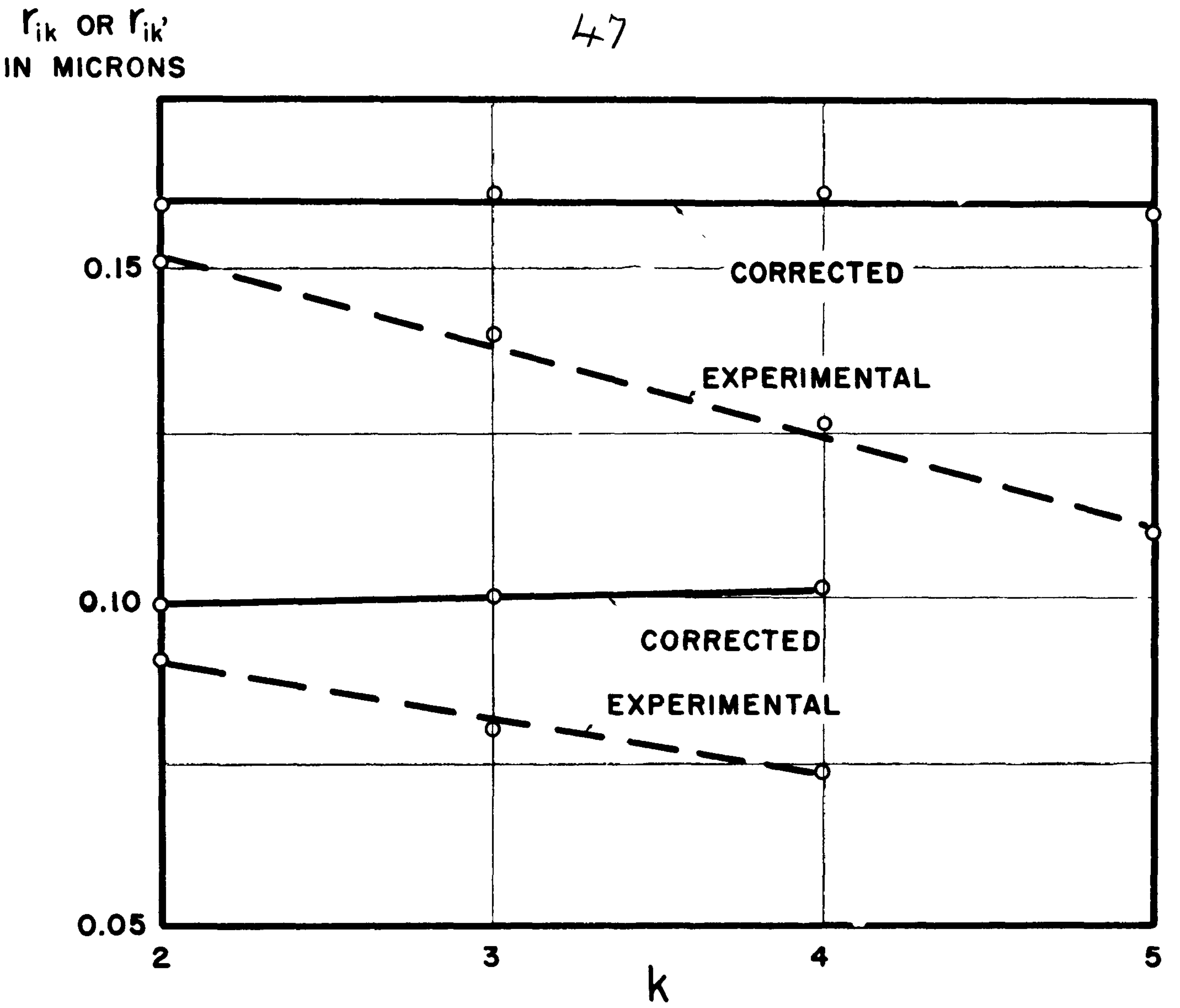

r_{ik} OR $r_{ik'}$
IN MICRONS
0.15
0.10
0.05
2
3
4
5
k
CORRECTED
EXPERIMENTAL
CORRECTED
EXPERIMENTAL

Fig. 4.9

APPENDIX B

Liquid Diffusion as a Possible Cause for Time Lag in the Growth of DOP-Toluene Droplets

by

Howard Reiss.

I. Introduction

This report contains a mathematical investigation of the possibility that the growth of DOP droplets in an atmosphere of Toluene vapor can be delayed because the diffusion of DOP molecules to the surface of the growing droplet is a time consuming process. The term "delay" implies a temporal period of at least several minutes, so that if it can be shown that the drop grows to completion in a fraction of a second, even when the growth is diffusion controlled, it will not be possible to blame a time lag on liquid diffusion.

In this report this fact will be demonstrated, and consequently no time delay can be ascribed to the liquid diffusion process.

II. Mathematics

At first, the problem of calculating the growth rate of DOP drops in Toluene vapor seems difficult, because of the need to take Raoult's law into account, the need for the simultaneous solution of connected liquid and gaseous diffusion problems, and, finally, the complications arising from the existence of a moving boundary. However, all of these difficulties can be removed.

Consider Figure 1. The growing drop receives material essentially from the control mixture of DOP and toluene. The transfer of material takes place through the medium of the vapor phase. However, the process of vapor diffusion occurs on the average, 100,000 times as rapidly as the liquid diffusion process. As a result, the adjustment in the vapor phase occurs instantaneously, relative to a variation in the liquid phase. For all practical purposes, the situation is identical with that in which the DOP drop is actually immersed in the control mixture (see Figure 2). The toluene from the mixture can therefore be considered to diffuse by means of a liquid-liquid process into the drop. The need for considering a gaseous diffusion process has therefore been obviated, and with it the need for taking Raoult's law into account.

If the distance from the center of the drop, immersed in the control mixture, is denoted by r, and the time by t, then c(r,t), the concentration of DOP, plotted versus r for various values of t, will resemble the curves of Figure 3. At the zero of time the curve will be discontinuous, corresponding to a droplet of pure DOP of initial radius, x, immersed in a 1/9 th by volume mixture of DOP in Toluene. As time passes the curves for t_1, t_2, t_3, t_4 and t_5

45

will result, the boundary of the drop being defined by the values of x_1, x_2, x_3, x_4 and x_5, corresponding to the points at which the concentration of DOP is reduced, effectively, to zero;(i.e., to that of the master solution,V.K.L.). In this way the moving boundary can be handled, i.e. it is merely necessary to follow the points x_1, x_2, x_3, etc. to follow the growth of the drop.

If the curve corresponding to t_5 where the distance, h, is a very small fraction of the 8/9 ths DOP concentration, available as the initial diffusional driving force, occurs for t_5 very small, the growth process is completed in a very small period of time. In fact, it is virtually complete at t_5.

In order to evaluate c(r,t), the following boundary value problem must be solved.

$$\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r} = \frac{1}{D}\frac{\partial c}{\partial t}$$

$$c(r,o) = \begin{cases} C_{DOP} & \text{for } o \leqslant r < x \\ 1/9\, C_{DOP} & \text{for } x < r \leqslant \infty \end{cases} \qquad (1)$$

Here, D is the coefficient of diffusion, C_{DOP} is the concentration of DOP molecules in pure DOP at room temperature. We will assume that the control mixture is 1/9 DOP by volume. The solution of this problem is

$$c = 1/9\, C_{DOP} + 8/9\, C_{DOP} \left[\sqrt{\frac{Dt}{\pi}} \left(\frac{e^{-\frac{(r+x)^2}{4Dt}} - e^{-\frac{(r-x)^2}{4Dt}}}{r} \right) + \int_{\frac{r-x}{\sqrt{2Dt}}}^{\frac{r+x}{\sqrt{2Dt}}} \frac{1}{\sqrt{2\pi}}\, e^{-v^2}\, dv \right] \qquad (2)$$

The integral on the right can be evaluated using a table of probability functions (see Lange's handbook, 4th edition). This solution assumes the validity of Fick's law. Obviously this law does not hold accurately for the system in question, but as long as an order of magnitude only is required, equation (2) will be very useful.

Assuming:

$D = 5 \times 10^{-6}$ cm^2/sec.
(almost certainly a lower limit, and not more than 2×10^{-6} cm^2/sec.

$t = 0.01$ sec.

$C_{DOP} = 1.51 \times 10^{21}$ molecules/cc.

$x = 2 \times 10^{-5}$ cm.

c(r,t) was computed. This plot is too flat for convenient graphing. The values for c(r,.01) at different values of r are given in Table 1.

Table 1

r	c(r,.01)
0	$1/9\ C_{DOP} + 8/9\ C_{DOP}(1.7 \times 10^{-4})$
$.2 \times 10^{-5}$ cm	"
.4 "	"
.6 "	$1/9\ C_{DOP} + 8/9\ C_{DOP}(1.6 \times 10^{-4})$
.8 "	"
1.0 "	"
1.2 "	"

It is seen that the h of Figure 3 is in this case 1.7×10^{-4} of $8/9\ C_{DOP}$, the available driving gradient, at a value of time so small as .01 sec. In other words, the growth is complete in less than .01 sec.; for all practical purposes, it is probably over in a much smaller time than this.

Any error introduced by a possible 50% error in the value of D, or by assuming the validity of Fick's law, cannot possibly change the meaning of this result. No time lag can be associated with the liquid diffusion process.

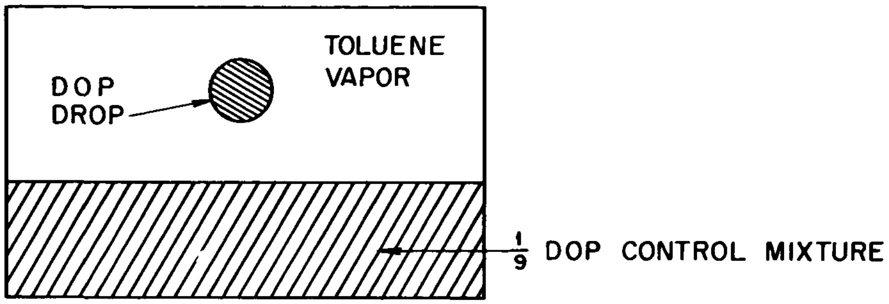


FIGURE 1

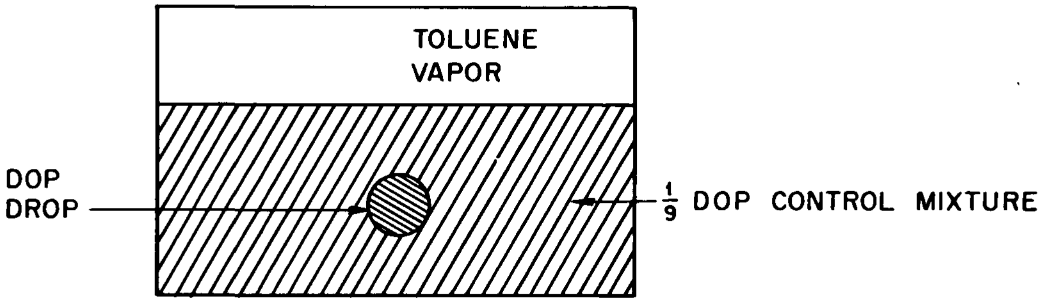


FIGURE 2

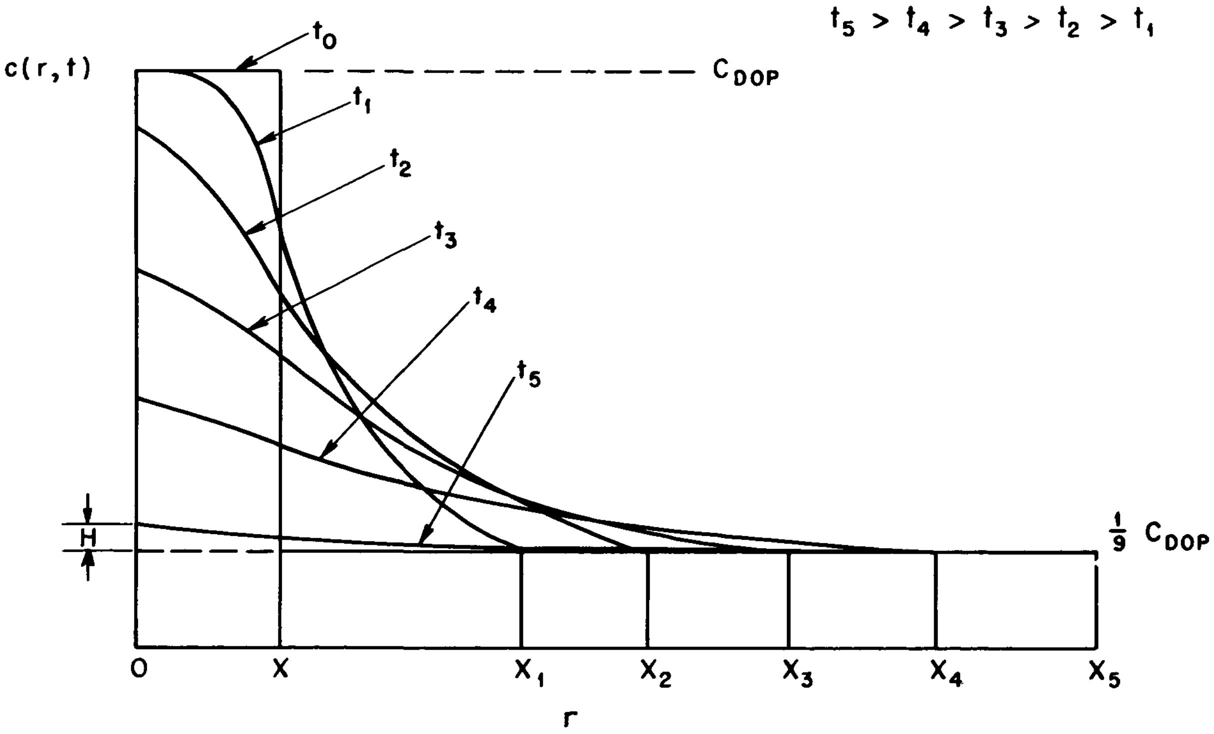


FIGURE 3

FILTRATION OF FINE MONODISPERSE AEROSOLS

by

Ruth Gruen, Guy Goyer and Mary L. Young

Experimental Details

In this investigation, the following types of various filters were considered: Chemical Corps No. 5 (CC-5), Whatman No. 2 (W-2), α-web carbon-impregnated paper, glass ("Gl"), a hand-made glass filter, a rayon type, and A.E.C. No. 1 (otherwise known as "Roll 13"). The majority of experiments were performed with the reproducible CC-5 filter since aerosols filtered through this paper offer a penetration percentage in all cases in a range convenient for optical examination. The behavior of other filters was compared to this as a standard. The performance of these filters was checked with three different aerosols; namely, dioctyl phthalate (DOP), oleic acid and solid stearic acid.

1. General Remarks Regarding the Aerosols Under Consideration.

a. Preparation

The aerosols were prepared in the usual manner in the LaMer-Sinclair generator (1). The boiler and reheater temperatures, the current through the nuclei-producing coil, and the rate of air flow are adjusted to values appropriate for the desired size and concentration of the aerosol particles to be studied. In order to obtain constant operating conditions during the filtration measurements, it is essential to allow the boiler and reheater to reach their final temperatures gradually over a period of a few hours. The use of a thermoregulator enables a boiler temperature with a ± 0.2°C variation to be maintained. A flow rate of 2 liters per minute, of which one liter/minute is applied to the nuclei source, was utilized.

For the majority of measurements, a current of 3.0 amps. through the sodium chloride-coated wire coil was used for the production of nuclei. With D.O.P. as aerosol, it is necessary to apply a current of 2.90 or 2.95 amps. to produce particles of radii greater than 0.3 microns. This is an experimental value and must be determined for each individual nuclei source and may change with the age of the coil.

---

1. La Mer, V.K. and Sinclair, D. Chem. Rev. 44, 245 (1949).

A variation of linear velocity of the aerosol was made by changing the area of the filter. For this purpose four filter holders of areas 1.19, 2.56, 7.05 and 13.00 cm^2 (later replaced by a holder of 13.25 cm^2 cross-section) were constructed to produce for a flow of 2 liters/min. linear velocities of 28.0, 13.0, 4.7 and 2.6 cm/sec., respectively. For the "G1" filter, an aluminum ring was used in the filter holder to decrease the effective filter area and thereby increase the aerosol linear velocity to 31.2 cm/sec. This procedure is not recommended.

b. Measurement of Particle Radius

Since the methods available for the measurement of the radius of aerosol particles vary in the range of size to which they may be applied, it is necessary to employ three separate types for particles in the 0.03-0.6 micron interval. For a detailed description of each, see(1,2,3)(also Section IV).

---

2. V.K.La Mer, Edward C.Y. Inn, Irwin Wilson, J. Coll. Sci. 5, 471 (1950).

3. I. Johnson and V.K. La Mer, J.Am. Chem. Soc. 69, 1184 (1947).

As a check upon the reliability of the values obtained by these different techniques, the radii of particles in overlapping ranges are obtained by the various methods available. The specific techniques are listed below, together with the range of particle radius in which they are effective:

Growth Method: $0.03 \text{ micron} \leqslant r_1 \leqslant 0.35 \text{ micron}$, where r_1 represents the radius of initial particle

Polarization: $0.12 \text{ micron} < r \leqslant 0.16 \text{ micron}$

Higher Order Tyndall Spectra: $r \geqslant 0.18 \text{ micron}$

The size of the aerosol particles under examination is determined prior to, during and subsequent to a filtration experiment as another check upon the steady conditions of operation. The aerosol particles remained constant in size on passage through the filters.

c. Measurement of Aerosol Particle Concentration

The concentration of particles (no. of particles/cc) in the unfiltered aerosol is measured by the standard transmission technique. (For a thorough discussion of this method see (1)). The concentration used throughout this analysis is of the order of 10^6 particles/cc.

The photographic method, applied to filtered aerosols of

7420 50

very low concentrations, is described in (4).

---

4. P.K. Lee and V.K. La Mer, Progress Report No. 5, Air Force contract AF-19(122)-164, (1951).

---

2. Filtration Analysis.

The remaining part of this discussion concerns itself with the actual filtration measurements and all details related directly thereto.

a. Preparation of Samples for Filtration Measurements

A disc of the diameter of the filter holder is cut from the sample to be examined. This disc is then placed within the holder and the screws of the latter fastened securely to prevent leakage.

No other precautions are necessary in the case of the CC-5 filter since this filter is apparently unaffected by humidity variations. The W-2 paper, however, exhibits poor reproducibility, which may be due to a pinhole effect (See Sections VI and VII of this report). To eliminate a possible variation of behavior with humidity this filter was dried 36 hours at 110°C and 72 hours in a desiccator at room temperature. No noticeable change was found.

b. Measurement of Percentage Penetration

Three methods are used to measure the percentage penetration of an aerosol through a given filter; namely, the 90° Scattering Penetrometer, the Forward Angle Penetrometer (5) and the photographic technique. The first is applied to the majority of experiments where an appreciable concentration of filtered aerosol exists. For the very efficient filters where only a few particles pass through the material, the photographic method offers particular advantages. The application of the Forward Angle Penetrometer to this filtration study is discussed in Section V.c.

The 90° Scattering Penetrometer

A schematic diagram of this apparatus is shown in Fig. 1. The unfiltered aerosol from the generator enters the glass cell, A, from which it is sent through the brass filter holder into the glass cell, B, and then to the exhaust. The cells A and B are identical in construction, each having a volume of 40 cc. The light scattered

---

5. Handbook on Aerosols, Atomic Energy Commission, (1950).

in each chamber from a beam of parallel monochromatic light is observed at right angles to the beam by two 1P21 multiplier phototubes. The circuits involving these tubes are shown in Fig. 2. In this way, it is possible to compare the light scattered by filtered and unfiltered aerosols and thereby obtain a measure of the concentration of each in their respective chambers. The intensity of scattered light, falling upon the photosensitive surface of each tube is actually measured by the amount of bucking current necessary to balance exactly the photocurrent of the tubes. When this equilibrium has been attained, the milliammeter in the plate circuit of the 6SN7 twin triode tube will register zero. The reading of the potentiometer in this plate circuit is a direct measure of this bucking current.

Throughout this discussion the following symbols will be used:

N_1 = the potentiometer reading for unfiltered aerosol in cell A and dry, dust-free air in cell B;

N_2 = the potentiometer reading for unfiltered aerosol in cell A and filtered aerosol in cell B.

Thus, the percentage penetration of an aerosol through a filter is defined as

$$\frac{N_1 - N_2}{N_1} \times 100.$$

Preliminary to any measurement with this penetrometer, the plate circuits of the phototubes must be balanced for identical light sources to eliminate the effect of tube variations. To achieve this, the circuits are adjusted when the scattered light from the same monochromatic beam in each chamber containing unfiltered aerosol is observed. The sensitivity of tube A is set at a minimum since this tube will receive at all times the light scattered by unfiltered aerosol, whereas the sensitivity of tube B is chosen arbitrarily. As a first step, the multiple switch is set so that both grids of the 6SN7 tube are grounded ("P" position) and the plate current adjusted to zero. This is for zero signal at this twin triode. Next, with a signal on one grid (i.e., with the signal from one phototube applied to the corresponding grid of the triode) and the other grid grounded (setting "A", for example), the plate current of the triode is again brought to zero. This is repeated in reverse for the other phototube (setting "B", for instance). With signals on both grids (i.e., both phototubes connected in the circuit), corresponding to position "N" of the switch, the reading on the milliammeter in the plate circuit of the triode is recorded as the "zero position."

To ascertain whether the sensitivity of the tube B is appropriate, the potentiometer reading is taken for the case of unfiltered aerosol in cell A and dry, dust-free air in cell B. A reading of 100-200 divisions on the potentiometer is desired, a smaller deviation rendering the apparatus insensitive and a larger one leading to unstable operating conditions. The sensitivity of tube B must fall within this working range; if not, it must be readjusted and the circuit rebalanced.

The following procedure is recommended for all cases where the percentage penetration is invariant with time (i.e., for a period of 10 minutes):

1. The zero position is determined by the method outlined above.

2. The reading N_2 is recorded (for filtered aerosol in cell B and unfiltered aerosol in cell A).

3. N_1 is found (for unfiltered aerosol in cell A and dry, dust-free air in cell B, the filter holder being disconnected from the line).

4. The penetration percentage is calculated. This process requires about 30 seconds and is desirable since tube B must adjust itself to a gradual change in light intensity, receiving light first from the unfiltered aerosol, then from the filtered, and finally from air. Several readings of penetration are necessary for a given set of operating conditions and must be repeated when any of the parameters is varied.

When the percentage penetration is time-dependent, a different procedure is advisable. For a given radius of the aerosol under consideration, a plot of the penetration percentage vs. time must be made. The values obtained for several samples of filter paper are averaged for this graph and the curve extrapolated to zero time. These studies are carried out only for the smallest linear velocity of the aerosol as filtration characteristics change more radically with larger linear velocities, with the result that any extrapolation to zero time would be unreliable. This method of investigation is applied to DOP filtered through α-web, C-impregnated paper and stearic acid aerosol through CC-5 filter.

When it is necessary to study the variation of the percentage penetration with time, the following technique is helpful;

1. The zero position is found by the usual method.

2. N_1 is found with the filter holder disconnected from the line.

3. The filter holder is now connected to the line, the air stream being removed and replaced by the unfiltered aerosol which is sent through the filter into chamber B. After 20 sec., during which time the cell is filled uniformly, N_2 is recorded and noted every 30 seconds thereafter for 2 minutes.

4. Steps 1, 2 and 3 are repeated until 10 minutes of filtration have elapsed.

This procedure is repeated for various samples of the same filter paper and the results averaged. The usual studies are made regarding the effect of linear velocity and radius of the aerosol upon the time variation of percentage penetration and a comparison of different aerosols made. It should be noted that the 20-second waiting period offers ample time for the cell to reach equilibrium since a flow rate of 2 liters/minute implies that the cell of volume 40 cc would be filled shortly after 1 second. Observation of the milliammeter scale reveâls that approximately 10 seconds are necessary for the true equilibrium to be reached.

In all filtration experiments it is necessary, for a given filter paper sample, to measure the percentage penetration several times. For the CC-5 paper about three values are sufficient because of its high reproducibility whereas the less reliable W-2 filter often requires about seven measurements before any reasonable conclusions can be drawn. The various values obtained are averaged arithmetically and the result called the "penetration percentage." For doubtful results, the following rejection policy was pursued: the average is calculated without this doubtful value and the deviations of each experimental result found and averaged. The doubtful value is rejected if its deviation from the average is greater than four times the average deviation of all the other values. If the deviation of this questionable penetration percentage from the average is less than four times the average deviation, the average must be recalculated to include this value.

Table I lists the results of a typical experiment using D.O.P. aerosol filtered through CC-5 paper. This illustration emphasizes the number of readings necessary to obtain reliable values of percentage penetration and the use of the rejection criterion for discarding the measurements on filter No. F69-3. Table II gives the results of a similar experiment on DOP aerosol through W-2 paper. It is interesting to note that these readings appear to fall in two distinct groups: one, clustered about 23.0% penetration and the other, about 27%.

Photographic Technique

A photographic method of studying aerosols, involving the use of a forward angle scattering camera, has been developed in this Laboratory by Mr. P.K. Lee (4). This technique assumes particular importance in the case of a highly efficient filter, such as A.E.C. No. 1, "Roll 13", since the intensity of scattered light from the filtered aerosol is below the limit detectable with the 90° Scattering Penetrometer. For this filter only a few aerosol particles escape into cell B.

This approach was applied to the A.E.C. No. 1 and CC-5 filter A series of exposures of the unfiltered and filtered aerosol streams is taken for each paper and the number of particles appearing in each exposure is calculated and averaged. The "penetration percentage" in this technique is defined as 100 times the ratio of the average number of unfiltered aerosol particles. In the case of A.E.C. No. 1, it is necessary to take multiple exposures in order to find any particle at all after filtration This introduces the necessary precaution that no stray particles from previous experiments be present in the chamber.

Table I

Typical Experiment of DOP aerosol Penetration Percentage Using CC-5

	N_1	N_2	$100\,\frac{N_1-N_2}{N_2}$	Average %
F-61	175,170	155, 150	11.5, 11.7	11.6
F-62-2	170, 173, 172	151, 152, 151	11.2, 12.2, 12.2	11.9
F-69*-3				
F-69-4	181, 179	158, 157	12.8, 12.3	12.6
F-69-5**	165, 161, 160.5, 166, 180	147, 140, 140.5, 142, 150	10.9, 13, 12.5, 14.5, 11.7	12.5
F-69-6	163, 152,	143.5, 133	12.0, 12.5	12.2
F-69-7	167.5, 157	146.5, 137	12.6, 12.7	12.6
			Average Penetration % (over all samples)	12.2 ± .3

Flow = 2.1 lit/min.

Nuclei source current = 2.8 amp.

Area = 13 cm^2

Velocity = 2.7 cm/sec.

* F-69-3 rejected as 12.2 - 10.6 = 1.6 > 4 a.d.
4 a.d. = 1.2

** Notice 5 readings were taken for this filter as the penetration percentage varied considerably. All these readings were used for average penetration percentage of this sample as pass the criterion rejection test.

