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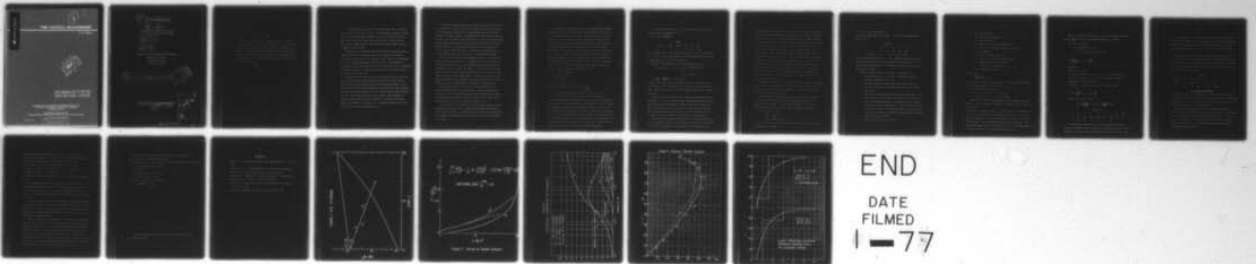
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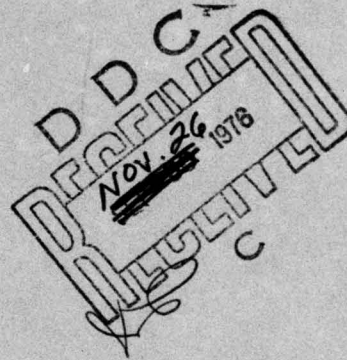
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FINE PARTICLE MEASUREMENT

T. A. Rich



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PRESENTED AT THE AEROSOL MEASUREMENTS WORKSHOP
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by

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Atmospheric Sciences Research Center
State University of New York at Albany

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ABSTRACT

A diffusion box with means for applying a voltage to remove all charged particles is used to get the transmission of an aerosol without voltage (T_D) and with voltage (T_{DD}). A number of combinations of two component aerosols would give a similar behavior and a simple way is shown to determine such pairs. A cumulative size distribution curve of fine particles can be found graphically which will behave similarly to the test aerosol.

The fine particles in an aerosol are arbitrarily taken to be those smaller than 5×10^{-6} cm in "radius." If the aerosol is brought to 100% humidity and then suddenly expanded, the air is cooled and the excess water vapor forms water drops around each particle. While the fine particles are submicroscopic, the water drops can be counted (or photographed) by various means.

There has been some question about the formation of drops on hydrophobic particles. Liu reported that clean oil drops do not serve as condensation centers but that in normal air their surface is contaminated in a short time and water drops can form on them. The comparisons of Liu between the Pollak CN meter and his electrical device give a comforting reassurance that the two independent methods check one another and that both count all the particles.

The great wonder in fine particle measurements is not that there are occasional baffling inconsistencies but that there is so much that is predictable even with outrageously over-simplified assumptions. In the early kinetic theory similar assumptions were made and yet many phenomena were rather accurately explained. In the kinetic theory it was reasonable to expect the molecules of a gas to be the same. The assumption of a spherical shape might not be quite right, but in any given test they acted like a sphere of a certain size. A somewhat different size could be found from viscosity, diffusion, etc.

The variety of shapes and sizes in natural aerosols is so great that it is necessary to find some kind of an average for calculations as well as a comprehensible description. Photomicrographs show a bewildering variety of crystals, needles, lacy aggregates and occasionally a spherical particle. The literature, more often than not, refers to an average radius without apology, and assumes that the reader realizes that this does not mean the aerosol is spherical but rather that in the circumstances it acts as spheres of that size would. It may not be a good practice, but no better way has been found, and there is a respectable precedent.

One of the first steps in any measurement problem is to decide what use will be made of the results. A precision of 1 or 2% is desirable in measuring, say, the loss in connecting tubing even though the accuracy needed may be only 10 or 20%. The number of particles cm^{-3} near a high traffic road will show such great variations in time and space that even changes of 50% are without significance. A passion for accuracy per se may be self-defeating or misleading. Accuracy and precision are instrument characteristics, but significance is the result of intelligent use.

The so-called dirty air of a large city usually has less than 10 parts per hundred million of dirt by weight. The fine particles have less than a tenth of this mass and are in lower concentrations by weight than many gaseous pollutants. They have little effect on many of the characteristics of air, such as density, viscosity, etc.

A clear concept of the reactions in a fine particle detector is more important for most people than a scientifically impeccable explanation. The following treatment is oversimplified in the details and overdetailed in discussing concepts with the hope of easing the task of the newcomer to the field.

For purposes of illustration, it will be assumed that the ambient temperature is 20°C and the pressure 1000 millibars. The device will be a tube, lined with a wet blotter, in which the aerosol is confined. A piston is used to expand the volume. An axial light beam will be attenuated by the cloud formed after expansion and a light measuring device is calibrated to indicate particles cm^{-3} . Several forms of expansion are in use, but all can be converted to the piston equivalent.

