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THE DIFFUSION BATTERY METHOD FOR AEROSOL PARTICLE SIZE DETERMINATION

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HEALTH PHYSICS DIVISION

THE DIFFUSION BATTERY METHOD FOR AEROSOL PARTICLE SIZE DETERMINATION

Jess W. Thomas

PROTECTIVE EQUIPMENT EVALUATION PROGRAM

(In Cooperation with the Army Chemical Corps)

E. G. Struxness, Group Leader

DATE ISSUED

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ABSTRACT

The object of the work described in this report was to design and construct several diffusion batteries and to investigate the validity of the diffusion method for size determination of sub-micron homogenous aerosols. Two parallel plate diffusion batteries were made and used for particle size determination in the 0.1 micron radius range. The aerosol particle size as determined by the batteries was compared with the size as determined by a standard light scattering method. Results agreed to within 30 percent.

Circular tube batteries were made and used to check the applicability of the method to diffusion of particles as small as gas molecules. The diffusion coefficients of gas molecules obtained by this method agreed well with the literature values.

It was concluded that the diffusion battery is a valuable instrument for study of the particle size of aerosols from atomic sizes up to particle radii of about 0.5 microns. Two batteries, with graphs of operating parameters, are now available for use in filter efficiency studies.

INTRODUCTION

At present very little is known about the health hazard caused by inhalation of sub-micron smoke or dust particles. Drinker and Hatch[1] state that vast numbers of particles below 0.25 micron radius are generated by industrial processes and they consider this sub-micron dust to be quite dangerous. Also, little is known about the efficiency of filters for particles under 0.1 micron radius. This lack of knowledge has been due to (1) difficulties in generating homogeneous aerosols, and (2) the lack of convenient and reliable methods for determining particle sizes under 0.1 micron radius.

Particles below 0.1 micron radius are too small for direct microscopic observation. Likewise, the standard light scattering techniques[2] cannot be used. Consequently, the methods now in use depend on observation of the particle with the ultramicroscope or electron microscope. These methods are tedious and are not well suited for use in filter paper efficiency investigations. Recently LaMer[3] has developed an unique method in which the particles are "grown" by use of an appropriate solvent, the "grown" size measured by standard methods, and the original size then calculated from the known growth factor.

---

1. Drinker, S. B. and Theodore Hatch, Industrial Dust, New York, McGraw-Hill, 1936, p. 55-59.
2. Handbook on Aerosols, Washington, D.C., Government Printing Office, 1950, p. 106-116.
3. LaMer, V.K., E.C.Y. Inn, and I. B. Wilson, "The Methods of Forming, Detecting, and Measuring the Size and Concentration of Liquid Aerosols in the Size Range of 0.01 to 0.25 Microns Diameter, "J. Colloid Science 5, 471 (October, 1950).

An alternate method which has been very little used, particularly in this country, is the diffusion battery technique. This method has several outstanding advantages; (1) the aerosol particle is measured without collection or alteration of the individual particles; (2) the method can be made rapid, provided only that the aerosol mass concentration may be measured rapidly; and (3) there is no lower limit to the size which is measurable. However, this method does not seem to have ever been given a direct experimental test against a standard light scattering method. This work was therefore undertaken to investigate the practicality and validity of the diffusion method.

A sketch of a typical battery is shown in Figure 1. For a battery having these dimensions, the effect of gravity is negligible for particles under 0.3 microns radius. The operation of a battery such as this is based on the Brownian motion of the aerosol particle. As the aerosol particle moves, in streamline flow, through the long narrow channels as shown, the random Browian movement of the particle causes it to displace from its original position in the air flow streamline. The most probable displacement from a streamline is a zero; but the average displacement is proportional to the square root of the travel time. Consequently, some of the particles are displaced sufficiently to reach the walls of the battery. It is assumed that once the particle reaches the battery wall, it will stick to the wall. This is an assumption generally made in aerosol investigations.[4,5]

4. Rodebush, W. H., I. Langmiur and V. K. LaMer, Filtration of Aerosols and the Development of Filter Materials, Sept. 4, 1942 (OSRD 865).
5. Radushkevich, L.V., "A Study of the Kinetics of Aerosol Coagulation by the Diffusion Method," Acta Physiochemica URSS 6, 161-182 (1937).

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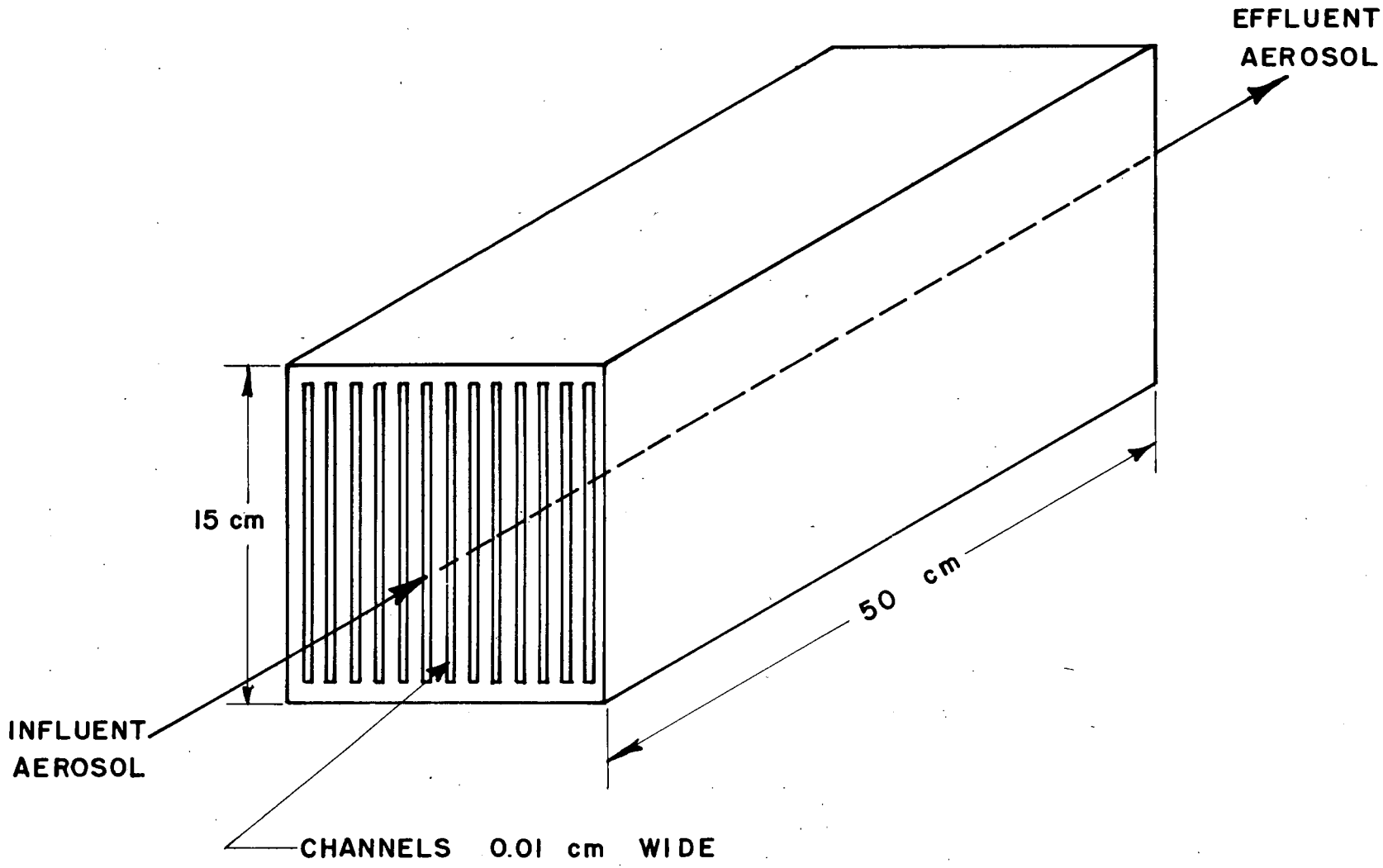

FIGURE I. TYPICAL DIFFUSION BATTERY

Since the efficiency of filter papers increases with time when using a solid test aerosol, the assumption seems verified. If particles were dislodged from the surface of the filter, the efficiency would tend to decrease with increasing testing time.

In this manner, some of the influent smoke particles are removed by the battery as they travel along the channels, and a fraction F of the influent particles appear in the battery effluent. It is easy to visualize in a qualitative way that since the magnitude of the Brownian movement increases with decreasing particle size, that the smaller the particle the more sorption by the wall and the lower the value of F.

This dependence of F on the particle size of the aerosol is the basis of the diffusion battery method. The usual procedure has been to use equations relating F and the diffusion constant of the aerosol, and then to calculate the particle size from the diffusion constant. This is done by use of the Einstein relation with modifications for the slip of particles between air molecules (Appendix I).

It is also possible to use the battery for determining the mass of the individual aerosol particle.[6]

---

6. DeMarcus, W. C. and J. W. Thomas, Theory of a Diffusion Battery, Oct. 16, 1952 (ORNL 1413).

HISTORICAL

Equations for the Circular Battery

Probably the first investigation of the relation between the fraction F penetrating the battery and the diffusion constant D was made by Townsend[7] in 1900. Townsend used a circular battery, or tube, in his work. His objective was to determine the diffusion coefficients of ions in air and different gases. The gaseous ions were sorbed by the wall of his diffusion tube while enroute through it, analogous to the removal of aerosol particles by a battery wall. In the notation of this report, the equation developed by Townsend is given below. Q is the volumetric (cm^3/sec) flow rate and Z the battery length in cm. The diffusion constant D is expressed in cm^2/sec.

$$F = 0.78\, e^{-\alpha} + 0.097\, e^{-6.1\,\alpha}$$
$$\alpha = \frac{3.66\ \pi\ DZ}{Q} \qquad (1)$$

It is interesting to note that the diameter of the tube does not enter in the above equation. On first thought this does not seem reasonable. However, consider a tube of fixed length Z at a given volumetric rate Q. Tripling the diameter of the tube would make it necessary, on the average, for each particle to diffuse three times as far before contacting a wall; but this would also reduce the linear (cm/sec) air velocity by a factor of 9, giving the particle 9 times as much time for diffusion. Since the "diffusing" distance is proportional to the square root of the time, the net result is the same mass transfer to the wall, leaving F unaffected.

7. Townsend, J. S., "The Diffusion of Ions into Gases," Transactions Royal Society 193-A, 129-158 (1900).

In 1948 Gormley and Kennedy[8] rederived Townsend's equation, obtaining

$$F = 0.819\, e^{-\alpha} + 0.0975\, e^{-6.1\alpha} + 0.0325\, e^{-16\,\alpha} \qquad (2)$$

with α the same as in equation (1). This equation applies for values of F below 0.78. For values of F above 0.78 another equation applies.[8]

Equation for the Parallel Plate Battery

In 1935 Timoney, working with Nolan and Guerrini[9], developed an equation for the parallel plate battery. This type battery is more suitable than the circular battery for working with relatively large particles ($\sim$ 0.01 to 0.5 microns radius). The equations developed by Timoney are given below:

$$F = 1.066\, e^{-\alpha} + 0.0065\, e^{-12.1\,\alpha}$$
$$\alpha = \frac{3.67\ bDZ}{aQ} \qquad (3)$$

2a = distance between parallel plates

b = height of the rectangular channel (perpendicular to the direction of air flow)

Z = length of channel (in direction of the air flow)

Q = volumetric flow rate through one channel

D = diffusion constant of aerosol

F = fraction penetrating battery

This equation is obviously not applicable for small values of α (high F), since for this condition the value of F may exceed 1.00, which is physically

8. Gormley, P. G. and M. Kennedy, "Diffusion from a Stream Flowing Through a Cylindrical Tube," Proc. Royal Irish Academy 52-A, 163-169 (1949).
9. Nolan, J. J. and V. H. Guerrini, "The Diffusion Constants and Velocities of Fall in Air of Atmospheric Condensation Nuclei," Proc. Royal Irish Academy 43A, 4-24 (1935).

impossible. Recently, at this laboratory, W. C. DeMarcus was requested to re-derive this basic equation. DeMarcus obtained the following equation.[6]

$$F = 0.915\, e^{-\alpha} + 0.059\, e^{-11.8\,\alpha} + 0.026\, e^{-80\,\alpha} \qquad (4)$$

$$\alpha = \frac{3.77\ bDZ}{aQ}$$

After this work was done, a later paper by Nolan and Nolan[10] was found, in which Gormely corrects the original Timoney-Nolan equation, obtaining

$$F = 0.910\, e^{-\alpha} + 0.053\, e^{-11.4\,\alpha} \qquad (5)$$

$$\alpha = \frac{3.77\ bDZ}{aQ}$$

This equation checks the DeMarcus equation very closely. For values of F under 0.90, there is a difference of less than 1 percent in F for the same value of D in the two equations.

Experimental Use of Diffusion Batteries

Nolan and Guerrini[9] used three different parallel plate diffusion batteries to determine the size of atmospheric condensation nuclei. In the different batteries, the distance between the parallel plates varied, from 0.05 cm to 0.60 cm. They found the radius of the nuclei to be 0.0285 microns. In addition, Nolan and Guerrini estimated the mass of the

10. Nolan, J. J. and P. J. Nolan, "Diffusion and Fall of Atmospheric Condensation Nuclei," Proc. Royal Irish Academy 45-A, 47-63 (1938).

nuclei. This pioneering investigation was subject to several errors, which were discussed in later papers by Nolan and Nolan[10] and Nolan and Kennan.[11] As reported in the latter paper, diffusion coefficients in the range 7×10^{-7} to 8×10^{-4} cm^2/sec were measured, corresponding to particle sizes of from 0.004 microns to 0.23 microns radius.

In 1937 Radushkevich applied the diffusion battery method to the study of aerosol coagulation, using a battery consisting of 400 glass therometer capillaries, inside diameter 0.01 cm and length 20 cm. Radushkevich measured ammonium chloride smoke particles of about 0.1 micron radius. He checked the radii values obtained by his diffusion method by counting the number of particles present in a given volume of aerosol and determining the mass concentration. The results agreed rather closely, and Radushkevich concluded that particle diffusion within a circular tube followed Townsend's theory. In a later paper, he[12] describes a static method for aerosol diffusion constant determination. In this method the aerosol is drawn into an ultra microscope cell for continuous observation. The diffusion coefficient is deduced from the rate of decrease of particle concentration with time.

---

11. Nolan, P. J. and E. L. Kennan, "Condensation Nuclei from Hot Platinum: Size, Coagulation Coefficient and Charge Distribution," Proc. Royal Irish Academy 52-A 171-190 (1949).
12. Radushkevich, L. V., "A New Method of Determining the Mobilities and Radii of Smoke Particles," Acta Physicochemica URSS 11, 265-276 (1939).

In 1943 Rodebush, Holley, and Lloyd[13] used a parallel plate diffusion battery for measurement of the radii of radioactive triphenyl phosphate smokes. Particle sizes down to 0.001 micron radius were measured. The battery penetration equation used by Rodebush differs somewhat from the one derived by DeMarcus.[6] Since the DeMarcus equation agrees very closely to that independently derived by Gormely[8], et. al., the DeMarcus equation is considered to be the more reliable. The values of the constants A, B, and C of the Einstein equation used by Rodebush are obsolete. (Appendix I).

In some of the above mentioned papers there is confusion about the dimensions a and b of the battery. In equations of the type (3, 4, 5,) the dimension a is one-half the distance between the parallel plates; the dimension b is the entire height of the rectangular channel (perpendicular to the direction of air flow).

With the exception of the work of Radushkevich with the circular tube battery, there appears to be no data in the literature in which the battery method is compared to other methods for determining particle size.

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13. Rodebush, W. H., C. E. Holley, Jr., and B. A. Lloyd, Progress Report on Filter Penetration by Aerosols of Very Small Particle Size, University of Illinois, Nov. 24, 1943 (OSRD-2050).

EXPERIMENTAL

Plan of Investigation

Although it is difficult to build even a parallel plate battery for use with particle sizes as large as 0.15 microns radius, it was decided to attempt this, since particles of this size may be generated with the standard "DOP" apparatus and their size measured with the "owl".[2] The construction difficulties are due to the large battery surfaces and close tolerances required for measuring the relatively small diffusion rate of 0.15 micron particles. To investigate end effects, a second battery was made similar to the first one except of much shorter length. This allowed cancellation of end effects when using the two batteries alternately on the same smoke. The first battery (for 0.15 micron smoke) was designated the "large" battery. The second was designated the "small" battery.

At the other extreme, it is possible to check the battery equations and methods using the ultimate in small particles, that is, gas molecules. This work is described in Appendix II.

Battery Design Criteria

The large diffusion battery was designed so that the F-values obtained in its use were in the range 0.05 to 0.80. This is a fundamental design criteria since (1) penetrations of less than about 5 percent may be difficult to measure accurately, depending on the type detector used, and (2) the error in the desired parameter D as a function of the experimentally measured parameter F increases greatly as F approaches 1.00. The

relation between F and α is given on page 17. Since $\alpha = \frac{3.77\ bDZ}{aQ}$. the percent error in α equals the percent error in D. For a F of 0.90, a 1 percent error in F will cause a 12 percent error in D. However, if F equals0.50, a 1 percent error in F will cause only 2 percent error in D.

Other important design characteristics are: (1) a low pressure drop through the battery; (2) the existence of streamline flow; and (3) as small a volume as possible in the end adapters.

A low pressure drop is obviously desirable, since a large pressure drop would appreciably change the air velocity and mean free path of the air molecules. This would complicate the calculations greatly. Pressure drops of less than 20 cm H_2O should be permissible, since such a drop is small compared to atmospheric pressure (1000 cm H_2O). Appendix III gives the pressure drop calculations as a function of battery dimensions.