Table II

Experiment of DOP Penetration Percentage Measurements

Using W-2 Filter

(The experiments show two distinct groups of penetration %).

	N_1	N_2	$100\,\frac{N_1-N_2}{N_1}$	Average %
F40-1	217, 230.5 231.5	165, 177.5, 177.5	24, 23, 23.3	23.4
F40-2	222.5, 225, 233, 226	166.5, 166.5 169, 165	25.2, 26.2, 27.5, 27.0	26.5
F40-3	221, 220	161, 160	27.1, 27.3	27.2
F40-4	215, 217	151, 152.5	29.7, 29.7	29.7
F40-4	215, 219.5	157, 159	27, 27.6	27.3
F40-5	219, 217, 211	159.5, 160, 155	27.2, 26.3, 26.5	26.7
F40-6	221, 215	170, 166	23.1, 22.8	23.0
F40-7	218, 210	167.5, 161	22.7, 23.3	23.0
F40-8	217, 215	167.5, 165	22.8, 23.3	23.0

F = 2.11 liters/min.

Lin. velocity = 2.7 cm/sec.

r = 0.14 micron

Notice two groups:	F40-1, 6, 7, 8	lower penetration
	F40-2, 3, 4, 5	higher penetration

These two group effects appear quite often in W-2 penetration measurements.

FORWARD ANGLE TYNDALLOMETER

A few experiments on filtration of aerosols were performed with a Forward Angle Tyndallometer similar to the one designed by La Mer and Sinclair (5), in this laboratory as a check for the penetration measurements obtained by the right angle scattering apparatus. The results show agreement between the two instruments.

Instrumental

A schematic diagram of the apparatus is shown in Fig. 3. The source s is a six-volt headlight bulb whose filament is imaged by the condenser C at the aperture A of the scattering chamber. A black opaque disc, 1-1/4" in diameter, is glued to the lens L_1 of the condenser to block the central rays. The light scattered by the aerosol particles at the point A is focussed onto the photomultiplier tube (1P21) through two 1/4" diameter diaphragms D_1 and D_2. A sheet of diffusing paper P around the phototube permits the use of most of the photosensitive surface. Neutral light filters F of known transmission are also used to reduce the intensity of the scattered light by the unfiltered aerosols.

For an empty cell, filled with dried, dustless air, no stray light is measurable on the microammeter. Stray light was reduced by the use of the twin diaphragms and by the lining of the inside of the apparatus with black velvet.

The detector is a 1P21 RCA photomultiplier tube fed by a bank of dry cell batteries through a circuit similar to that used by Kerker and La Mer (6). However, the dynode resistors have been increased to 100 K to decrease the current drawn through the tube and three 300-volt batteries (Eveready No. 493) are used as a power supply. The output voltage is varied from 600 to 850 volts through a megohm variable resistor, which permits, by the adjustment of the reading for the unfiltered aerosol to 100 on the meter, to read per cent penetrations directly on the meter.

For a given aerosol particle radius, the photocurrents read on the meter are proportional to the concentration of the aerosol in the chamber, provided the loss of intensity of the direct beam due to scattering is negligible. For this latter reason, the inlet and outlet of the aerosol have been placed directly in line to prevent the attenuation of the direct beam. A gentle suction at the outlet keeps the aerosol in a well-defined stream and prevents it from filling the whole chamber.

---

6. M. Kerker and V.K. La Mer, J. Am. Chem. Soc. 72, 3516 (1950).

V. b.

Experimental

A few penetration measurements were carried out with this instrument and the results compared with those obtained by right angle differential scattering as shown in the following table:

Aerosol	Size	Filter Paper	Linear vel. in cm/sec.	% Penetration Right Angle Scattering	% Penetration Forward
Stearic acid	.18	CC-5	2.6	18.8 ± .5	18.2 ± .3
Stearic acid	.18	CC-5	4.7	20.5 .4	18.4 .5
Stearic acid	.18	CC-5	13.1	15.3 2	15.2 1.1.
D.O.P.	.3	alpha-web carbon impregnated	2.6	37	36
Oleic acid	.5	CC-5	1.9	9.8	10.3

Discussion

These data together with those obtained by the photographic method and the Forward Angle Tyndallometer, provide a means of checking the reliability of the right angle scattering apparatus. They show agreement within the limit of experimental precision, and check the values of the penetration measurements reported in this paper.

It must be pointed out that the relative error on the Forward Angle Tyndallometer readings should be greater than on the right angle scattering apparatus due to the fact that the latter uses a differential measuring circuit and the former an absolute intensity measurement. Slight changes in aerosol concentration and size, possibly caused by a variation of the nuclei source current, will show much more in the Tyndallometer.

Very low penetrations cannot be measured with this apparatus due to the too small concentration of the generated aerosol. Only an increase of concentration would make the measurement possible.

The concentration could be increased by increasing the amount of DOP vapor and the number of nuclei. However, it is impossible to increase the boiler temperature higher than 130°C using air as a carrier because of the oxidation of DOP to phthalic anhydride during the process. An inert gas, such as nitrogen or argon, used as the carrier gas would permit the heating of the DOP to a higher temperature as proved possible by H. Griswold (Chicopee Mfg. Corp.). Increasing the evaporation surface of the DOP in the boiler would also permit a greater total vapor output. The particle size range could be kept to the one investigated up to now by increasing the total nuclei output. The effect on the monodispersity of the generated aerosols of such changes in the operating conditions of the generator would still have to be studied. Coagulation and secondary scattering may impair the advantages looked for in this method.

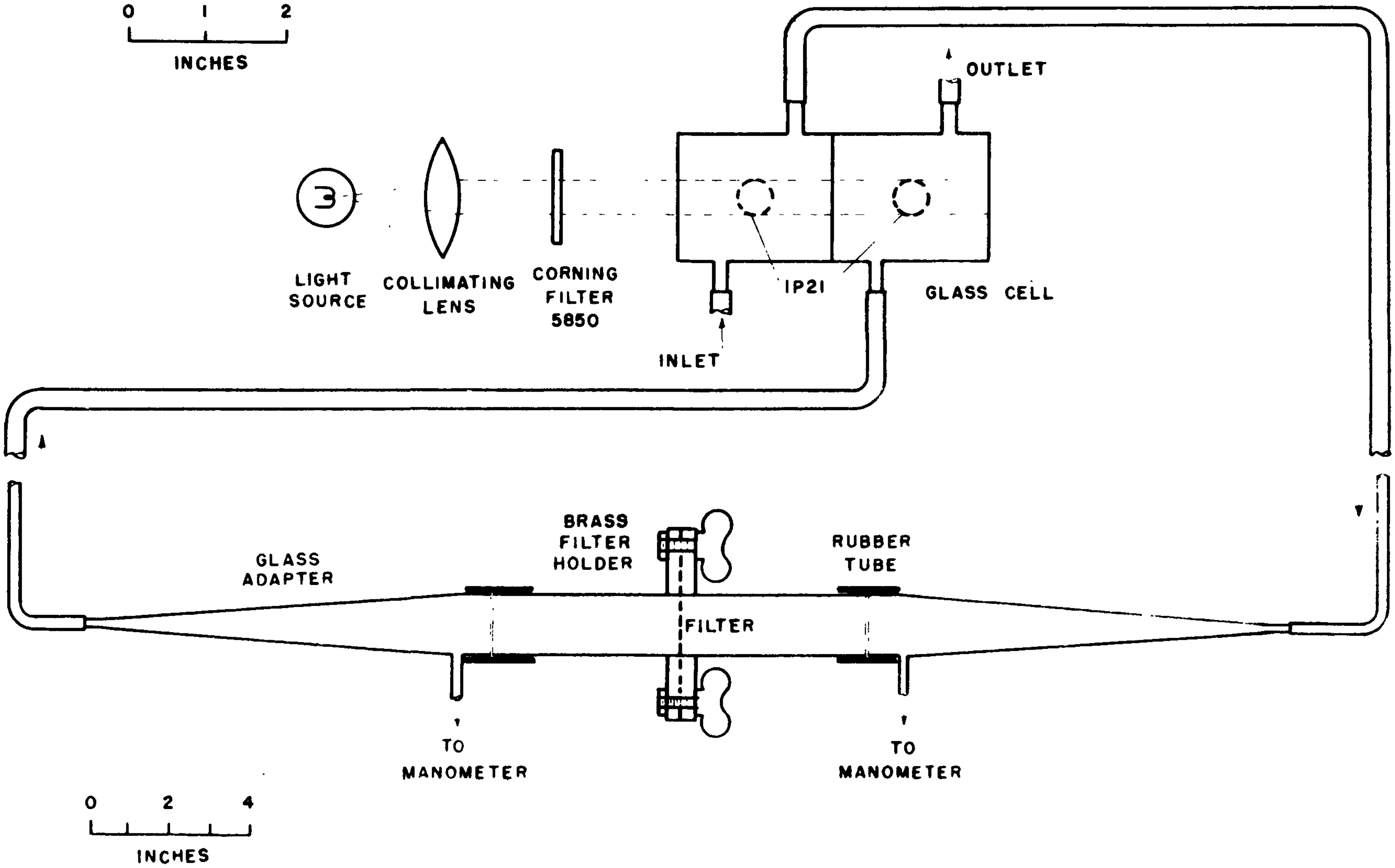

0 1 2
INCHES
OUTLET
LIGHT SOURCE
COLLIMATING LENS
CORNING FILTER 5850
1P21
GLASS CELL
INLET
BRASS FILTER HOLDER
GLASS ADAPTER
RUBBER TUBE
FILTER
TO MANOMETER
TO MANOMETER
0 2 4
INCHES

Fig. 5b.1

FILTRATION ELECTRONIC SET UP

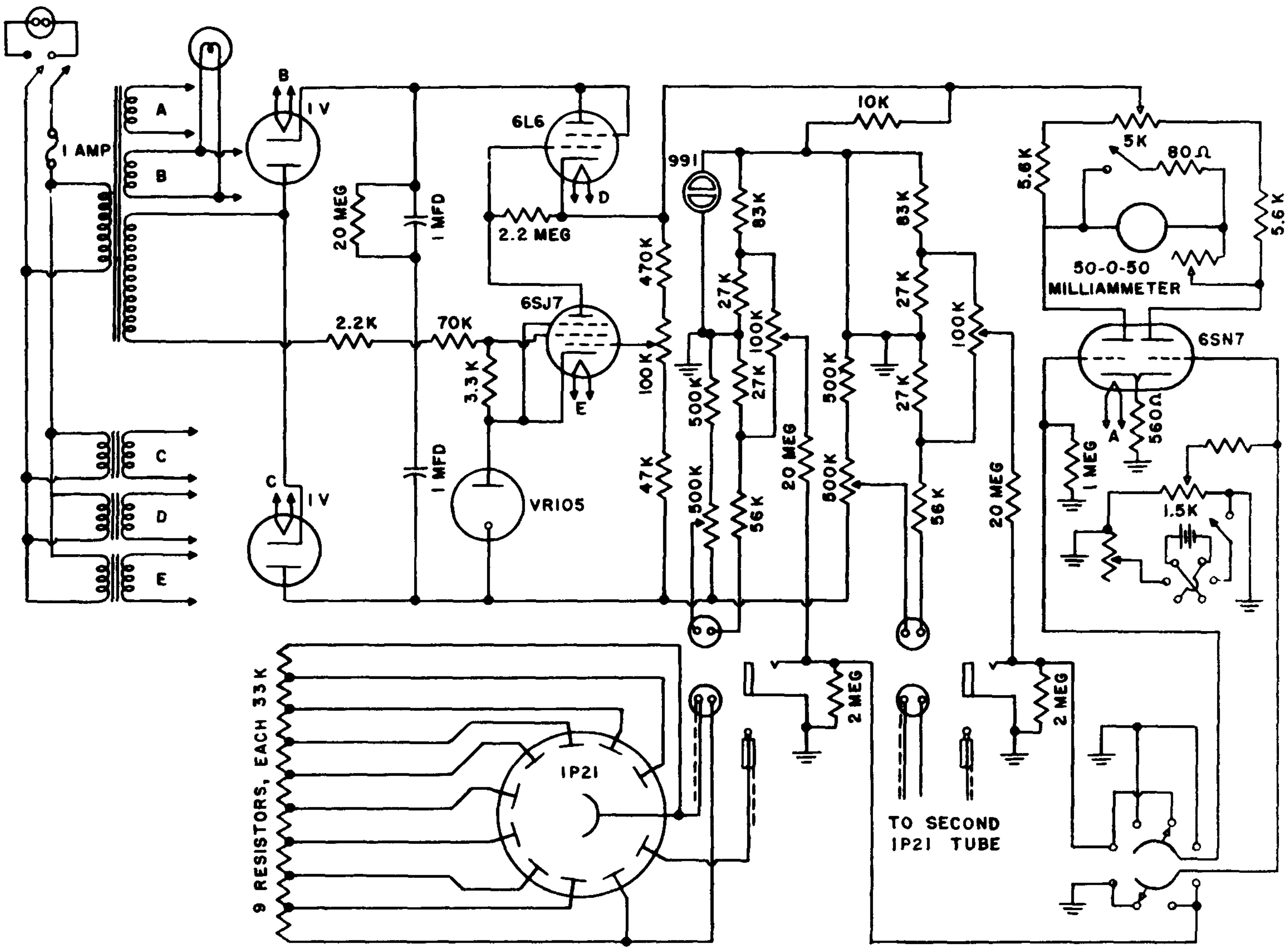


Fig. 5b.2

64

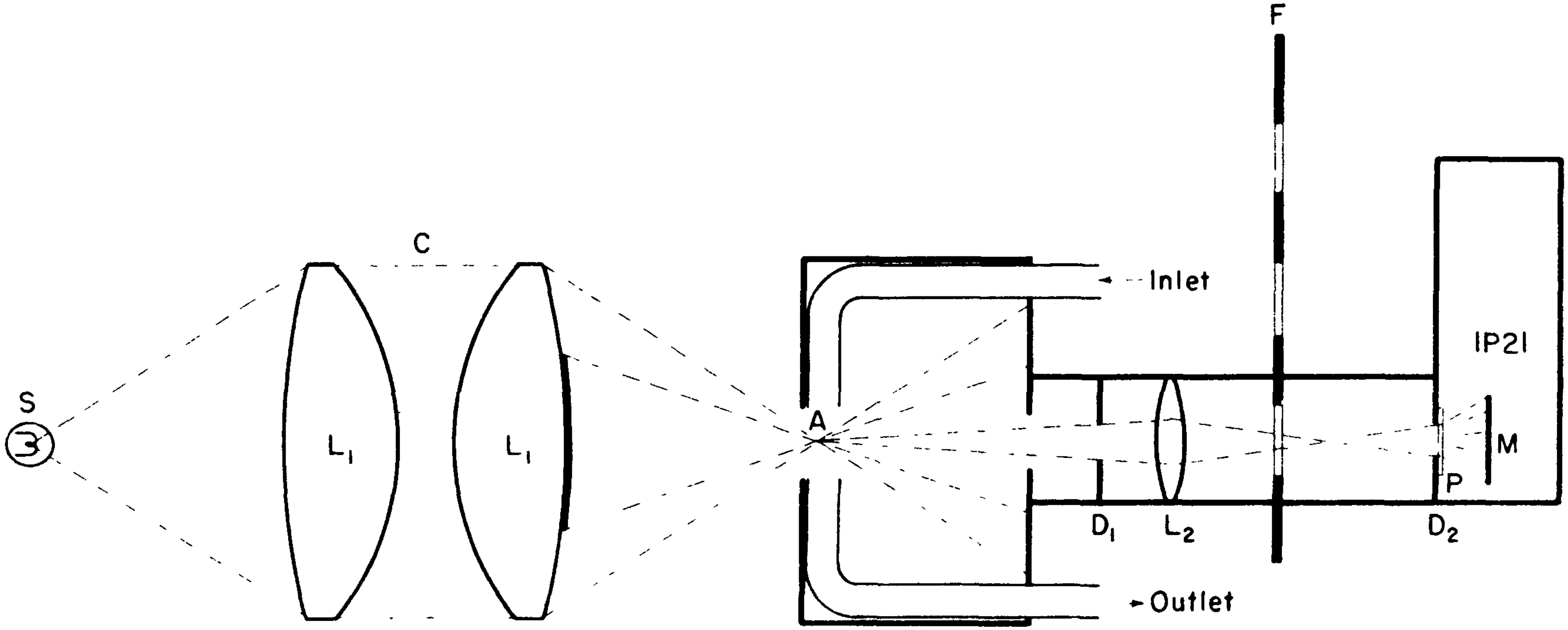


Fig. 5b.3

SUMMARY AND CONCLUSIONS

The results and conclusions reached in this research will be divided into several categories, according to the type of filter under examination. These large classifications will then be subdivided into sections comprising all the relations investigated for each filte Since the CC-5 paper offers characteristics most suitable for this study, it will be discussed in detail, the behavior of other filters being compared to it. As a final summation, a table, listing all the principal qualities of the filters, will be presented.

1. Scope of this Investigation.

In this research, CC-5 filter was tested with dioctyl phthalate (DOP), oleic acid and stearic acid aerosols, whereas Whatman No. 2 (W-2), alpha-web carbon-impregnated, A.E.C. No. 1 ("Roll 13"), "G1", hand-made glass, and rayon filters were studied with DOP aerosol exclusively.

2. Properties Common to all Filters.

a. Percentage Penetration vs. Radius of Aerosol.

In all cases, the percentage penetration was observed to decrease monotonically with increase of the aerosol particle radius; that is, no maximum in the penetration per cent vs. radius curve appears (See.Figs. 2, 10, 14, 19 and 20). This relationship exists whether or not the filter exhibits time-dependent penetration properties. It also applies to the CC-5 filter with stearic acid as aerosol, provided the penetration values are extrapolated to zero time. A hand-made glass filter, examined with DOP aerosols of radii 0.14 and 0.35 micron, showed the same decrease in percentage penetration. A rayon filter demonstrated very high penetration (between 85 and 100% with DOP) with large variations. A 5-fold increase of this filter thickness did not markedly improve its efficiency. A.E.C. No. 1 ("Roll 13"), on the other hand, is so effective a filter that variation due to radius could not be studied quantitatively under the conditions of operation employed (flow rate, concentration, etc.) and particularly with the instruments of detection presently available.

b. Percentage Penetration vs. Linear Velocity of Aerosol.

With the exception of W-2 filter paper which will be discussed later, the various filters tested showed an increase of percentage penetration with increase of linear velocity in the range of particle radius from 0.03 to 0.35 micron. This effect becomes less pronounced as the radius is increased. Table I lists some typical data for CC-5 and hand-made glass filters with DOP aerosol and illustrates this relationship.

Table I

Filter	Aerosol	Radius (microns)	Velocity	P*	ΔP
CC-5	DOP	0.05	2.7 13.1	29.7) 32)	2.3
CC-5	DOP	0.30	2.7 13.1	16.5) 16.5)	0
Hand-made Glass No. 1	DOP	0.14	2.7 13.1	49.0) 61.5)	11.5
Hand-made Glass No. 1	DOP	0.35	2.7 13.1	28.3) 30.6)	2.3

* Penetration Percentage

Similar results are obtained with oleic acid aerosol. For both aerosols filtered through CC-5 paper, this tendency is reversed for particles of radii greater than 0.35 micron; in other words, for these large particles, the penetration percentage decreases with increasing linear velocity. This paper also shows a so-called "isopenetration region" in which, for particle radii from 0.25 to 0.35 microns, penetrations invariant with respect to linear velocity are obtained when the latter is varied from 2.6 to 28.0 cm/sec. A more thorough discussion of the properties of each filter paper with the various aerosols is presented in the sections to follow. The time variation of the penetration characteristics of α-web C-impregnated paper rendered this filter useless for this study since extrapolation to zero time for high linear velocities becomes practically impossible. This is also true for CC-5 paper with stearic acid aerosol. Experiments with "G1" filter have only an orienting, qualitative value since an aluminum ring was used to increase the linear velocity of the aerosol by decreasing the filter area.

An analytical filter, such as the Whatman-2 paper, exhibits a decrease in percentage penetration with increase of linear velocity for the entire range of particle radii under investigation.

3. Chemical Corps No. 5 (CC-5) Filter Paper.

a. Dioctyl Phthalate Aerosol (DOP).

A total of 74 filtration experiments was carried out with this paper as filter and DOP as aerosol.

The percentage penetration of DOP through this paper is invariant with time as may be seen from some typical data represented in Fig. 1. Here the fluctuations of the experimental values about the average occur with no marked tendencies in any direction for a period of 7-1/2 minutes. It was also observed that no significant change took place over a period of 2-1/2 hours of continuous filtration.

The normal logarithmic decrease of penetration with filter thickness was also obtained.

A survey of the penetration percentage vs. radius relationship yielded curves such as that shown in Fig. 2a. This monotonic decrease in per cent penetration with radius has been described above.

It is worthwhile to mention at this juncture that the CC-5 filter exhibits highly reproducible penetration values for a given radius, such a conclusion being reached from an examination of the frequency distribution curve of the percentage average deviation of the experimental values (Fig. 3). A curve of this type is constructed in the following manner: the arithmetic average per cent penetration for different filter samples is calculated for a given radius, the deviation of each experimental value from this average found, and the average of these deviations determined. The percentage average deviation is defined as 100 times the ratio of the average deviation to the average per cent penetration. This procedure is repeated for all the radii investigated and the frequency of occurrence of each per cent average deviation tabulated. A graph of the results of such a study is shown in Fig. 3 (also Fig. 15 for W-2 paper). Examination of Fig. 3 reveals that the majority of cases show a per cent average deviation of less than 2.5%. The shape of this curve points to the excellent behavior of this filter. Since the 90° Scattering Penetrometer possesses a limit of precision of this same order of magnitude, the filter may yield results even more reproducible than this test would indicate.

(1) Effect of variation of linear velocity

Another subject of interest in the investigation of this filter is the variation of percentage penetration with the linear velocity of the aerosol for different particle radii. Fig. 5 shows the results obtained for the velocities 2.7, 4.7, 13.0 and 28.0 cm/sec. It may be noted that for radii smaller than 0.33 micron these curves possess a definite maximum with a very sharp initial increase in penetration percentage in the small velocity range. For velocities greater than 13.0 cm/sec., the per cent penetration begins to decrease slightly. For a particle of radius 0.21 micron, a penetration of 16.4% was obtained for a linear velocity of 42 cm/sec (this velocity was produced by increasing the flow rate from 2 to 3 l/min) and represents a decided decrease below the penetration value of about 20% for a velocity of 2.7 cm/sec. No general conclusions can be drawn, however, regarding the behavior of the other curves in the very high velocity range since this was the only experiment performed in this region. An aerosol particle of radius 0.33 micron experiences a penetration independent of the linear velocity within the limited range of velocities whereas larger particles show a decrease in penetration percentage with increasing linear velocities.

Fig. 4 shows another method of representing the data already discussed. In this case, the per cent penetration is plotted against the radius of the aerosol particle for the four different linear velocities. This figure shows more clearly the so-called "isopenetration region" for particles whose radii fall in the 0.25 - 0.35 micron range. Here the four curves are effectively coincident, indicating that the penetration is independent of linear velocity for this particle size. Larger variations appear in the very low and very high velocity regions.

b. Oleic Acid Aerosol.

A total of 24 experiments with this aerosol yielded results practically identical with those for DOP. The normal decrease of percentage penetration with increasing particle radius is plotted in Fig. 10. Fig. 11 shows this relation for the four different linear velocities. It should be emphasized at this point that these curves are based on fewer data and are less reliable statistically than those in Fig. 4 and 5. (The solid line, however, for the lowest velocity of 1.9 cm/sec is an average curve, taken from many more experiments, and is therefore more reliable than the other three). Perhaps for this reason, the isopenetration region is less well-defined. The results of the treatment of the data in Fig. 12 show oleic acid aerosol to behave similarly to DOP. Nevertheless, in spite of the statistical considerations, these curves do appear to have less sharp maxima with initial slopes which are much less steep.

c. Stearic Acid Aerosol.

A total of 19 experiments was performed with stearic acid aerosol.

This semi-solid aerosol shows filtration properties similar to the other aerosols already discussed if the clogging action, evident from the rapid increase of pressure drop with time discussed below, is taken into consideration. In other words, the normal monotonic decrease in penetration per cent with increasing particle radius is obtained, provided that the per cent penetration is extrapolated to zero time. This is illustrated in Fig. 2 where the curve may be seen to be practically parallel to that for DOP aerosol.

A definite clue to the origin of this clogging effect may be seen in Figs. 6, 7, 8 and 9. In Fig. 6, the variation of the per cent penetration with time for particle radii of 0.19, 0.33, 0.42 and 0.64 microns is shown for a linear velocity of 2.6 cm/sec. For the smallest particle, the penetration is constant with time, only the normal fluctuations about the average appearing. For the larger particles, the penetration per cent decreases sharply with time. For the case of the 0.33 micron particle, the penetration per cent appears to be constant for about 2 minutes before clogging begins to take effect. In Fig. 6, the pressure drop variation could not be studied since this quantity was too small to be detected by the ordinary nitrobenzene manometer. Fig. 7 pictures the time variation of the percentage penetration for the first three particle sizes for a linear velocity of 4.7 cm/sec. In this case, the penetration decreases almost linearly with time and a pressure drop, large enough to be observed, is obtained for particles of 0.30 and 0.50 microns.

The results for a linear velocity of 13.0 cm/sec for particle radii of 0.19, 0.25 and 0.35 microns are shown in Fig. 8. Here a sharp decrease in the curve for the 0.19 micron particle appears and a slight change in the curvature of these plots may be noted, particularly for the case of the 0.35 micron particle. Now a pressure drop may be observed for the 0.20 micron particle, a very steep slope appearing for a radius of 0.50 micron. Fig. 9 shows a very definite change in the curvature of the per cent penetration curves for radii of 0.21 and 0.35 microns. Extremely sharp increases in pressure drop are in evidence for particles from 0.18 to 0.50 microns, These findings are all consistent with the view that the higher the velocity, the greater the mass concentration - roughly proportional to the cube of the radii of the droplets - the more rapidly does the pressure drop increase and the penetration decrease with time. The stearic acid droplets evidently crystallize in the pores of the filter.

4. Whatman No. 2 Filter Paper.

A total of 45 experiments was performed with DOP aerosol filtered through this paper.

This paper shows penetration characteristics differing from those above. They are invariant with time, and exhibit only the normal fluctuations about the average of 16.3%, as illustrated in Fig. 13, for these operating conditions.

A study of the variation of penetration percentage with radius for a specific linear velocity yields a (normal) decrease with increasing r (See Fig. 14) but a very wide spread exists in the penetration values obtained for any particular radius. The frequency distribution (Fig. 15) for this paper shows the results to be unreliable relative to other papers. In this case, the curve possesses a maximum for an average deviation per cent from 1.5 - 4.5%. This signifies that an error of this amount is most probable when a study of the percentage penetration is made, and emphasizes the poor reproducibility of the filter. The poor reproducibility may be due tc a pin-hole effect or to variations in filter thickness.

In order to obtain a value of the per cent penetration for a given sample of this paper, it was necessary to take anywhere from four to ten readings and to dry the papers in an oven before testing. Very often these values would appear to be divided into two distinct groups (See Table II, Section V.a). None of these values could be rejected, however, since their deviation from the average was less than four times the average deviation (the criterion of rejection). To eliminate one more disturbing factor, a thorough drying of the filter was attempted, but the penetration group effect still persisted.