In Fig. 1 the Dee¹ condensation diagram is shown. The grams of water vapor per cubic meter at 100% humidity is plotted against the air temperature going from 4.85 at 0°C to 17.3 at 20°C . The aerosol at $P_1 = 1000$, $T_1 = 20^{\circ}\text{C}$ has a volume V_1 . The piston increases the volume to (aV_1) at pressure and temperature P_2 , T_2 .

$$1) \quad P_1 V_1^{1.4} = P_2 (aV_1)^{1.4}$$

$$2) \quad P_1 V_1 T_2 = P_2 (aV_1) T_1$$

$$3) \quad P_1 = a^{1.4} P_2$$

$$4) \quad T_1 = a^{0.4} T_2$$

If $T_1 = 293^{\circ}\text{K}$ and $T_2 = 273^{\circ}\text{K} = 0^{\circ}\text{C}$, $a = 1.193$

$$P_2 = 780 \text{ mb.}$$

$$5) \quad \text{The water vapor density at } P_2, T_2 \text{ is } \rho_a = 14.5 \text{ gm m}^{-3}$$

$$6) \quad \text{For } T = 0^{\circ}\text{C}, H = 1, \rho = 4.85 \text{ so the } H = 14.5/4.85 = 3.0$$

This supersaturation of 3.0 means that the rate of molecules leaving a water drop at 0°C has been reduced in the proportion of $4.85/17.3$ while the bombardment of water vapor has decreased by only $14.5/17.3$. The air contains 16% less water vapor than before expansion, not more water vapor as the word supersaturation seems to imply. It may also be noted that the particles are at 20°C initially and see only 84% humidity. The air molecules at 0° will rapidly cool the particles; at about 17°C the water vapor will start to condense on the larger particles.

For small particles that are or act like water drops, there is an H_c and r_c where condensation starts

$$7) H_c = \exp\left(\frac{1.1 \times 10^{-7}}{r_c}\right)$$

TABLE I

r_c (cm) 10^{-7}	2×10^{-7}	5×10^{-7}	10^{-6}	10^{-5}	10^{-4}	
H_c	3	1.7	1.25	1.12	1.01	1.001

For the example given a 10^{-7} particle would have to cool to air temperature (0°C) to start growth, whereas a 2×10^{-7} particle would have to cool to approximately 8° , and 5×10^{-7} to about 13° .

The heat of condensation must be carried away by the air

$$L_V(\Delta\rho_a) = M_{\text{air}} \times C_V \times \Delta T_a; \quad M_{\text{air}} = 1254 \text{ gm/m}^3 \text{ at } 5^\circ\text{C}$$

$$C_V = 0.171$$

$$L_V = 575 \text{ cal/gm}$$

$$8) \frac{\Delta\rho_a}{\Delta T_a} = \frac{1254 \times 0.171}{575} = 0.373 \text{ gm m}^{-3}/^\circ\text{C}$$

A line of this slope starts at 14.5 gm m^{-3} at 0°C to 9.3 gm^{-3} at 14°C .

The intersection of this with the $H = 1$ curve is at 11.4° and the total water condensed = $14.5 - 10.3 = 4.2 \text{ gm m}^{-3}$ because at this point condensation stops.

These figures are for water drops. The particles may behave quite differently - a lacy structure would have capillary channels; the material may be hygroscopic or hydrophobic so there can be little dependence on Eqn. 7 as a measurement of size. There is a high likelihood that the device described here would record down to 2×10^{-7} cm radius, but there is going to be some uncertainty at the lowest level of detection.

The Wilson cloud chamber is essentially a condensation nuclei meter, but the condensation nuclei are ions rather than particles. These start to be effective condensation centers when $H > 4$. At high values of H ,

so-called spontaneous nucleation occurs. When $H \rightarrow 8$ in clean and (hopefully) ion free air, a fine cloud appears. For fine particles $H \rightarrow 4$ is as high an H as should be used. It will also be noted that in the example used here the temperature fell to 0°C ($H = 3$). Things are complicated enough without the confusion of vapor pressure over ice vs. vapor pressure over water, so most commercial units use 1.2 as a maximum expansion. The Pollak counter uses a somewhat lower expansion (and his laboratory in Dublin was frequently 17 or 18°C). These are rather cowardly reasons for stopping at 1.2. A better reason is that particles in the range of 10^{-7} and smaller will not last long in natural air, and their losses in the necessary connecting tubing, humidifiers, etc. are high. There is some merit in the argument that these smallest sizes are too ephemeral for field work, although of great importance in following the conversion of gases to bigger particles.

The speed of expansion is a factor, as well as the amount of expansion. With a slow expansion, growth starts early on the biggest particles and the condensed vapor reduces the supersaturation to such an extent that the smaller particles never do grow.

The Dee diagram does not give information on the rate of growth of water drops, but it shows vividly that the initial growth does not deplete the vapor supply. For the example used here, the total condensable water vapor is 4.2 gm m^{-3} and R_m = maximum size of drops.

$$\begin{aligned} 9) \quad \frac{4}{3} \pi R_m^3 Z &= 4.2 \times 10^{-6} \\ R_m &= .0100/Z^{1/3} \text{ cm} \\ R_m &= 100/Z^{1/3} \text{ microns} \end{aligned}$$

It will be a convenience to express the drop radius as a fraction of the maximum radius as G where

10) $R = GR_m$ cm drop radius

Here the condensed vapor is $\frac{4}{3} \pi G^3 R_m^3 Z = 4.2 G^3$ and the remaining vapor $14.5 - 4.2 G^3$.