The maintenance of a streamline flow in the battery will normally not be a problem, due primarily to the low flow rate which is necessary to allow time for diffusion. For very small particles (< 0.001 microns radius) higher flow rates are possible and the maintenance of streamline flow must be taken into consideration. For a battery such as that shown in Figure 1, the Reynolds number** is under 10 for flow rates under 5 liters per minute through the battery.

The volume in the battery end adapters is important, since it is a factor causing a lag in the response of the battery. The volume of the end adapters should be as small as possible, consistent with the maintainance of an even flow in all parts of the battery channels.

** See page 815 of reference (34) Appendix III. "--- for((non-circular) passages running full the indications are that the transition from viscous to turbulent flow occurs when (Re) is ----- 2100 to 2300."

Battery Construction

Drawings of the large battery and its end pieces are shown in Figure 2 and 3. A separate drawing was not made for the small battery, since it is merely a shortened version of the large one. Graphite (carbon) was chosen as the construction material for the battery plates since it is relatively easy to machine to the extremely close tolerance necessary (± 0.00015" in thickness over an area of about 50 in^2). It also has the advantage of a small temperature coefficient of expansion. Figure 4 shows the assembled battery without the end pieces. To assure rigidity, heavy stainless steel plates were placed on both sides of the battery. A supporting ridge of graphite was machined through the middle of each plate parallel with the direction of air flow. Twelve stainless steel bolts hold the large battery together.

The battery dimensions specified on the drawings are as follows:

	Large Battery	Small Battery
Width of channel (2a)	0.0102 cm	0.0102 cm
Height of channel (b)	12.70 cm	12.70 cm
Length of channel (Z)	49.9 cm	5.08 cm
Number of channels (n)	19	19

The spacings (2a) of the channels in the assembled battery were checked with a microscope. A strong light source was placed under the battery and the width of each channel measured at several different points. The values obtained were averaged to give the following: Large battery, 2a = 0.0095; small battery, 2a = 0.0092. These values are considered to be

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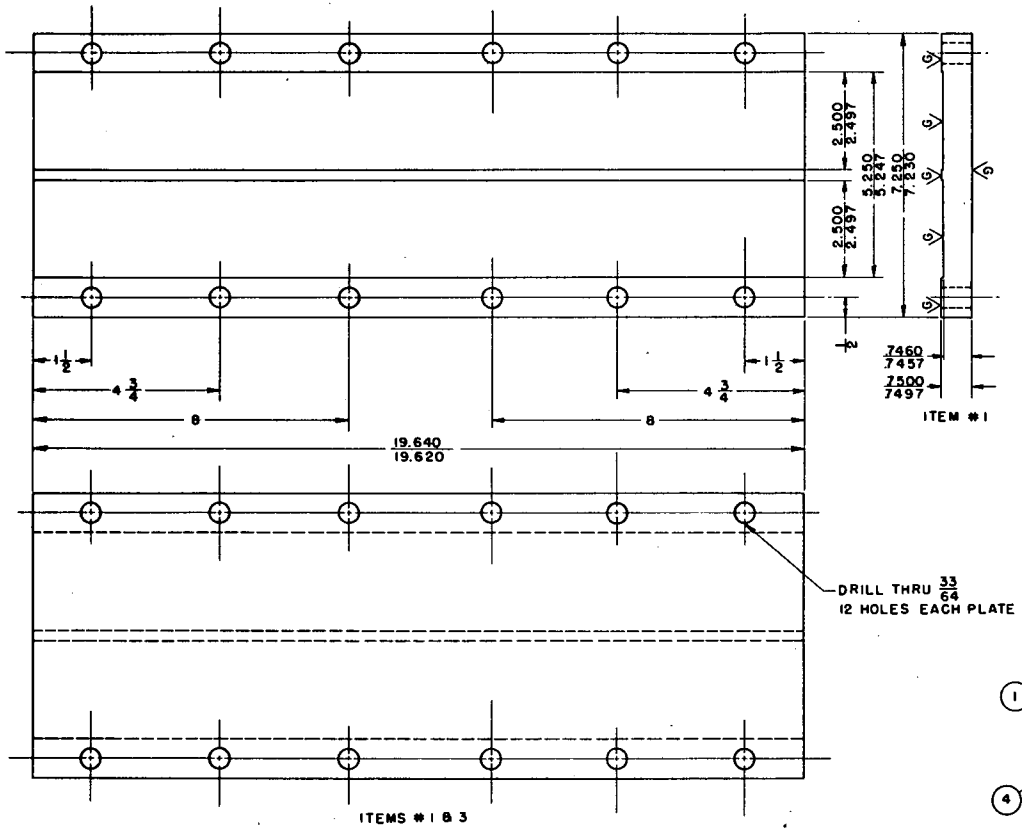
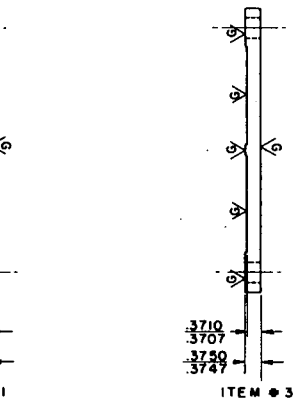
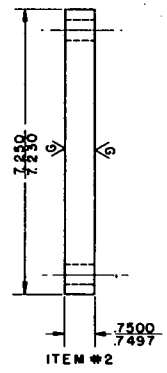
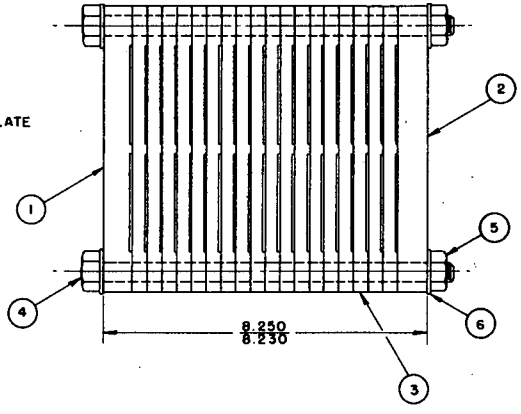
ITEM	QUAN.	MATERIAL	DESCRIPTION
1	1	S. ST.	PLATE
2	1	S. ST.	PLATE
3	18	CARBON	PLATE
4	12	S. ST.	BOLT $\frac{1}{2}$-13 x $9\frac{1}{2}$
5	12	S. ST.	HEX. NUT $\frac{1}{2}$-13
6	24	S. ST	WASHER

NOTES:
1. CHECK SPACING BETWEEN EACH PLATE WITH A MICROSCOPE WHILE ASSEMBLING.
2. SPACING BETWEEN PLATES MUST BE UNIFORM AND CONSTANT THROUGHOUT.
3. ALL SURFACES TO BE FLAT AND PARALLEL TO EACH OTHER.









BATTERY PLATE
ASSEMBLY & DETAILS
FIG. 2

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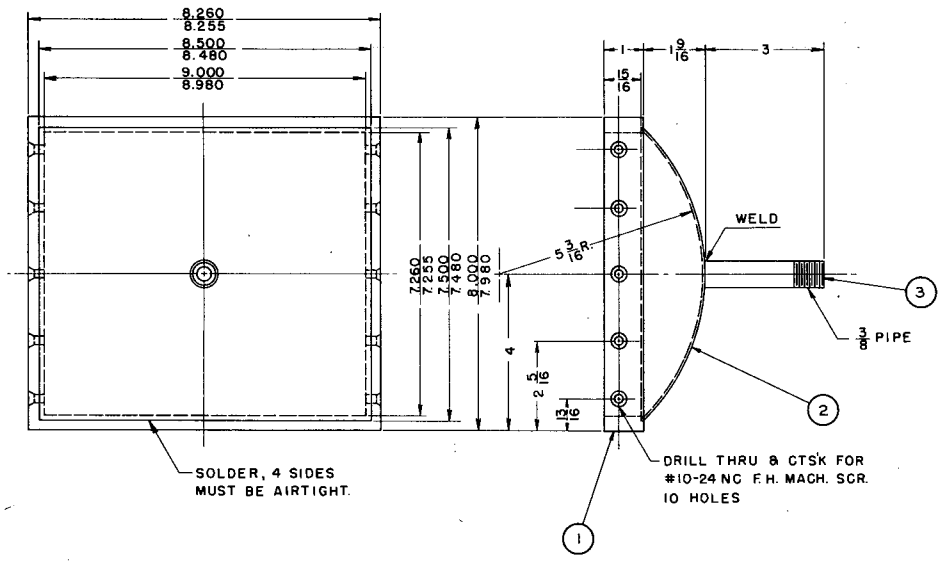
ITEM	QUAN.	MATERIAL	DESCRIPTION
1	2	S. ST.	FRAME
2	2	S. ST.	H000-20 GA.
3	2	S. ST.	$\frac{3}{8}$ PIPE

NOTE:
THESE HOODS MUST FIT
DIFFUSION BATTERY E-SK 17000



BATTERY END PIECES
FIG. 3

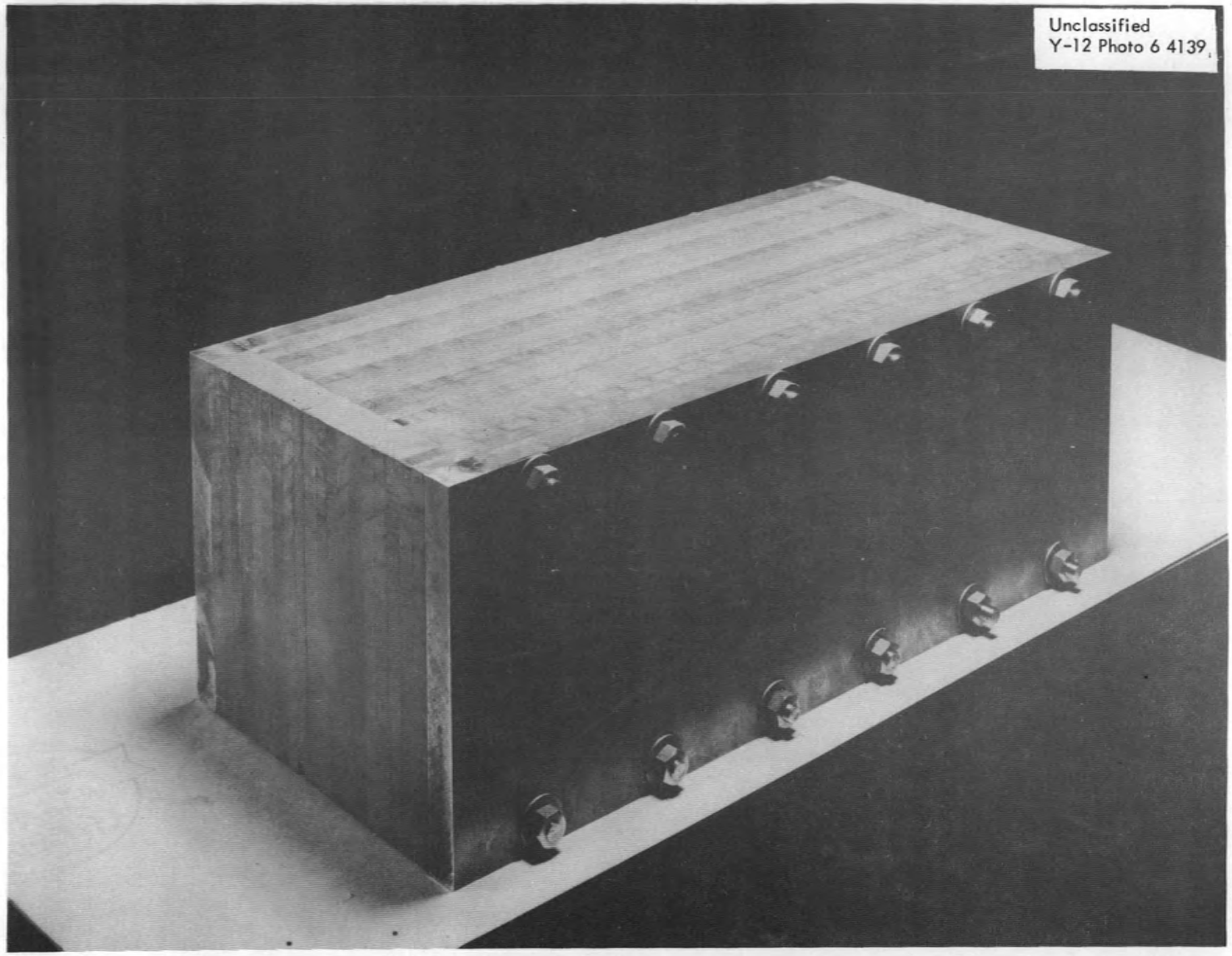


Fig. 4. Assembled Battery Without End Pieces.

low, since this method would measure the narrowest part of the channel. By these measurements the most probable deviation of each channel width from the average width was 0.0004 cm for either battery.

The channel spacings, as calculated from the pressure drop measurements (Appendix III), are: Large battery, 2a = 0.00994; small battery, 2a = 0.00970. Since the existence of end effects would tend to lower the value for 2a determined in this manner, these values can be considered the lower limits on the dimension 2a. For purposes of calculation 2a was considered to be 0.0100 cm for the large battery, 0.0098 cm for the small battery.

It was intended to make both batteries exactly alike, except for the length Z, but during construction of the batteries one extra slit was placed in the large battery, giving it 20 channels while the small battery has 19 channels. During a streamlining experiment, the length of the large battery was reduced to 47.3 cm. The final operating dimensions of the batteries are given below:

	Large Battery	Small Battery
Width of channel (2a)	0.0100 cm	0.0098 cm
Height of channel (b)	12.70 cm	12.70 cm
Length of channel (Z)	47.3 cm	5.08 cm
Number of channels (n)	20	19

Calculated Performance Curves

The equation of either battery has the form

$$F = 0.915\, e^{-\alpha} + 0.059\, e^{-11.8\,\alpha} + 0.026\, e^{-80\,\alpha} \quad (6)$$

This equation is graphed in Figure 5. Since experimentally a, b, Z are measured in cm and Q is measured in liters per minute through n channels, it is convenient to express α as follows:

$$\alpha = \frac{3.77\ bDZ}{aQ} = 0.226\ \frac{nbDZ}{aQ_t} \qquad (7)$$

n = number of channels

a,b,Z = battery dimensions, cm

D = diffusion constant, cm^2/sec

Q = flow, cm^3/sec, through one channel

Q_t = flow, liters per minute, through n channels

For the large battery, when the values of n, b, Z and a are substituted,

$$\alpha = 543{,}000\ \frac{D}{Q_t} \qquad (8)$$

For the small battery,

$$\alpha = 56{,}540\ \frac{D}{Q_t} \qquad (9)$$

Figures 6 and 7 show the relation between the fraction of influent aerosol penetrating the batteries and the diffusion constant for several values of Q_t. By use of the graphs in Appendix I the fraction penetrating the battery is plotted as a function of the particle size for each battery, Figures 8 and 9.

Smoke Testing Apparatus

A Chemical Corps "DOP" apparatus[14] was used to generate an aerosol for test purposes. This apparatus is designed to generate a

14. Operation of Apparatus, Canister Testing, MIT-E3. (CWS Directive No. 334) Chemical Corps, Army Chemical Center, Md., 1946.

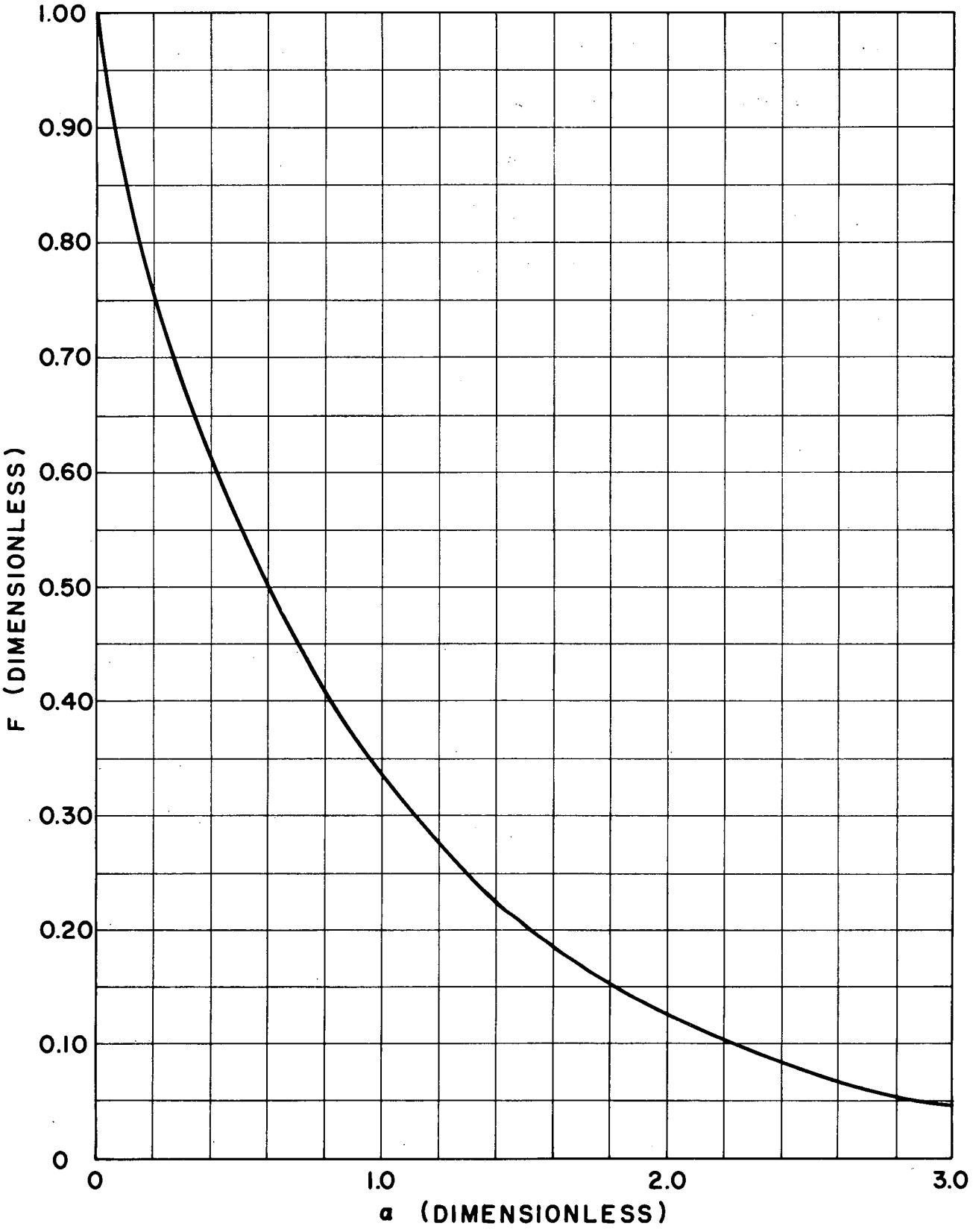


FIGURE 5

PLOT OF EQUATION

$$F = 0.915\,e^{-a} + 0.059\,e^{-11.8a} + 0.026\,e^{-80a}$$

homogeneous aerosol, particle radii 0.15 microns and produces the smoke by sudden simultaneous cooling and dilution of warm DOP vapor. Particle size is measured by use of the owl[2]. Smoke concentrations and/or penetrations are measured with the NRL-E3 smoke penetrometer[15], equipped with a Brown recorder. The "servo owl"[16] developed in this laboratory was used to control particle size. In another series of test the "LaMer type" generator as modified by E. Grassel[17] of this laboratory was used.