A survey of the variation of the penetration per cent with particle radius for different linear velocities reveals that there is a sharp decrease in penetration with increasing radius for all linear velocities and that no "isopenetration region" exists (See Fig. 16). Fig. 17 shows the results of this study for particles of 0.26 and 0.12 microns. The pressure drop across the W-2 filter is much greater than that across the CC-5 paper for the same operating conditions. For a velocity of 28.0 cm/sec, this drop is so great that a decrease in the flow rate in the generator results, because of back pressure, and a readjustment of this flow rate is necessary for further operation of the generator. This represents an undesirable technique and should be avoided.

5. Alpha-Web Carbon-Impregnated Paper.

Twelve experiments were performed upon this paper with DOP as the test aerosol.

A study of the influence of time of filtration upon the value of the per cent penetration for different particle radii showed that even with a liquid aerosol, such as DOP, the per cent penetration increases with time and that this effect is more prominent for larger radii (See Fig. 18). A brief explanation of the technique employed to obtain this plot is necessary for a thorough understanding of its significance. The per cent penetration is measured as a function of time for a particular radius and a particular filter sample. A smooth curve is passed through the points so obtained and the procedure repeated for several filter samples. Next the values of per cent penetration for a certain time, t, are averaged from these curves for all the samples, and a point obtained. This is carried out for several t's and the results plotted in Fig. 18 for a certain radius. This method is used for particles of radii 0.12, 0.18, 0.32 and 0.48 microns.

The effect of passage of time is further emphasized by a plot of per cent penetration vs. particle radius for zero time (a), and a time of 90 seconds (b), Fig. 19. In the former case, the usual curve is obtained whereas the latter exhibits a curvature the reverse of the normal and illustrates the erroneous results produced when the time dependence of the penetration is ignored. We believe this effect may be the reason a maximum in the filtration-radius curve was obtained (1) with this filter using stearic acid as the test aerosol.

---

1. W.H. Rodebush, I. Langmuir and V.K. La Mer, O.S.R.D. Report 865, Sept. 1942.

Legends for Figures

Fig. 1. Time dependence of D.O.P. aerosol penetration through Chemical Corps No. 5 filter (CC5).

Flow rate: 2 liters/min.
Filter area: 13.25 cm^2
Linear velocity: 2.5 cm/sec.
Particle radius: .13 microns

Fig. 2. Variation of aerosol penetration with particle radius using CC5 filter.

(a) D.O.P. aerosol
(b) Stearic acid aerosol (extrapolation of penetration values to zero time is used).

Flow rate: 2.1 liters/min.
Filter area: 13 cm^2
Linear velocity: 2.7 cm/sec.

Fig. 3. Frequency distribution of percentage average deviation of D.O.P. aerosol penetration through CC5 filter. (Measure of reproducibility of CC5 filter with respect to penetration of liquid aerosols).

Flow rate: 2.1 liters/min.
Filter area: 13 cm^2
Linear velocity: 2.7 cm/sec.

Fig. 4. Variation of D.O.P. aerosol penetration percentage with particle radius for various linear velocities using CC5 filter

Flow rate: 2 liters/min.

	Linear velocity	Filter area
(a)	2.7 cm/sec.	13 cm^2 (average curve, see Fig. 2a)
(b)	4.7	7.05
(c)	13.0	2.56
(d)	28.0	1.19

Fig. 5. Variation of D.O.P. aerosol penetration percentage with linear velocity using CC5 filter.

Flow rate: 2 liters/min.
Particle radius: (a) 0.08 microns
(b) .13
(c) .21
(d) .33
(e) .49

9. Microscopic Analysis of Filters.

Samples of fibers from various filters were spread out on glass slides and examined under a light microscope (magnification 400x). For the filtration analysis, samples were prepared from filters before and after passage of the aerosol through the paper.

a. CC-5 and W-2 Filters with DOP as Aerosol.

Examination of fibers from papers through which DOP aerosol of particle radius 0.5 micron had been passed for 15 min. revealed no droplets attached to them.

A simple experiment proved the presence of DOP in the CC-5 paper. Samples of this filter fiber before and after the passage of this aerosol of large particle size through the paper were prepared. Five droplets of toluene were deposited on each of the slides. After about five minutes the toluene droplet on each slide was transferred to a clean slide and allowed to evaporate. The droplet from the slide prepared after the passage of the DOP aerosol, left a large stain on the slide, showing that DOP had been present in the filter but was not detectable with the microscope. DOP evidently wets these fibers and is distributed over the length of the fiber.

b. CC-5 with Stearic Acid as Aerosol.

Stearic acid aerosol of radius 0.6 micron and 28.0 cm/sec linear velocity was passed through this filter for a few minutes. On examination of fibers of this filter under the microscope, clusters and larger concentrations of aerosol particles could be seen at intersections and thin ramifications of fibers. The contrasting behavior of stearic acid aerosol as compared to DOP is evident in both the filtration data and the microscopic analysis.

c. A.E.C. No. 1 ("Roll 13") with Nujol Aerosol.

Passage of Nujol aerosol of radius 0.2 micron for 10 minutes through this filter did not yield any particles visible under the microscope.

d. Physical Appearance of the Fibers.

The fibers of the CC-5 and rayon filters appear to have diameters of the sameorder of magnitude although the latter are much smoother. The W-2 fibers seem to be non-uniform whereas those of A.E.C. No. 1 consist of two distinct types: one is of the same order of magnitude as the rayon fibers and the other is a needle-like fiber of much smaller diameter. This latter class is probably responsible for the high efficiency of the filter. For a more complete discussion of filter composition, see Section II.

10. Photographic Counting of Filtration Characteristics.

This method of analysis yielded substantially the same results as the 90° Scattering Penetrometer for the CC-5 filter and offers no advantages above and beyond this apparatus for all other filters, offering high penetrations. In the case of highly efficient filters, this technique is desirable because the aerosol which penetrates is seen, and although only semi-quantitative results have been obtained, the method warrants further investigation.

Legends for Figures

Fig. 1. Time dependence of D.O.P. aerosol penetration through Chemical Corps No. 5 filter (CC5).

Flow rate: 2 liters/min.
Filter area: 13.25 cm^2
Linear velocity: 2.5 cm/sec.
Particle radius: .13 microns

Fig. 2. Variation of aerosol penetration with particle radius using CC5 filter.

(a) D.O.P. aerosol
(b) Stearic acid aerosol (extrapolation of penetration values to zero time is used).

Flow rate: 2.1 liters/min.
Filter area: 13 cm^2
Linear velocity: 2.7 cm/sec.

Fig. 3. Frequency distribution of percentage average deviation of D.O.P. aerosol penetration through CC5 filter. (Measure of reproducibility of CC5 filter with respect to penetration of liquid aerosols).

Flow rate: 2.1 liters/min.
Filter area: 13 cm^2
Linear velocity: 2.7 cm/sec.

Fig. 4. Variation of D.O.P. aerosol penetration percentage with particle radius for various linear velocities using CC5 filter

Flow rate: 2 liters/min.

	Linear velocity	Filter area
(a)	2.7 cm/sec.	13 cm^2 (average curve, see Fig.2a)
(b)	4.7	7.05
(c)	13.0	2.56
(d)	28.0	1.19

Fig. 5. Variation of D.O.P. aerosol penetration percentage with linear velocity using CC5 filter.

Flow rate: 2 liters/min.
Particle radius: (a) 0.08 microns
(b) .13
(c) .21
(d) .33
(e) .49

Figures

Fig. 6. Time dependence of filtration with stearic acid aerosol through CC5 filter.

Flow rate: 2 liters/min.
Linear velocity: 2.6 cm/sec. (Filter area: 13 cm^2).
Particle radius: (a) 0.19 micron
(b) .35
(c) .42
(d) .64

Fig. 7. Time dependence measurements with stearic acid aerosol through CC5 filter.

Flow rate: 2 liters/min.
Linear velocity: 4.7 cm/sec. (filter area: 7.05 cm^2).
Variation of penetration percentage with time:
Particle radius: (a) 0.19 micron
(b) .35
(c) .42

Change in pressure drop with time:
Particle radius: (d) .50 micron
(e) .30

Fig. 8. Time dependence measurements with stearic acid aerosol through CC5 filter.

Flow rate: 2 liters/min.
Linear velocity: 13.0 cm/sec. (Filter area: 2.56 cm^2).

Variation of penetration percentage with time:
Particle radius: (a) 0.19 micron
(b) .25
(c) .35

Change in pressure drop with time:
Particle radius: (d) 0.20 micron
(e) .30
(f) .50

Fig. 9. Time dependence measurements with stearic acid aerosol through CC5 filter.

Flow rate: 2 liters/min.
Linear velocity: 28.0 cm/sec. (Filter area: 1.19 cm^2).
Variation of penetration percentage with time:
Particle radius: (a) 0.21 micron
(b) .35
(c) .18

Changein pressure drop with time:
Particle radius: (d) 0.30 micron
(e) .50

Figures

Fig. 10. Variation of oleic acid aerosol penetration with particle radius using CC5 filter.

Flow rate: 1.5 liters/min.
Filter area: 13 cm^2
Linear velocity: 1.9 cm/sec.

Fig. 11. Variation of oleic acid aerosol penetration percentage with particle radius for various linear velocities using CC5 filter.

	Flow rate	Linear velocity	Filter area
(a)	1.5 liters/min.	1.9 cm/sec.	13 cm^2
(b)	2.	2.6	13 (average curve, see Fig. 10).
(c)	2.	13.	7.05
(d)	2.	28.	1.19

Fig. 12. Variation of oleic acid aerosol penetration percentage with linear velocity using CC5 filter.

Flow rate: 2 liters/min.
Particle radius: (a) 0.14 micron
(b) .24
(c) .33
(d) .52

Fig. 13. Time dependence of D.O.P. aerosol penetration through Whatman filter (W-2).

Flow rate: 2 liters/min.
Filter area: 13 cm^2
Particle radius: 0.26 micron
Linear velocity: 2.6 cm/sec.

Fig. 14. Variation of D.O.P. aerosol penetration percentage with particle radius using W-2 filter.

Flow rate: 2.1 liters/min.
Filter area: 13 cm^2
Linear velocity: 2.7 cm/sec.

Fig. 15. Frequency distribution of percentage average deviation of D.O.P. aerosol penetration through W-2 filter. (Measure of reproducibility of W-2 filter with respect to penetration of liquid aerosols).

Flow rate: 2.1 liters/min.
Filter area: 13 cm^2
Linear velocity: 2.7 cm/sec.

Figures

Fig. 16. Variation of D.O.P. aerosol penetration percentage with particle radius for various linear velocities using W-2 filter.

Flow rate: 2 liters/min.

	Linear velocity	Filter area
(a)	2.7 cm/sec.	13 cm^2 (average curve, see Fig. 14).
(b)	13.	2.56
(c)	28.	1.19

Fig. 17. Variation of D.O.P. aerosol penetration percentage with linear velocity using W-2 filter.

Flow rate: 2 liters/min.
Particle radius: (a) 0.12 micron
(b) .26

Fig. 18. Time dependence of D.O.P. aerosol penetration through α-web carbon impregnated filter.

Flow rate: 2 liters/min.
Filter area: 13.25 cm^2
Linear velocity: 2.5 cm/sec.
Particle radius: (a) 0.12 micron
(b) .18
(c) .32
(d) .48

Fig. 19. Variation of D.O.P. aerosol penetration with particle radius using α-web carbon impregnated filter,

Flow rate: 2 liters/min.
Filter area: 13.25 cm^2
Linear velocity: 2.5 cm/sec.

(a) Data from extrapolation of penetration values to zero time.
(b) Data from readings at 90 seconds.

Fig. 20. Variation of D.O.P. aerosol penetration with particle radius using glass filter (G1).

Flow rate: 2 liters/min.
Linear velocity: (a) 2.6 cm/sec.
(b) 31.2

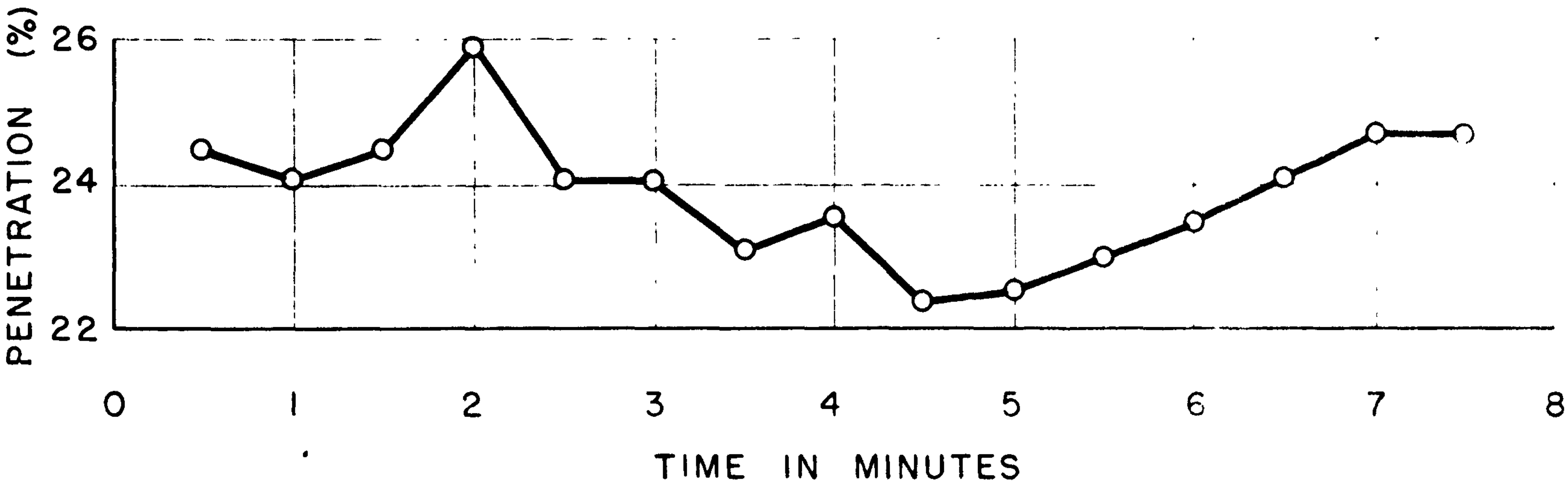


Fig. 5c.1

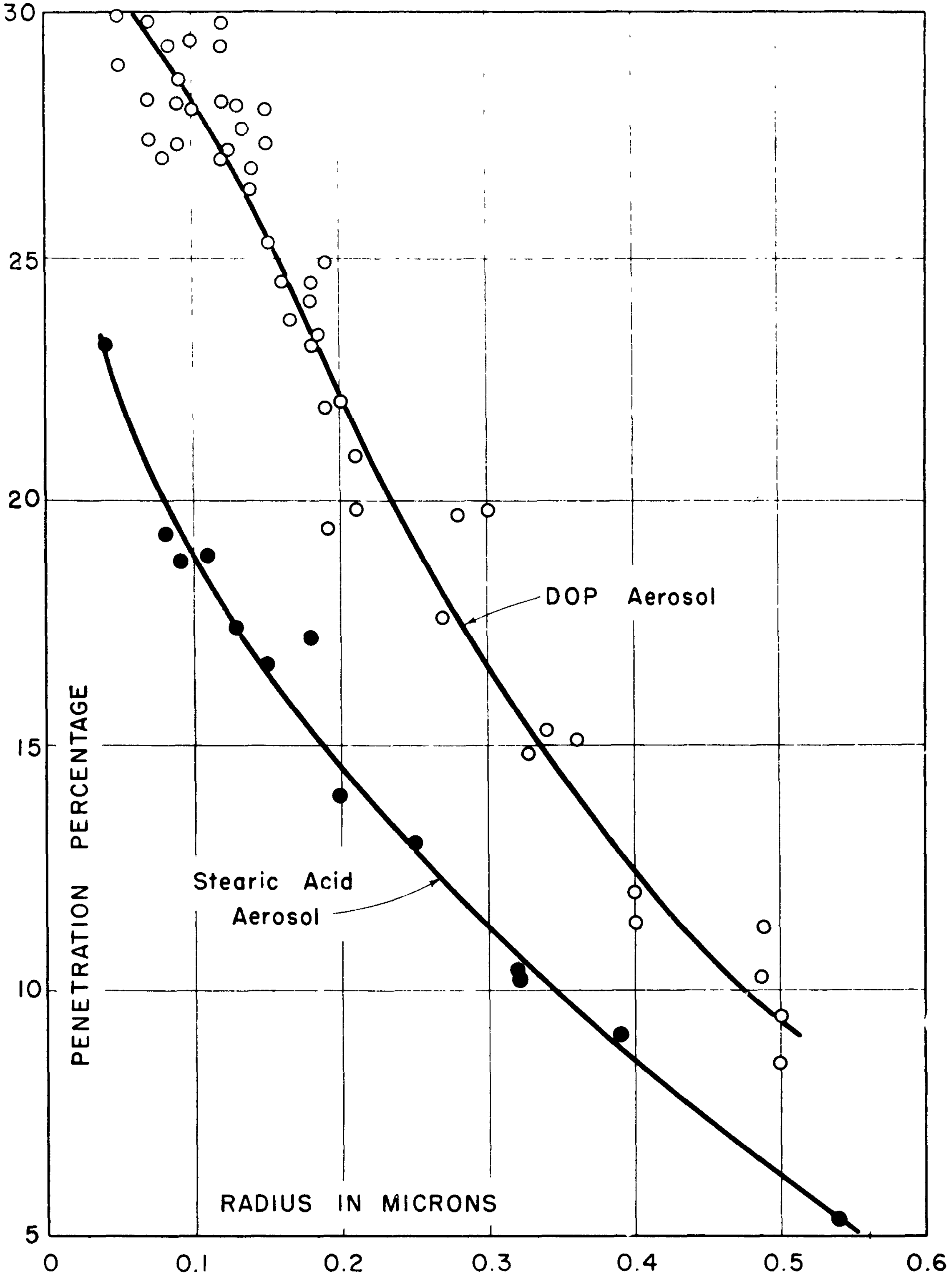

30
25
20
15
10
5
0
0.1
0.2
0.3
0.4
0.5
0.6
PENETRATION PERCENTAGE
RADIUS IN MICRONS
DOP Aerosol
Stearic Acid Aerosol

Fig. 5c.2

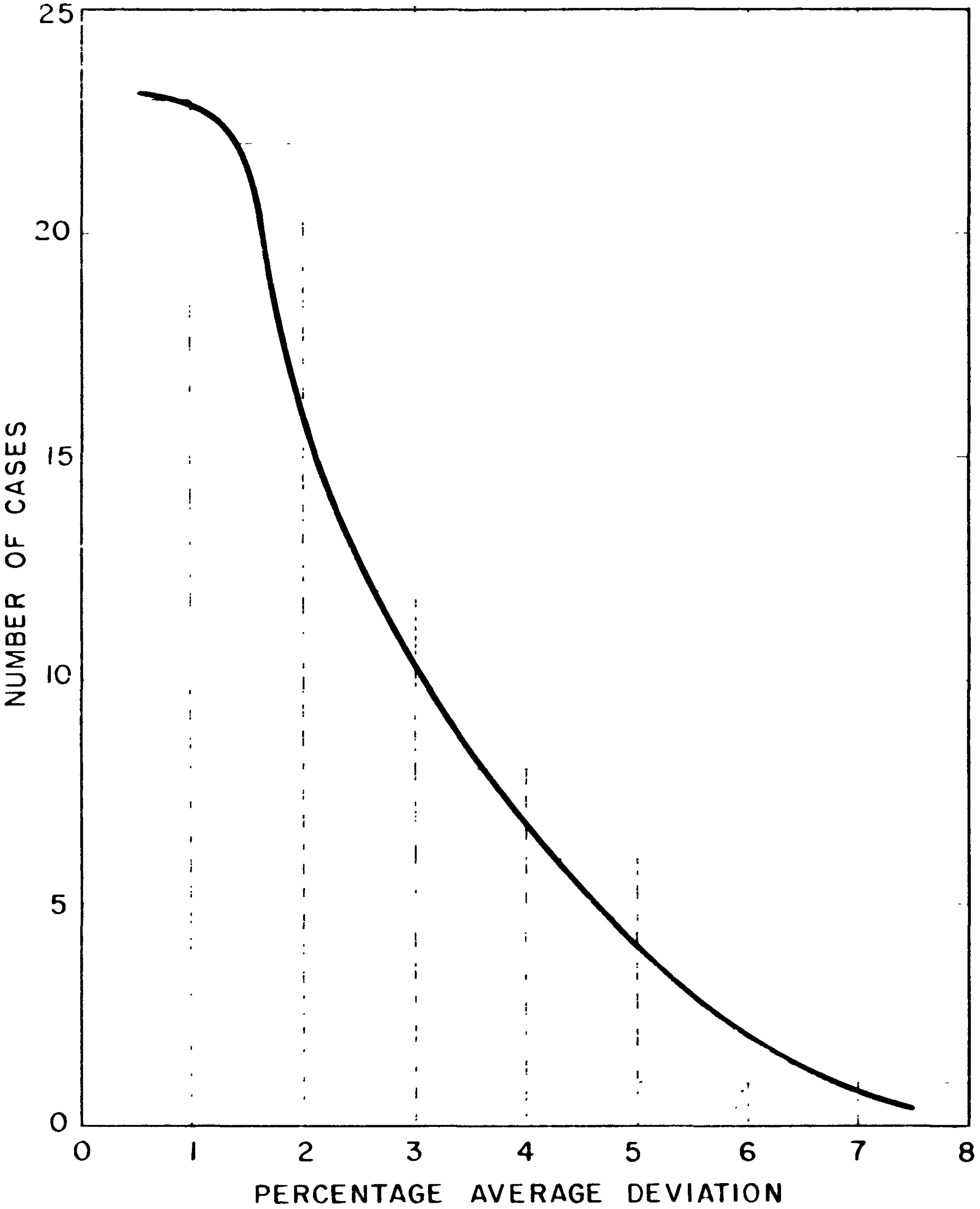


Fig. 5c.3

7420 74

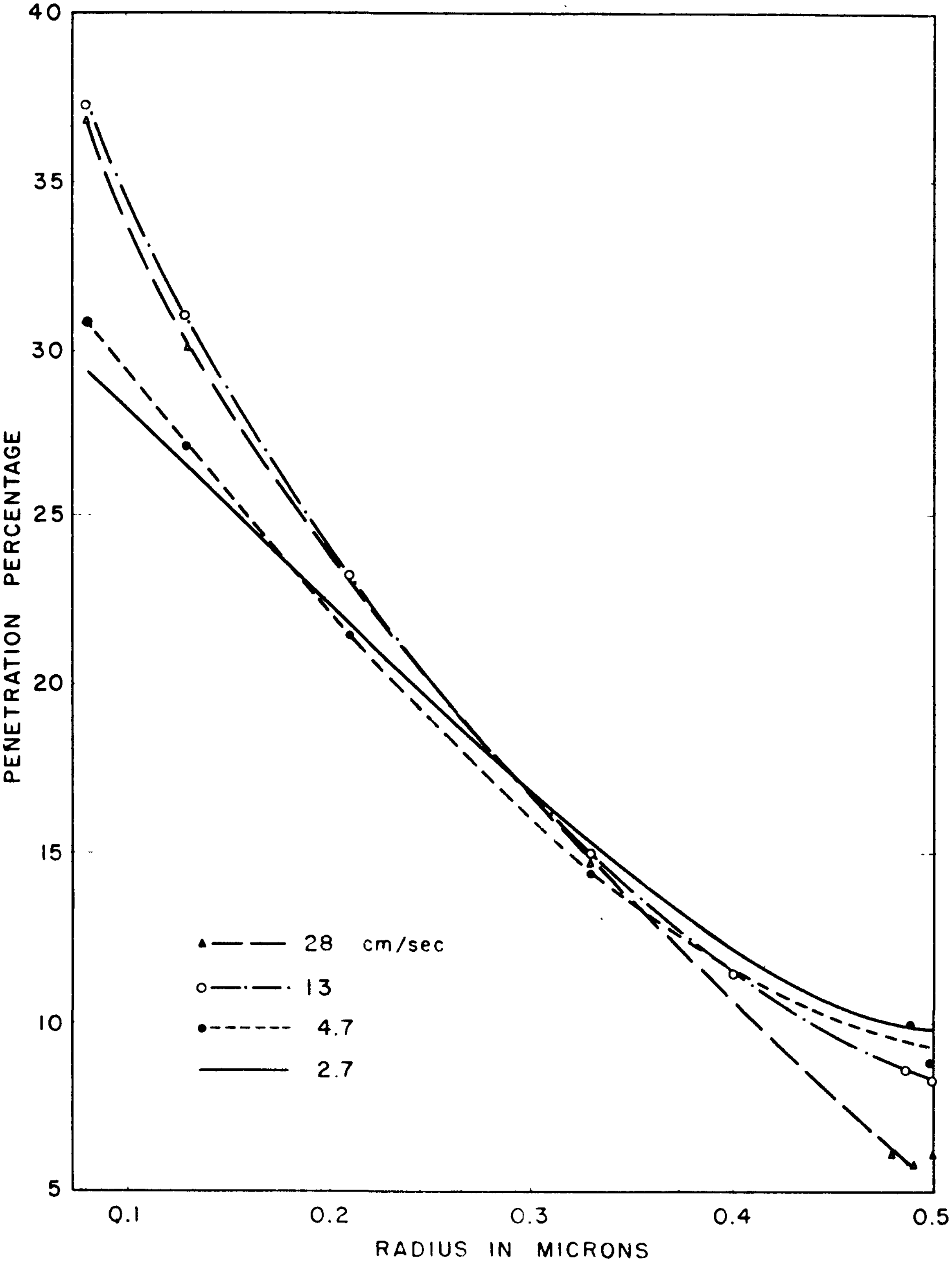

40
35
30
25
20
15
10
5
PENETRATION PERCENTAGE
0.1
0.2
0.3
0.4
0.5
RADIUS IN MICRONS
▲ 28 cm/sec
○ 13
● 4.7
2.7

Fig. 5c.4

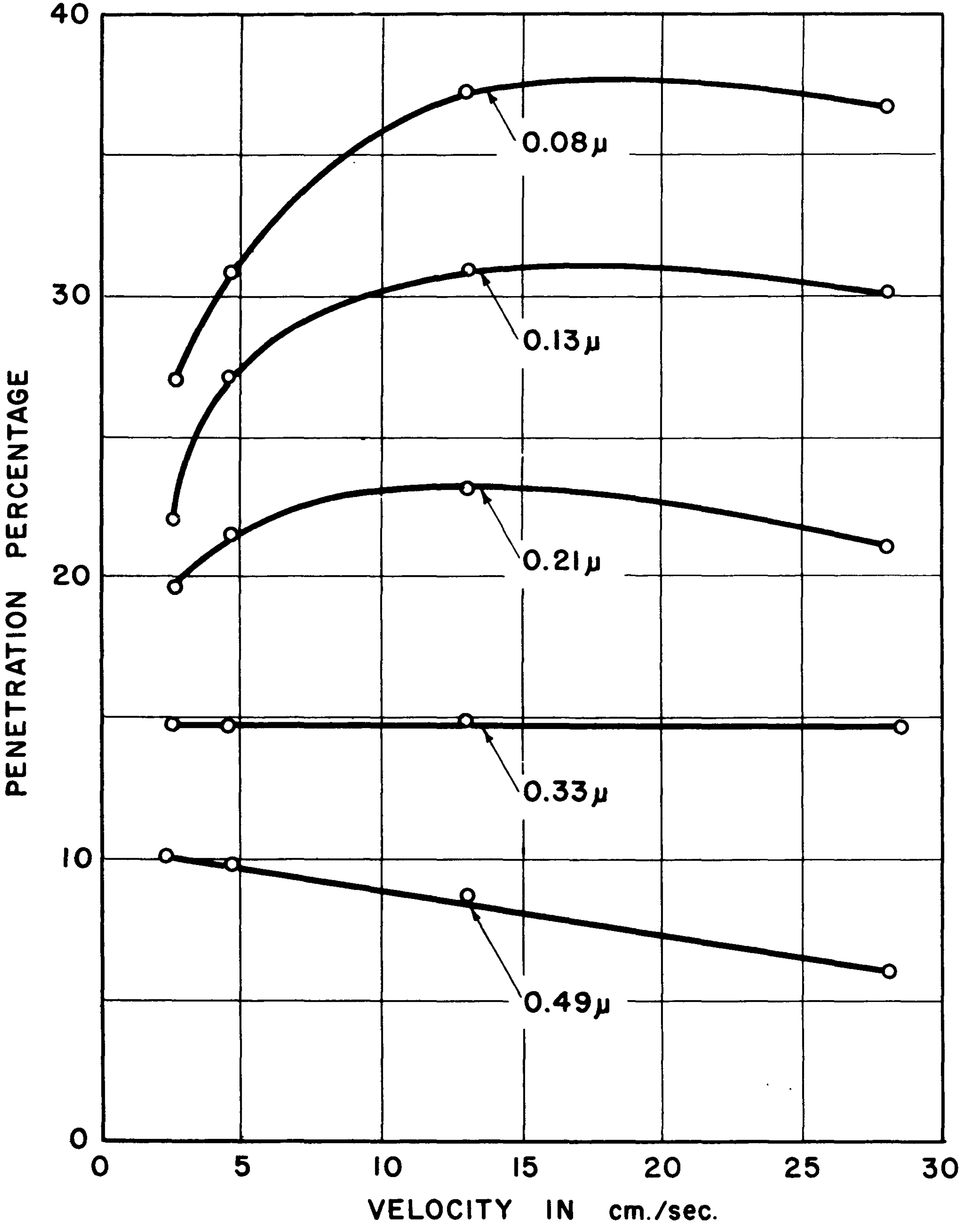

PENETRATION PERCENTAGE
0
10
20
30
40
VELOCITY IN cm./sec.
0
5
10
15
20
25
30
0.08µ
0.13µ
0.21µ
0.33µ
0.49µ

