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Porosimetry Data Interpretation

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Porosimetry Data Interpretation

by

J. M. Dickinson
H. D. Lewis

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POROSIMETRY DATA INTERPRETATION

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J. M. Dickinson and H. D. Lewis

ABSTRACT

Statistical models developed for particle "size" analysis are used for the interpretation of porosimetry data. A brief outline of the development of the finite interval and the log normal models is given, with emphasis on assumptions and conditions required for applicability to porosimetry data. Methods of calculations based on both models are illustrated.

INTRODUCTION

The results of the measurements of pore "size" and "pore size distribution" have often been reported in a graphical manner, occasionally with an inadequately or incorrectly defined "average pore size" indicated. One of the more commonly employed methods has been to use a plot of some measure of cumulative pore volume against a measure of pore "size". Methods employing plots of various distribution functions have also been used. Although useful information often can be obtained from such methods of data treatment, numerical representation of pore "size" and "pore size distributions" are necessary to achieve rapid and accurate comparisons between various graphites.

The procedures outlined in this report are based on the methods of particle "size" data analysis described by Lewis and Goldman⁽¹⁾ and Goldman et al.⁽²⁾ This report discusses the application of these methods to porosity data, and their interpretation, calculation, and utility. Examples of each are given.

EXPERIMENTAL

Porosity data obtained through the use of a mercury porosimeter were chosen to illustrate the use of these methods of data analysis, although data obtained from other instruments used to determine "pore size distributions" can be treated in a similar manner. The data were obtained in terms of the intruded volume of mercury corresponding to an applied pressure using an Aminco-Winslow Porosimeter that was rebuilt and calibrated at Los Alamos Scientific Laboratory (LASL).

The specimens were solid rods of graphite 0.5 in. diameter with their lengths adjusted to allow a maximum of 0.2 cc of mercury, the capacity of the measuring system, to be intruded into the specimen at the maximum pressure obtained during the experiment. Mercury porosimetry data were obtained on a number of different graphites including H4LM, ZTA, ATJ, AGOT, and AGOT that had been hot-worked at LASL. In addition, a number of specimens of experimental graphites made from graphite flour and a partially polymerized furfuryl alcohol binder were used.

The determination of a "pore size distribution" by mercury porosimetry implies the measurement of the

total pore volume in a certain pore "size" range in which "size" is defined as the diameter of a circular cross-section void into which mercury can be intruded at a given pressure. Intrusion pressures were converted to pore "sizes" using the porosimetry equation,

$$rp = -2\sigma \cos\theta, \quad (1)$$

as derived by Washburn.⁽³⁾ Values for σ , the surface tension, and θ , the contact angle between mercury and graphite given by Bocquet,⁽⁴⁾ were used. The working equation is then,

$$d = \frac{213}{p}, \quad (2)$$

where d is the pore "diameter" in microns and p is the applied mercury pressure in psi.

The phrases pore "size" and "pore size distribution" are ambiguous. Any discussion involving these phrases presupposes a definition of "size" upon which the experimental determination of the distribution of pore "sizes" in a sample can be based. The definition of pore "size" implies the determination or ad hoc definition of a characteristic pore "shape". The phrase "average pore size" then implies that the experimental data have been subjected to some statistical treatment by which an average pore "size" has been calculated. The methods used in treatment of pore "size" data can be analogous to methods used in treatment of particle "size" data. The discussions which follow are based on the methods of particle "size" data interpretation and analysis described in full detail in Ref. 1. Notation used for pore "size" data analysis is identical to that used for particle "size" analysis.

A plot of experimental data from a porosimetry run is shown in Fig. 1. The symbol $\sum_1^r v_i'$ represents the total or cumulative volume of mercury intruded into the pores through successively larger values of p . To convert the data to a more useful form for subsequent analysis, the measured values of p are converted to values of d using Eq. (2) and the intruded mercury volume is converted to the volume fraction, $\sum_1^r \frac{v_i'}{V}$, where V is

Fig. 1. Cumulative volume of mercury intruded into pores at successive values of p .

the total volume of mercury intruded. In order that the data represent cumulative volume fraction less than a given "size", the values of cumulative volume fraction,