Operating Procedure

Essentially, the procedure consisted of (1) setting up a stable test smoke, (2) observing battery penetration at different flow rates, and (3) calculating the diffusion constant and particle size from the battery penetration.

Smoke from the generator was drawn through the battery (or bypass), through the penetration meter and then through a capillary flowmeter to the vacuum line. Figure 10 shows the battery hookup. By using three way values the flow could be directed through the large battery, small battery, or bypass line. The valve on the bypass line allowed adjustment of the pressure drop, so that the effect of pressure on the penetrometer reading

15. Kundson, H. W. and L. White, Development of Smoke Penetration Meters, Naval Research Laboratory Report No. NRL-P-2642, Sept. 14, 1945.
16. Bradshaw, R. L., report in preparation (November, 1953).
17. Grassel, E. E., report in preparation (November, 1953).

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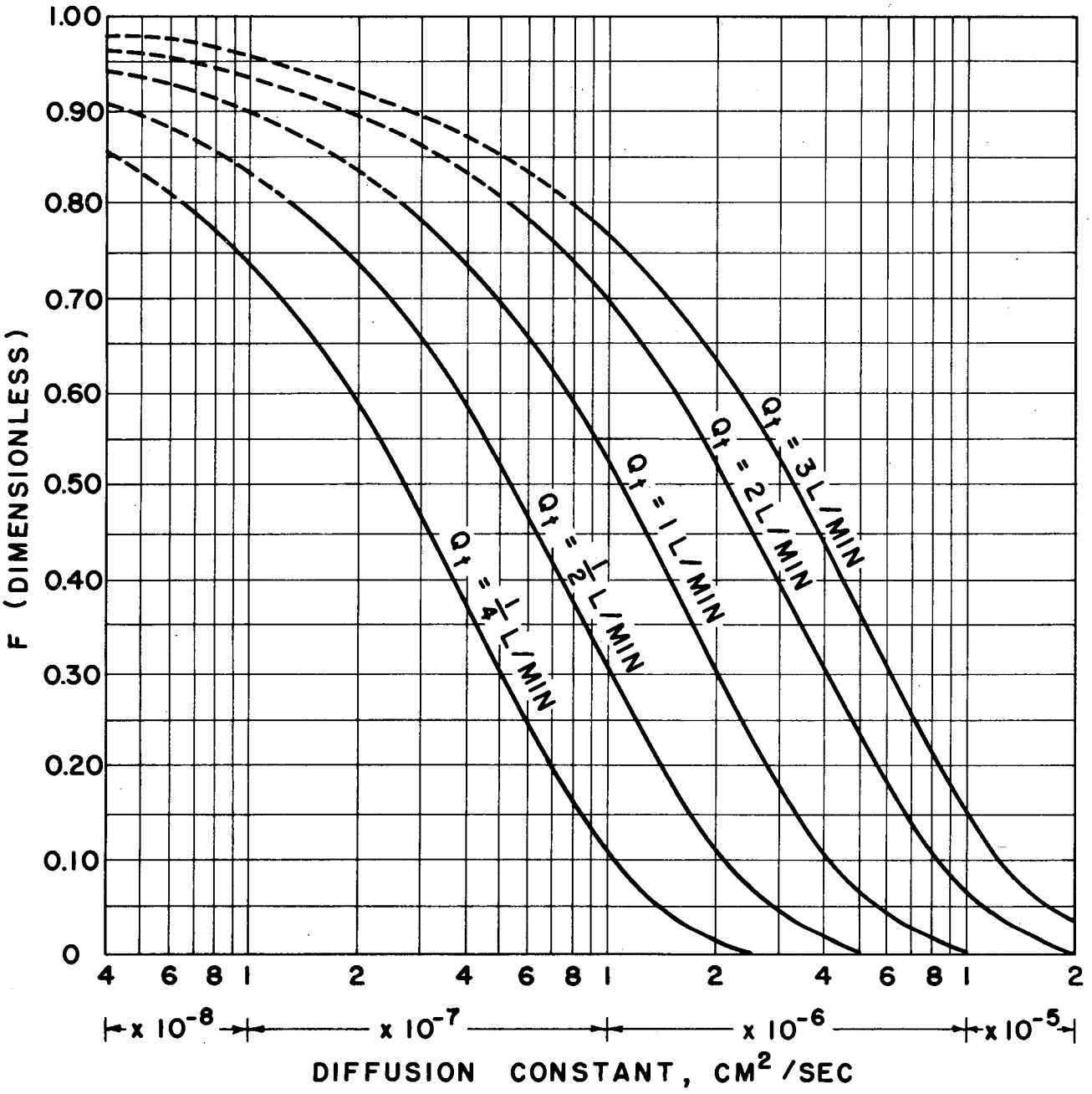