Fig. 5c.5

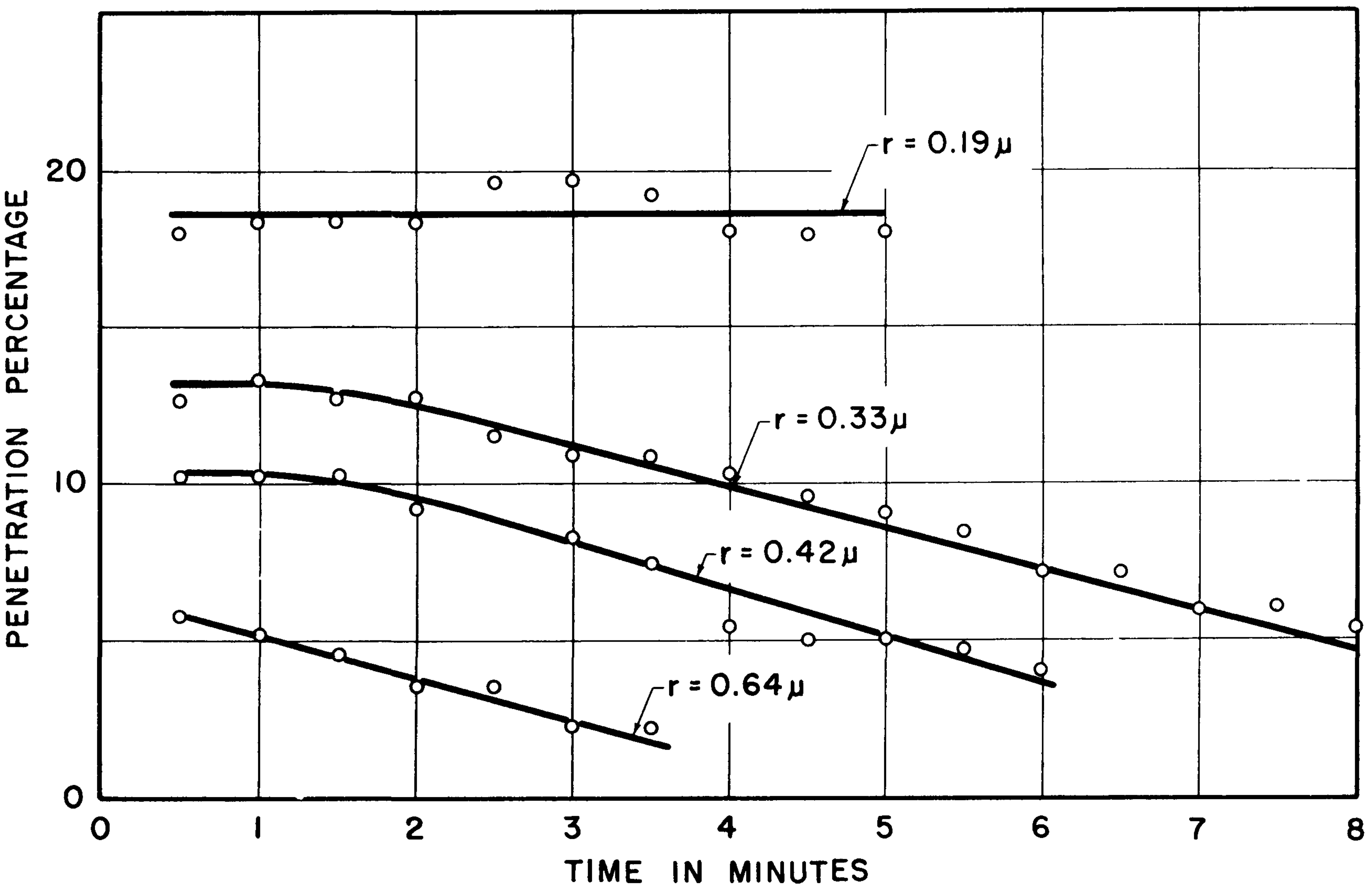

r = 0.19 μ
r = 0.33 μ
r = 0.42 μ
r = 0.64 μ
PENETRATION PERCENTAGE
20
10
0
0
1
2
3
4
5
6
7
8
TIME IN MINUTES

Fig. 5c.6

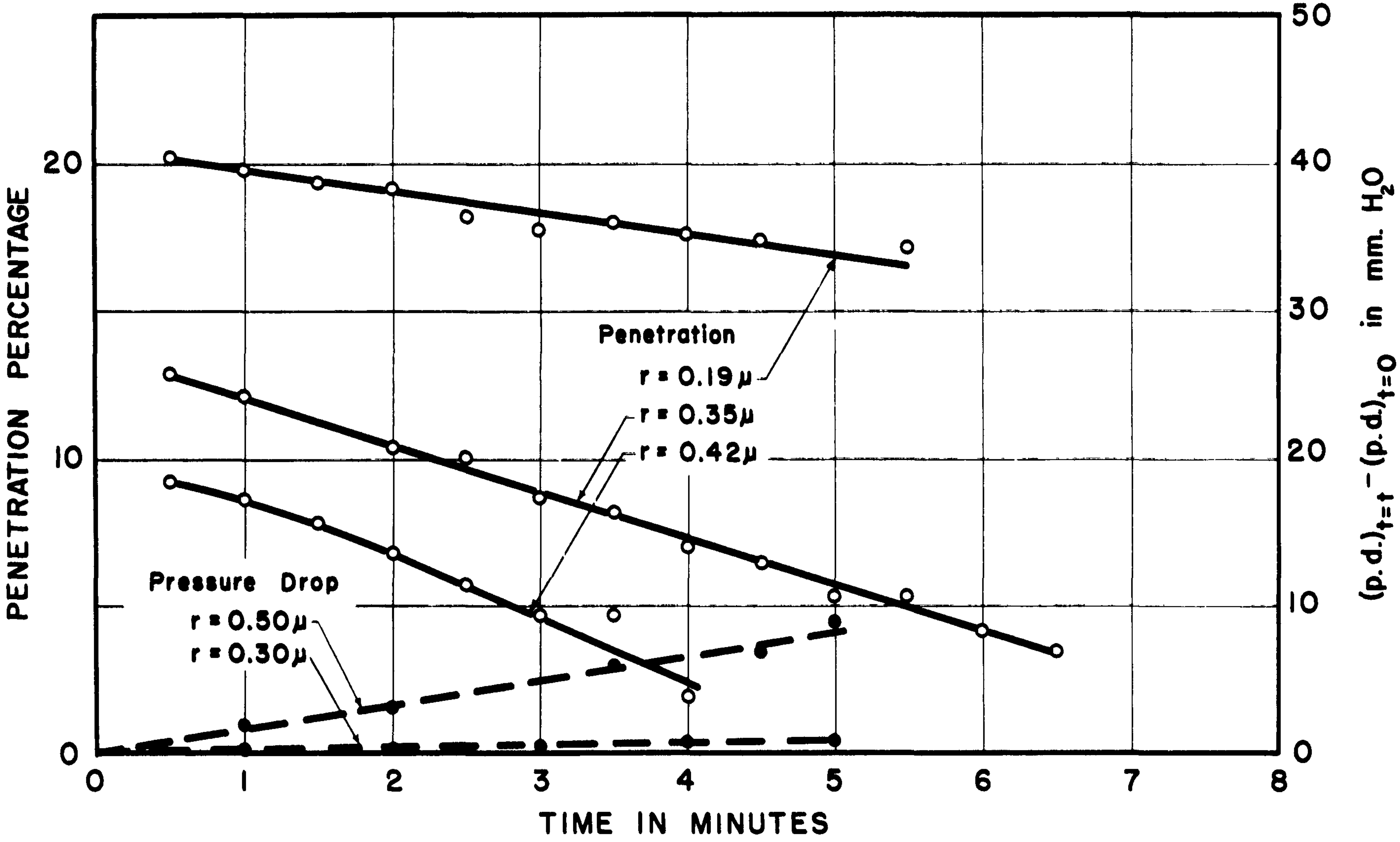

PENETRATION PERCENTAGE
0
10
20
0
1
2
3
4
5
6
7
8
TIME IN MINUTES
0
10
20
30
40
50
$(p.d.)_{t=t} - (p.d.)_{t=0}$ in mm. H_2O
Penetration
r = 0.19μ
r = 0.35μ
r = 0.42μ
Pressure Drop
r = 0.50μ
r = 0.30μ

Fig. 5c.7

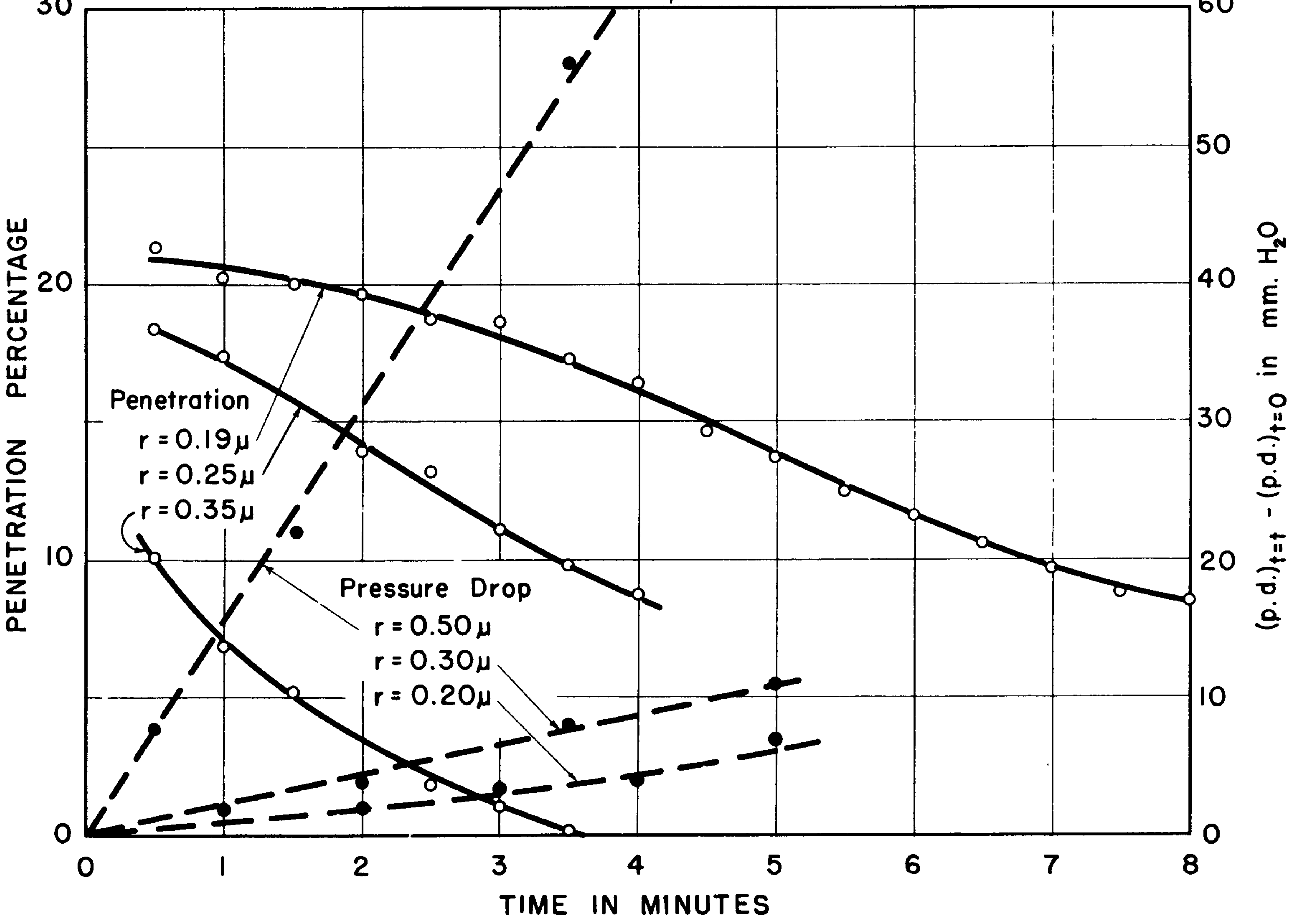

PENETRATION PERCENTAGE
30
20
10
0
(p.d.)$_{t=t}$ - (p.d.)$_{t=0}$ in mm. H_2O
60
50
40
30
20
10
0
Penetration
r = 0.19µ
r = 0.25µ
r = 0.35µ
Pressure Drop
r = 0.50µ
r = 0.30µ
r = 0.20µ
0
1
2
3
4
5
6
7
8
TIME IN MINUTES

Fig. 5c.8

85

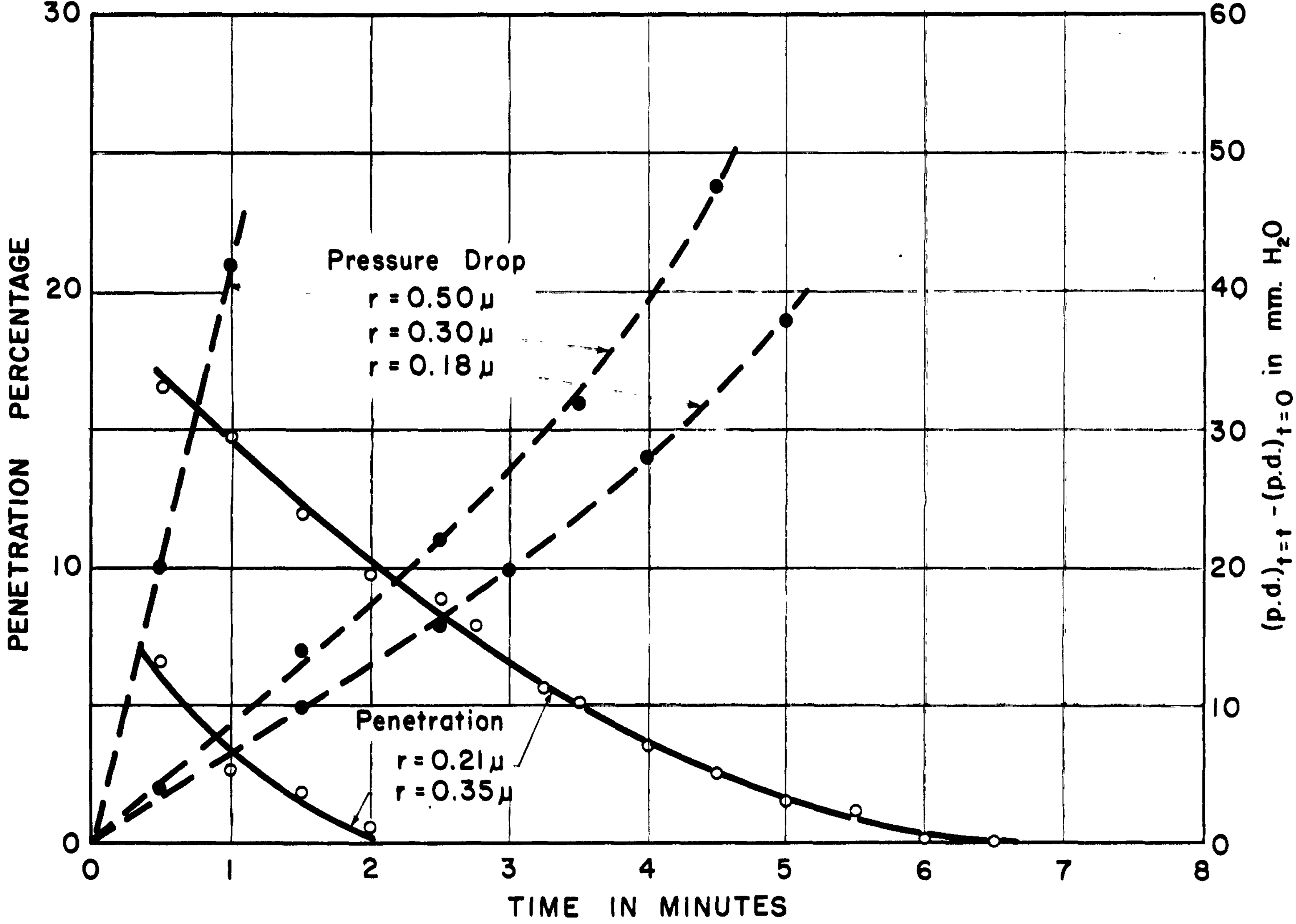

30
20
10
0
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
PENETRATION PERCENTAGE
TIME IN MINUTES
(p.d.)$_{t=t}$ - (p.d.)$_{t=0}$ in mm. H$_2$O
Pressure Drop
r = 0.50 μ
r = 0.30 μ
r = 0.18 μ
Penetration
r = 0.21 μ
r = 0.35 μ