TABLE II

G	.9	.7	.5	.3	.1
G^3	.73	.34	.125	.027	.001
$14.5 - 4.2 G^3$	11.4	13.	14.	14.39	14.496

This is shown plotted on Fig. 1. It is noteworthy that a drop can grow to 30% of its final size without reducing the water vapor by 1%. It is also a fortunate circumstance, or the speed of expansion would be a far more serious problem.

There are several stages in the growth of fine particles:

1. The particle cools to a point where condensation starts by molecular bombardment of cool air.
2. Molecular deposition of water which warms the particle to a point where heat of net condensation is equal to heat carried away by air.
3. When the drop radius approaches the mean free path length, there is a depletion of water vapor in the vicinity of the drop, as well as a temperature gradient. The mechanism is now ruled by diffusion and thermal conductivity. It can be shown that stages 1 and 2 are fractions of a milli-second and little error will be introduced by assuming the diffusion-thermal conductivity regime throughout the growth period.

11) $Q_w = Z_m L_v D(4\pi R)(\rho_a - \rho_d) \text{ cal m}^{-3} \text{ sec}^{-1}$

$$12) \quad Q_a = Z_m K(4\pi R)(T_d - T_a)$$

Q_w = heat due to condensation

Z_m = particles/meter³

L_v = latent heat at constant volume (575)

D = diffusion constant water vapor in air (.294)

R = drop radius

ρ_a = density of water vapor in air

ρ_d = density of water vapor at drop surface

K = thermal conductivity (5.88×10^{-5})

T_d = temperature of drop surface ($^{\circ}\text{C}$)

T_a = temperature of the air

Since $Q_a = Q_w$

$$13) \quad \frac{\rho_a - \rho_d}{T_d - T_a} = \frac{K}{LD} = .348$$

K , L , and D are functions of temperature. The values used are for about 5°C for reasons which will become evident later.

In the region of 11°C for $H = 1$

$$14) \quad \rho_d = 10 + .7 (T_d - 11) = 2.3 + 0.7 T_d$$

$$15) \quad (14 \rightarrow 13) \quad \rho_a - 2.3 - .7 T_d = .348 (T_d - T_a)$$

This would not apply strictly immediately after expansion, but the behavior of G vs. T_a makes it reasonable to evaluate for $T_a = 0$ $\rho_a = 14.5$
 $T_d = 11.64^{\circ}\text{C}$

At the end of condensation cycle $T_d = 11.4^{\circ}$ from Fig. 1, the evidence is that the drop temperature does not change much, if at all. If so, the numerical coefficient of 13 should equal Eqn. 8: 0.348 vs. 0.373, or a 7% discrepancy. The approximations used here are not that good. The condensation takes place over a range of 0°C to 11.4° air temperature and the drop temperature over a narrow range around 11.4°C .

The heat released by condensation is at a rate of $L \frac{dm}{dt}$ calories/sec. = $L_v Z(4\pi R^2) \frac{dR}{dt}$ and the air carries away $Z(4\pi RK)(T_d - T_a)$ cal/sec.

$$16) LRdR = K(T_d - T_a)dt$$

$$T_a = \left(\frac{4\pi R^3 Z}{3}\right) / .373 = 11.3 R^3 Z$$

$$T_d = 11.4 \frac{K}{L} (T_d - T_a) = 1.15 R^3 Z \times 10^{-6}$$

$$17) \int_0^r \frac{RdR}{1 - R^3 Z} = 1.15 \times 10^{-6} \int_0^t dt$$

when $R^3 Z \ll 1$

$$18) R^2 = 2.3 \times 10^{-6} t$$

If t is say 0.02 secs $R = 2.1 \times 10^{-4}$ cm and is independent of Z_m

if $Z_m \ll 1$. If $R^3 Z_m = 0.01$ $Z_m = 10^9$ particles/m³ or 1000/cm³

When $\frac{4}{3} \pi R^3 Z_m = 4.2$ gm/m³ as here

then $R_m^3 Z_m = 1$ and Eqn. 17 in terms of $G = R/R_m$ becomes

$$19) R_m^2 \int_0^G \frac{GdG}{1 - G^3} = 1.15 \times 10^{-6} \int_0^t dt$$

The solution of the integral is:

$$= \frac{1}{6} \ln \frac{1+G+G^2}{(1-G)^2} - .0101 \left(\tan^{-1} \frac{(2G+1)}{\sqrt{3}} - 30^\circ \right)$$

TABLE III

G	.1	.2	.4	.6	.8	.9	.95	.99
S	.005	.019	.0818	.198	.422	.648	.88	1.41
G ²	.01	.04	.16	.36	.64	.81		

A substantially linear scale up to 100,000 particles/cm³ is obtained in the General Electric CN meter by limiting the growth to 0.02 sec. There are full scale values 100,000; 30,000; 10,000; 3,000; 1,000. Each

scale can be adjusted so the departure from linearity from, say, 30,000 to 100,000 is not great. As the concentration increases and the available water is used up, the radius of the drops is proportional to $Z^{-1/3}$ and the light scattering area per drop to $Z^{-2/3}$, and the total scattering to $Z^{1/3}$.

In instruments such as Gardner and Pollak the condensation time is not limited (by design, at least) although the air will warm up from the 11.4° . When there are few particles the time to grow to a given fraction of final size increases and the warming from the 20° ambient may halt the growth sooner than indicated here.