FIGURE 6
BATTERY PENETRATION (F) VS. DIFFUSION CONSTANT, LARGE BATTERY

Drawing # 22174
Unclassified

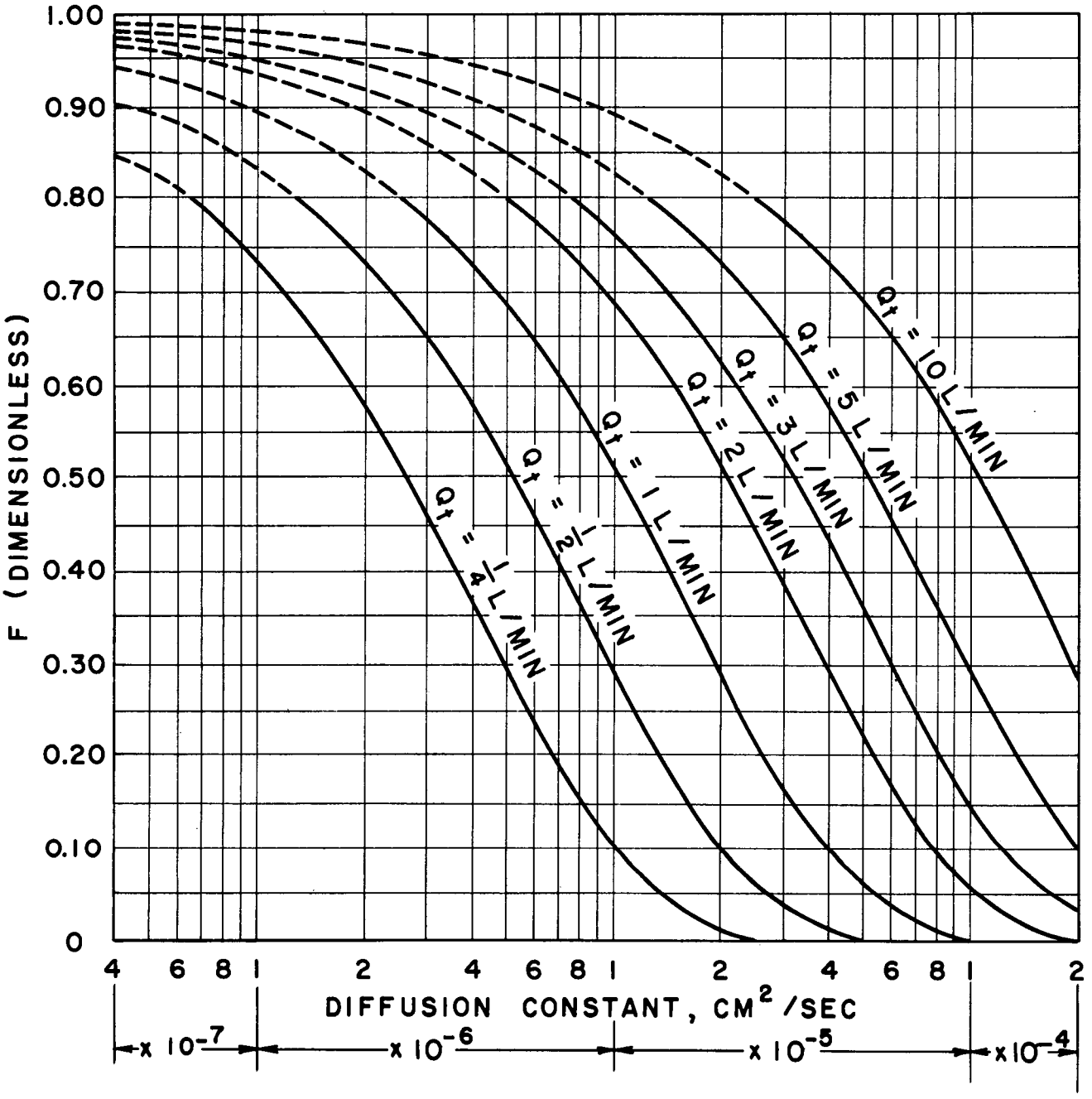

FIGURE 7

BATTERY PENETRATION (F) VS. DIFFUSION CONSTANT, SMALL BATTERY

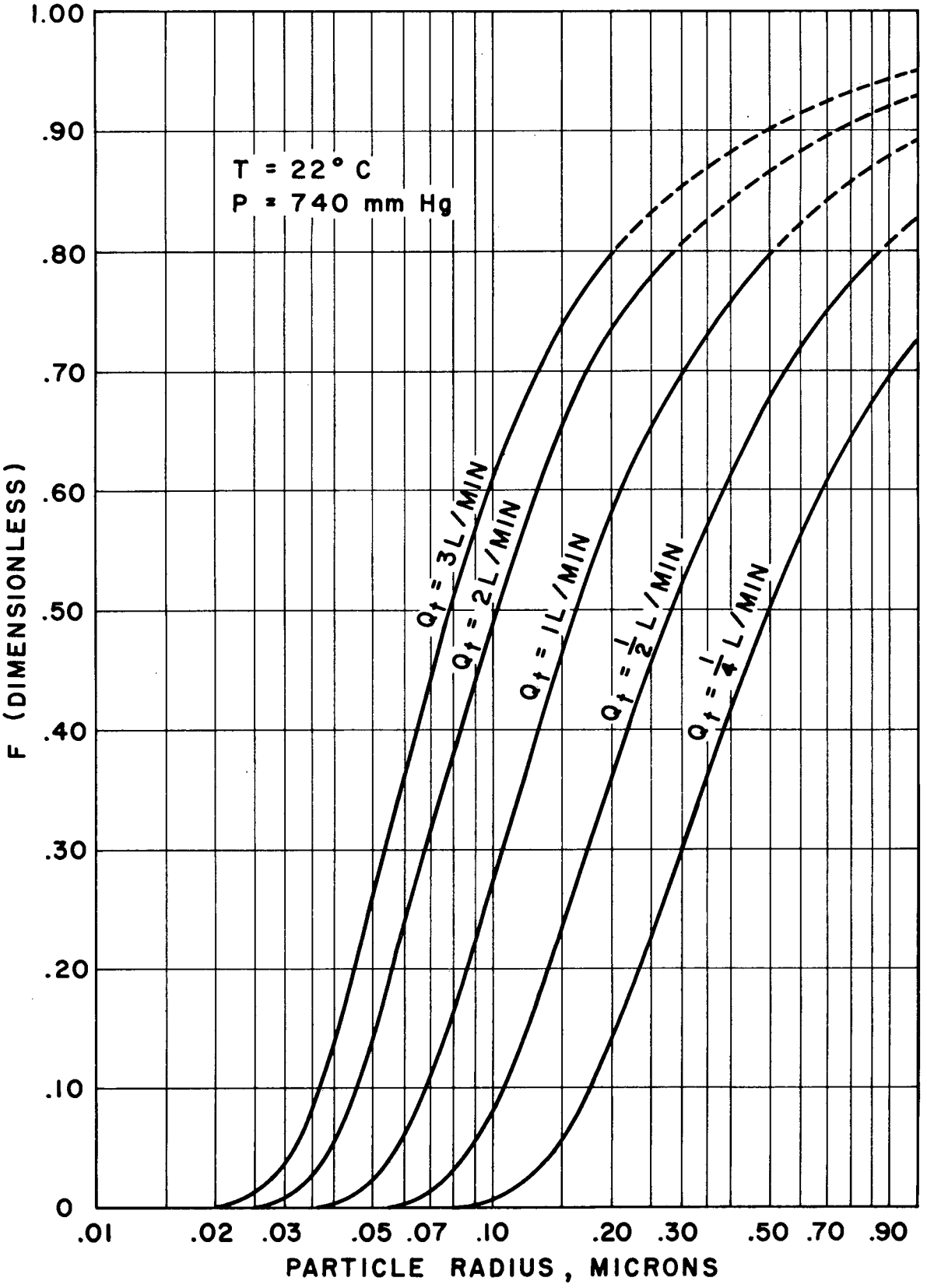

FIGURE 8
BATTERY PENETRATION VS. PARTICLE RADIUS, LARGE BATTERY

Drawing # 22176
Unclassified

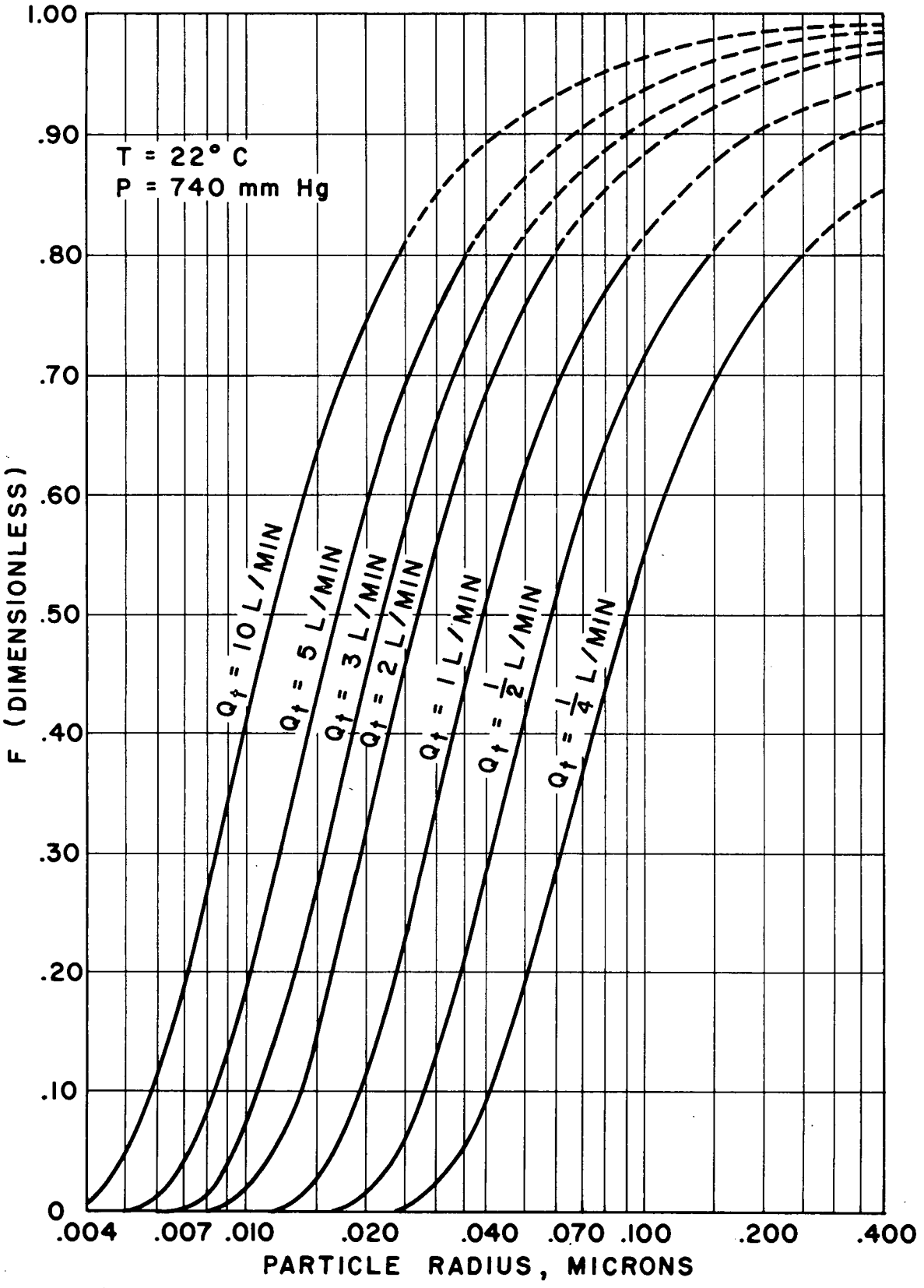

FIGURE 9
BATTERY PENETRATION VS. PARTICLE RADIUS,
SMALL BATTERY

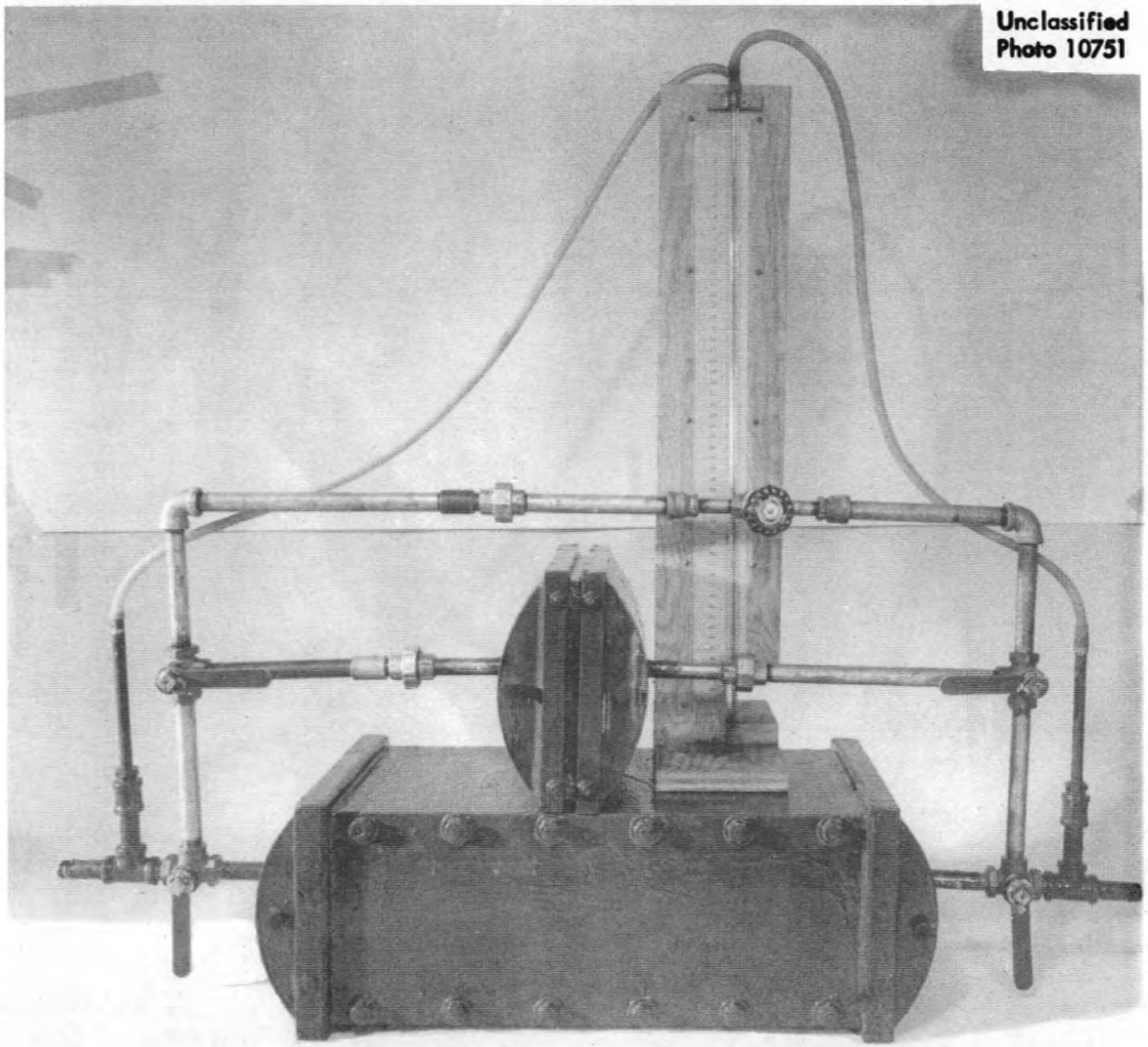

Fig. 10. Assembled Batteries.

could be determined. The manometer connected across the battery measured the pressure drop, and was used to confirm the flow rate as indicated by a capillary flowmeter. Leaks, of course, are detected by this arrangement.

The test for generator smoke stability, a sample of smoke was isolated in the smoke chamber[15] of the penetrometer and allowed to stand for 5 or 10 minutes. A change in the penetrometer reading indicated smoke instability. A rise in the reading was attributed to coagulation, due in turn to an excessively high smoke concentration. A fall in the reading indicated that evaporation of the particles was occurring. This occurs when the material used is too volatile (sulphur, for example) or when the particle size is too small.

After obtaining a stable smoke, the flow was directed through the bypass line at a known flowrate and the penetrometer reading noted. The flow was then directed through either of the batteries. After allowing time for sweeping out the end pieces, the penetrometer reading was again taken, and F, the fraction penetrating the battery, calculated. This process was repeated several times to minimize the effect of small fluctuations in smoke concentration from the generator. In most of the tests, readings were taken at several flow rates using both batteries. "Owl" readings were taken when using the DOP apparatus.

From the value of F and Q_t the diffusion constant and particle size were taken from graphs already prepared. The particle size as given by the battery was compared to the size calculated from the "owl" reading.

Battery Sweep-Out Time

Smoke was passed through each battery at flow rates of 1/2 and 2 liters per minute. After the battery penetration had reached an equilibrium value smoke free air was introduced instead of smoke without disturbing the pressure in any part of the system. The time required for the penetrometer reading to drop to 0.5 percent of its original value was observed. It was found that either battery, at a flow rate of 2 liters/min, required 4.0 min. to sweep out the aerosol (including the volume of the penetrometer cell and connecting lines), while at 1/2 liter/min., approximately 12 minutes were required.

Battery Performance Results

The results are summarized in Tables I, II, and III and Figures 11-15. In this data reference is made to the "corrected" battery. This is the large battery corrected for end effects. The method of calculating this correction is given on page 37, in the section entitled "End Effects".

Results of a series of tests using the DOP apparatus and a 42° DOP smoke (owl), equivalent to a particle size of approximately 0.18 microns radius, are shown in Table I and Figure 11, 12, 13.

To generate a large size DOP aerosol, a LaMer type apparatus was used. The particle size of the aerosol was estimated by drawing the aerosol through a 4-liter flask and observing the color of the light scattered by the aerosol at different angles to an incident light beam.

The boiler temperature of the generator was about 165°C. Four red bands[18] could be detected in the smoke. Results of battery tests on this smoke are given in Table II and in Figures 14 and 15.

Two experiments were made using the LaMer apparatus in which all conditions except the boiler temperature were kept constant. The results are given in Table III. In these two experiments the reheater temperature was maintained about 5°C above the boiler temperature. The flow over the nuclei source was 4 liters/min., with a diluting air flow rate of 25 liters/min. The flow rate through the battery was 1 liter/min. in all cases. The column "Relative Particle Size" in Table III shows the relative particle size when the size at a boiler temperature of 116°C (or 110°C) is considered unity. For example, the value 1.45 was obtained by taking the cube root of the vapor pressure of DOP at 130°C divided by the vapor pressure pressure of DOP at 116°C.

18. Handbook on Aerosols, Washington, D. C., Government Printing Office, 1950, page 84.

TABLE I

BATTERY DATA, APPROXIMATELY 0.18 μ SMOKE

(Owl Reading, 42°)

Flow Rate Liters/min.	Fraction Penetrating		Calculated Penetration "Corrected" Battery	Particle Radius, Microns	
	Large Battery	Small Battery		Large Battery	"Corrected" Battery
3	0.670	0.923	0.726	0.12	0.13
1/2	0.361	0.832	0.434	0.20	0.21
2	0.643	0.891	0.721	0.145	0.175
1	0.521	0.896	0.581	0.17	0.18
1	0.537	0.867	0.619	0.18	0.205
2	0.659	0.900	0.732	0.155	0.18
3	0.748	0.898	0.833	0.16	0.225

TABLE II

BATTERY DATA, APPROXIMATELY 0.4 μ SMOKE

(4 reds)

Flow Rate Liters/min.	Fraction Penetrating		Calculated Penetration "Corrected" Battery	Particle Radius, Microns	
	Large Battery	Small Battery		Large Battery	"Corrected" Battery
3	0.809	0.918	0.881	0.22	0.33
2	0.764	0.903	0.846	0.23	0.34
1	0.667	0.895	0.743	0.26	0.33
1/2	0.525	0.806	0.651	0.30	0.39
1/4	0.398	0.795	0.500	0.36	0.45
3	0.810	0.930	0.871	0.22	0.31

TABLE III

BATTERY PENETRATION VS PARTICLE SIZE

Nuclei Source	Boiler Temperature	Fraction Penetrating		Calculated Penetration "Corrected" Battery	Particle Radius		Relative Particle Size		Appearance of Smoke
		Large Battery	Small Battery		Large Battery	"Corrected" Battery	"Corrected" Battery	Calculated, DOP Vapor Pressure	
Volts	°C				Microns	Microns	Microns	Microns	
136 136	116 116	0.28 0.29	0.82 0.84	0.345	0.102	0.107	1.00	1.00	Bluish
136 136	130 130	0.39 0.39	0.87 0.87	0.45	0.125	0.13	1.21	1.45	Faint Color
136 136	148 148	0.53 0.55	0.89 0.89	0.605	0.18	0.195	1.82	2.30	Intense Color
136 136	162 162	0.63 0.63	0.90 0.91	0.695	0.24	0.265	2.47	3.10	Reds at ~60°, 140°
136 136	191 191	0.695 0.715	0.89 0.88	0.795	0.31	0.44	4.11	5.85	~ 4 reds
100 100	110 110	0.44 0.41	0.87 0.86	0.49	0.14	0.14	1.00	1.00	Not observed
100 100	123 123	0.55 0.54	0.86 0.87	0.63	0.18	0.21	1.50	1.42	Not observed
100 100	148 148	0.62 0.63	0.90 0.89	0.70	0.23	0.275	1.96	2.71	Not observed
100 100	170 170	0.68 0.71	0.83 0.86	0.825	0.30	0.54	3.86	4.40	Not observed