Fig. 5c.9

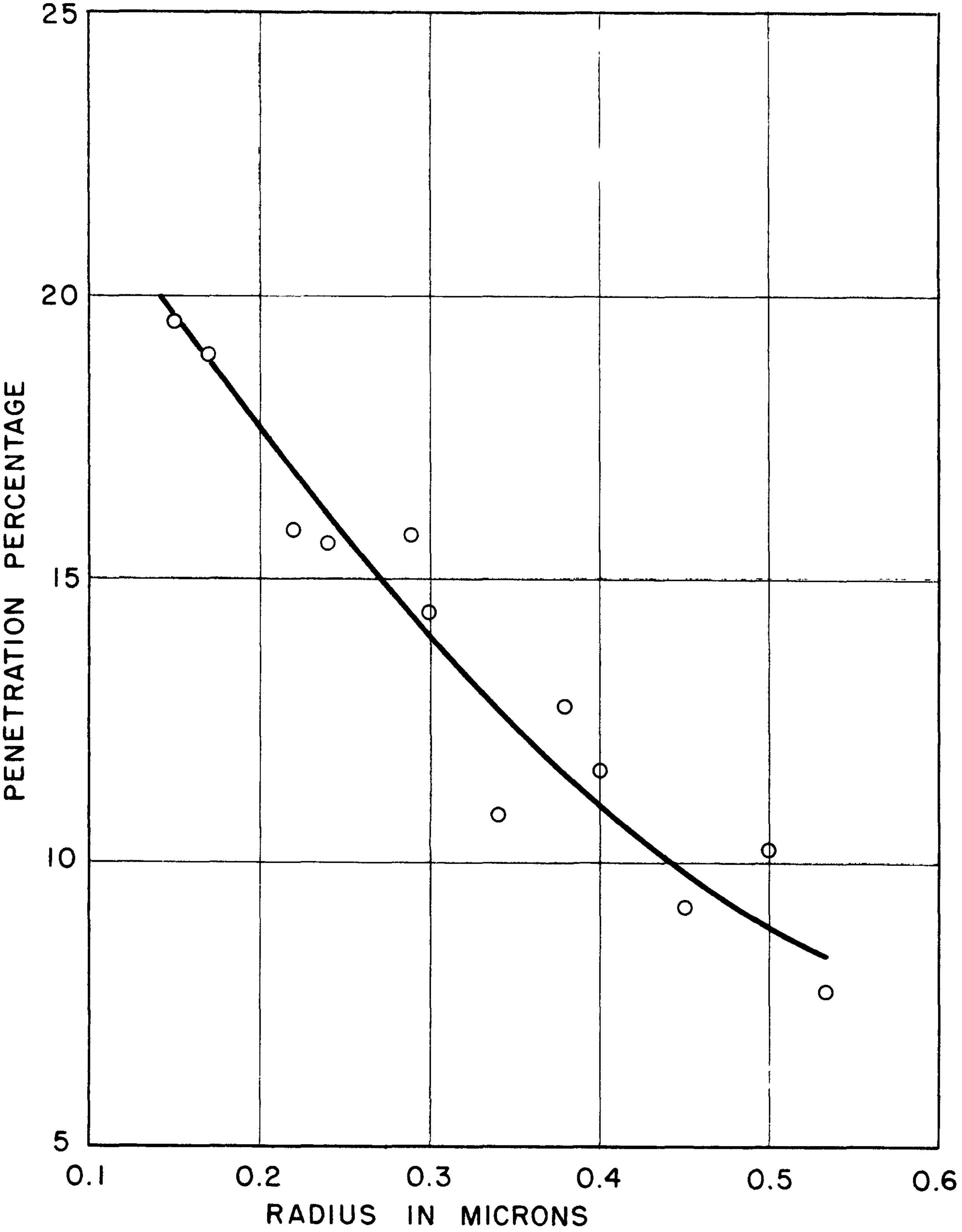

25
20
15
10
5
PENETRATION PERCENTAGE
0.1
0.2
0.3
0.4
0.5
0.6
RADIUS IN MICRONS

Fig. 5c.10

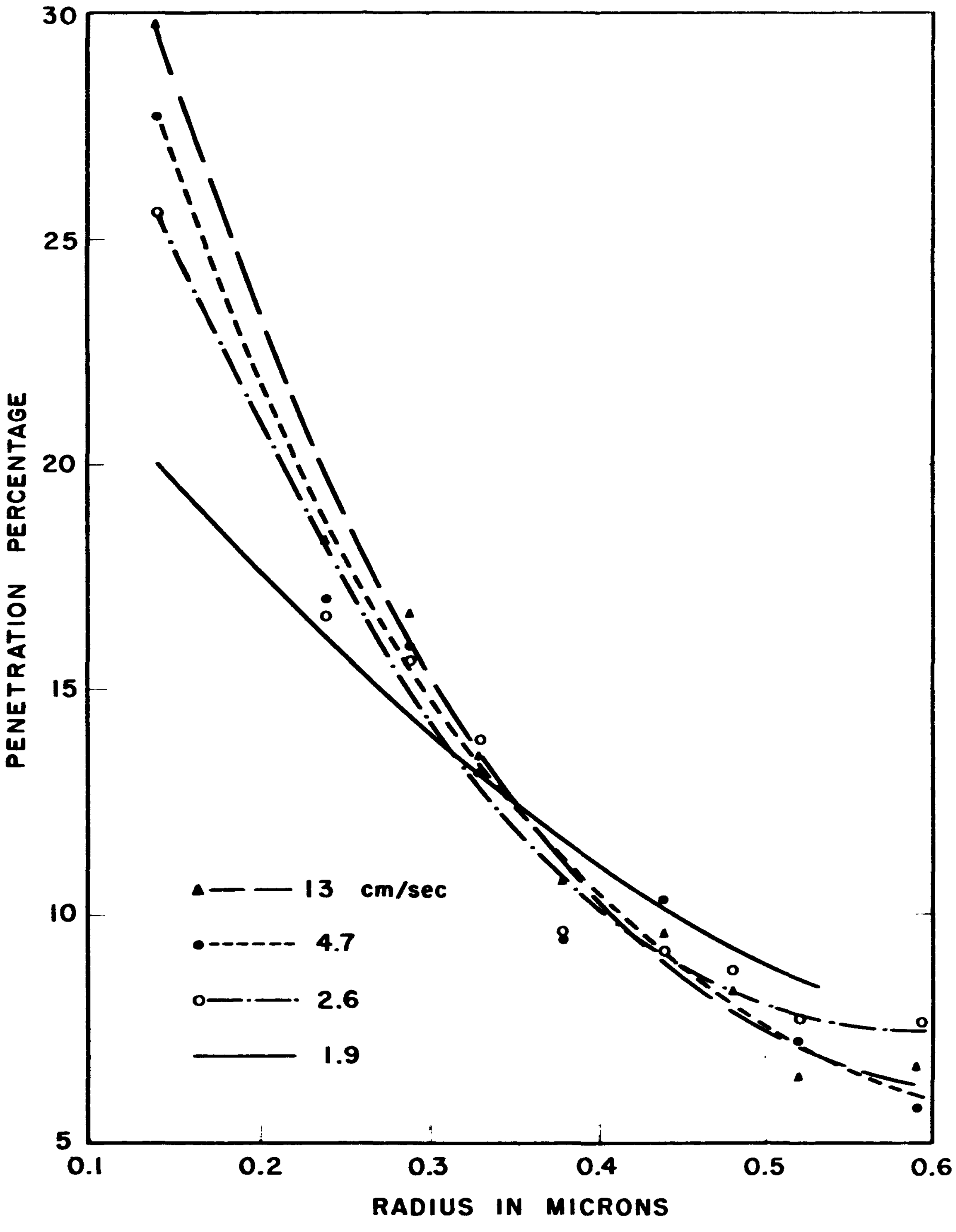

30
25
20
15
10
5
PENETRATION PERCENTAGE
0.1
0.2
0.3
0.4
0.5
0.6
RADIUS IN MICRONS
▲ 13 cm/sec
● 4.7
○ 2.6
1.9

Fig. 5c.11

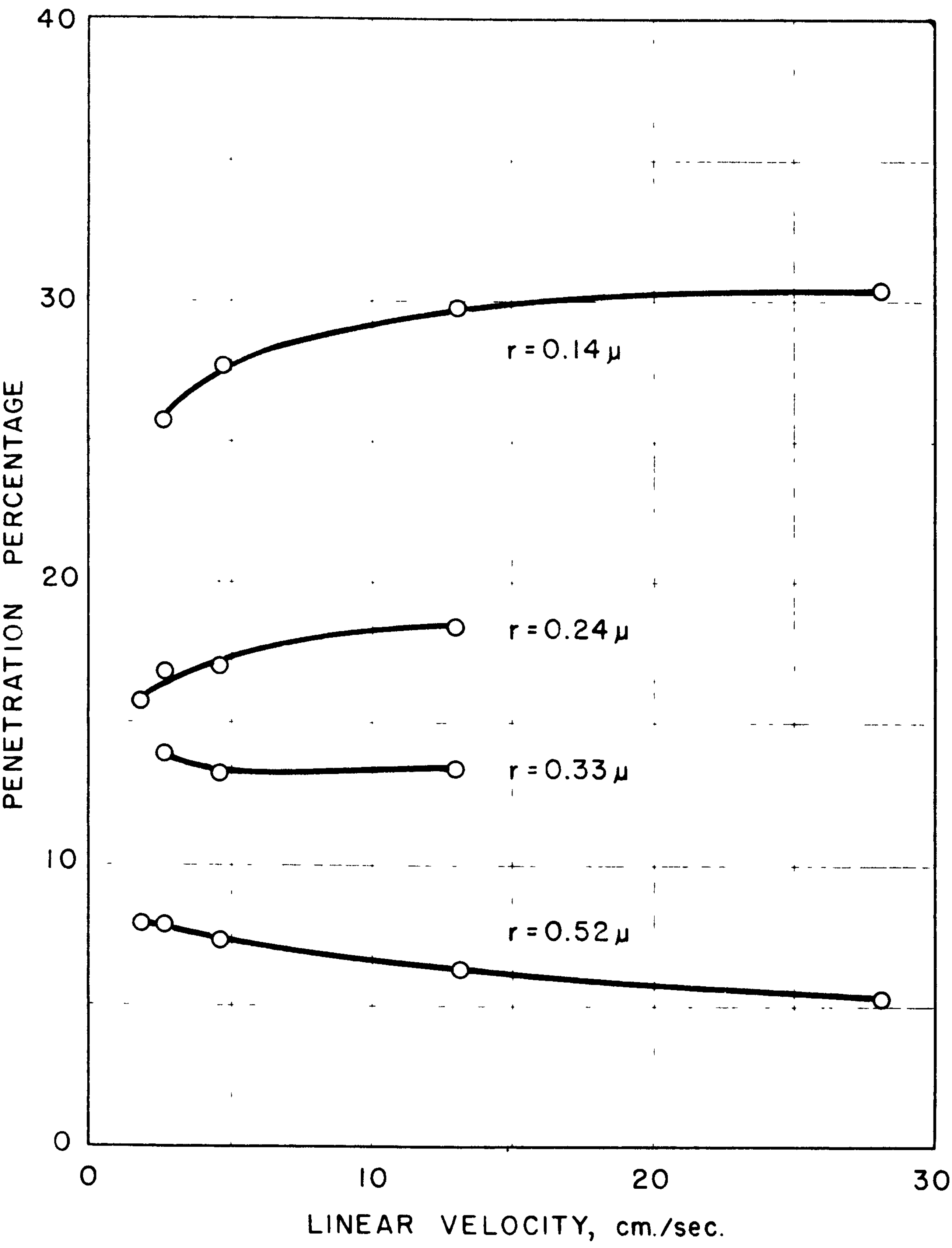

40
30
20
10
0
PENETRATION PERCENTAGE
0
10
20
30
LINEAR VELOCITY, cm./sec.
r = 0.14 μ
r = 0.24 μ
r = 0.33 μ
r = 0.52 μ

Fig. 5c.12

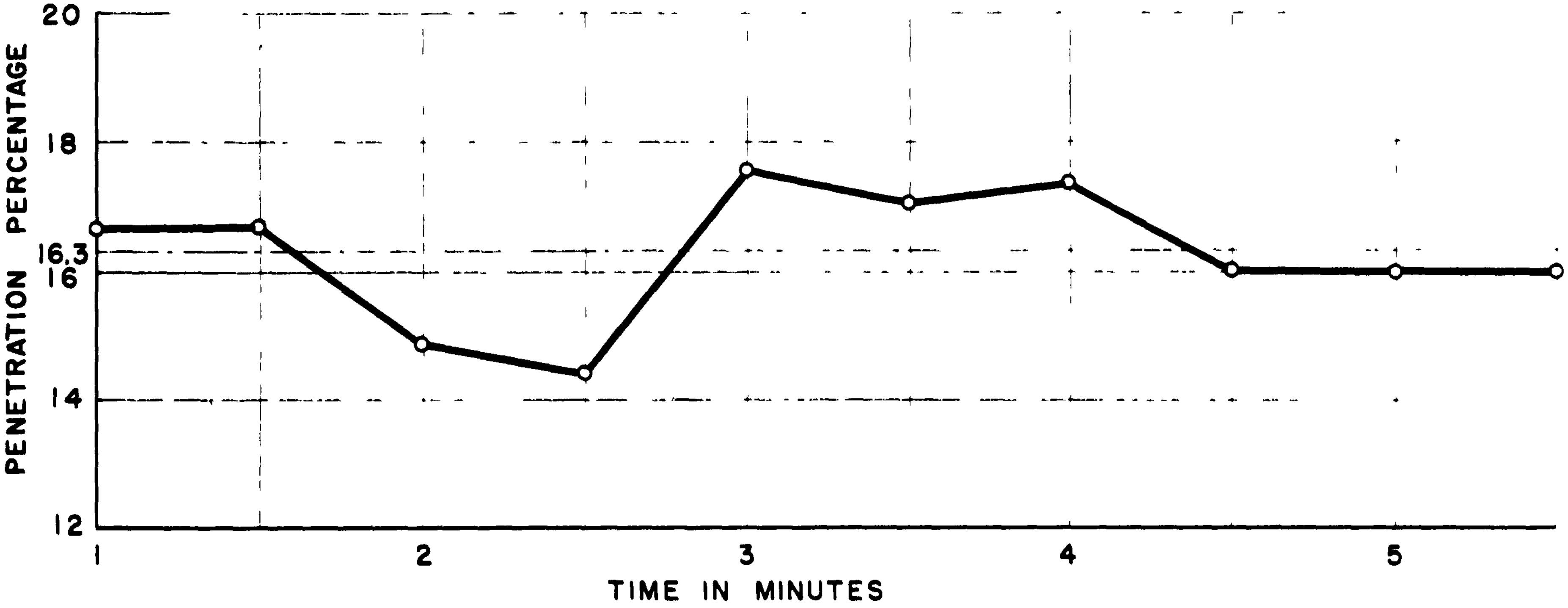

PENETRATION PERCENTAGE
20
18
16.3
16
14
12
1
2
3
4
5
TIME IN MINUTES

Fig. 5c.13

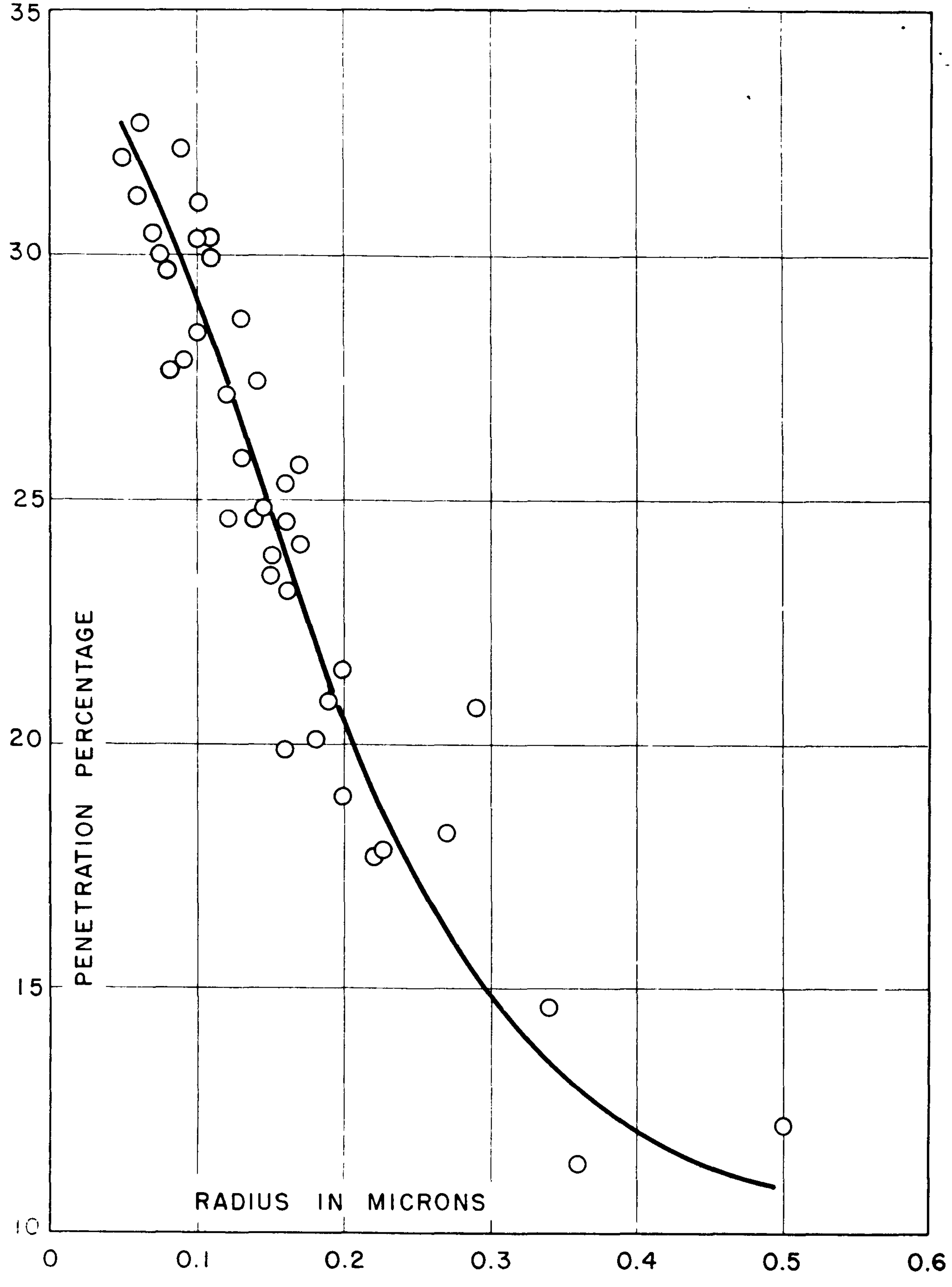

35
30
25
20
15
10
PENETRATION PERCENTAGE
RADIUS IN MICRONS
0
0.1
0.2
0.3
0.4
0.5
0.6

Fig. 5c.14

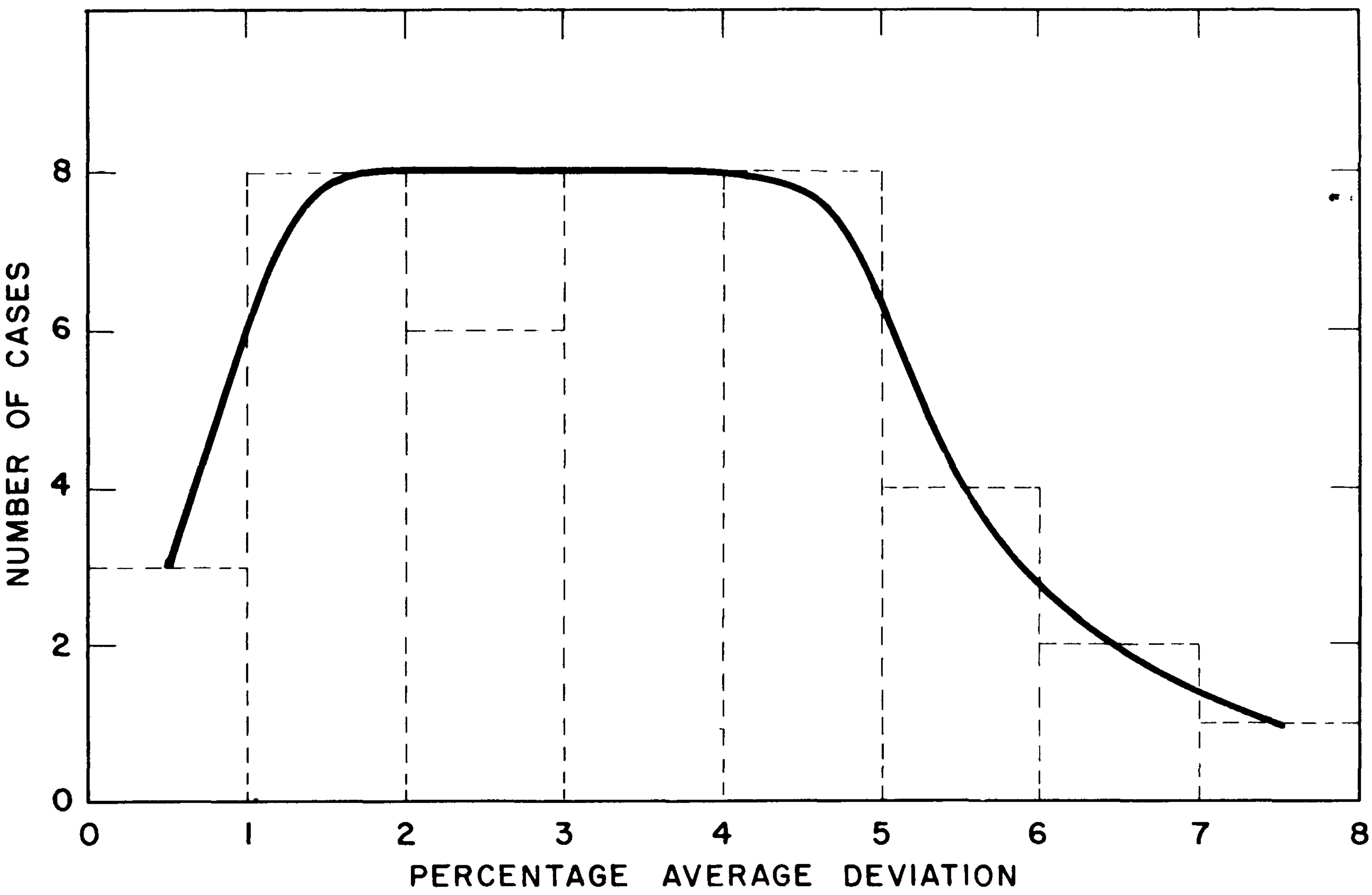

NUMBER OF CASES
0
2
4
6
8
0
1
2
3
4
5
6
7
8
PERCENTAGE AVERAGE DEVIATION

Fig. 5c.15

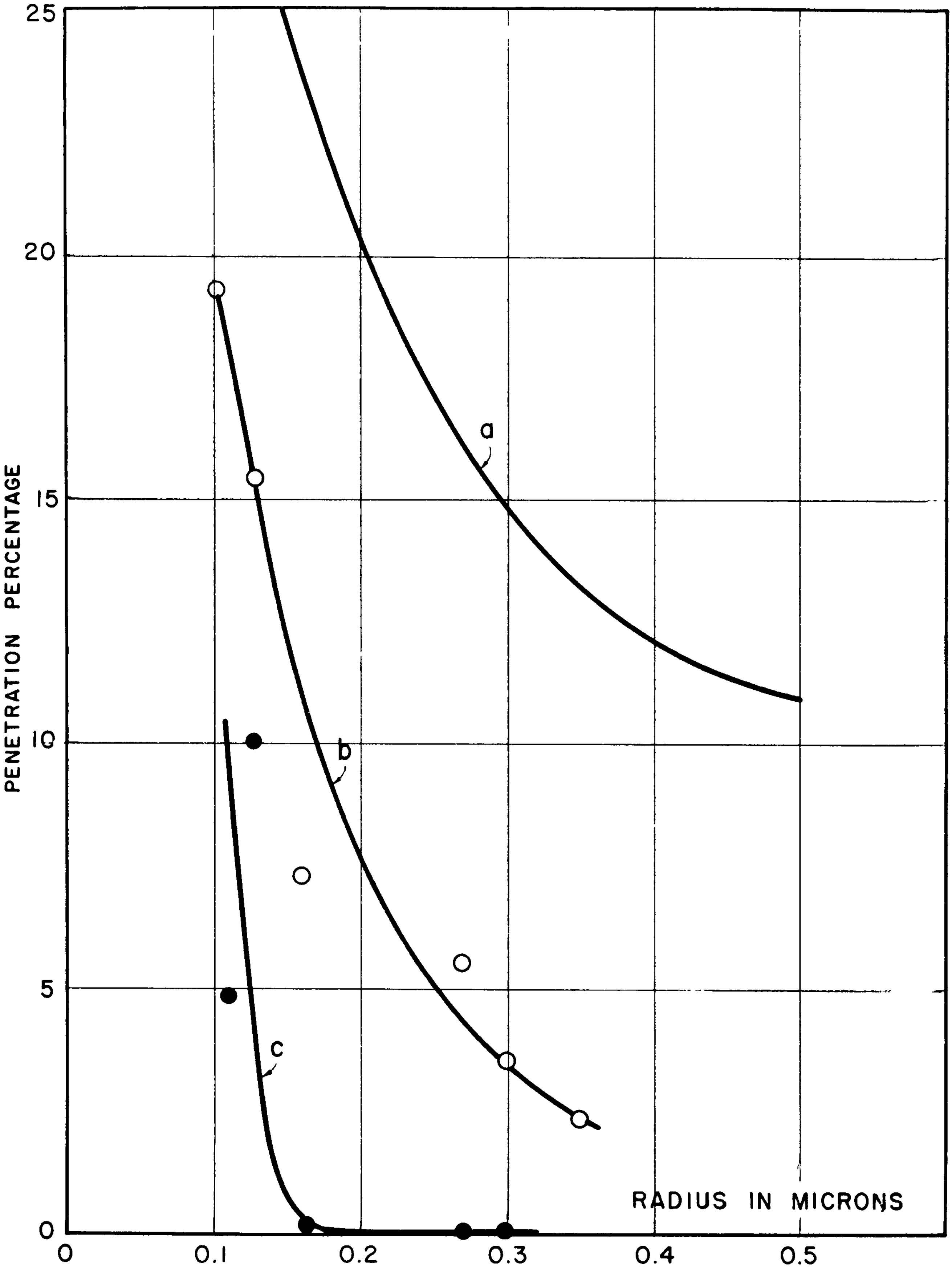

PENETRATION PERCENTAGE
25
20
15
10
5
0
0
0.1
0.2
0.3
0.4
0.5
RADIUS IN MICRONS
a
b
c

Fig. 5c.16

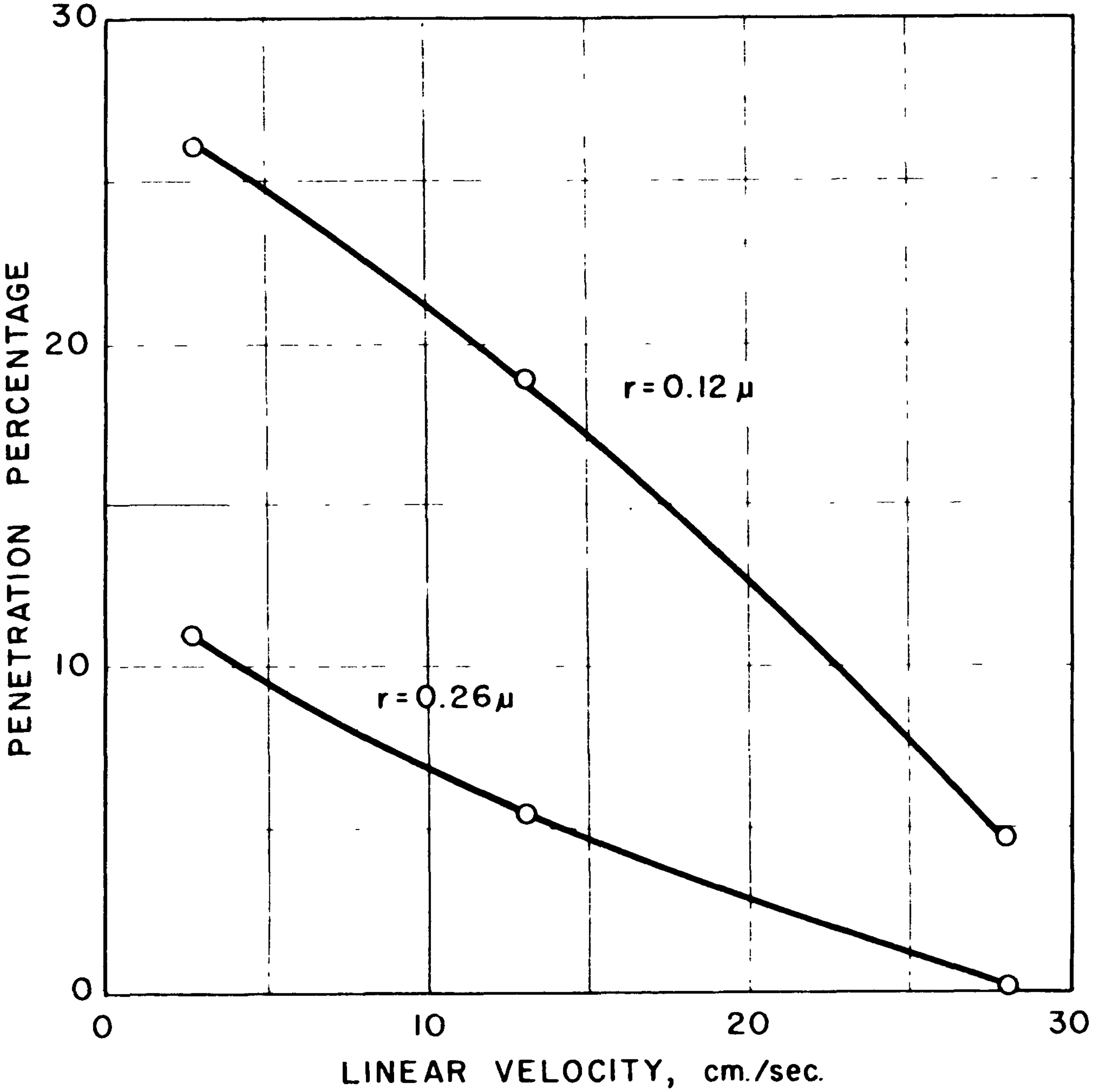

30
20
10
0
0
10
20
30
PENETRATION PERCENTAGE
LINEAR VELOCITY, cm./sec.
r = 0.12 μ
r = 0.26 μ