TABLE IV

Z/cm^3	10^3	10^4	5×10^4	10^5	10^6
R_m	10	4.64	2.71	2.15	1.0 μ
t	1.22	.26	.09	.056	.012 sec.

Size and Size Distribution

Size distribution is a higher order of absurdity than size itself. For purposes of calculation or comparison with other aerosols, an imaginary spherical aerosol of 1 or more components is specified that will act like the aerosol under test in certain situations.

The simplest case would be to find an imaginary spherical aerosol that would have the same diffusion loss as the test aerosol under the same set of conditions. The ideal case would be a curve of dZ/dr . In most cases it is impossible to determine more than three components before changes in the aerosol cause uncertainties greater than the accuracy further measurements could give.

Fuch² calculated the response of families of log normally distributed aerosols when subject to various diffusion losses. With the values of three diffusion losses (one high, one low, one 40-45%), a log normal distribution could be picked out that would most nearly duplicate the test aerosol. This is still only 3 points on a distribution curve, and one cannot place any great dependence on those results for the larger sizes. Megaw³ and others have shown the diffusion method does give good results for the fine particles. The larger particles constitute such a small fraction of the total numbers that no accurate evaluation of their effect can be made with a CN meter, and diffusion losses are small in themselves.

Again, this is not a criticism of getting representations of size distributions; but familiarity with the concept of a radius (as used here and in the literature) should not obscure the fact that aerosol particles are not necessarily spheres.

Another size dependent parameter is the fraction charged when the aerosol is in electrical equilibrium. Essentially this is an application of Boltzmann's law suggested by Fuchs.

$$20) \quad N_p = N_o \exp\left(-\frac{p^2 e^2}{2rKT}\right)$$

where e = electric charge, K = Boltzmann constant, P = number of electronic charges.

The results are shown in Fig. 3. For particles larger than 2×10^{-6} cm, the average energy per particle is $\frac{1}{2} KT$. The capacity of a sphere is numerically equal to its radius. The charge is $4.8 \times 10^{-10} p$, so electrical energy = $\frac{p^2 e^2}{2r}$.

Below 2×10^{-6} , or what amounts to the same thing, for singly charged particles Boltzmann's law falls off sharply (dotted lines of Figure 3). The assumption that the average energy is $\frac{1}{2} KT$ over the

whole range of sizes gives results which seem to give a reasonable check with experiment, or more conservatively, do not create many obvious inconsistencies.

$$21) F_u = 1 - 0.17 (r \times 10^6) \quad r < 2 \times 10^{-6}$$

$$22) F_u = 0.95 / (r \times 10^6)^{1/2} \quad r < 2 \times 10^{-6}$$

If an aerosol is passed between two plates with an adequate potential difference, only the uncharged particles will penetrate. If such a device is designed to have small diffusion losses, a high voltage will be required which is a serious disadvantage in the field where voltage breakdowns can occur in fog or condensation conditions. For some reason, such a device is called a denuder.

If the plates of a diffusion box are insulated, the device can be used as a denuder. Applying a moderate voltage to alternate plates, a combined diffusion-denuder is obtained that will work on low voltage⁴. A diffusion box that has 50% transmission for a 10^{-6} cm particle will require a flow for 20 to 30 seconds to reach steady state conditions. When voltage is applied, steady state requires only a few seconds. If after this sequence, the diffusion box is by-passed to get the unprocessed air to the CN meter, the three readings can be obtained rapidly. The percent transmission through the diffuser is plotted in Fig. 4 against the percent transmission through the diffusion-denuder.

In Fig. 4 a monodisperse aerosol would fall on the curve. For example, if the particles were all 1×10^{-6} cm radius, there would be 50% transmission for the diffuser-denuder used as an illustration. The fraction of 1×10^{-6} particles that are uncharged (and therefore could

pass through the diffuser-denuder) is $1 - .17 = .83$, or $T_{DD} = 41.5$.

Similarly, if the size were $r = 3 \times 10^{-6}$, $T_D = 86$, $T_{DD} = 47$ (from Fig. 4).

If 75% of an aerosol were $r = 1 \times 10^{-6}$, $T_D = .75 \times 50 = 37.5$

and 25% were $r = 3 \times 10^{-6}$, $T_D = .25 \times 86 = 21.5$, or $\Sigma T_D = 59$

For T_{DD} for $r = 10^{-6} = .75 \times 41.5 = 31.1$ $\Sigma T_{DD} = 43$

for $r = 3 \times 10^{-6} = .25 \times 47 = 11.8$

Note that this lies on a line from $r = 1$ to $r = 3$ and 75% of the distance from $r = 3$.

If an unknown aerosol read $T_D = 59$, $T_{DD} = 43$, then it would act like a two component aerosol of 75% of $r = 10^{-6}$ and 25% of $r = 3 \times 10^{-6}$. A cumulative step function of this is shown in the lower half of Fig. 5 worksheet. A curve balancing the areas around the step function is drawn in by eye.

A straight line from $r = 0.5 \times 10^{-6}$ through the 59,43 point indicates a two component aerosol of 18%, 0.5×10^{-6} and 82% of 1.6×10^{-6} cm. The step function is shown in the upper half of Fig. 5. A smooth curve again balances the areas around the step function. The circled points are from the 75-25% two component curve.