Drawing # 22177
Unclassified

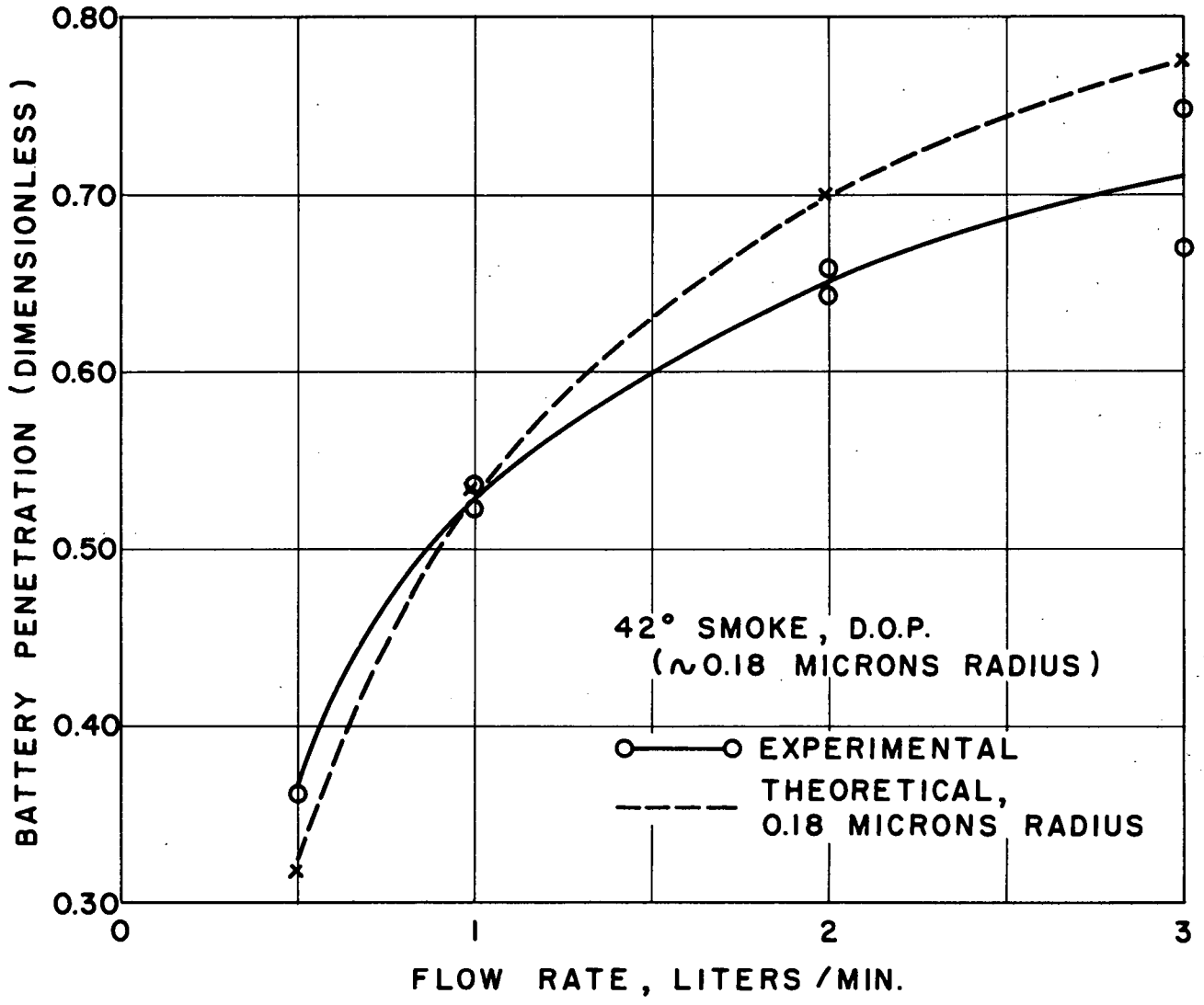

FIGURE 11
PENETRATION VS. FLOW RATE, LARGE BATTERY

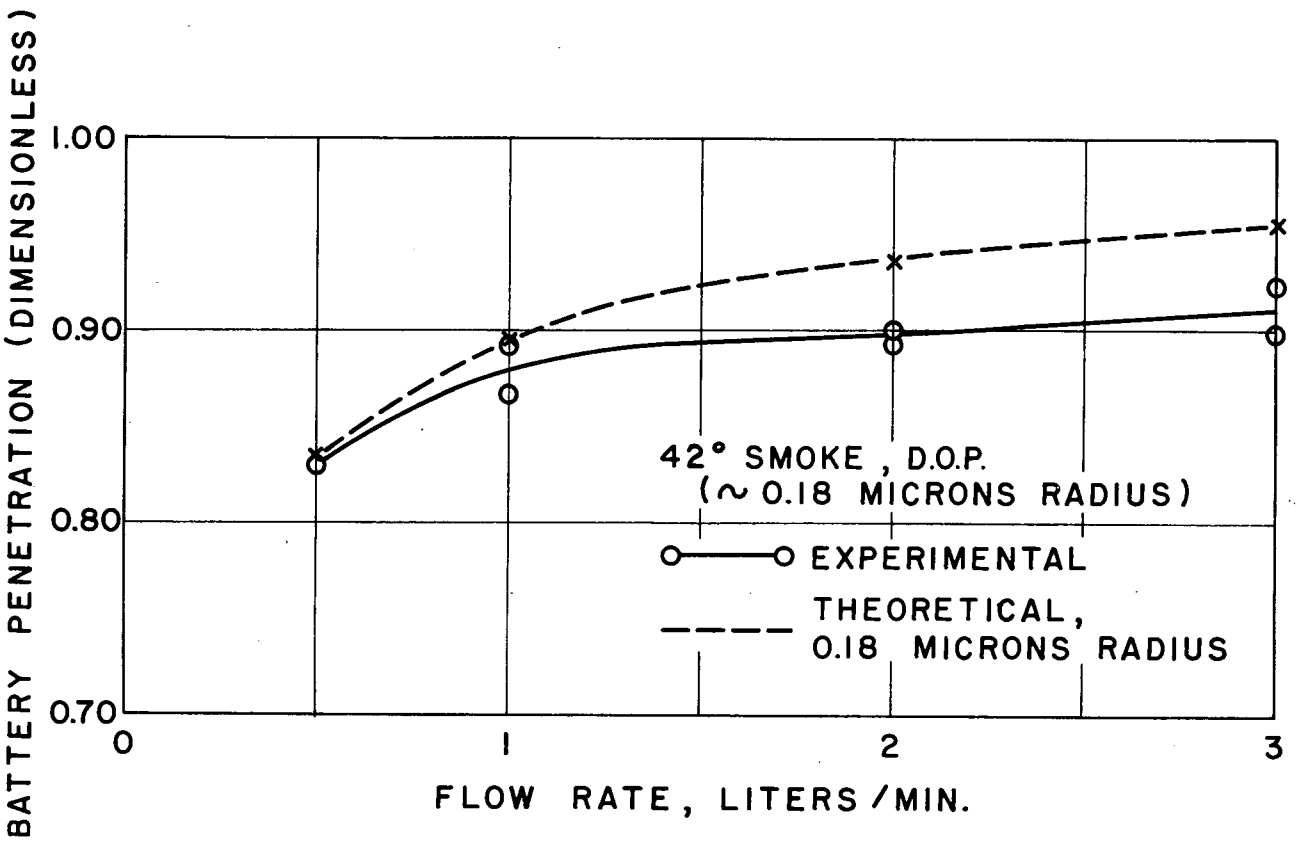

FIGURE 12
PENETRATION VS. FLOW RATE, SMALL BATTERY

Drawing # 22179
Unclassified

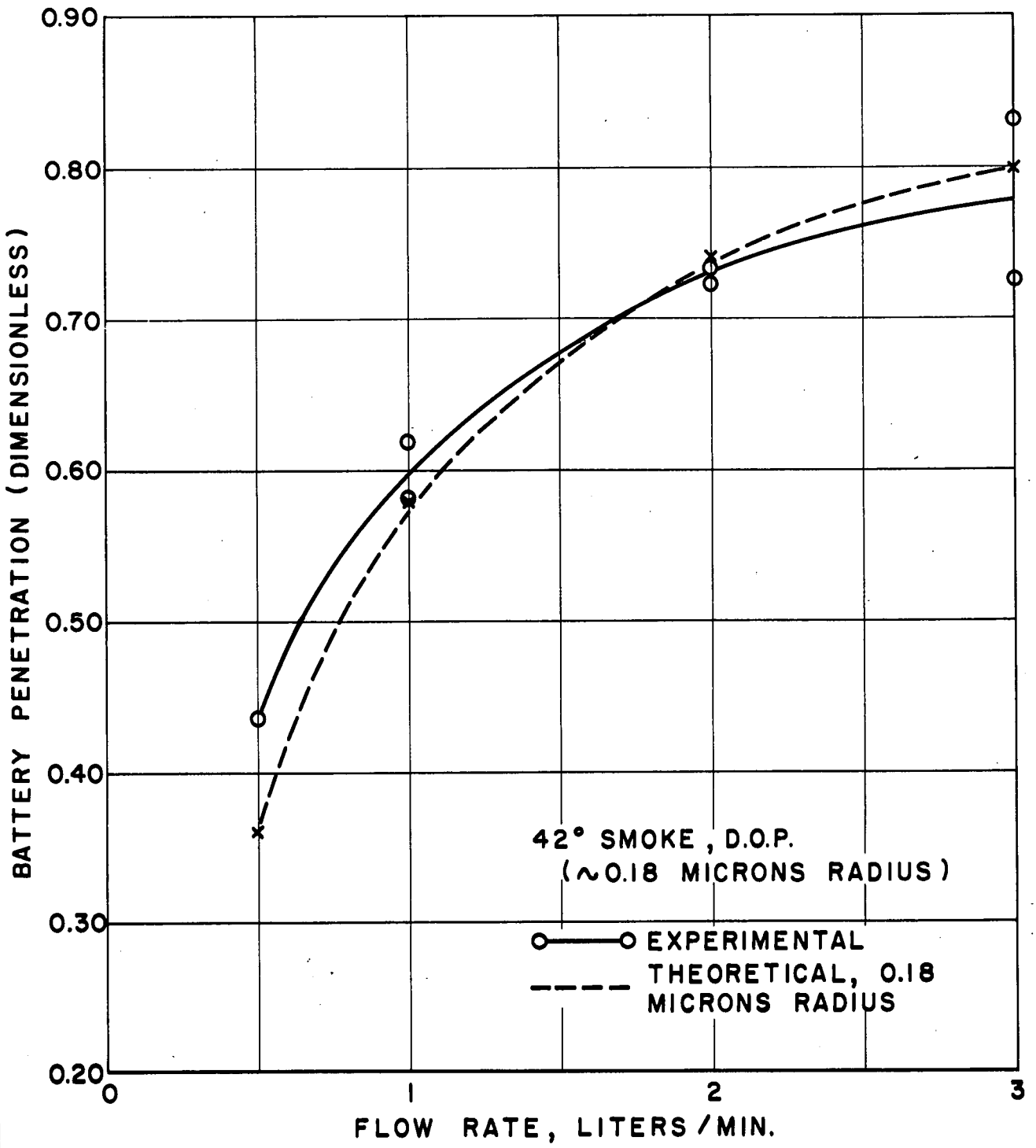

FIGURE 13

PENETRATION VS. FLOW RATE, "CORRECTED" BATTERY

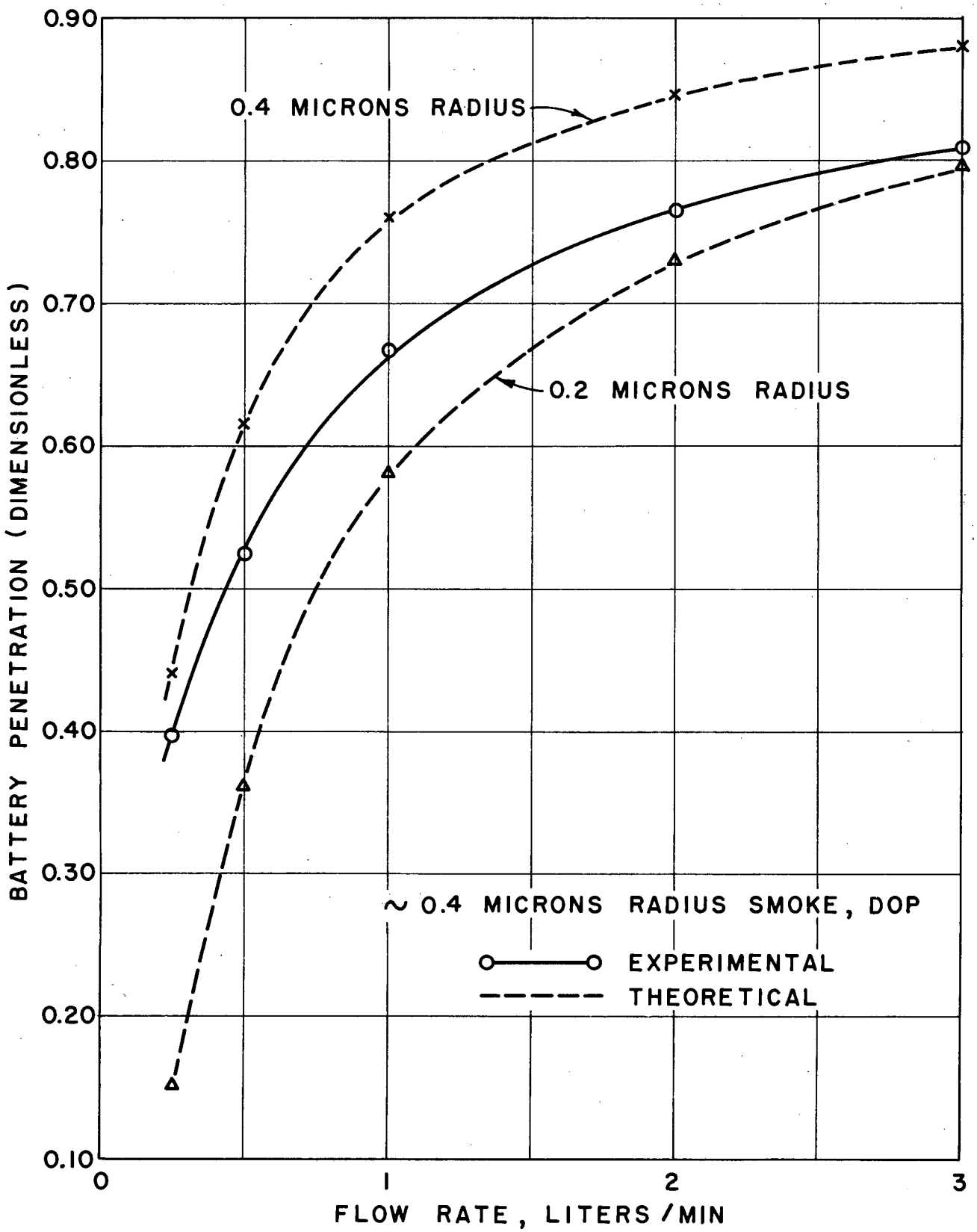

FIGURE 14
PENETRATION VS. FLOW RATE, LARGE BATTERY

Drawing # 22181
Unclassified

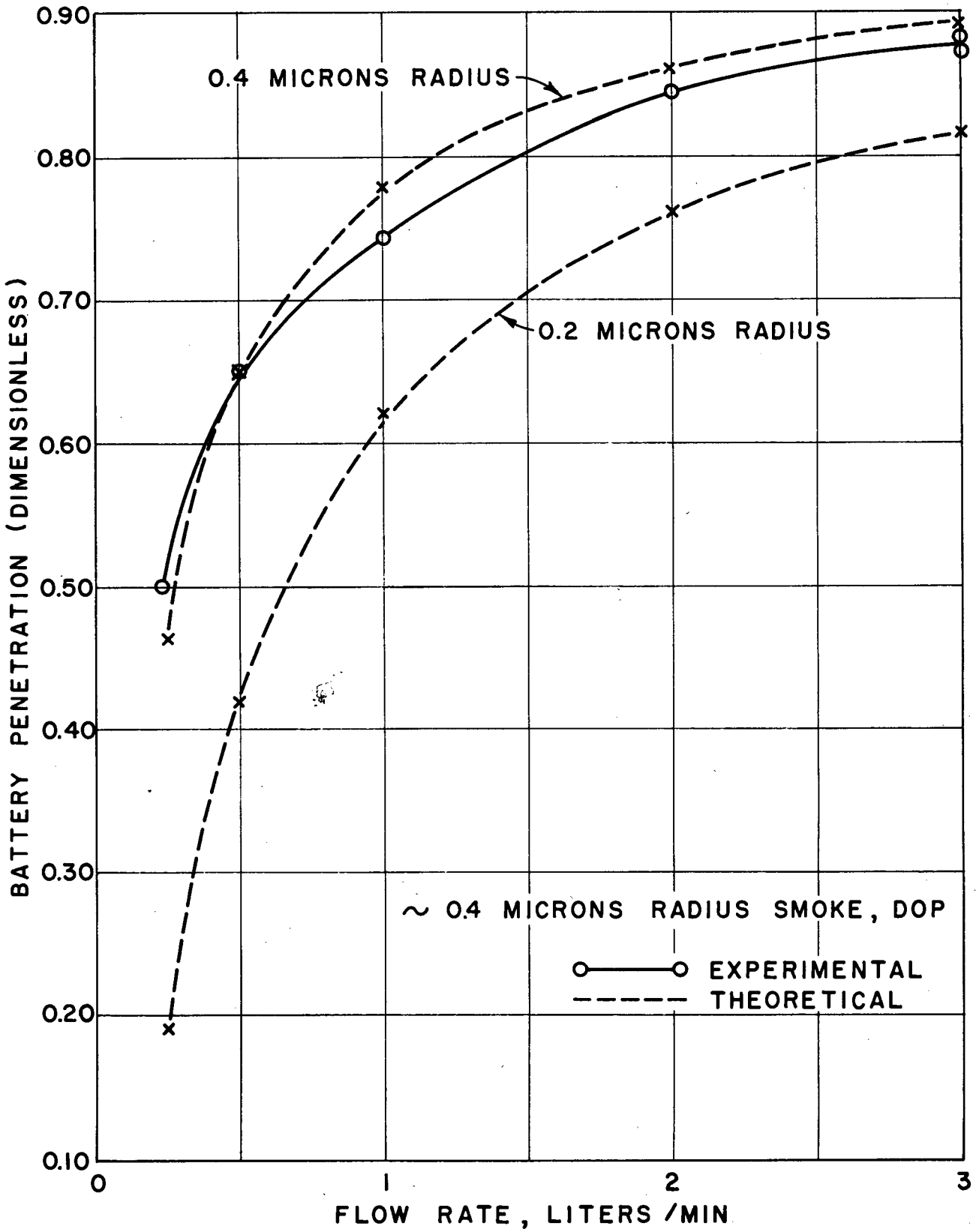

FIGURE 15

PENETRATION VS. FLOW RATE, "CORRECTED" BATTERY

DISCUSSION

Comparison of Experiment with Theory

The battery gives particle sizes close to the sizes as determined by light scattering techniques. However, a definite discrepancy exists between theory and experiment. In every test with either battery, including some preliminary results not reported here, the experimental penetration vs. flow rate relation (F vs. Q) shows a deviation from theory which is always in the direction of apparent increasing diffusion coefficients with increasing flow rates. The effect of various disturbing factors on the battery performance is discussed in the following sections.

End Effects

The end effect problem was attacked by use of two batteries essentially alike except for their length Z. As stated previously, the small battery had 19 channels and the larger battery 20. The small battery had a slit width of 0.0098 cm, and the large battery 0.0100 cm. The length of the small battery was 5.08 cm. It was originally planned to make the small battery exactly like the large one except for the length Z. However, it is possible to get an "effective length" for the present small battery, which is the length the small battery would have if it had the same number of channels and same slit width as the large battery, and the same performance curves (F vs. D at different Q_t's) as the present small battery. This "effective length" was obtained as shown below:

$$(5.08)\left(\frac{19}{20}\right)\left(\frac{0.0100}{0.0098}\right) = 4.92 \text{ cm}$$

It is not strictly permissible to use a small battery of different cross sectional properties for correction of the performance of a longer battery, but in this case the difference in cross sectional properties is so small as to be negligible. In any case, this amounts to a small correction to a correction, and the error introduced here is small compared to experimental errors.

It is considered that the same aerosol mass transfer to the battery wall occurs in the first 4.92 cm of the large battery as occurs in the entire length of the small battery. Therefore, at a point 4.92 cm down the large battery in the Z-direction, the influent aerosol concentration will be the same as the concentration at the exit of the small battery. Designating the last (47.3-4.9) = 42.4 cm of the large battery as the "corrected" battery, the following relation holds:

$$F\,(\text{corrected battery}) = \frac{F(\text{large battery})}{F(\text{small battery})}$$

Since the corrected battery has a different Z value, the curves of Figures 6 and 8 do not directly apply. However, for a given F and Q_t the D values may be read from Figure 6 and multiplied by the factor

$$D(\text{corrected battery}) = \frac{47.3}{42.4}\,D(\text{large battery}) = 1.16\,D(\text{large battery})$$

An estimate of the end effects may be obtained by considering the distance down the battery in the Z-direction necessary to establish streamline flow. In a monograph edited by Goldstein[19] a sketch is given showing

19. Goldstein, S., Modern Developments in Fluid Dynamics, Volume I, Oxford, the Clarendon Press, 1938, p. 308 - 310.

the flow distribution between parallel plates as a function of the distance downstream and other parameters. According to this figure, the batteries used in this work should have a parabolic flow distribution at a distance of less than 0.005 cm downstream, for flows (Q_t) under 10 liters/min. Since the linear velocity at a Q_t of 10 liters/min. is about 60 cm/sec, the time available for mass transfer due to non-streamline flow in the inlet is only about 10^{-4} sec. It does not seem, from this calculation, that a measurable diffusion mass transfer could exist at the entrance due to non-streamline flow.

The experimental results, however, indicate that an end effect exists. This is particularly apparent from a comparison of Figures 14 and 15. The smoke size, as estimated from the number of reds, was about 0.4 microns radius and possibly larger. The particle size as given by the "corrected" battery was much closer to this value than the particle size as given by the large uncorrected, battery.

The existence of an end effect is confirmed by the results of Table III. As the particle size of the smoke is increased, the difference between the corrected and uncorrected results becomes larger and larger. This indicates that particles are being removed from the air stream in the inlet, probably by impaction, (inertial deposition), and as would be expected, the larger the particle size, the greater the removal by impaction.

Effect of Smoke Inhomogeneity

If the battery is used on a heterogeneous smoke, the battery will indicate an apparent particle size somewhere between the maximum and minimum size present in the aerosol. Table IV shows the effect on battery penetration of various hypothetical smoke mixtures. In these compilations, it was assumed that all particles, regardless of size, had unit light scattering power when detected by the penetrometer. The effect of changing light scattering response with particle size would merely shift the percentage comparison of the hypothetical mixture. This is shown by the following example:

Assume 100 particles enter battery, 50 having a size so that $F = F_1$ and 50 having a size so that $F = F_2$. For unit light scattering power in the detector, the apparent F would be:

$$\frac{\text{Output}}{\text{Input}} = F = \frac{50\,(F_1) + 50\,(F_2)}{100}$$

Now let the particles having the size corresponding to F_1 have a light scattering power of 3 relative to the particles having a size corresponding to F_2:

$$\frac{\text{Output}}{\text{Input}} = F = \frac{(50)\,(3)\,(F_1) + 50\,F_2}{(50)\,(3) + 50} = \frac{75\,(F_1) + 25\,(F_2)}{100}$$

It is obvious that if the first mixture, above, had been composed of 75 percent particles having a size corresponding to F_1 and 25 percent particles having a size corresponding to F_2, each size with the same light scattering power, the same result as given in the second case would have been observed.