Fig. 5c.17

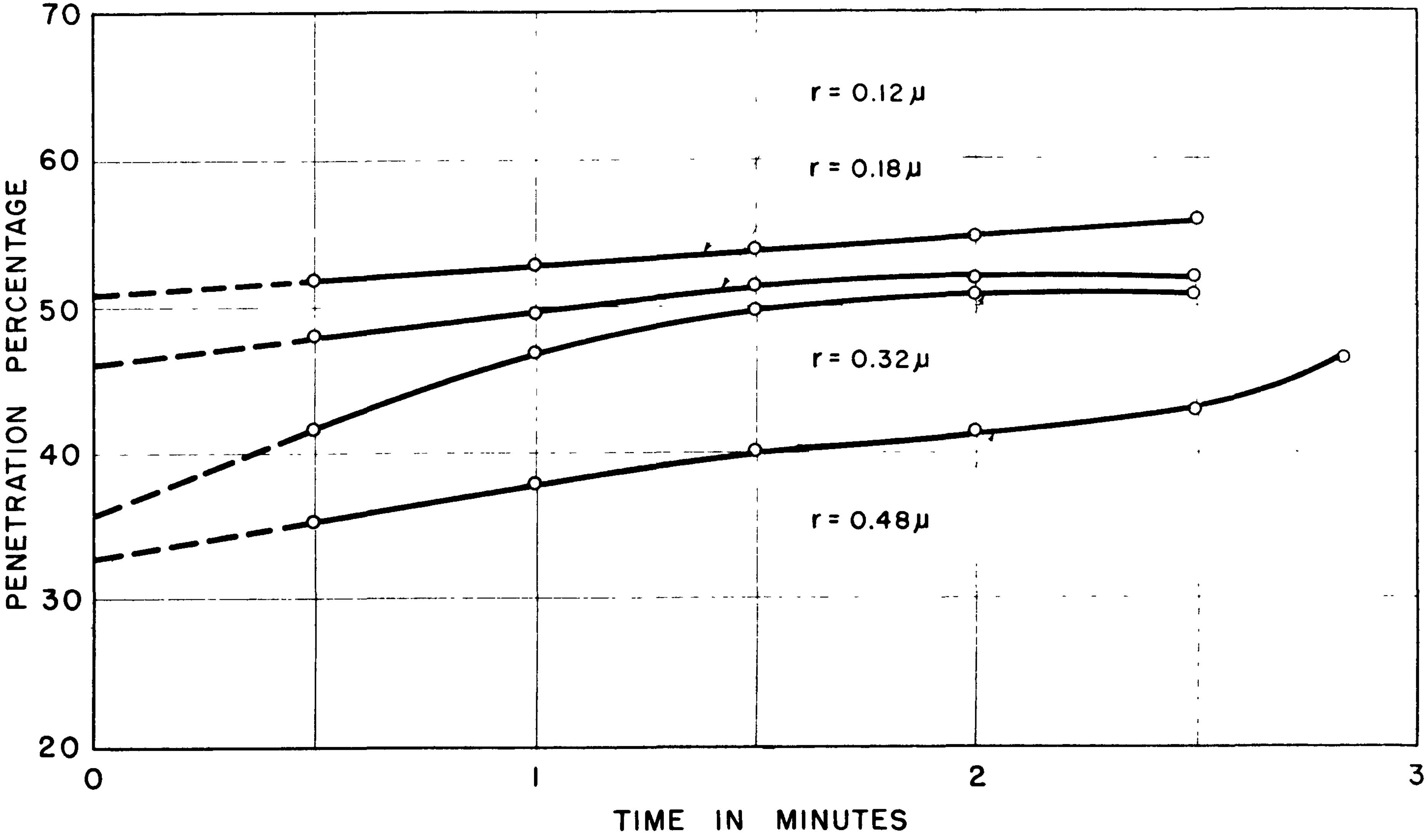

70
60
50
40
30
20
PENETRATION PERCENTAGE
0
1
2
3
TIME IN MINUTES
r = 0.12 μ
r = 0.18 μ
r = 0.32 μ
r = 0.48 μ

Fig. 5c.18

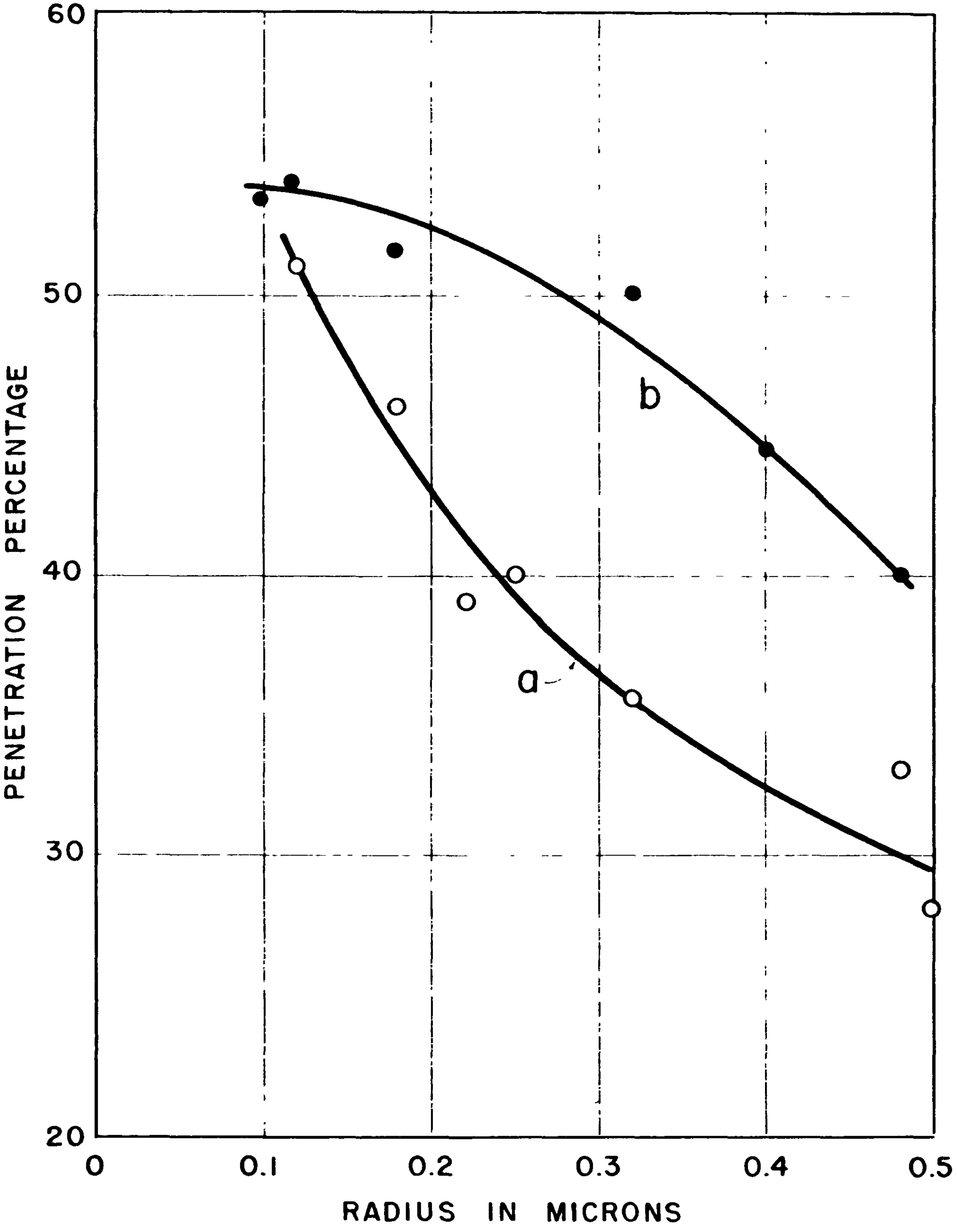
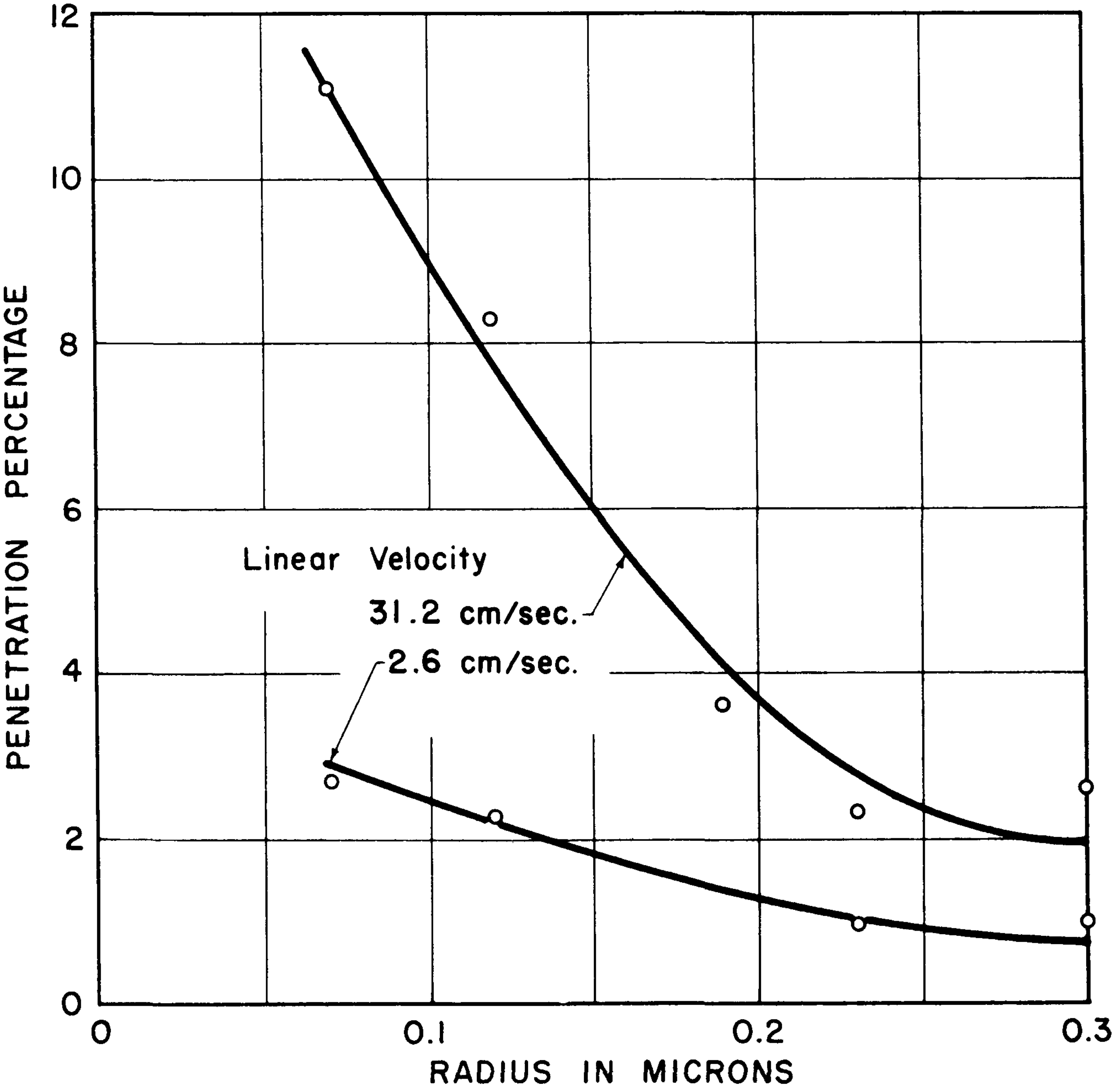

60
50
40
30
20
PENETRATION PERCENTAGE
0
0.1
0.2
0.3
0.4
0.5
RADIUS IN MICRONS
b
a

Fig. 5c.19



12
10
8
6
4
2
0
PENETRATION PERCENTAGE
Linear Velocity
31.2 cm/sec.
2.6 cm/sec.
0
0.1
0.2
0.3
RADIUS IN MICRONS

Fig. 5c.20

SOURCES OF ERRORS IN FILTRATION MEASUREMENTS

1. Production of Aerosol and Particle Radius Determination.

a. Production of aerosol.

The variation of the filtration characteristics with the particle radius constitutes a primary part of our studies. A monodisperse aerosol is required. All factors that decrease the degree of monodispersity will render the determination of the particle radius less reliable and are consequently sources of errors.

These factors are: fluctuations in boiler temperature, air flow rate through the generator, and nuclei emission for a given nuclei source current.

All of these sources of errors are minimized in the following manner: The generator is allowed to come to equilibrium several hours before starting a filtration experiment. A frequent check of flow rate, nuclei current and boiler and reheater temperatures is made during the experiment. The thermoregulator provides an improved temperature control (see Section III, Production of Aerosols).

b. Measurement of Particle Radius.

The determination of the particle radius of monodisperse aerosol by growth, polarization and Higher Order Tyndall Spectra (H.O.T.S.) methods is subject to error. For detailed discussion on this subject see "Sources of Errors" in the Growth Method Section (IV) of this Report.

2. Linear Velocity.

All the filtration experiments were performed for a linear velocity defined by the aerosol flow rate and by the area of the filter. Variations in linear velocities are eliminated by controlling the flow rate. Variation of half a division on each of the two flow gauges used will cause a ± 0.06 cm/sec change in the 2.56 cm/sec velocity, when filter of 13 cm^2 area is used.

In the case of filters with large pressure drop, the control of flow rate is rendered difficult by the back pressure. The flow drops as soon as the filter is connected to the line and has to be raised in order to again reach the desired linear velocity. This frequent change of flow causes a decrease in the degree of monodispersity. It was only in the case of the W-2 filter of 1.19 cm^2 area that the back pressure was observed and the necessary corrections made.

3. Losses of Aerosol.

All losses and leakages of aerosol along the rubber tubes, the glass cells (see Fig. 1, Sec. V.a), and other parts of the filtration circuit should be eliminated. Leakage in the filter holders or losses in the part of the circuit between the two glass cells directly affect the penetration percentage value. In the case of solid aerosols like stearic acid, precipitation at constrictions and on the inner walls of the rubber tubes becomes especially troublesome for large particle sizes. The use of wide and short tubing plus the elimination of all constrictions and sharp edges in the glass cells will greatly diminish the errors introduced by losses.

4. Filtration Measurements.

a. Aerosol Stream.

All foreign particles should be eliminated from the stream. This is easily achieved by drying the air and filtering it before it enters the generator. It is also important to check whether the aerosol has swept out any of the filter particles or loose fibers.

b. Light Source and Measuring Instruments.

The following experiments were performed in order to study the stability and response of the two penetrometers:

(1) Dilution experiments permit the study and comparison of the behavior of the filtration instruments using light scattered from the aerosol beam without the filter. All the variations due to the differences in properties of various samples of filter are thus eliminated.

(2) Study of fluctuation in the light source.

(3) Constant scatterer: In order to study the performance of the penetrometers, experiments involving materials yielding constant scattering were carried out. In this case, both the variations due to the bad reproducibility of the filter samples and fluctuations in the aerosol beam were absent.

(1) Dilution Experiments.

The DOP aerosol coming from the generator at 2 l/m was mixed in a glass flask with dust-free air of the same flowrate. To insure good mixing, the mixture was sent to a second flask. The aerosol diluted by 50% was then used in the dilution experiments. Calibrated Fisher are Porter flowmeters were used. The results of the experiment are shown in Table I.

The Forward Angle Tyndallometer readings (See Section V.b) were first taken for the pure and then for the diluted aerosol. Each value is an average of four readings, the deviation from the average given in the table.

In the case of the 90° penetrometer, the circuit is balanced each time with undiluted aerosol. The quantity, N_2, (see Sec. V.a), is found by passing the mixture through cell B. The results are tabulated and the differences between the reading on the two instruments calculated.

Table I

Dilution Percentage

Particle Size in microns	90° Penetrometer	Forward Angle Tyndallometer		Δ
0.19	49.5			
	48.5			
0.28	49.2	49.7	± 1.2	- 0.5
	50.0	47.5	± 1.4	+ 2.5
	48.3	48.3	.8	.0
	48.5	47.6	.8	+ .9
	48.5	45.9	.4	+ 2.6
	19.6*	18.1*	1.3	+ 1.5
	49.4	50.4	1.2	- 1.0
	56.9*	53.7	1.2	+ 3.2
	48.9	43.9	0	+ 5.0
	53.2	52.7	1.0	+ .5
	62.8*	63.0*		- .2
0.33	48.8	47.0	± 0.5	+ 1.2
	50.5	50.4	.1	+ .1
	48.6	47.7	.1	+ .9
	49.3	48.0	.3	+ 1.3
	46.5	47.6	.6	- 1.1
	45.8	45.3	.3	+ .5
0.36	47.8			
	45.8			
	46.8			
	50.3			
	49.5			
	49.5			

* rejected

(a) 90° Penetrometer

A total of 25 dilution experiments was performed to test the instrument. The average dilution percentage calculated is 48.8 ± 1.2 (or 48.8 ± 2.5%). Three readings were rejected. Notice that for CC-5 the average deviation averaged over various samples of filter varies between 0 and 2.5, while it varies between 4 and 8 for W-2 (See Fig. 15, Section V.c). This shows that the CC-5 does not introduce appreciable variation.

(b) Forward Angle Tyndallometer (F.A.T.)

Out of the 15 dilution experiments performed to test the instrument, two were rejected due to the large deviation from the average. The average dilution percentage is 48.4 ± 2.0 (or 48.4 ± 4.1%).

(c) Comparison of the results obtained with the two instrument

The average dilution percentages of 48.4% for F.A.T. and 48.8% for the 90° Penetrometer show good agreement between the two instruments.

The average difference between the corresponding readings on the two instruments is 1.35% dilution.

Out of 25 dilution experiments with the 90° Penetrometer and 15 for F.A.T., only 6 and 5 respectively show dilution % $\ngtr$ 50. There seems to be a constant error which appears simultaneously in the readings on both instruments which can be accounted for by losses of aerosol particles in the diluting process as discussed above.

The relative average deviations are 2.5% and 4.1% for the 90° Penetrometer and F.A.T., respectively. This is understandable in view of the fact that the 90° Penetrometer uses a differential measuring circuit and the F.A.T. measures an absolute intensity. Slight changes in the aerosol concentration due possibly to a non-uniform nuclei emission will affect the F.A.T. much more than the 90° Penetrometer.

Fluctuations in the air or aerosol flows constitute an error in the original dilution percentage. A variation of half a division on the flow gauge can be observed and corrected. For 50% dilution, the maximum possible error due to change in flow rates through the three flow gauges is ± 1.2 of the dilution value.

(2) Light Source.

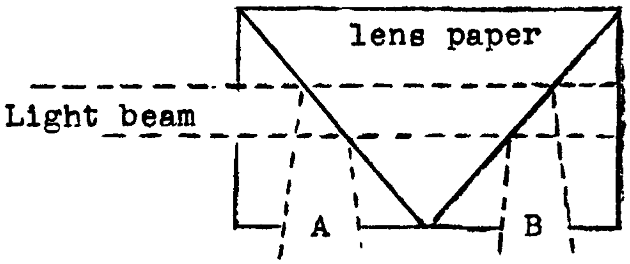
The intensity output of the light source used with the 90° Penetrometer was studied for constancy of illumination. A six-volt headlight bulb is fed by a regulated d.c. voltage from the power supply of the penetrometer. A Photovolt (Model 512) photometer was used to measure the intensity of the light source over periods of ten minutes, at consecutive hours.

The light intensity increases slowly in the course of an afternoon and oscillates about a mean value in any interval of 10 minutes by a factor of 2%. The differential circuit used in the 90° Penetrometer should be independent of fluctuations of light source; however, because the two photomultipliers are used under different sensitivity conditions, an equal change in light intensity in the two cells does not imply an equal change in photocurrent output from the two photomultipliers.

The same light source fluctuations are much more significant in the F.A.T. where absolute measurements are made.

(3) Constant Scatterer.

Stability and reliability of the penetrometers were studied by the use of constant scatterers made of lens papers set in the scattering cell in the following manner:



Pinholes were made in the first lens paper in order to equalize the light falling on the two photomultipliers which were operated in the same sensitivity range as when used in actual penetration measurements. The transmissions of neutral light filters of known optical density were measured with the 90° Penetrometer circuit by filtering the scattered light beam in cell B. This procedure reproduces the conditions of measurement of filtration as they are performed with aerosols.

The transmissions of the neutral light filters were also measured using a constant scatterer in the F.A.T. However, in this experiment, the direct beam was filtered instead of the scattered beam as in the 90° Penetrometer. But as the scattered light from a constant scatterer is a linear function of its illumination, no appreciable error is committed here.

The transmission measurement results are given in the following table:

TABLE II

90° Penetrometer	Forward Angle Tyndallometer
42.4 ± 1.6 (or ± 3.8%)	42.0 ± .4 (or ± 0.9)
23.3 ± 0.3 (or ± 1.3%)	22.4 ± .2 (or ± 0.9)
7.5 ± 0.6 (or ± 8.0%)	7.0 ± .04 (or ± 0.6)

The absolute transmission of the filters was measured with a Beckman spectrophotometer, and integrated over the wavelength range limited by the Corning Filter No. 6850, used in the incident light beam.

Stability. It is seen that the variations around the average values are much larger for the 90° Penetrometer than for the F.A.T. The averages given above are for a series of at least 25 experiments on each filter. During this series of experiment, the 90° Penetrometer sometimes showed good and some other times very poor stability.

The accuracy of the penetration measurements is shown to be impaired by an error due to fluctuations in the electronic circuit itself.

Reliability. The per cent errors in transmission measurements obtained with the 90° Penetrometer and the F.A.T. were calculated assuming the Beckman results exact.

Per cent error vs. transmission per cent

% transmission	90° Pen.	F.A.T.
47.8	- 11.3%	-12.13%
23.6	- 1.27%	- 5.08%
6.7	+ 11.9%	+ 4.48%

It is seen that a constant error is brought in the penetration measurements, the magnitude of which seems to depend on the per cent penetration. Notice that the 50% dilution experiments show a constant error of only 2.5%. However, it should be noted that in the transmission measurements, the light intensity falling on photomultiplier B is only dependent on the transmission per cent of the neutral light filters whereas in the penetration experiments, the light intensity falling on photomultiplier B is not only dependent on the per cent penetration, but also on the particle size of the aerosol. Thus the light intensity range is much wider in the transmission measurements. Hence, if the fact that large penetrations are encountered for small sizes and small penetrations for large particle sizes, reduces the illumination range to a small value where the phototube response is linear, the actual penetration error might not be as large as the transmission measurements show.

5. Conclusions.

From these experiments the conclusion can be reached that the maximum possible error is no more than 10% of the penetration percentage as shown by the transmission measurements, and the probable error is of the order of 2 - 4% of the penetration percentage as shown by the dilution experiments.

INVESTIGATION OF PRESSURE DROP ACROSS FILTERS

This portion of the report concerns itself with the examination of the pressure drop across the filters and the importance of this parameter in the development of a theory of filtration. The latter will be treated fully in Section VII. A resume of the chronological contributions to the theory of the flow of viscous fluids is given with emphasis on results, pertinent to the filtration problem. Important conclusions, regarding the type of flow present and the effect of pinholes, follow from this investigation.

1. Introduction.

The study of the pressure drop across filters is valuable in several respects. First of all, for physiological reasons, the pressure drop in gas mask canisters must be kept below a certain limit. Edgewood Arsenal set the permissible pressure drop through canisters at 3.5 cm of water for a flow of 85 liters per minute through an area of about 400 cm^2 (1). Thus, filters, which show a pressure drop larger than this limit will be undesirable for canisters no matter how good their other properties are. Secondly, a study of the pressure drop as a function of the linear velocity of the aerosol reveals whether the flow in the pores of the filters is laminar or turbulent. Lastly, it might be mentioned here that the drop in pressure across a filter yields some information regarding the type of filtering action present. If the pores of a filter are of a size of the same order of magnitude as the aerosol particles, the pores would become clogged with an accompanying increase in pressure drop. Such a filter, operating exclusively on screening action, is useless for aerosols because of this block to air flow. It is therefore evident that a study of the pressure drop is an easy means of checking the operation of a filter.

2. Scope of This Investigation.

A study was made of the pressure drop across the following filters:

a. Chemical Corps No. 5 (CC-5)

A majority of the experiments were performed on this paper because of its high reproducibility.

b. Whatman No. 2 (W-2)

c. Fiberglass filters
Handmade filters from A.D. Little Co.
Owens-Corning Glass Corp. filter.

---

1. Langmuir, I., Nat. Def. Comm., Office of Scientific Research and Development, OSRD No. 865, Serial No. 353, Part IV, p. 23.

d. A.E.C. No. 1 (Roll 13)

Filter, used in the standard DOP tester, shows highly efficient filtration characteristics.

For a detailed discussion of the structure of these filters, see Section VII.

3. Experimental Details.

The brass filter holders, described in Section V, were used in the pressure drop experiments to vary the aerosol linear velocity. The apparatus was modified, however, by the insertion of glass adapters of different design to insure laminar flow in the holder. These filter holders with their new adapters are pictured in Fig. 6.1. An extreme form of the original adapter was used to produce turbulence in the holder for special studies discussed later. This arrangement is shown in Fig. 6.4.

The air, used in the experiments, was taken from the compressor outlet, dried through a $CaCl_2$ tube, and passed through Fischer-Porter flow gauges to the adapter and filter holder, as shown in Fig. 6.2. For regulated, steady flow a cylinder of water was used for overflow of the air at the compressor outlet. The pressure drop across the filter was measured with a nitrobenzene manometer. The flowmeters were calibrated with a Precision Wet Tester (Precision Scientific Co., Chicago).

For the case where turbulence exists in theholder, it is necessary to run a blank determination to find the pressure drop in the holder without a filter in order to deduct this from the total drop obtained with the filter in place. In this manner the pressure drop across the filter alone may be found. While this procedure is required for every measurement under turbulent conditions, it is advisable to run such a check at the beginning of any set of pressure drop determinations to insure valid results.

4. Results.

The data from these experiments are plotted in Fig. 6.3 for CC-5, W-2, and A.E.C. No. 1 filters. Each point represents the arithmetic average of the results for 3-5 samples of filter paper. As a check upon the validity of the results for the four different holders, it was found that for a particular sample a given linear velocity yielded the same pressure drop in all four holders. It was necessary to perform more experiments upon the holders of smaller areas since in these inhomogeneities and minute pinholes in the filters become more important and cause appreciablefluctuations.

The major result of this study is that the pressure drop varies directly as the first power of the linear velocity for the filters investigated. The significance of this will be discussed later.

The effect of turbulent flow in the holder upon the laminar flow conditions in the filter pores was studied with the apparatus of Fig. 6.4, which produces turbulence in the holder for all but the very smallest velocities. The data obtained are listed in Table I, together with those found with the standard glass adapters. No pressure drop was observed with the latter with the filter absent. The agreement of the results indicates that turbulence in the holder apparently does not affect the pressure drop across the filter since both techniques yield the same value for the filter alone.

Table I

Rates in liters/min.	Pressure drop in cm nitrobenzene measured with: glass adapter	Apparatus -Fig. 6.4
0.42	0.06	0.04
1.22	0.10	0.06
2.05	0.18	.16
3.10	0.27	.30
4.24	0.39	.39
5.25	0.51	.49
6.7	0.66	.60
7.6	0.72	.72
8.6	0.80	.78
9.65	0.93	.90

5. Theoretical Considerations.

An extensive historical review of the viscous fluid flow through porous media has been given recently by Iberall[2]. Some of the important equations will follow, together with some results of other investigators in this general field of viscous fluids. D'Arcy in 1856 first expressed the pressure drop as a function of the velocity of flow of a viscous fluid through a porous medium in the equation

---

[2] Iberall, A.S., J. Res. Nat. Bur. Stds. 45, 398 (1950).

$$\frac{A\Delta p}{lF} = c\mu \qquad (1)$$

where Δp = pressure drop between the ends of a cylindrical plug of the porous medium

l = length of the plug

A = cross-sectional area of the plug

F = fluid flow through the plug in volume per unit time

μ = absolute viscosity of the fluid

c = constant.

Iberall also describes the extensions of this equation by Dupuit and Slichter to include the porosity of the medium. Following the concept of Schiller of a mean hydraulic radius and Blake's work on the flow through granular beds, Kozeny in 1927 derived the equation

$$\frac{\Delta p}{l} \cdot \frac{A}{F} = c' \frac{\mu s^2}{\varepsilon^2} \qquad (2)$$

where s is the surface per unit volume of a porous medium in contact with the fluid ($s = \varepsilon/r$) and the porosity, ε, is the ratio of the volume occupied by voids available to the fluid in a porous medium to the total volume. The mean hydraulic radius, r, may be defined as the ratio of the volume of a medium filled with a fluid to the surface within the medium in contact with the fluid.

The Kozeny equation was modified by P.C. Carman[3] to the form

$$\frac{\Delta p}{l} \; \frac{A}{F} = k \frac{\mu s_o^2 (1 - \varepsilon)^2}{\varepsilon^3} \qquad (3)$$

in which the value of k was found to be about 5 for granular materials of low porosities and s_o is the "specific" surface exposed to the fluid (surface exposed to the fluid per unit volume of solid material). Eq. (3) was applied to fibrous materials by Wiggin, Campbell and Maass[4] and by Fowler and Hertel[5].

---

[3] Carman, P.C., J. Soc. Chem. Ind. 57, 225 (1938); 58, 1 (1939).

[4] Wiggin, E., Campbell, W., Maass, O., Can. J. Res. 17, 318 (1939).

[5] Fowler, J., and Hertel, K., J. App. Phys. 12, 503 (1941).

The Kozeny, or hydraulic radius, theory was developed for all porous media since the only possible variations lie in the shape and configuration of the fluid path or in the shape and orientation of the material particles and these differences are taken into account in the constant k. Langmuir[1] shows how this constant varies with the geometrical construction of a filter. According to Iberall, it appears that this theory has a limited range of applicability since data on fibrous materials, obtained by Sullivan in 1942, showed a breaking down of the theory at high porosities.

The theory of viscous drag offers a different approach to the problem. Emersleben[6] in 1925 treated mathematically the hydrodynamic problem of the viscous drag of a fluid on a certain array of parallel fibers. In 1928, Burke and Plummer obtained a law for the dependence of permeability of a porous medium on its porosity by using the drag on spheres. Although data at that time seemed to support the hydraulic radius theory, the most recent experiments on materials of high porosity seem to verify that of viscous drag. In reality, probably nether theory is entirely correct but each will have a limited range of application.

Langmuir utilized the viscous drag concept to calculate the flow resistance as a function of the drop in pressure through the filter, analogous to the electrical case of Ohm's Law. He considered the simplest possible hypothetical filter model, having an evenly spaced cylindrical fiber structure. A further simplification was made by selecting the axes of the fibers parallel to the direction of flow of the fluid. The volume of the filter is divided into a honey-comb of hexagonal prisms, each containing one coaxial fiber. Since the velocity of the viscous gas is zero at the surface of the filament, the velocity distribution near this surface is unaffected by a change of prism to a cylinder of equal cross-section, thereby reducing the problem to that of laminar flow of gas through the space between two long coaxial cylinders of different diameters.