There is reasonably close agreement for this example but this distribution is not necessarily the actual distribution. From data available, there could have been either of the two component aerosols as the skew distribution shown. The skew distribution is far more likely and a convenient method of comparing aerosols, but there is very little data involved and caution is indicated in taking face value results. The other side of the coin is that more accurate distributions are more costly and one should have some tangible use for the more accurate data.

Fuch's book⁵ contains a wealth of information on diffusion and diffusion losses. The DeMarcus equation is

$$T_o = .915 \exp(-1.89\mu) + .059 \exp(-22.3\mu) + .026 \exp(-152\mu) \text{ where } \mu = D\chi/h^2\bar{U}$$

D = diffusion coefficient cm^2/sec

χ = length in cm

h = half separation of plates in cm

$\bar{U}$ = average velocity in cm/sec

The diffusion constant is approximately

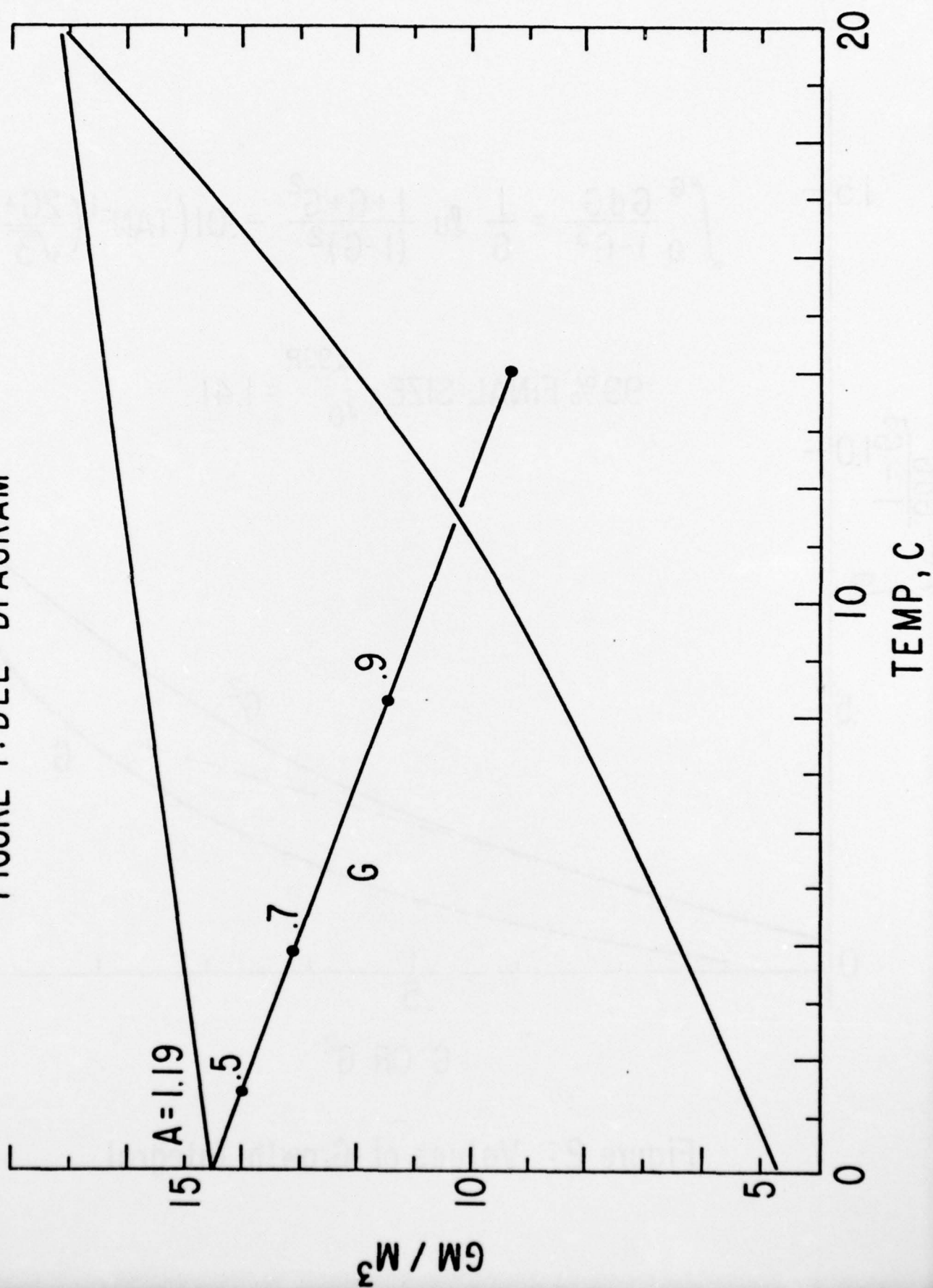
$$D = \frac{12 \times 10^{-12}}{r} \left(1 - \frac{10^{-5}}{r}\right)$$

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3. Megaw, et al. Measurement of diffusion coefficient of homogeneous and other aerosols. J.R.A., No. 3, pp. 113-123, 1963.
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FIGURE 1: DEE DIAGRAM