TABLE IV

EFFECT OF SMOKE INHOMEGENUITY

Smoke* Composition	F (battery penetration)**			Smoke* Composition	(F (battery penetration)**		
	Q_t = 1/2	Q_t = 1	Q_t = 3		Q_t = 1/2	Q_t = 1	Q_t = 3
50 percent 0.200 μ 50 percent 0.146 μ	0.296	0.516	0.760	90 percent 0.64 μ 10 percent 0.092 μ	0.662	0.770	0.881
100 percent 0.170 μ	0.290	0.516	0.755	100 percent 0.443 μ	0.644	0.770	0.885
90 percent 0.200 μ 10 percent 0.146μ	0.349	0.566	0.784	10 percent 0.64 μ 90 percent 0.092 μ	0.123	0.290	0.611
100 percent 0.193μ	0.349	0.566	0.785	100 percent 0.104 μ	0.091	0.290	0.622
10 percent 0.200 μ 90 percent 0.146 μ	0.243	0.468	0.736	50 percent 0.64 μ 50 percent 0.146 μ	0.480	0.642	0.822
100 percent 0.150μ	0.240	0.468	0.732	100 percent 0.245 μ	0.450	0.642	0.824
50 percent 0.200 μ 50 percent 0.092 μ	0.208	0.404	0.684	90 percent 0.64 μ 10 percent 0.146 μ	0.680	0.792	0.896
100 percent 0.131μ	0.177	0.404	0.695	100 percent 0.50 μ	0.678	0.795	0.900
90 percent 0.200μ 10 percent 0.092 μ	0.331	0.543	0.769	10 percent 0.64 μ 90 percent 0.146 μ	0.280	0.493	0.748
100 percent 0.182 μ	0.323	0.543	0.773	100 percent 0.162 μ	0.268	0.493	0.750
10 percent 0.200 μ 90 percent 0.092 μ	0.086 0	0.266	0.599				
100 percent 0.100μ	0.077	0.266	0.602				
50 percent 0.64 μ 50 percent 0.092 μ	0.392	0.530	0.746				
100 percent 0.177μ	0.308	0.530	0.768				
100 percent 0.185μ	0.368	0.552	0.778				

*Particle radius is given in microns.

**Calculated for 22°C, 740 mm, Q_t in liters per minute, for the large battery.

Two conclusions may be drawn from the table. (1) A pure smoke always shows a slightly larger difference between the F values at low and high flow rates than a heterogeneous smoke which has the same F at an intermediate point. This effect would be interpreted, in an actual run, as the battery showing increasing diffusion coefficients with increasing flow rates. (2) The amount of deviation of the F-Q relation for mixtures from the F-Q relation for pure smokes is remarkably small. In other words, the battery is relatively insensitive to smoke inhomogenuity.

Coagulation and Evaporation Effects

The stability of the smokes used was determined by isolation of the smoke in the penetrometer and observation of the time rate of change of its reading. Most of the smokes used were rather stable, that is, the penetrometer reading changed less than 1 percent per minute. This indicated little evaporation or coagulation. The small effects due to coagulation or evaporation were also in a large measure cancelled out by use of the two-battery technique. Since the end pieces of the batteries are exactly alike, the transit time through each battery is virtuallythe same and when using the penetration through each, to calculate the F-value for the corrected battery, the effect of coagulation or evaporation is largely cancelled out. Thus, it is believed that the F-Q discrepancy is not due to evaporation or coagulation.

Electrical Effects

It is not to be expected that DOP particles from the LaMer generator are charged before entering the battery[20]. However, the possibility exists that the friction of the air moving between the graphite plates would cause a charge to accumulate on the particles. As the flow rate increases the amount of charging would increase, and this may explain the F-Q discrepancy.

Other Effects

The assumption that all particles which contact the wall adhere is probably open to question. However, if this assumption were not true, the result would be a too high penetration at high flows. This has never been observed. The battery was not always operated at exactly 22°C, and 740 mm Hg, however, a room temperature or pressure change would cause no deviation in the F-Q relationships. (Provided, of course, that all F's at different Q's were taken at the same temperature and pressure).

The remote possibility that the aerosol might be flowing directly through the graphite was investigated and it was found that this effect is insignificant. Calculations were made on the effect of irregular battery plate spacing and this effect estimated to be small. A study of possible thermal currents in the battery was not made but due to the relatively high flow rate through the battery, thermal effects were thought to be negligible. The smokes used in the battery were thought to be rather

20. LaMer, V. K., et. al., "Filtration of Monodisperse Electrically Charged Aerosols," Columbia University, June 30, 1952 (NYO-514).

homogeneous as judged by the intensity and position of the reds observed. Table IV shows that the smokes used would have to be very inhomogeneous before any appreciable effect would be apparent in the F-Q relation.

Cause of F-Q Relation Discrepancy

As stated before, the experimental results using DOP smoke show that as the flow rate Q increases, the apparent diffusion constant D increases, even after cancellation of end effects by the two battery technique. The results with gases (Appendix II, Table II,) show no such effect. The results given in Appendix II indicate that the battery theory is correct within experimental error. Therefore, it would seem that with aerosols some process other than diffusion is causing either (a) too low a mass transfer at low flow rates, or (b) too high a mass transfer at high flow rates. The previous discussion indicates that at least a large part of this discrepancy cannot be attributed to (1) inertial deposition at the battery entrance, (2) smoke inhomogenuity (3) other minor effects.

The cause for the discrepancy has not been found in the present work. Possibility (b) above, that there exists too high a mass transfer at high flow rates seems most likely. This may be due to frictional electrical effects, which would probably cause increasing non-diffusion mass transfer with increasing flow rates.

Value of Battery for Particle Size Determinations

A rough estimate of the accuracy of the diffusion battery method shows that corrected far end effects, the battery will give a particle size within 30 percent of the true value. At particle sizes below $\sim$ 0.1 micron radius, the end effects should be negligible. The battery, corrected for end

effects, can be used to indicate unambiuously whether or not one test smoke is larger than another. With an sensitive method for the determination of mass concentration, it should be possible to determine approximate particle sizes from 0.5 micron down to gas molecule size, 0.0003 microns radius.

Filter Performance Implications

A question controversial at the present time is the existence or non-existence of a particle size for maximum penetration through a filter. If the battery itself is considered a "filter," the results of this work show that a size for maximum penetration does exist. This is evident from the experimental results shown in Table III. As the particle size increases, the penetration through the battery also increases. Since the spacing of the plates is 100 microns, obviously particles larger than 50 μ radius could not penetrate. Due to inertial deposition at the inlet of the battery, it is probable that particles of $\sim$ 5 μ radius would be efficiently deposited at high flow rates. It may be said, therefore, that the size for maximum penetration for the large battery is in the approximate range 1 to 5 μ radius. In the case of the small battery, where the mass transfer by diffusion is smaller compared to the mass transfer by other effects, the size for maximum penetration would occur at a lower value of the particle radius. According to Table III, the size for maximum penetration for this battery is $\sim$ 0.3 microns.

CONCLUSIONS AND RECOMMENDATIONS

The diffusion battery method checks the light scattering for particle size determination to within better than ~30 percent. The method is good for particle sizes under ~0.5 microns radius. The existence of a size for maximum penetration through the battery has been demonstrated. Two batteries, with graphs of operating parameters, are now available for use in filter efficiency studies.

It is recommended that if further work is done to improve battery performance, that (a) to cut down the time lag much smaller end pieces be used, and (b) the possible frictional electrical effect be investigated.

ACKNOWLEDGMENTS

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APPENDIX I

Relation Between Diffusion Constant and Particle Size

The Einstein-Stokes equation applies for particles which are large compared to the mean free path of an air molecule;

$$D = \frac{KT}{6\pi\eta r} \tag{1}$$

D = diffusion constant, cm^2/sec

K = Boltzman's constant (1.38×10^{-16} erg/°C)

T = absolute temperature, °K

η = viscosity of air, poises

r = radius of particle, cm

For particles below about 5 micron radius it is necessary, to apply the so-called Cunningham correction for the slip of particles between air molecules. λ is the mean free path of an air molecule. This gives

$$D = \frac{KT}{6\pi\eta r}\left[1 + A\frac{\lambda}{r}\right] \tag{2}$$

The quantity A has been studied by many investigators. Millikan, in conjunction with the famous oil drop experiment, studied the quanity A very carefully[21], and proposed the equation

$$A = A_0 + B e^{-c\frac{r}{\lambda}} \tag{3}$$

21. Millikan, R. A., "The General Law of Fall Through A Gas," Phy. Rev. 22 (2nd Series) 1-23 (1923).

This equation was verified by Millikan for values of $\frac{\lambda}{r}$ ranging from 0.1 to about 100. The high values of $\frac{\lambda}{r}$ were studies by lowering the air pressure so that λ become large compared to r. If the radius of the particle is very small, and the medium is air at atmospheric pressure, the same high values of $\frac{\lambda}{r}$ are obtained. Assuming that Millikan's verification of the equation applies also to this case, as seems very likely, we may calculate that this equation is expected to hold down to particle radii of about 0.001 microns.

Millikan determined the quantity $A\lambda$ experimentally[22], and then calculated A using the then accepted value of the mean free path[23] (9.42×10^{-6} cm at 760 mm, 23°C). He obtained the values[21] $A_o = 0.864$, $B = 0.290$, and $C = 1.25$. From the values and formulae given by Partington[24] and Kennard[25] we may take the presently accepted value of the mean free path of an air molecule at 23°C, 760 mm to be 6.53×10^{-6} cm. Correcting Millikan's values for the presently accepted value of the mean free path, there is obtained

$$A_o = 0.864 \left(\frac{9.42 \times 10^{-6}}{6.53 \times 10^{-6}}\right) = 1.24$$

$$B_o = 0.290 \left(\frac{9.42 \times 10^{-6}}{6.53 \times 10^{-6}}\right) = 0.42$$

$$C = 1.25 \left(\frac{6.53 \times 10^{-6}}{9.42 \times 10^{-6}}\right) = 0.87$$

22. Millikan, R. A., "The Isolation of an Ion," Phy. Rev. 23, p. 379 (1911).
23. Millikan, R. A., "Coefficients of Slip in Gases," Phy. Rev. 21 (2nd Series), p. 223 (1923).
24. Partington, J. R., An Advanced Treatise on Physical Chemistry, London, Longmans (1949).
25. Kennard, E. H., Kinetic Theory of Gases, New York, McGraw-Hill (1939).

The quantity A_o varies a small amount with the nature of the droplet[21,26]. However, Millikan states that the sum (A_o + B) is the same within two to three percent for most types of particles. Since in equation (3) the second term can vary only between O and +B, the maximum variation in A with different kinds of particles amounts to about 30 percent. Langmuir[27] summarizes the results of various observers and given the values A_o = 0.62, B = 0.22, and C = 2.2. Langmuir corrected his values to a mean free path of 1.31×10^{-5} cm at 20°C, 760 mm Hg. Converting his values to the presently accepted value of the mean free path, there is obtained A_o = 1.25, B = 0.44, and C = 1.09. These are the values that are used in this report. They are believed rather accurate for oil particles down to about 0.001 microns radius, and within 30 percent for other particles. This gives the final equation,

$$D = \frac{KT}{6\pi\eta r}\left[1 + A\frac{\lambda}{r}\right] \tag{4}$$

$$A = 1.25 + 0.44\, e^{-1.09\frac{r}{\lambda}} \tag{5}$$

For air at 22°C, 740 cm Hg, equation (4) reduces to (r in cm, D in cm^2/ sec).

$$D = \frac{11.9 \times 10^{-12}}{r}\left(1 + A\frac{6.7 \times 10^{-6}}{r}\right) \tag{6}$$

It is of interest to consider the case of particles as small as gas molecules, where $\lambda >> r$. In this case the exponential term $(-1.09\frac{r}{\lambda})$ becomes essentially equal to 1. Also, the first term in equation (4) becomes negligible, giving

$$D = \frac{KT\lambda}{6\pi\eta r^2}\left(A_o + B\right)$$

26. Wasser, V. E., "Das Widerstandgesetz kleiner Kugeln in reibenden Medien," Physik. Zeitschr. 34, 257-278 (1933).
27. Langmuir, Irving, "Filtration of Aerosols and Development of Filter Materials," (Part IV) OSRD-865, Sept. 4, 1942.

Partington[24] given the equation

$$\lambda = \frac{1.25\,\eta}{\sqrt{\rho P}} \tag{7}$$

λ = mean free path

η = viscosity (of air)

ρ = density (of air)

P = pressure

Using this equation, and substituting the values of the constant, there is obtained

$$D = 1.41 \times 10^{-13} \left(\frac{T^{3/2}}{P r^2}\right)\left(\frac{1}{\sqrt{M}}\right) \tag{8}$$

T = absolute temperature

P = pressure

M = molecular weight (of air)

r = radius of diffusing particle.

This equation is similar to the semi-empirical equation given by Sherwood[28] which is used for calculation of gas diffusion constants from molecular volumes. For air at 22° C, 740 mm Hg, the equation reduces to

$$D = \frac{13.5 \times 10^{-17}}{r^2} \tag{9}$$

Using equation (9), the predicted values of the particle radius for a diffusion constant D are compared with same values given in the literature[29, 30]

28. Sherwood, T. K., Absorption and Extraction, New York, McGraw-Hill (1937) p. 18.
29. Mack, Edward, Jr., "Cross Sectional Areas of Molecules," J. Am. Chem. Soc. 47, p. 2473 (1925).
30. Klotz, I. M. and D. K. Miller, "Diffusion Coefficients and Molecular Radii," J. Am. Chem. Soc., 69, 2557-58 (1947).

TABLE I-1

Molecule Size from Diffusion Constant

Compound	Diffusion Constant* Literature	Molecule Radius Literature μ	Molecule Radius, Equation (9) μ
Iodine	0.108	0.00023	0.00035
n-Octane	0.060	0.00038	0.00047
Napthalene	0.061	0.00037	0.00047
Toluene	0.084	0.00030	0.00040
Diphenyl	0.073	0.00032	0.00043
Chloropicrin	0.088	0.00028	0.00040
HCN	0.197**	0.00020	0.00026

* 25° C, 760 mm
** Converted to 25° C, 760 mm

Even in this extreme case, the radii predicted by equation (9) are not in error by more than ~ 50 percent. It seems reasonable to conclude that equation (4) is accurate for oil particles in air down to about 0.001 microns radius, and that the equation is accurate to better than 30 percent for other materials in this size range. Below 0.001 microns radius, the equation is probably accurate to within 50 percent. A plot of equation (6) is given in Figures I-1, I-2, I-3, and I-4.