The quantity, β, the fraction of the filter volume occupied by the fibers, is defined as

$$\beta = (r_F/r_1)^2 \qquad (4)$$

where r_F is the radius of the fiber and r_1 is the radius of a cylinder having the same cross-sectional area as that of a hexagonal prism of the filter model.

If, analogous to Ohm's Law in the electrical case, the resistance, R, is defined as

---

[6] Emersleben, O., Physik. Z. 26, 601 (1925).

$$R = \frac{p_A \Delta_p}{F_p} \quad \text{, in which} \tag{5}$$

p_A = arithmetic average of pressures at both ends of the tube pressure drop

F = flow rate (vol./sec.)

p = actual pressure at any point along tube,

then, following the treatment of Langmuir, the resistance becomes

$$R = 4 \mu l \beta \phi / A r_F^{\,2}$$

where μ = viscosity of gas

A = area of filter

$\phi = 1/(- \ln \beta + 2\beta - \beta^2/2 - 3/2)$.

On examination of the theory of the movement of ellipsoids through fluids, Langmuir concludes that the effect of transverse position of the fibers with respect to the direction of flow is to increase the resistance by a factor not greater than 2. He also finds that a random, non-uniform distribution of fibers tends to lower R. Such factors as stranding or non-parallelism of filaments, which give a less uniform fiber distribution, have a net effect of decreasing the resistance. Langmuir estimates the magnitude of changes in resistance produced by altering the cross-section of the fibers by use of Perrin's equation for the forces which act on small ellipsoids moving through viscous media. Calculations show that the resistance offered by a ribbon-shaped filament falls within a few per cent of that of a cylindrical fiber having the same length and area, proving that the perimeter of the cross-section determines the resistance. This viscous drag theory is particularly valuable for materials of high porosity. In this case the resistance to flow can be found by summing the fluid drags on each element. For materials of lower porosities, adjacent elements modify the flow pattern around a particular element, but if this mutual interference effect between particles could be taken into consideration, the drag theory could be applied to all porosities. Such has not been accomplished mathematically with the result that this theory should fail at low porosities.

Iberall considers the permeability of a random distribution of circular cylindrical fibers of the same diameter on the basis of the drag on individual elements. He obtains the result

$$\frac{\Delta p}{l} \frac{A}{F} = \left(\frac{16\mu}{3}\right) \left(\frac{1 - \varepsilon}{\varepsilon d^2}\right) \left(\frac{4 - \ln R}{2 - \ln R} \right) \qquad (6)$$

where R = local Reynolds number = $\frac{v\, d\, \rho}{\mu}$

d = fiber diameter

v = velocity of fluid stream distant from the filament

ρ = fluid density

μ = viscosity of fluid

ε = porosity of medium

In this equation thepressure drop is not strictly proportional to the average linear velocity. The factor which is proportional to the resistivity is

$$\frac{16}{3} \cdot \frac{4 - \ln R}{2 - \ln R} .$$

Since the theories of hydraulic radius and of viscous drag require specific information regarding the structure of the filter, an exact, detailed analysis of the problem cannot be made. Nevertheless, the discussion by Langmuir has indicated that a simplified model of the filter is sufficient to yield significant results regarding the resistance of the filter to fluid flow. Since he has proved a change from longitudinal to transverse flow, or from circular to ribbon-shaped fibers, does not alter the order of magnitude of the resistance, it is possible to consider a filter composed of parallel capillaries for which the analysis of flow of viscous fluids through tubes is applicable. It should be noted that the structure of the actual filter is quite different from this hypothetical case. This treatment will enable the immediate determination of the type of flow through the filter since the results for laminar and for turbulent flow differ so radically.

The basic equation, covering laminar flow of viscous fluids through tubes is known as Poiseuille's Law. Here the pressure drop, Δp, measured between two parallel cross-sections of distance l apart, is given as

$$\Delta p = 8 \mu l v / r^2 \qquad (7)$$

where μ = the viscosity of the medium, r is the radius of the tube, and v is the average linear velocity through the tube. This equation is derived on the assumption that the cross-sections between which the pressure drop is measured are situated sufficiently far from the ends of the tube to avoid end effects. Thus, for laminar flow in the tube the pressure drop is proportional to the first power of the average linear velocity.

Corrections to Poiseuille's Law will now be considered. In 1839, Hagen[7] showed that it isnecessary to add a term in v^2 to the expression for the pressure drop in tubes so that

$$\Delta p = \alpha v + \beta v^2 \tag{8}$$

Poiseuille's Law is actually valid only for long, narrow tubes[8]. Hagenbach[9] in 1860 attributed the term βv^2 to the acceleration of the fluid. When a fluid of approximately zero initial linear velocity is withdrawn from a container through a tube, the pressure drop is

$$\Delta p = 8 \mu v l/r^2 + \rho v^2 \tag{9}$$

(See Reference (10) for example, for a complete discussion.)

For the problem under consideration in this report the gas has an initial linear velocity quite different from zero and some acceleration is experienced by the gas since the effective area of the filter is smaller than the goemetrical area. Although this term is almost completely compensated for when the gas decelerates on leaving the filter, some energy may be dissipated as heat in the pores of the filter. According to Prandtl and Tietjens[10], the parabolic distribution of velocity in the tubes upon which Poiseuille's Law is based is not established immediately when the fluid enters the tube and the pressure drop per unit length of the tube is larger before this parabolic distribution is attained.

Hagenbach's correction is unimportant in this problem since the data obtained show the pressure drop proportional only to the first power of the linear velocity.

Another important point to be considered under Poiseuille's Law is turbulence. When the rate of flow through a capillary exceeds a certain limit, turbulence replaces laminar flow and Poiseuille's Law no longer holds. This occurs when the Reynolds' number R reaches

---

[7] Hagen, G., Pogg. Ann. d. Phys. u. Chem. (2) 16, 423- (1839).

[8] Handbuch d. Exp. Phys. IV⁴, 45 (1932).

[9] Hagenbach, E., Pogg. Ann. (4) 109, 385 (1860).

[10] Prandtl and Tietjens, Applied Hydro- and Aeromechanics, McGraw Hill Book Co., 1934, p. 24.

a value near 2000*. This number is defined as

$$R = 2 r v \rho/\mu . \tag{10}$$

In order to insure laminar flow conditions, it is best to have R less than 1000. The Reynolds' number is also important in that the distribution of velocities, when expressed in dimensionless coordinates, is the same in two different tubes when the Reynolds' numbers in the two tubes are the same.

When turbulence does occur, the pressure drop, instead of being directly proportional, according to Poiseuille's Law, now varies as the 7/4 power of the linear velocity.

The Fanning Equation[11] incorporates the two types of flow in one expression

$$\Delta p/l = 2f \rho v^2/gd \tag{11}$$

where for turbulent flow

$$f = 0.06 (\mu/d\rho v)^{0.2} \tag{12}$$

and for laminar flow

$$f = 16 (\mu/d\rho v). \tag{13}$$

In these relations d is the diameter of the conduit and g the acceleration due to gravity. A combination of equations (11) and (13) yields Poiseuille's Law while (11) and (12) show the pressure drop is proportional to the 1.8 power of the average linear velocity for turbulence. The values, given in the literature, for the exponent of the velocity for turbulence are not consistent but seem to lie in the range 1.8 - 2.0(10).

---

* Actually, there is no sharp boundary between the two kinds of flow since the geometry of entrance, roughness of surfaces, bends, etc., influence the conditions for turbulence.

[11] Chilton, T.H. and Colburn, A.P., Am. Inst. Chem. Eng. 26, 182 (1931).

Conclusions:

Although the hypothetical filter model of parallel capillaries is an ideal case, the wide variation so obtained between the pressure drop-linear velocity relationship for laminar flow and for turbulence is very significant. Since the data obtained in the experiments show only a first power proportionality, the existence of laminar flow in the filters is established. The fact that this relationship holds when definite turbulence is produced in the filter holder shows that laminar flow exists in the pores of the filters at all times.

The Reynolds' number was found by a rough calculation to be very much smaller in the pores of the filter than in the holder.

Pinholes:

Knudson and White[12] in their analysis of filter pinholes specify that flow is laminer through the pores of a filter and turbulent through pinholes. For the case of large holes the flow is obviously turbulent through the filter since a major proportion will be routed through the pinholes. Thus, when these holes dominate the behavior of a filter, the Reynolds' number will be increased until turbulence occurs, at which time the pressure drop will be proportional to the square of the linear velocity.

Apparently, the entire group of filters under consideration in this study exhibits no pinhole effect as the v^2 relationship is absent. Since the W-2 filter is known to contain pinholes, their size must be below the limit for turbulence to set in. Stafford and Smith[13] have observed this v^2 term for the case of artificially constructed pinholes of large diameter.

---

[12] Knudson, H.W., and White, L., Naval Research Lab. Report No. P-2642 (1945).

[13] Stafford, Earl and Smith, Walter J. - Performance Characteristics of Dry Fibrous Air Filter Media - paper read at A.C.S. Symposium on Dispersions of Gases - Baltimore, Maryland, December 29, 1950.

113

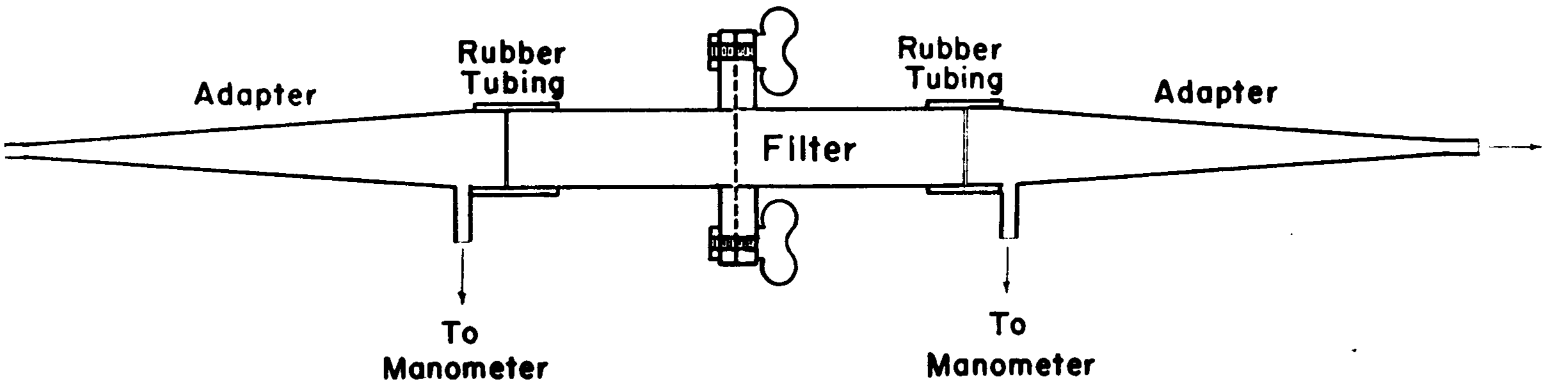

Rubber
Tubing
Rubber
Tubing
Adapter
Adapter
Filter
To
Manometer
To
Manometer

Fig. 6.1

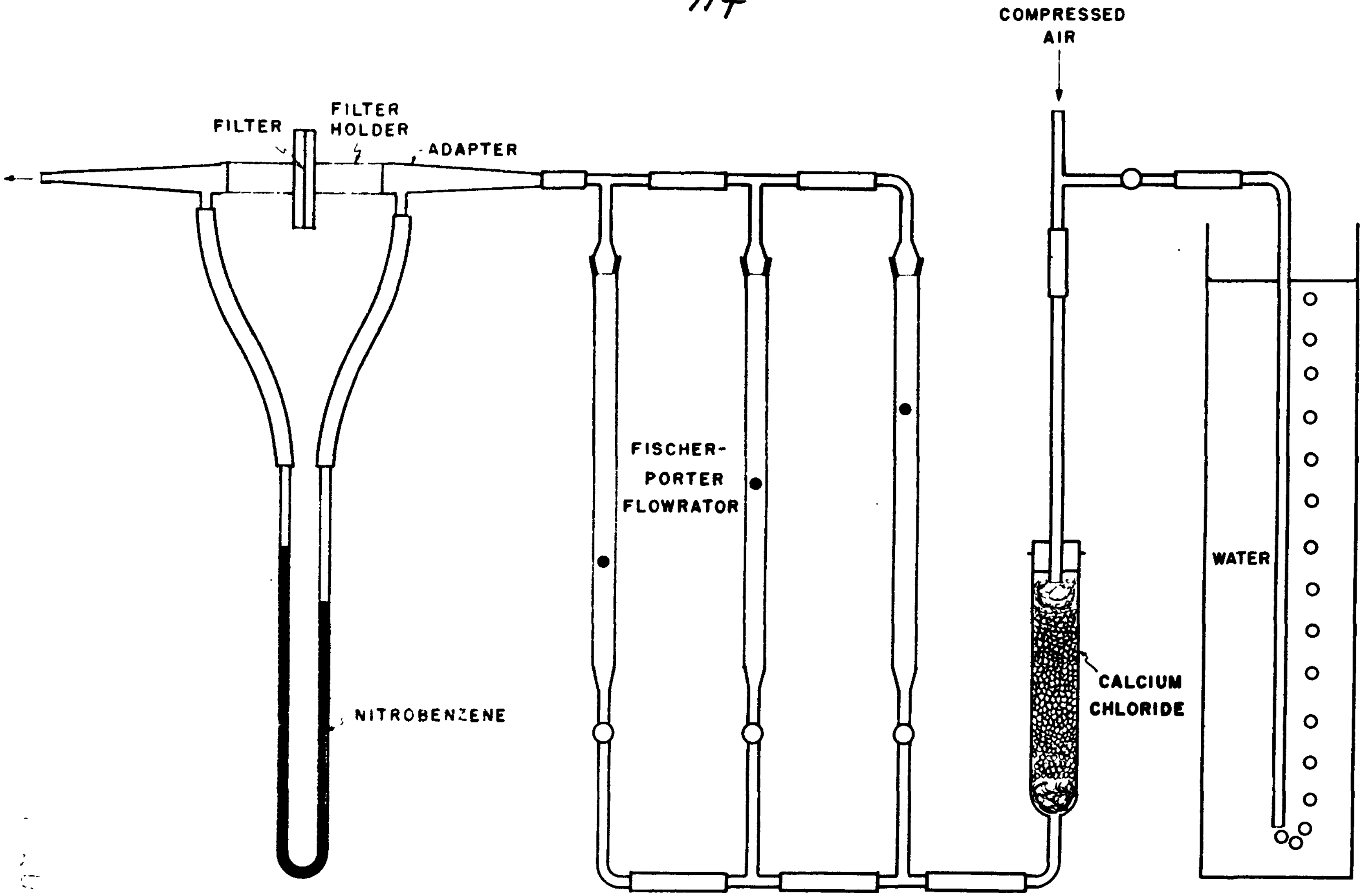

COMPRESSED AIR
FILTER
FILTER HOLDER
ADAPTER
FISCHER-PORTER FLOWRATOR
WATER
CALCIUM CHLORIDE
NITROBENZENE

Fig. 6.2

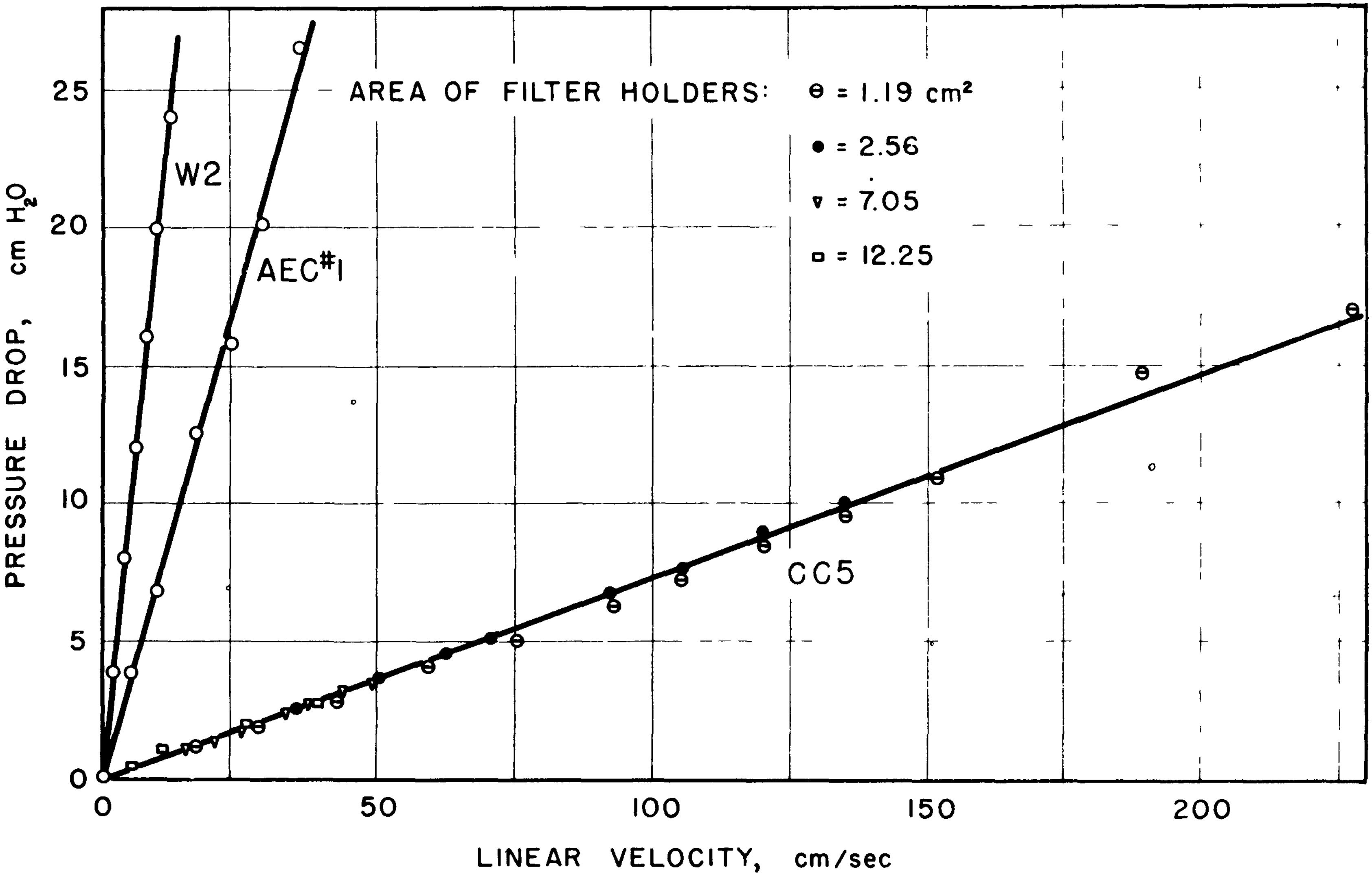

PRESSURE DROP, cm H_2O
0
5
10
15
20
25
LINEAR VELOCITY, cm/sec
0
50
100
150
200
W2
AEC#1
CC5
AREA OF FILTER HOLDERS:
⊖ = 1.19 cm²
● = 2.56
▿ = 7.05
▫ = 12.25

Fig. 6.3

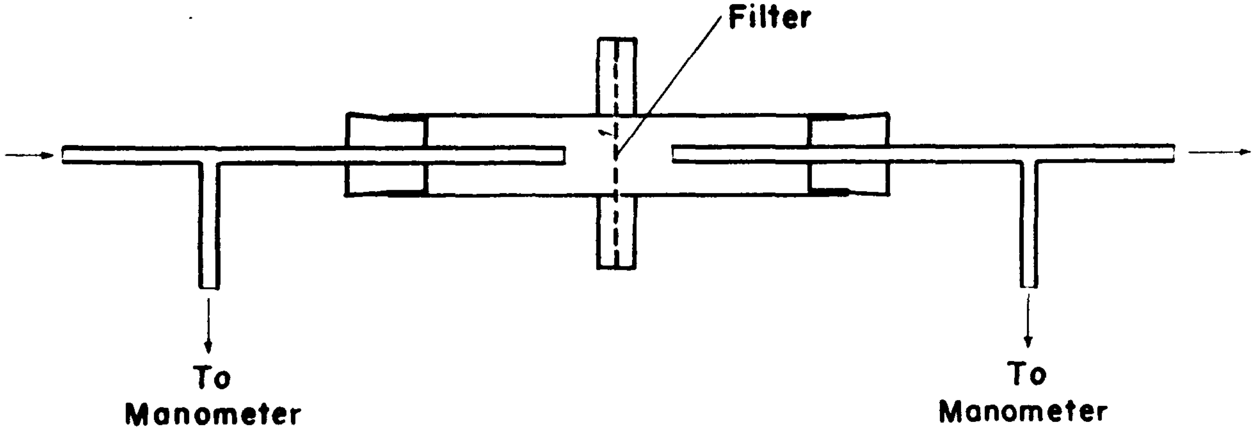


Fig. 6.4

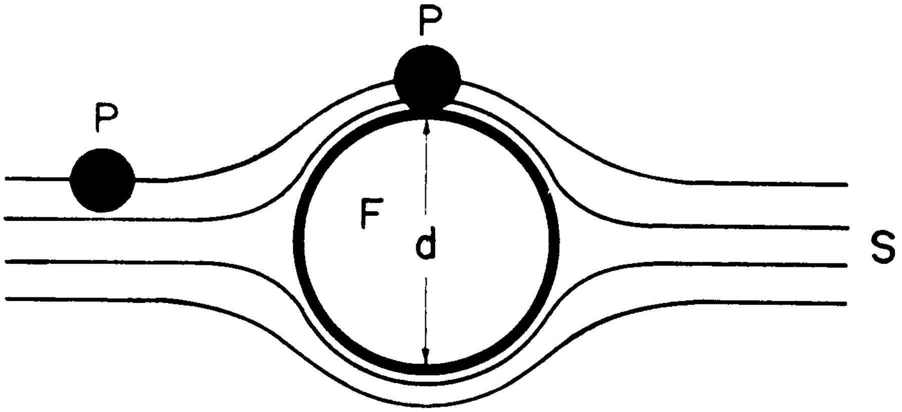
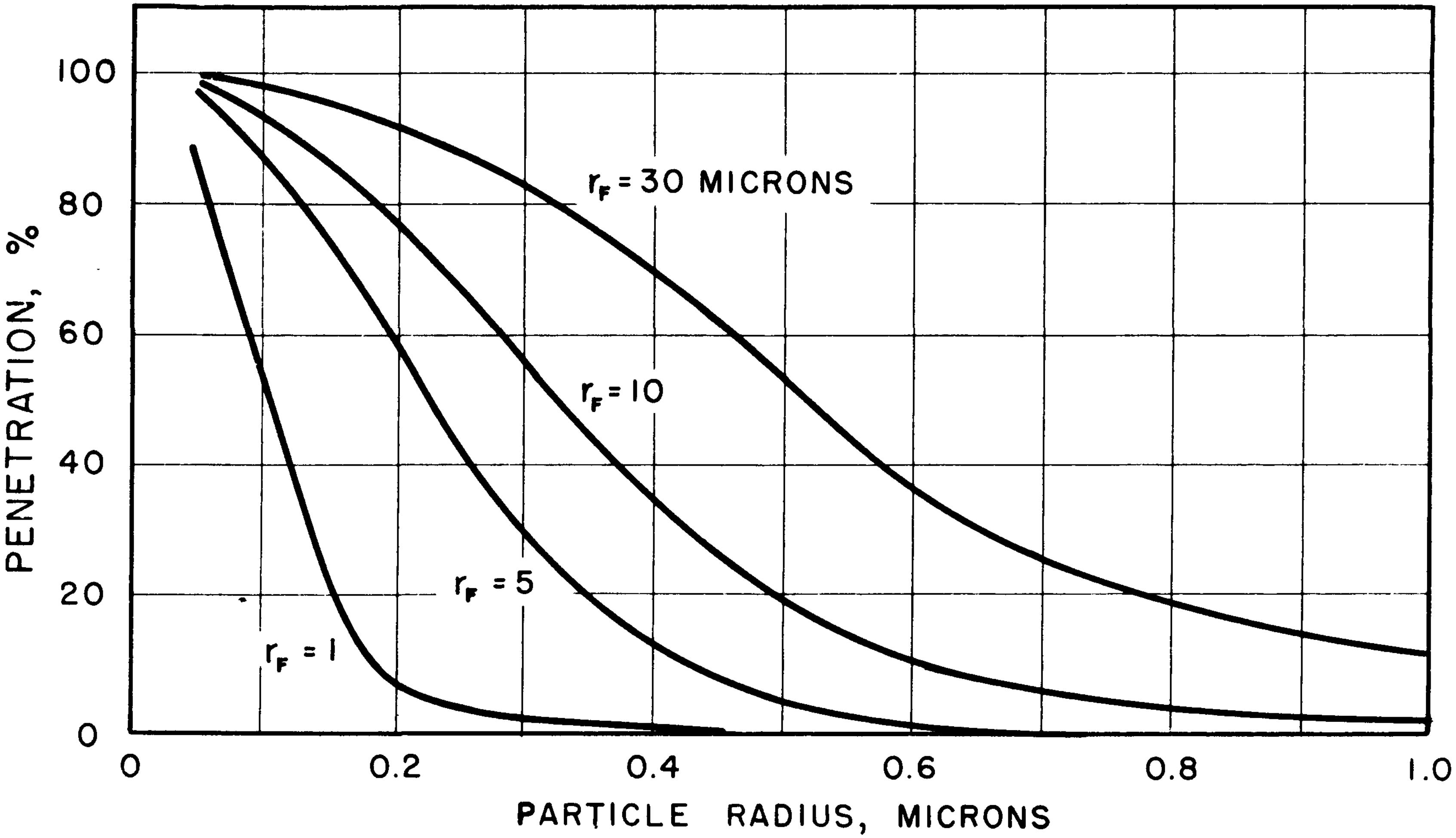


Fig. 6.5



PENETRATION, %
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1.0
PARTICLE RADIUS, MICRONS
r_F = 30 MICRONS
r_F = 10
r_F = 5
r_F = 1

Fig. 6.6

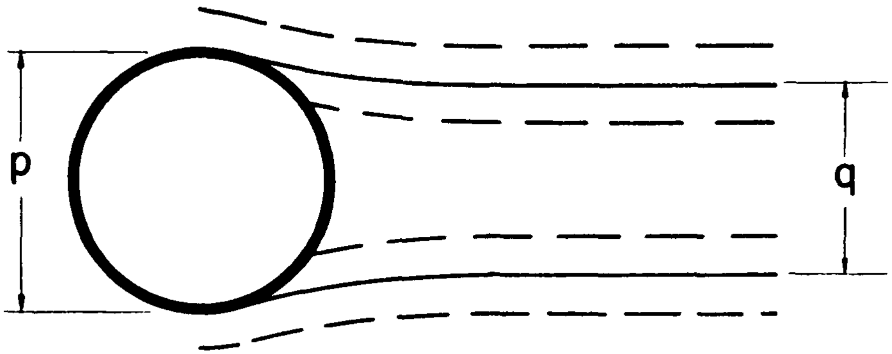


Fig. 6.7

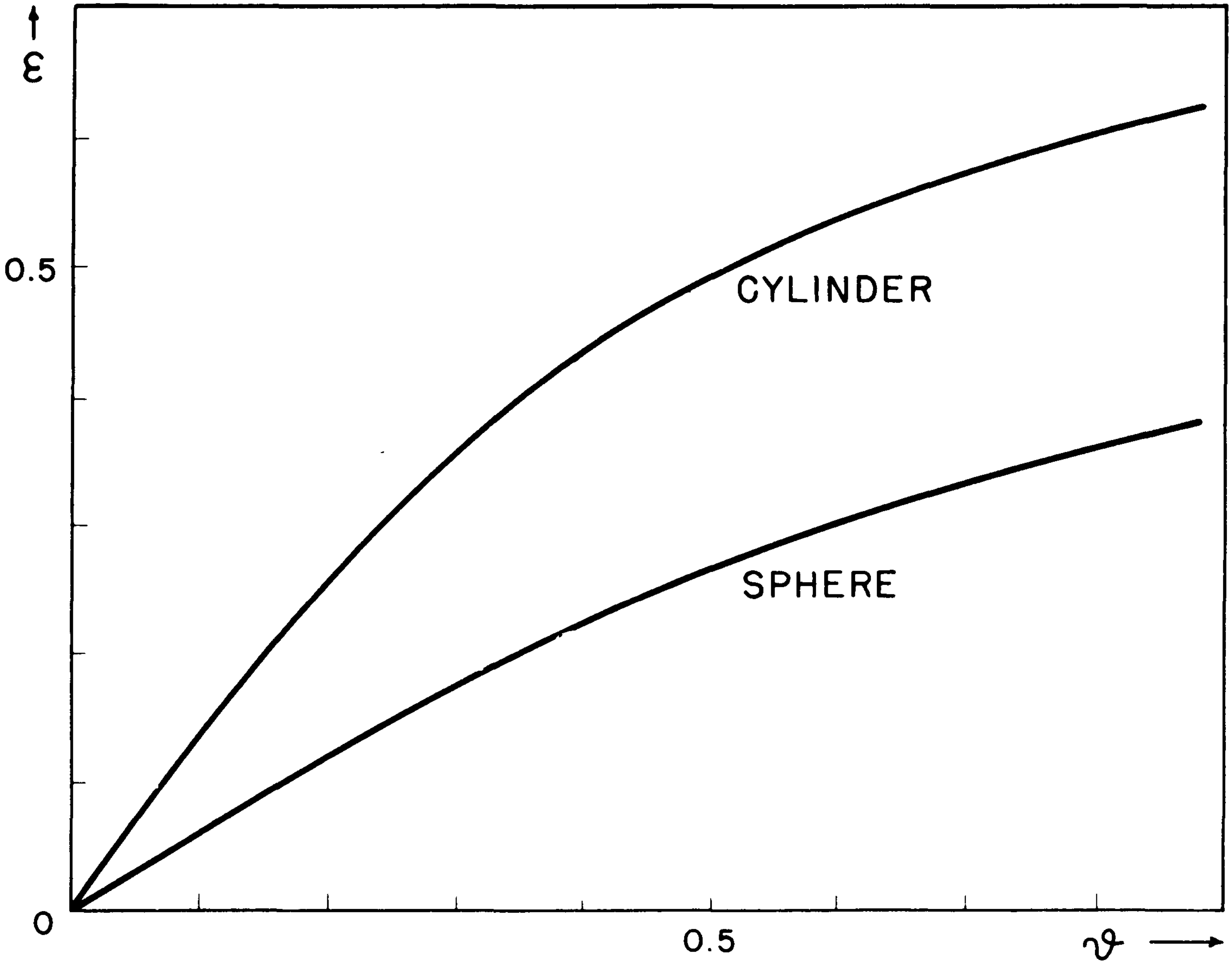


Fig. 6.8

Introduction.