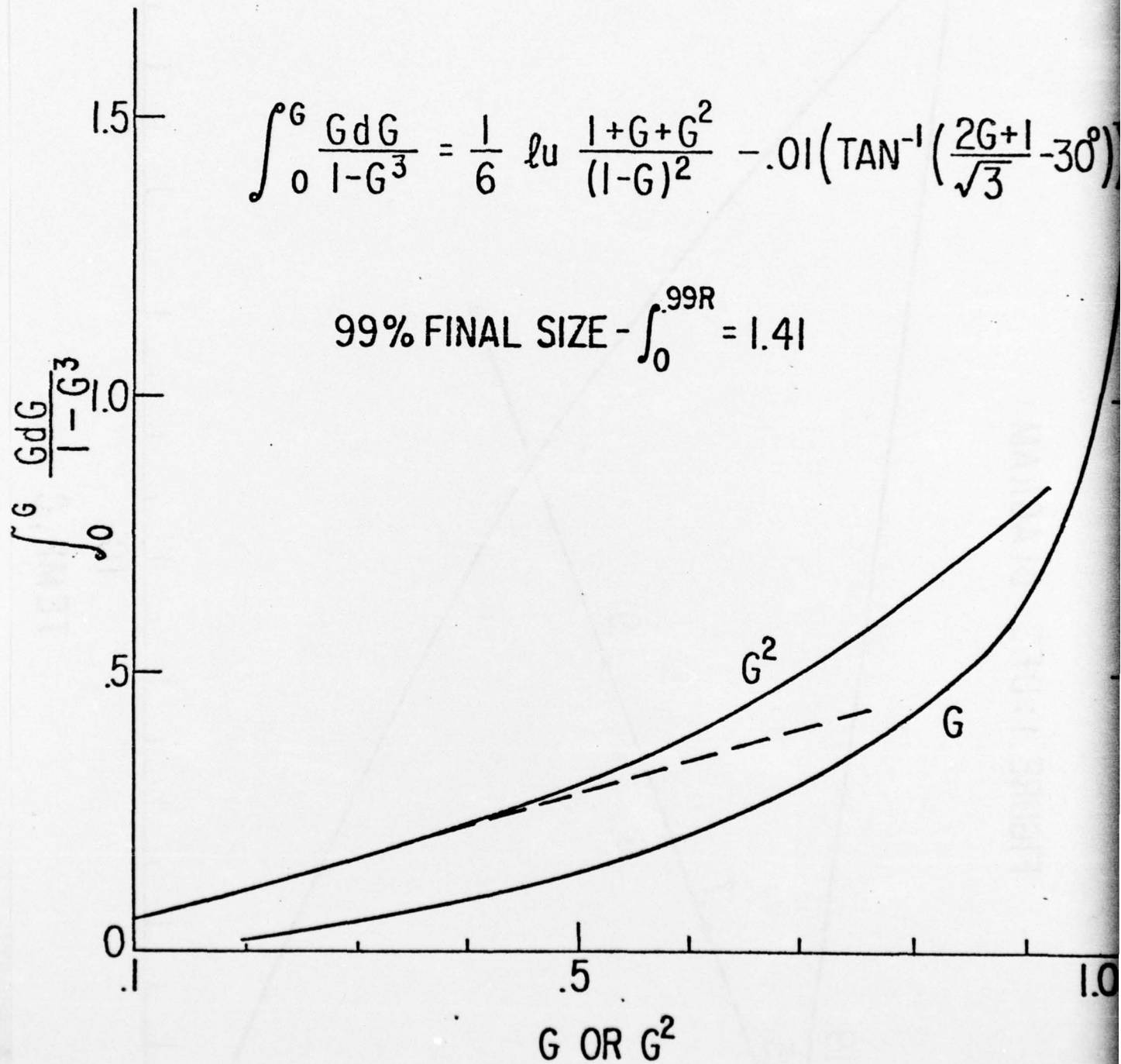


Figure 2: Values of Growth Integral

Figure 3