Drawing # 22182
Unclassified

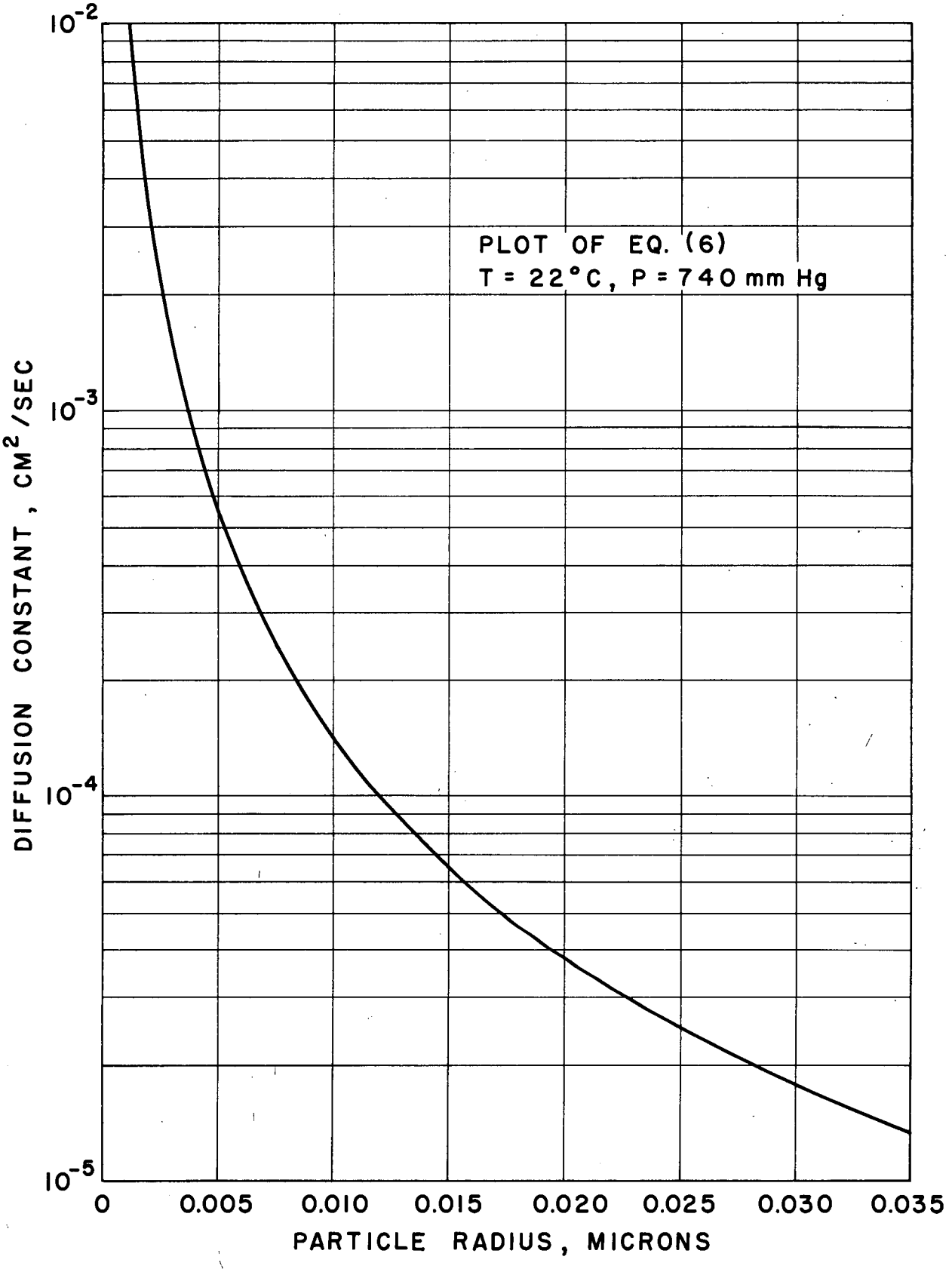

FIGURE I-1
DIFFUSION CONSTANT VS. PARTICLE SIZE

Drawing # 22183
Unclassified

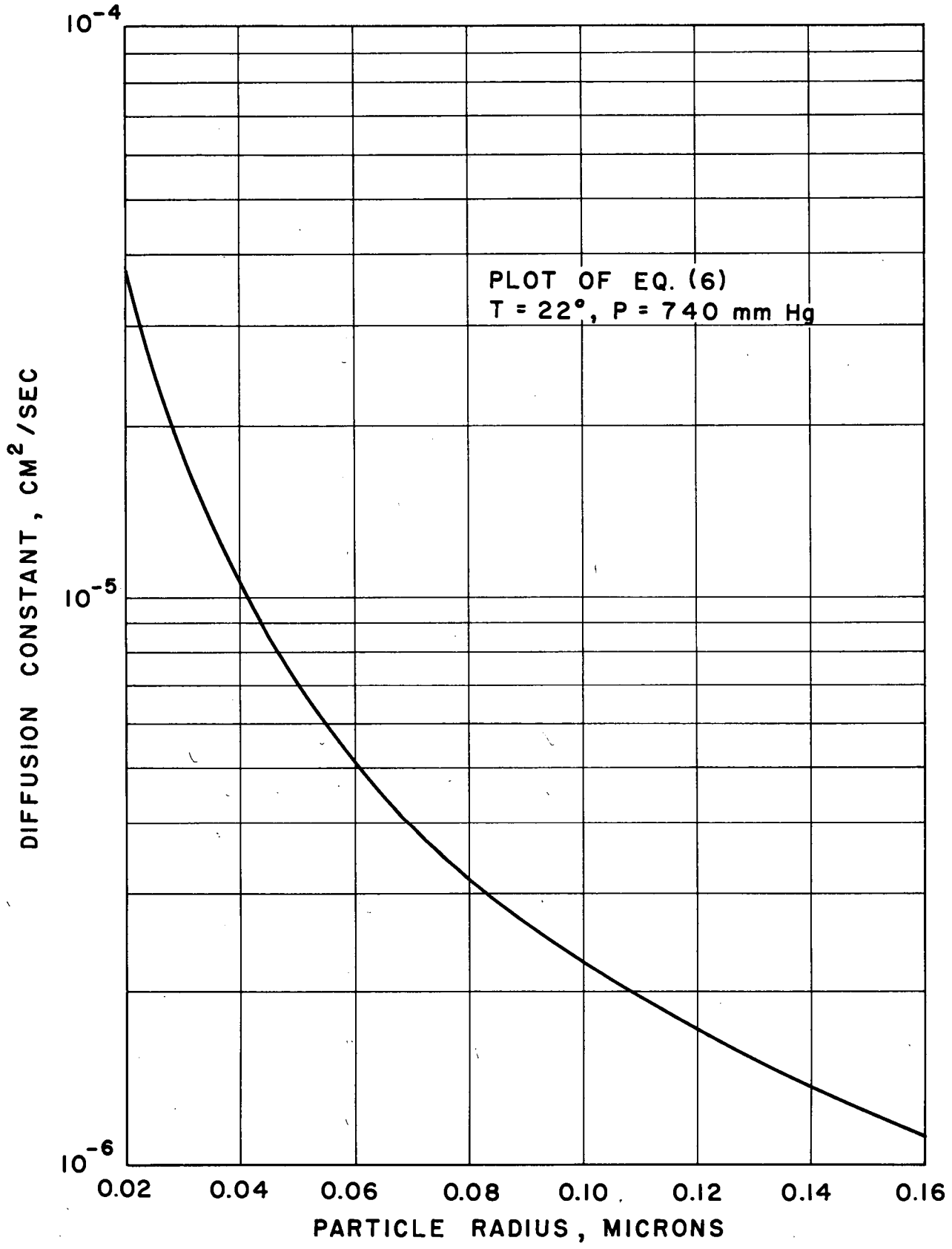

FIGURE I - 2

DIFFUSION CONSTANT VS. PARTICLE SIZE

Drawing # 22184
Unclassified

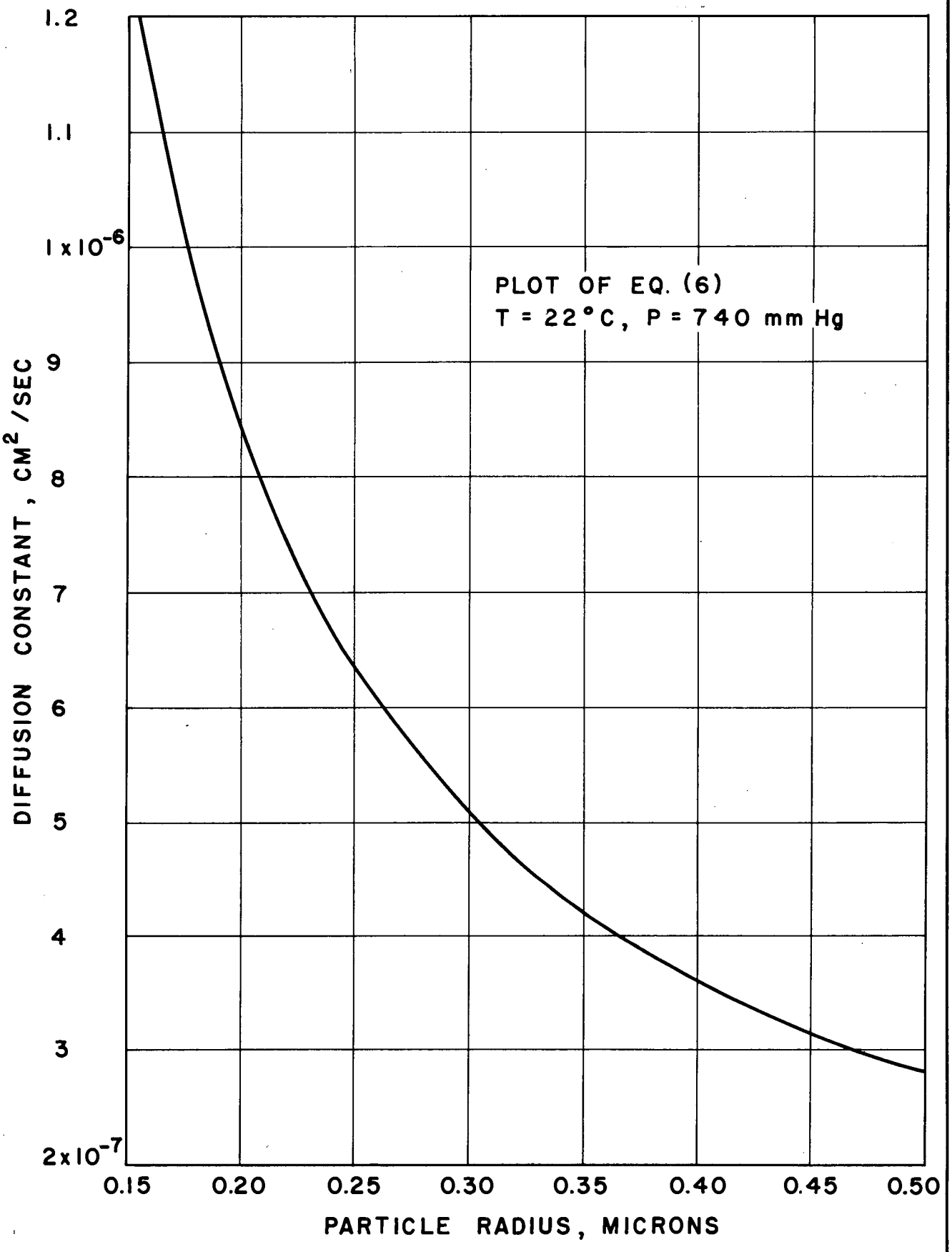

FIGURE I-3
DIFFUSION CONSTANT VS. PARTICLE SIZE

Drawing # 22185
Unclassified

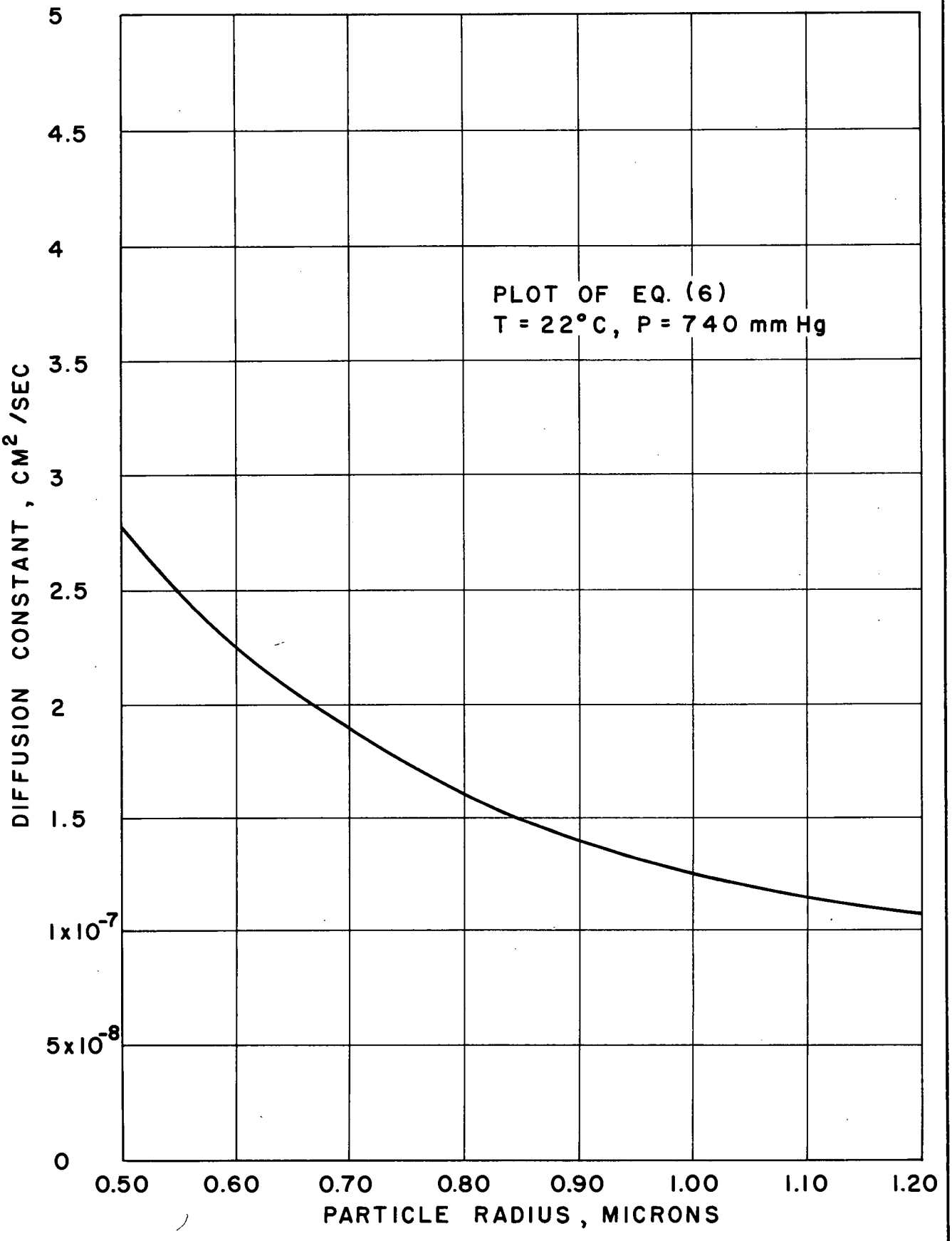

FIGURE I-4
DIFFUSION CONSTANT VS. PARTICLE SIZE

APPENDIX II

Diffusion Constants of Gas Molecules

Introduction. The object of this work was to test the battery equations using the ultimate in small particles, that is, gas molecules. In this work it was necessary to use a battery surface capable of absorbing quantitatively all of the diffusing gas molecules which contacted it. Streamline flow was assured by adjusting conditions so that the Reynolds number was always under 100.

Preliminary Experiments. The first gas investigated was SO_3. A preliminary test was made in which a dry air-gas mixture was passed through a small circular tube containing a cylindrical section of dry Type 6 paper. It was found that, although the SO_3 reacted with the paper, as the test proceeded the paper became saturated and desorbed, or failed to absorb, the SO_3 gas molecules. An attempt was made to eliminate this difficulty by introducing a small amount of water into the paper to hold all SO_3 as H_2SO_4. An objection to this method was the slow evolution of H_2O molecules from the paper, with formation of a visible aerosol in the tube. This, of course, invalidated the measurements. Evidently what was needed was an absorber with a negligible vapor pressure. It was finally demonstrated by E. E. Grassel of this laboratory, that oleic acid, a compound of negligible vapor pressure, would absorb SO_3 quantitatively. Use of oleic acid improved the procedure, but results were still erratic and it was found necessary to (1) use a large diameter tube to allow sufficient capacity for absorption (milligram quantities of gas were being

absorbed in a relatively small paper), (2) use longer inlet and exit tubes to avoid entrance and exit effects, and (3) counterset the paper in the tube so that the air streamlines were not disturbed. With these improvements an apparatus which gave fairly consistent and reproducible results was finally obtained.

For the NH_3 test saturated copper sulfate solution was used to impregnate the paper. Evidently this reacts rapidly with NH_3, as no trouble was had with desorption from the paper. In the NH_3 test it was not necessary to keep the paper and air stream dry as the evaporating water molecules from the surface of the paper do not have a tendency to form an aerosol with the approaching NH_3 molecules.

During these experiments very little trouble was experienced from absorption and desorption of the test gas on the glass walls of the apparatus. Since the gas concentrations were of the order of 1-5 mg/l, and the tests were operated for 15-30 min, equilibrium between absorption and desorption on the glass was soon obtained, minimizing these effects. The final apparatus and procedure used are described in the next section.

Apparatus. The apparatus is shown in Figure II-1. The diffusion battery consisted of a piece of Type 6 paper, wrapped into a cylindrical shape, inside diameter 3.5 cm. The length of the paper was either 14.6 or 5.8 cm. To insure streamline flow through the battery, the inlet section to the battery was made 80 cm long, and the exit section 45 cm long, as shown in Figure II-1. The Type 6 paper was impregnated with oleic acid for the SO_3 test, and with a saturated copper sulfate solution for the NH_3 test. These impregnates allowed complete absorption of

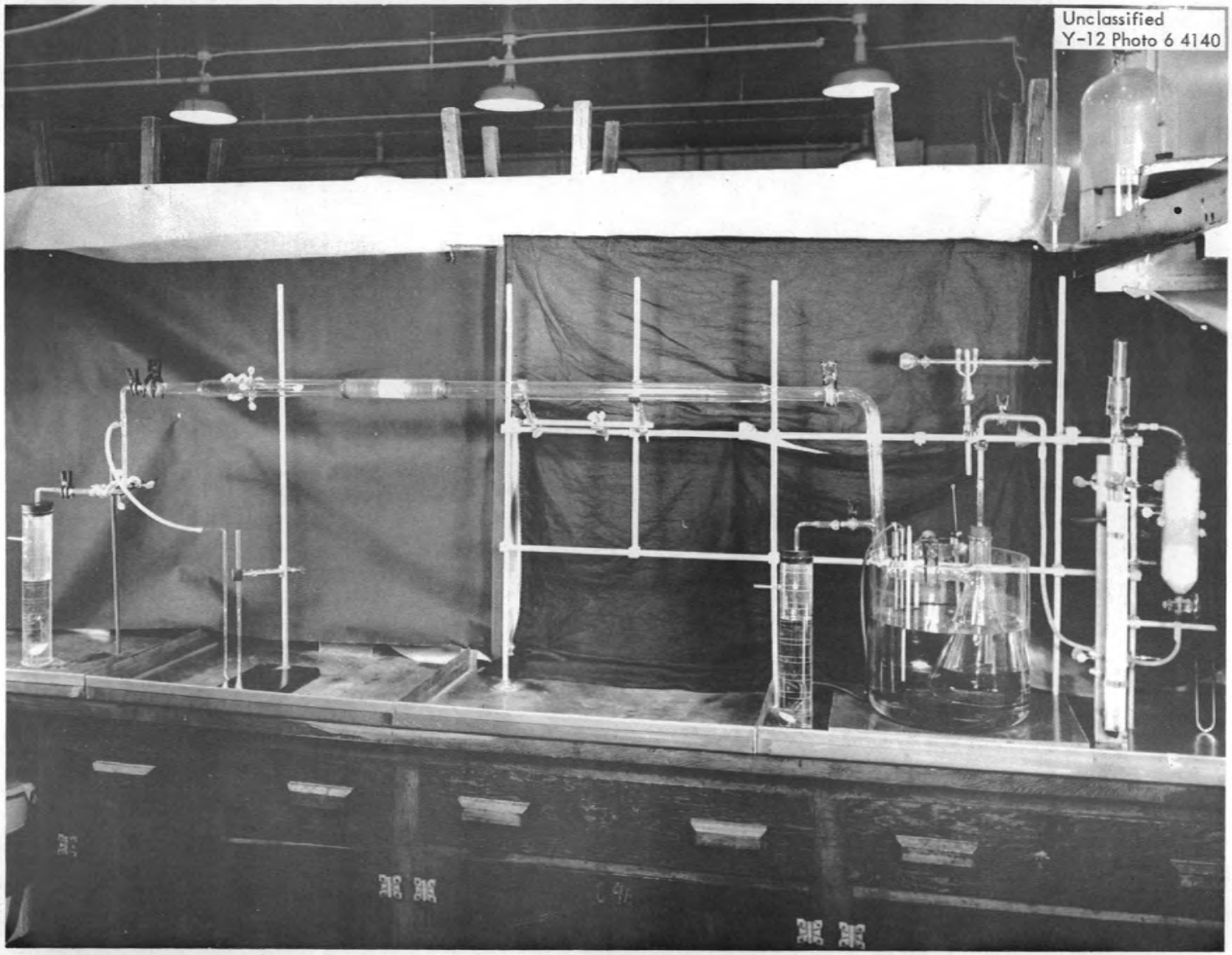

Fig. II - 1. Gas Diffusion Constant Apparatus.

all gas molecules contacting the surface of the paper. For treating the influent air a tube filled with layers of ascarite, silica gel and dehydrite was used. This enabled dew points of less than -50° F to be obtained. The ascarite removed all detectable CO_2 from the influent air.