In this section, the various postulated mechanisms of filtration are described and the relative importance of each discussed in the light of the experimental results obtained. Whenever feasible, a mathematical development is furnished for a given mechanism but an all-embracing exact theory of filtration is very complicated with no explicit solution even for laminar flow. A semi-quantitative explanation, however, of the operation of the various filters follows from some general considerations of these filtration mechanisms, since it is possible to evaluate their function qualitatively in all cases, with some mathematical results for the less complicated theoretical analyses.

The experimental procedure for the determination of the filtration characteristics of the papers under consideration is described in Section V(a). In order for a paper to function properly as an aerosol filter, its pores must be large compared to the size of the aerosol particles to prevent a large pressure drop across the filter and clogging of the pores. Because of this requirement, the screening action present in analytical filters is excluded; instead, the particles must be deposited by collisions with the fibers. It is necessary to assume that with moderate rates of gas flow every aerosol particle that comes in contact with the surface of the filter will stick to it regardless of relative size of the particle and the distance between the fibers[1]. In other words, gravitational and other effects due to particle inertia are negligible compared to surface forces and those producing Brownian movement. With this in mind, the following mechanisms will be discussed: (a) direct interception, (b) inertial deposition, (c) diffusion, (d) electrostatic attraction, and (e) Stokes' Law deposition. A brief explanation of the term "filtering action" and its significance in describing a filter will precede this discussion.

A. Penetration and Filtering Action.

The most widely used criterion for the evaluation of filter performance is its penetration characteristic. If n_0 represents the number of unfiltered aerosol particles per unit volume and n the number of filtered aerosol particles per unit volume, the percentage penetration is defined as

$$P = (n/n_0)\cdot 100 \qquad (1)$$

and is measured according to the methods described in Section V(a).

---

[1] Rodebush, W.H., Handbook on Aerosols, A.E.C., Washington (1950), p. 117.

Very often another quantity is preferred to measure filtering action; namely, γ, which is defined by

$$n = n_o \exp(-\gamma) \qquad (2)$$

γ offers an advantage over the penetration since it increases directly in proportion to the thickness of the filter, provided its thickness is uniform throughout its volume. This was verified experimentally (See Section V(c)).

The value of the penetration, P, can be reduced or that of γ increased by the use of a greater filter thickness, but the accompanying increase of the pressure drop limits the freedom of alteration of this parameter.

B. Deposition by Direct Interception.

Since the gas moves in streamlines through a filter, the volume between the fibers may be considered to contain an infinite number of flow lines. Fig. 6.5 (Section VI) shows a single fiber of diameter d and a particle P of radius r, following one of the S streamlines. For the moment, effects due to the inertia of the particle will be neglected. The condition for contact of any particle with a fiber of the filter is that its flow line shall pass within a distance r of a fiber.

If this were the only mechanism at work in the filtration of aerosols, then the penetration, P, would be independent of the linear velocity, v, of the gas since for laminar flow the shapes of the stream lines do not change with changing flow rates.

The assumption that all particles follow the streamlines is not valid for all particle sizes and velocities. For large particles and high gas velocities, the paths of the centers of the particles will not coincide with the gas flow lines. The paths of heavy particles do not curve as rapidly and may cause a particle to come into contact with a fiber, even if the flow line does not come within a distance r of the fiber. Gravitational forces also may cause a deviation of the particle from the streamline. Small particles, on the other hand, may wander away from this flow line by diffusion. Because of the relatively simple mathematics involved, the results for the case of all particles following prescribed streamlines will be described first.

Under the operation of the direct interception mechanism alone the penetration varies inversely as the size of the particles, but the exact relation can be found only by a detailed knowledge of the shapes of the streamlines near the fibers.

Langmuir[2] was able to derive an expression for the effect

---

[2] I. Langmuir, Nat. Def. Comm. Office of Scientific Research and Development, OSRD No. 865, Serial No. 353

of direct interception of aerosol particles upon the filtering action for a filter composed of fibers whose axes are parallel to the surface of the filter and possessing layers of these fibers, each out of step with another (or randomly distributed). He obtained

$$\gamma = \frac{AR\ r^2}{\pi \mu\ r_F} \left[1 - (\tfrac{2}{3})\mathcal{E}_o^{\,o} + (\tfrac{7}{12})\,\mathcal{E}_o^{\,2} \ldots \right] \qquad (3)$$

where R, the flow resistance of the filter, is defined as

$$R = \frac{\Delta p}{F} \quad \text{for small pressure drops,} \qquad (4)$$

A is the area of the filter, r is the radius of the large particle, r_F is the radius of the filter fibers, Δp is the pressure drop, F the volumetric flow, and

$$\mathcal{E}_o = {}^{r}/_{r_F}. \qquad (5)$$

Incidentally, the specific surface resistance, RA, is

$$RA = \frac{A\Delta p}{F} = \frac{\Delta p}{v} \qquad (6)$$

which is the pressure drop per unit velocity, known from the pressure drop experiments.

A simplification of Eq. (3) can be made in the case of CC-5 paper, whose fiber radius is of the order of 10 microns. Since the particle radius ranges from 0.05 to 0.6 micron, $\mathcal{E}_o$ will be very small compared to 1 and higher order terms can be neglected. Thus, Eq. (3) becomes

$$y = \frac{AR\ r^2}{\pi \mu r_F} = Cr^2 \qquad (7)$$

where

$$C = \frac{A\ R}{\pi \mu r_F} \qquad (8)$$

For CC-5, AR = $\Delta p/v$ is found experimentally to be 7.2 x 10^{-2} cm H_2O/cm. sec^{-1}.

The value of C calculated for different values of r_F is given in Table I.

Table I

r_F (microns)	10^{-7} C
1	12.4
5	24.8
10	12.4
30	4.1

Substitution of the value of γ from Eq. (7) and expression in terms of P yield

$$\log \left[P/100 \right] = -2.303\ C\ r^2 \qquad (9)$$

From this equation, P can be calculated for different r's. The results are given in Table II and plotted in Fig. 6 (Sec. VI).

Table II

Penetration P in per cent

r (microns)	r_F microns 30	10	5	1
0.05	99.5	98.4	96.8	84.8
0.1	98.0	93.6	87.7	51.8
.2	91.6	76.5	59.1	7.2
.3	82.2	55.3	30.6	0.3
.33	79.4	48.9	23.9	
.4	70.8	34.9	12.2	2.7×10^{-3}
.45	64.6	26.4	6.9	
..5	57.5	19.3	3.7	
.6	45.7	9.4	0.9	
1.0	11.4	0.1	1.9×10^{-3}	

From Fig. 6 (Sec. VI), we see that the penetration decreases with increasing particle size for a given fiber radius. The penetration, likewise, decreases with decreasing fiber radius for a given particle size. The smaller the fibers the better will be the filtering action due to the mechanism of direct interception.

C. Stokes' Law Deposition.

Another mechanism of importance for heavy particles is the Stokes' Law deposition. If a particle is large enough to exhibit a sufficiently great Stokes' rate of fall, it will no longer follow its particular streamline in the air flow. Rodebush[1] shows how this mechanism enters into the problem of filtration and discounts the argument that a particle would be as likely to fall away from as toward a fiber. If the air flow were stopped suddently, all the larger particles would deposit on the upper surfaces of the filter fibers in a very short time since the distances traveled are necessarily short. Rodebush points out that the direction of flow is immaterial and that the deposition rate varies with particle size and concentration and total area projected by the upper surfaces into a horizontal plane. The concentration is inversely proportional to the depth of penetration of the filter and the rate of deposition is independent of the rate of flow, although for very high flow rates the deposition time is long compared to the time of passage through the filter. If a particle has a radius less than 0.3 micron, this mechanism is of little importance.

Stokes' law may be written

$$mg = 6\pi r \mu \, ds/dt \qquad (10)$$

or, on integration,

$$S = mgt/6\pi r \mu \qquad (11)$$

where S is the vertical displacement, t is the time, r is the radius of the particle, and g the acceleration due to gravity.

Table III lists values of S for different linear velocities and particle sizes.

Table III

r in cm	V in cm/sec	
10^{-4}	8.4×10^{-3}	8.4×10^{-4}
10^{-3}	8.4×10^{-1}	8.4×10^{-2}

If the distance between the fibers is of the same order of magnitude as the diameter of the fibers (which is a reasonable assumption for the CC-5 filter), this distance is about 10^{-3} cm. Accordingly, the deposition due to Stokes' law of fall will not be important for our particle size range 2.10^{-6} - 6.10^{-5} cm, except for very low velocities. The penetration will then decrease with increasing particle size and decreasing velocity.

D. Deposition Due to Diffusion.

A mathematical treatment of this effect is given by Langmuir[2]. The calculations are complicated and no explicit expression for the filtering action is obtained. For a qualitative understanding of the filtration curves obtained in this investigation, the following general considerations will suffice. One should expect the deposition due to diffusion to be largest at small velocities, since the slower the gas passes through the filter, the more time the particles will have for diffusion away from the streamlines and consequently be caught by the fibers. One should also expect the deposition to be larger the smaller the particles, because small particles diffuse more rapidly than large ones. This means that the deposition due to diffusion will be most effective in the region where deposition due to direct interception is smallest. According to the Einstein relation, the particles will fluctuate around the streamlines according to the equation

$$\overline{\Delta x^2} = 2Dt \tag{12}$$

In order to estimate the average distance a particle will diffuse away from its original location as the aerosol passes through the filter, a few values of $\overline{\Delta x^2}$ are calculated, for different particle sizes and velocities, valid for a 0.07 cm sheet of CC-5 filter, making use of the values for D given by Langmuir[1]. These latter values are given in Table IV:

Table IV

r in microns	D in cm^2/sec
0.05	6.80×10^{-6}
0.1	2.21×10^{-6}
0.3	5.03×10^{-7}
0.6	2.24×10^{-7}

The values of $(\overline{\Delta x^2})^{1/2}$ in cm x 10^{-4} are listed in Table V:

Table V

	r in microns			
V cm/sec	0.05	0.1	0.3	0.6
1	9.8	5.6	2.7	1.8
10.	3.1	1.8	.83	.56
30.	1.8	0.1	.48	.32

If the distance between the fibers in CC-5 is of the same order of magnitude as the diameter of the fibers (about 10 microns), Table V shows that for low velocities of flow and small particle size, the particles travel a large share of this distance. Even for larger flow rates and particle sizes, the deposition due to diffusion is unimportant. It should be emphasized that $\overline{\Delta X^2}$ represents the net mean square distance a particle moves in a time t. In general, however, a particle has at times been at distances greater than x from its origin. Here it is desired to calculate the number of particles reaching the surface only once. Diffusion serves to increase the effectiveness of a filter for small particles and to increase penetration with increasing velocity. This is in accord with the experimental results and will be discussed in detail later with respect to the specific filters.

E. Deposition Due to Inertial Effect.

Large particles will not follow the streamlines when bending around the fibers in a filter. Due to inertia, such particles will tend to continue in their original direction. This effect will increase for increasing particle size and for increasing velocity. The laws of deposition for this effect have been studied extensively by Albrecht[3] and Sell[4] and tested by La Mer and Hochberg[5].

---

[3] F. Albrecht, Physik. Zeitschr. 32, 48 (1931).

[4] W. Sell, Forschungsheft 347, Forschung auf dem Gebiete des Ingenieurwesens (1931).

[5] V.K. La Mer and S. Hochberg, Chem. Rev. 44, 341 (1949).

Sell studied experimentally the form of and distance between the streamlines around different kinds of bodies in their path and calculated the paths of particles along these lines according to the laws of aerodynamics, using the pictures of the stream field obtained experimentally. He defined the dimensionless property θ, characteristic for the deposition of particles on cylinders or spheres, as

$$\theta = x_{\infty}/d \qquad (13)$$

where x_{∞} is the stopping distance (i.e., the distance through which a particle with velocity v when introduced in a medium at rest will continue before stopping), and d is a property characteristic of the resisting body. For a given cylinder or a sphere, the diameter is usually chosen for d.

The stopping distance x_{∞} is given as

$$x_{\infty} = r^2 \rho \; v/4.5\mu \qquad (14)$$

where the symbols have the same meaning as before.

The quantity $\mathcal{E}$ is defined by

$$\mathcal{E} = b/d \tag{15}$$

where d is the diameter of the cylinder or sphere and b is the distance between the streamlines which just touch the body, measured at such a distance from the body that the streamlines remain parallel (Fig. 6,8). The value of $\mathcal{E}$ is the same when the dimensionless ratio θ is unchanged.

Sell's results for a cylinder and a sphere are given in Fig. 6.8 and show that $\mathcal{E}$ increases with increasing θ, although the relation isnot linear.

Combining (13) and (14) we obtain

$$\theta = r^2 \rho \; v/4.5 \mu \; d. \tag{16}$$

In the size region where this effect is predominant, the penetration will thus decrease with increasing velocity. This has been verified experimentally; for 6C-5, for example, particles of radii above about 0.35 microns show decreasing penetration with increasing velocity, while the particles of smaller size exhibit the opposite behavior (see Deposition due to Diffusion).

Albrecht's treatment of the deposition due to inertia, while similar to Sell's, is more theoretical and is not based upon the experimentally determined streamline distribution. Albrecht predicts no deposition for small values of θ ($\theta < 0.09$), whereas Sell points out that this cannot be correct since the central streamline is a straight line, which bends very sharply to both sides of the cylinder. Even an extremely small particle when following the central streamline, has to be deposited because of its inertia. The same holds true for those particles proceeding along streamlines close to the central one. Sell's explanation seems to be more correct, and these particles in this report will be included with those deposited by direct interception.

Langmuir also criticises Albrecht's interpretation because he has based his calculations on the perfect fluid theory of flow near a cylinder and has not taken into account that the tangential as well as the radial velocity approach zero at the surface of the resisting body. In revising Albrecht's treatment, Langmuir finds 0.27 as the critical value instead of 0.09. A calculation shows that this would imply no deposition due to inertia in the range of operation in this investigation, but this obviously is not the case!

Rodebush concludes that particles of less than 0.5 micron radius and velocity equal to 3.5 cm/sec will not be deposited by inertia because the stopping distance in this case is only 10^{-5} cm. For particles of smaller velocity or size, there should of course be a still smaller chance for deposition by the inertia effect.

In conclusion, it appears there is no agreement whatsoever between the different authors on this deposition effect. Since the experimental results obtained in this laboratory show that for CC-5 filter the penetration decreases with increasing velocity for a particle size above 0.35 microns, it follows that deposition by inertia must be important in this region, since it is the only velocity-dependent effect showing this behavior. (Stoke's law deposition would show the opposite velocity-dependent effect). It is primarily in respect to the quantitative importance of inertial deposition at low particle radii that our interpretation differs from that of Langmuir and Rodebush. Also, we do not agree with Langmuir that electrostatic attraction can be completely neglected.

F. Deposition Due to Eledtrostatic Attraction.

Certain filters, especially those made of wood and resin, carry electric charges. These filters will of course retain particles due to electrostatic attraction. This will be the case even if the particles are originally uncharged, as in the case under consideration, because neutral particles will polarize in this strong field and be attracted to the fibers. There is also some evidence that certain filters will be charged by friction when the air passes through the filter. The velocity with which a particle will be drawn toward the charged fibers is proportional to the square of the radius[1]. Therefore, large particles should be removed to a larger extent than small ones by this electrostatic effect. Analogous to deposition due to Stoke's law fall, deposition due to electric attraction should decrease with increasing velocity. This effect appears to be important for the present filters and aerosols, but the subject merits more careful investigation before this view can be accepted. The deposition of particles of large size and low velocity where the effect should be important is attributed chiefly to direct interception and inertia (and perhaps to some extent to gravity). For other filters, however, this deposition effect probably is of great importance. A fundamental investigation of electrostatic deposition is under way and will form the basis of a future report.

G. Turbulent Surface Deposition.

Although turbulence should cause some additional surface deposition, it has been shown that the flow through the filters is laminar, no matter what conditions exist in the holder, rendering this effect negligible in this investigation.

H. Summary.

In general, the results of this analysis of the various effects governing deposition of particles on fibers are as follows: The principal phenomena at work are diffusion, direct interception and inertial deposition. The first assumes prominence in the small particle range and causes an increase of the penetration of aerosol with increasing particle velocity. The mechanism of direct interception operates in all particle ranges, but is of major importance in the intermediate size zone. For this case, the penetration is not a function of the particle velocity. In the range of large radii the inertial deposition effect predominates and causes the penetration to decrease with increasing particle velocity, but our experimental data show that the influence of inertial deposition persists to much smaller particle radii than Langmuir and Rodebush have stated. The role of electrostatics cannot be ignored but has been beyond the realm of this immediate investigation.

The penetration versus particle radius curves, obtained for the CC-5 filter (see Fig. 4,(Vc)), show reasonable agreement with these conclusions. Particles of about 0.35 micron radius experience almost no variation of penetration with linear velocity, while for smaller particles the penetration increases with increasing velocity. For larger particles, the penetration decreases when the velocity increases. In order to explain the insensitivity of the penetration to velocity in the region around 0.35 micron radius, the following suggestions are offered:

1. Both deposition due to diffusion, which is most important for small particles, and deposition due to inertial effects, which has the greatest influence in the large particle range, become negligible in this intermediate size zone. This means that all particles follow the streamlines and that the deposition for this particle size is due to direct interception alone, and consequently is independent of velocity.

2. The deposition due to diffusion and inertia approximately balance each other in this region, which implies that, when the velocity is increased, the deposition due to diffusion decreases by an amount just equal to the increase in deposition due to inertia.

The second interpretation seems more logical since the value of penetration from the theoretical curves for deposition due to direct interception alone ismuch larger than the penetration actually observed for this particle size (about twice as large).

Particles smaller than 0.35 micron in radius will now be considered. If deposition due to diffusion were the only mechanism of retention of such particles, the penetration should decrease with decreasing particle size. It has already been shown, however, that deposition due to direct interception is an important effect in this range. Deposition due to this latter mechanism decreases as the square of the radius as the particle size decreases. It cannot, therefore, be concluded that the penetration should decrease with decreasing particle size with a maximum in the penetration versus particle size curve. This maximum, which is predicted theoretically by Langmuir, is not found in the experiments performed in this laboratory which cover a large range of particle sizes (from 0.03 to 0.6 micron). A α-web carbon-impregnated paper which had been found to give such a maximum with stearic acid aerosol produced also on careful examination the same kind of curves as found for the other filter papers when DOP aerosol was used.

The influence of the velocity-dependent deposition effects is better understood by considering a plot (Fig.5,12(V)of penetration vs. velocity for different particle sizes. Such a graph shows that the penetration of small particles first increases as the velocity increases the deposition due to diffusion being the most important effect. As the velocity increases, however, deposition due to inertia will increase and the penetration will finally decrease. Particles of intermediate size show almost no variation of penetration for varying velocity, the two velocity-dependent effects approximately balancing each other.

For larger sizes deposition due to inertia is the most important mechanism and the penetration consequently decreases with increasing velocity (See Fig. 5,12, Sec. Vc).

I. The Whatman Filter (W-2).

This filter is an ordinary analytical filter. It does not operate as a sieve when applied to the filtration of small aerosols because the size of the pores is large compared to the size of the aerosol particles. The size of the fibers in this filter is approximately the same as for CC-5. Since the pressure drop is much higher than for CC-5, it follows that the average pore size must be smaller, i.e. the fibers are more closely packed. Therefore, the importance of deposition due to diffusion and inertia will increase because the particles will have a shorter distance to diffuse and be trapped and the streamlines will bend more sharply, increasing the deposition due to inertia. Fig. 16(Vc) shows a plot of penetration vs. particle radius for DOP aerosol through this filter. The penetration decreases in all particle ranges with increasing velocity. This might be due to some extent to the fact that the deposition due to inertia is the dominating velocity-dependent effect since the streamlines are very distorted, but the most likely explanation is a pinhole effect. A decreasing penetration with increasing velocity was found (by Stafford and Smith, A.D. Little Co.) for filters with artificial pinholes, while the same filter without the pinholes showed the opposite behavior. This is probably due to the fact that since the flow through a pinhole will be turbulent, a larger portion of the gas will go through the filter as the velocity is increased. Penetration through filter pores is proportional to first power of the particle velocity, while that through pinholes increases with the square of the velocity.

J. The "Gl" Glass Filter.

This filter shows an increase in penetration for an increase in velocity for all particle sizes. This can be understood from the following considerations. This filter has very small fibers (about 1 micron diameter). The streamlines will therefore be bent very little making the deposition due to inertia unimportant and leaving deposition due to diffusion as the only velocity-dependent effect. This filter is also thicker than the CC-5 filter, allowing more time for diffusion to take place during passage of the aerosol through the filter. Since diffusion is the only important velocity-dependent effect in operation, this filter must show increasing penetration for increasing velocity for the whole range. It was mentioned (letter to V.K. La Mer from Owens-Corning Glass Corp. April 5, 1950), that the filtering efficiencies of this pap are markedly improved if blended with fibers of diameter 5 microns, in the ratio 1:3. This result is more easily understood because now deposition due to inertial effects will also take place; the streamlines will be more distorted around the larger fibers. This effect is expecte to be most pronounced for particles of larger size.

K. Other Filter Characteristics.

Some other types of filter were investigated experimentally. They showed approximately the same behavior as the CC-5 filter and the same interpretation can therefore be made.

ACKNOWLEDGMENT SECTION VIII

This report is a continuation of the investigation initiated in 1948 by the Protective Division (Dr. Eugene Ramskill) of the Naval Research Laboratory, on the Production of Very Fine Monodisperse Aerosols in the Sub-Tyndall Region, O.N.R. contract (Columbia University), July 1, 1948-49, published by V.K. La Mer, Edward C.Y. Inn and I. Wilson in J. Colloid Science 5, 471 (October, 1950).

The present investigation was supported in part by funds from the Atomic Energy Commission under contract At(30-1)-651 with Columbia University from July 1, 1949 through March 31, 1951, on the initiation of the Chemistry Research Division (Dr. Kenneth Pitzer) of the Atomic Energy Commission.

Dr. Pierre Gendron and Miss Ruth Gruen were responsible in 1949-50 for constructing apparatus, extending the growth method of determining particle size to DOP aerosols, and for the filtration measurements showing the absence of a maximum in the radius penetration curves as reported in Progress Report NYO-511, January, 1950, abstracted in Nuclear Science Abstracts 5, No. 755 (1951).

Dr. Guy Goyer replaced Dr. Gendron in the summer of 1950, in the matter of production of apparatus, maintenance of working conditions and immediate supervision of filtration. Miss Gruen continued the filtration measurements and later (Spring, 1951) was assisted by Miss Joan Kruger.

The sections of the report have been written by various members. In the winter of 1950-51, an investigation of the underlying theory and interpretation of the data was undertaken by Hans Holtan, Jr. This report, rewritten and revised by Mrs. Mary L. Young, forms the basis of Sections VI (Pressure Drop), VII (Theory of Filtration and part of Section V (Experimental).

Sections III (Production of Aerosols, IV (Growth Method) and V (Experimental) are due primarily to Dr. Goyer and Miss Gruen with revisions by Mrs. Young. Appendix B (Section IV) is by Dr. Howard Reiss. Appendix A (Section IV) - Kelvin Effect - is by Victor K. La Mer and Miss Gruen, but all members of the staff participated in clarifying the problem as it developed.

The director is responsible for the initiation, planning and overall direction of the investigation, for revision of much of the manuscript, and for writing the Abstract, Introduction and Appendix A. He also acknowledges many helpful discussions and suggestions over the past decade from Drs. Irving Langmuir and W. H. Rodebush.

The drawings were made by Mr. P.K. Lee and our best thanks are due the secretary, Miss Castagneri, for her care in reproducing the report.