ELECTRICAL PROPERTIES OF AEROSOLS

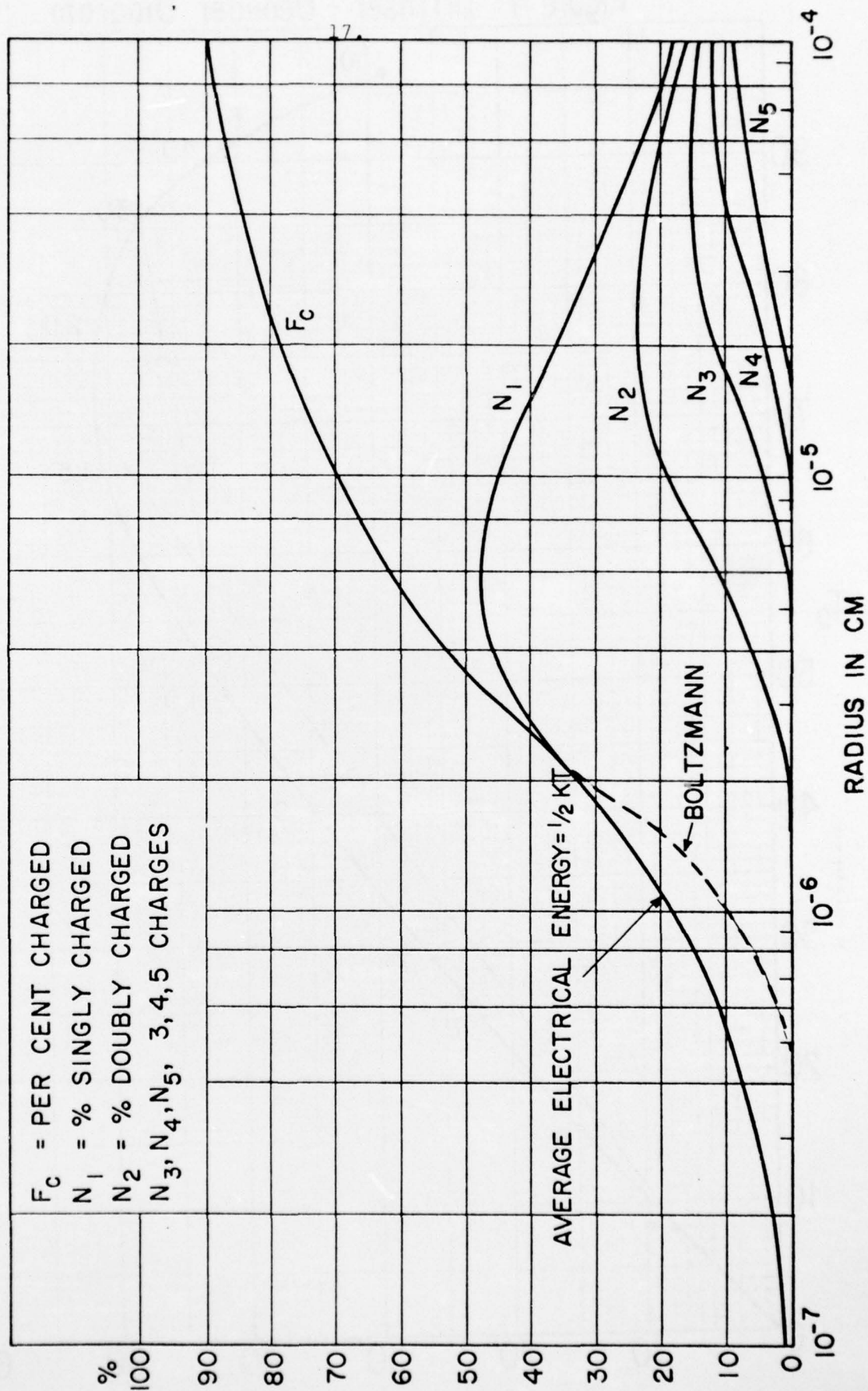
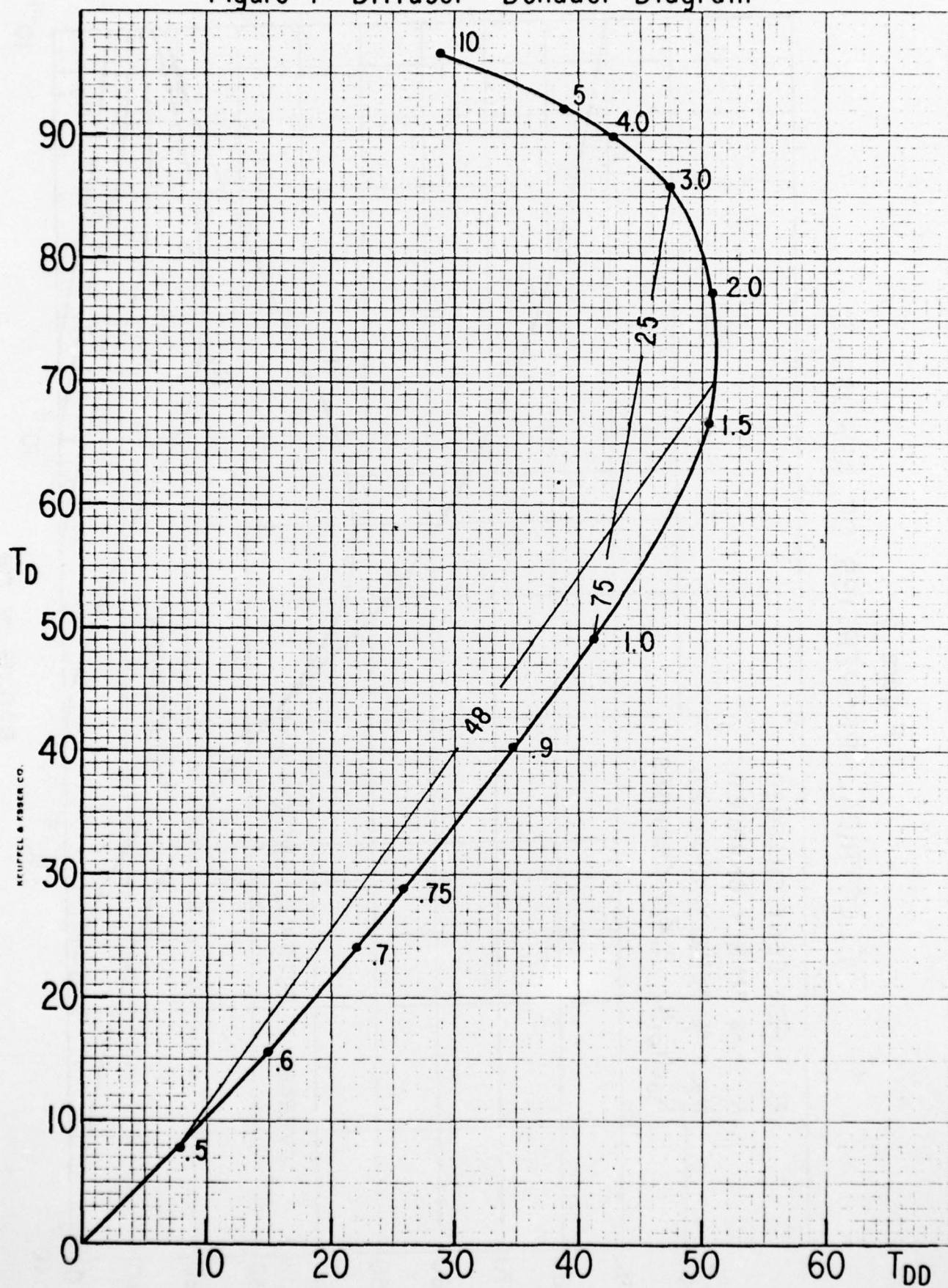