The gas generator was a modified 2-liter filtering flask, immersed in a constant temperature bath. Influent air to the generator passed over the liquid in the flask, establishing a gas concentration. For the SO_3 test, fuming sulfuric acid was used, containing about 20 percent free SO_3. For the NH_3 test, the generator contained concentrated ammonium hydroxide dilute by a factor of 60. The gas absorbers, or bubblers, were 500 ml graduated cylinders fitted with inlet and outlet tubes. It was necessary to fit the inlet tube to the bubbler with a medium porosity glass disc, so that when using SO_3 the gas would be sufficiently dispersed to prevent aerosol formation in the bubbler. Water was used to absorb the SO_3 gas, and a weak acid solution used for the NH_3 test. About 400 ml of absorber was used in either case. All parts of the apparatus in contact with the test gas, with minor exceptions, were made of glass, using ball joint connections. A flowmeter and several manometers were provided.

Procedure. Before or after each test a check was made to ascertain that the leaks were less than 0.1 percent of the flow rate and that the flow rate was at the desired value. When running the SO_3 test, the "Dewpointer" was utilized to check that the water content of the influent air was less than 0.05 mg/l.

After passing air at the desired flow rate over the liquid in the generator for about 10-30 minutes, equilibrium was obtained, and a concentration sample taken at the test flow rate. The sampling time was adjusted so that 10-30 mg of the gas were obtained for analysis.

The desired gas concentration having been obtained the flow was switched through the diffusion battery for about 15-30 minutes and 5 min penetration samples taken continuously. After taking the penetration samples, the flow rate was changed to another value, and the procedure repeated.

For the SO_3 test, the concentration and penetration samples were analyzed by titration against 0.05 N sodium hydroxide, using phenolphthalein as an indicator. Water was used as the absorber. For the NH_3 test, the bubblers were made up to contain 25.0 ml of 0.05 N H_2SO_4 and about 400 ml water. After absorption of the ammonia gas, the bubbler solutions were titrated to pH 6.5 using the "Fisher Titrimeter."

From the results of the concentration and penetration determinations, the fraction of gas penetrating the battery was obtained.

Results. As example of the results obtained in one run is given in Table II-1. The results are summarized in Table II-2.

Discussion. An experimental value for the diffusion constant of SO_3 could not be found in the literature, so this was calculated by empirical equations due to Sherwood[31] and Andrussow[32]. At the temperature and

31. Sherwood, T. K., Absorption and Extraction, 1st Edition, New York McGraw-Hill, 1937.
32. Andrussow, L., "Uber die Diffusion in Gasen," Z. Elektrochemie 54, 566-571 (1950), 55, 51-53 (1951).

TABLE II - 1

ORIGINAL DATA - SECOND NH_3 TEST

Length of Battery - 5.8 cm T = 25.7°C, P = 740 mm Hg

Flow Rate - 0.947 liters/minute:

Gas concentration - Start of test	2.11 mg/l
Gas penetration - 1st 5 minutes	0.65 mg/l
Gas penetration - 2nd 5 minutes	1.36 mg/l (error)
Gas penetration - 3rd 5 minutes	0.66 mg/l
Gas penetration - 4th 5 minutes	0.65 mg/l
Gas penetration - 5th 5 minutes	0.66 mg/l
Gas concentration - same flow rate	2.06 mg/l

Flow Rate - 1.950 liters/minute:

Gas concentration - new flow rate	1.78 mg/l
Gas penetration - 1st 5 minutes	0.95 mg/l
Gas penetration - 2nd 5 minutes	0.93 mg/l
Gas penetration - 3rd 5 minutes	0.94 mg/l
Gas concentration - end of test	1.76 mg/l

Average gas concentration - 0.947 liters/minute - 2.08 mg/l

Average gas penetration - 0.947 liters/minute - 0.655 mg/l

Fraction penetrating battery - 0.947 liters/minute - 31.4 percent

Average gas concentration - 1.950 liters/minute - 1.77 mg/l

Average gas penetration - 1.950 liters/minute - 0.94 mg/l

Fraction penetrating battery - 1.950 liters/minute - 53.2 percent

TABLE II - 2

DIFFUSION CONSTANT DETERMINATIONS

Gas Used	mg/liter	Battery Length cm	Flow Rate liters/min	Gas Penetrating Battery	Diffusion Constant cm^2/sec	
SO_3	6.75	14.6	0.950	17.4%	0.147	0.145
SO_3	5.59	14.6	1.960	37.6%	0.152	
SO_3	5.19	14.6	0.950	19.1%	0.138	
NH_3	2.40	14.6	0.947	9.2%	0.202	0.202
NH_3	2.07	14.6	1.950	34.9%	0.165	
NH_3	2.08	5.8	0.947	31.4%	0.229	
NH_3	1.77	5.8	1.950	53.2%	0.210	
NH_3	2.19	5.8	0.500	16.6%	0.200	
NH_3	2.04	5.8	0.750	27.4%	0.206	

NOTES

1. Temperature, 24 ± 2° C: Pressure, about 740 mm Hg.

2. Inside diameter of diffusion battery - 3.5 cm.

3. The diffusion constant was calculated from the percent gas penetration by Gormley's equation. (Page 8)

4. The brackets on the left indicate tests that were made consecutively, without turning off the apparatus.

5. The brackets on the right show the average diffusion constant determined for each gas.

pressure used in these experiments, Sherwood's equation gave 0.109 cm^2/sec as the diffusion constant of SO_3 and Andrussow's equation, 0.111 cm^2/sec. These values compare with the value of 0.145 cm^2/sec obtained in this work. Andrussow[2], in a recent paper, gives 0.190 cm^2/sec as the experimentally determined value of the diffusion constant of NH_3 at 0^oC, 760 mm Hg, equivalent to 0.222 cm^2/sec at the temperature and pressure used in these experiments. These values compared with the value of 0.202 cm^2/sec obtained in this work.

Conclusions. The diffusion constant of SO_3 as determined by this method appears to be in error by about 30 percent according to the empirical equations. However, these equations are not accurate, as may be seen from the graph given by Sherwood , page 16. The results obtained when using ammonia gas are considered more reliable, due to the better analytical technique used and the larger amount of data. Here, there is a 10 percent difference between the value found in this work and the experimental value given by Andrussow.

It was concluded that the equation for the circular battery is correct, or very nearly so, and that the discrepancies found above are due to experimental difficulties. The method described above is not a standard method and may be, in many cases, a more convenient method than the standard methods[33] for determination of the diffusion coefficient of gases and vapors.

33. Sherwood, T. K., Absorption and Extraction, New York, McGraw-Hill 1937 1st Edition, p. 20.

APPENDIX III

Pressure Drop in a Parallel Plate Battery

The formula for flow between two infinite parallel plates is readily available[34]. Converting this formula to metric units, and using the notation of this report

$$W = \frac{2}{3} a^3 b \left(\frac{\rho \Delta P}{\mu Z} \right)$$

W = weight rate of discharge, grams/sec

2a = spacing of the plates, cm

b = breadth (width) of the plates, cm

ρ = density of air, grams/cm^3

μ = viscosity of air, poises

Z = length of battery, cm

ΔP = pressure drop, dynes/cm^2

For air at 22°C, 740 mm Hg pressure, $\mu = 1.83 \times 10^{-4}$ poises and $\rho = 1.165 \times 10^{-3}$ grams per cm^3. Converting W into liters per minute per n channels, and P into centimeters of water, the equation becomes:

$$\Delta P = 4.68 \times 10^{-6} \left(\frac{Z}{a^3 bn} \right) Q_t$$

P = pressure drop across battery, cm H_2O

Z = battery length parallel to flow direction, cm

a = one-half spacing between parallel plates, cm

b = battery height perpendicular to flow direction, cm

Q_t = total flow through battery, liters per minute

34. Perry, J. H., Chemical Engineer's Handbook, New York, McGraw-Hill, 2nd edition, 1941, p. 818-819.

Figure III - 1 shows an experimental plot of ΔP against Q_t for the large battery. This curve may be used to determine indirectly the dimension a of the battery, which is difficult to measure accurately. The other quantities in the above equation are accurately known, $n = 20$, $b = 12.70$, and $Z = 49.9$.

The experimental curve given the following equation:

$$\Delta P = 7.50\ Q_t$$

Therefore

$$7.50 = 4.68 \times 10^{-6} \left(\frac{49.9}{(a^3)\ (12.7)\ (20)} \right)$$

and

$$2a = 0.00994 \text{ cm}$$

This battery was later reduced to a length of 47.3 cm, giving an expected experimental equation.

$$P = 7.10\ Q_t$$

Figure III - 2 shows the experimental plot of P against Q_t for the small battery. The equation is

$$\Delta P = 0.87\ Q_t$$

Solving for 2a as before,

$$0.87 = 4.68 \times 10^{-6} \left(\frac{5.10}{(a^3)\ (12.7)\ (19)} \right)$$

$$2a = 0.00970$$

Drawing # 22186
Unclassified

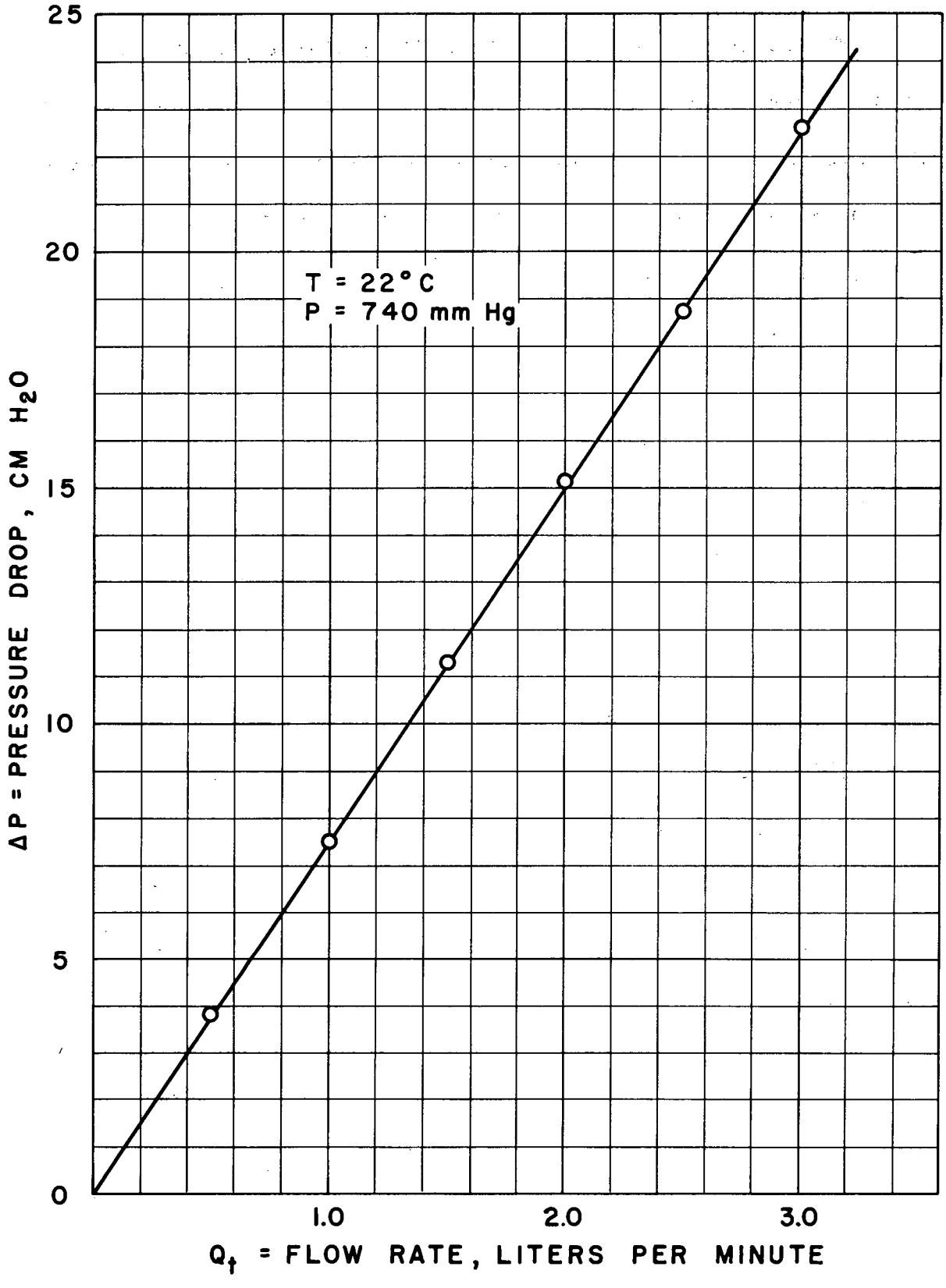

FIGURE III-1
PRESSURE DROP IN LARGE BATTERY

Drawing # 22187
Unclassified

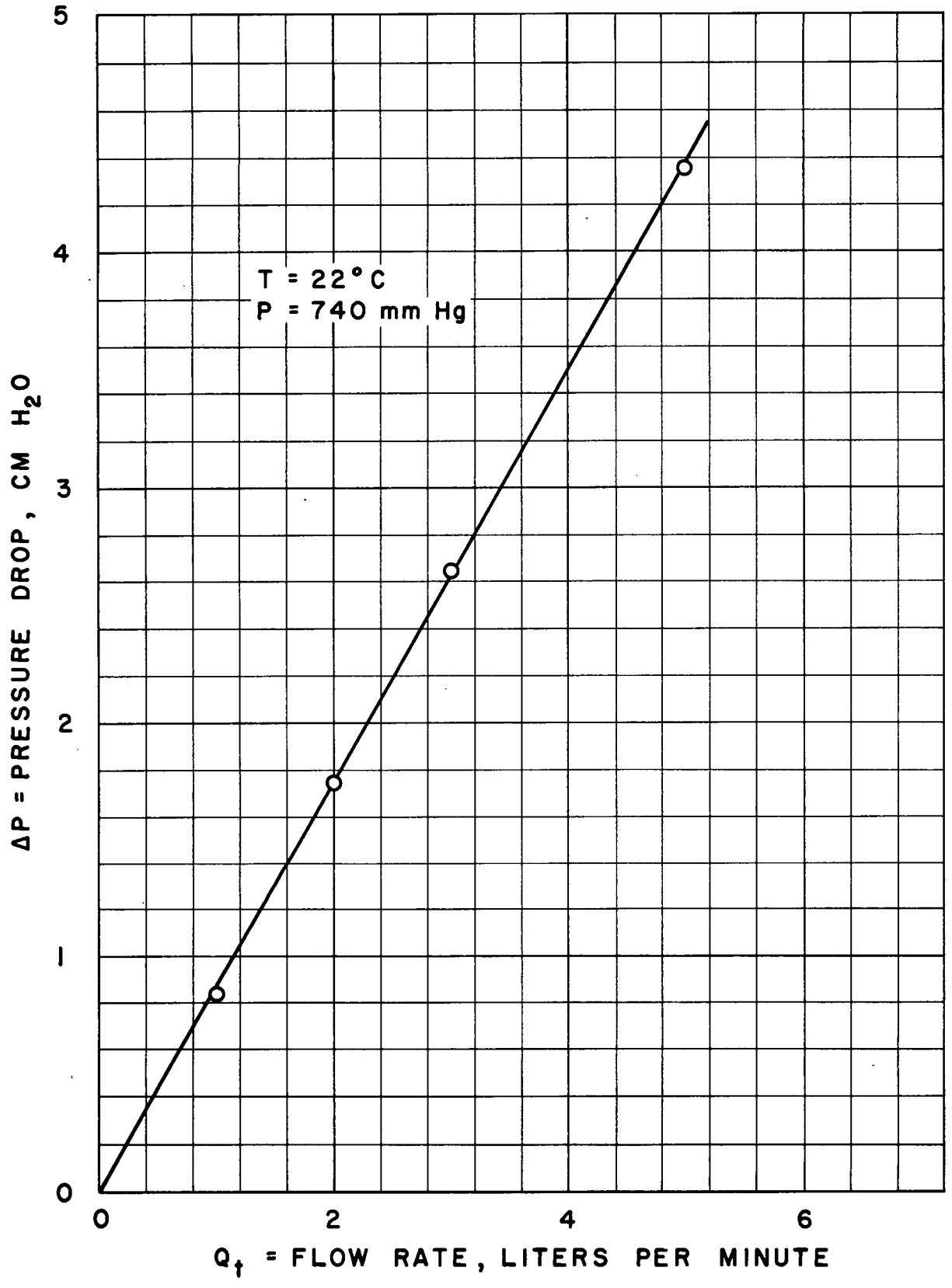

FIGURE III-2
PRESSURE DROP IN SMALL BATTERY