Figure 4: Diffuser - Denuder Diagram¹⁸



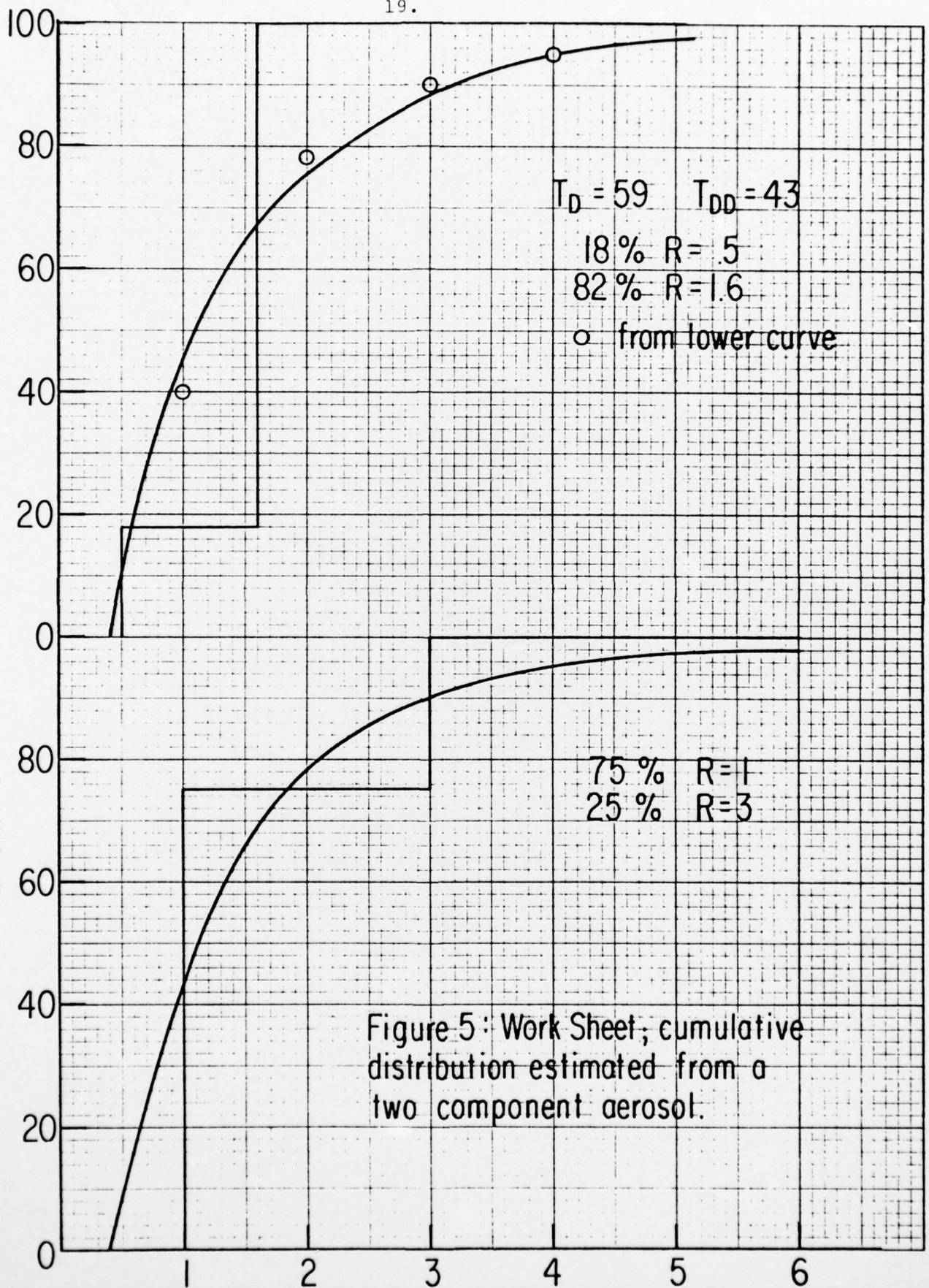


Figure 5: Work Sheet; cumulative distribution estimated from a two component aerosol.