$\sum_1^r \frac{v_i'}{V}$, are subtracted from unity, i. e.,

$$1 - \sum_1^r \frac{v_i'}{V} = \sum_1^r \frac{v_i'}{V}. \quad \text{These are then plotted vs the}$$

values $d_1^* < d_2^* < d_3^* \dots d_r^* \dots$ as shown in Fig. 2. V is

the total volume of mercury intruded, and $\sum_1^r \frac{v_i'}{V}$ is the

total volume fraction of mercury intruded into the sample through the i th "size" interval. The values of d_1 can be considered midpoint values of each of i "size" intervals, $i = 1, 2, 3, \dots, r \dots I$, having endpoint values of d_i^* and

d_{i+1}^* . The midpoint values are then $d_i = \frac{d_i^* + d_{i+1}^*}{2}$, as

illustrated in Fig. 2. The porosimeter then measures

Fig. 2. Volume fraction of mercury intruded into pores of size $d_1 < d_2 < d_3 \dots d_r \dots d_I$.

cumulative pore volume vs effective pore openings as "size". For example, the volume of all pores to the upper

endpoint of the 6th interval in Fig. 2 would be $\sum_1^6 \frac{v_i'}{V}$; the

volume fraction of pores in the 6th interval can be estimated as,

$$\frac{v_6'}{V} = \sum_1^6 \frac{v_i'}{V} - \sum_1^5 \frac{v_i'}{V}. \quad (3)$$

DEVELOPMENT OF THE STATISTICAL MODELS FOR "PORE SIZE DISTRIBUTIONS"

The representation in Fig. 2 of pore "size" data is not a representation of the pore "size" distribution in the strict technical sense. Neither does it offer an unambiguous definition of pore "size" because, in general, the pores in a particular sample are not all the same shape. We believe that the frequent misinterpretation of statistics computed from this type of data is because the diagram of Fig. 2 is usually called a "distribution". It is strictly only a cumulative volume fraction diagram, where the fraction of occurrence of pores in a given "size" interval (d_i^* , d_{i+1}^*) is represented by the measured pore volume fraction, $\frac{v_i'}{V}$. If the cumulative volume fraction diagram is to be related to the pore "size" distribution, the assumption must be made that volume of mercury intruded into pores in a given "size" interval is related to some average linear dimension characteristically measured for all pores in that "size" interval; i.e.,

$$v_i' = n_i C_3 d_i^3, \quad (4)$$

where n_i is the number of pores in the interval and C_3 is a volume shape factor relating d^3 to v .

If an optical count of the number of pores vs d could be made, and the simplifying assumption is made that the pores all had the same shape with a characteristic dimension d , a true sample distribution or histogram of pore "size" could be plotted from the experimental data. The histogram (sample distribution) and corresponding volume fraction diagrams then could be developed as shown schematically in Fig. 3 using Eq. (4).

Fig. 3. Schematic histogram and related volume fraction diagram.

Is it possible, then, to develop a statistical treatment of pore "size" data such that various sets of data can be compared in a more satisfactory manner than the qualitative comparison of data plots of the type shown in Fig. 1 or 2; i.e., can sample statistics related to the pore "size" distribution be computed and these numbers be quantitatively compared? We believe that sample statistics related to the pore "size" distribution can be computed and utilized in a meaningful manner as shown in the subsequent discussion.

To develop the pertinent statistics defining a set of pore "size" sample data, it is assumed that:

- (1) some hypothetical pore "size" distribution exists,
- (2) the distribution is
 - (a) uniquely defined by a known function which is itself defined by a unique set of parameters, or

(b) the defining function is unknown.

The model for case (a) will be called the functional model, and that for case (b) the finite interval model. The relationships between pore "size" distribution data and the distribution function are shown in Fig. 4. The use of the functional model simply implies the following approximation:

$$\frac{n_i}{N} (d_i^*, d_{i+1}^*) \approx \int_{d_i^*}^{d_{i+1}^*} h(d) dd. \quad (5)$$

That is, integration of the distribution function representing the sample data over the interval (d_i^*, d_{i+1}^*) gives a fraction approximately equal to n_i/N observed in the same sample data interval as indicated in Figs. 4(a) and 4(c).

Further, as illustrated in Figs. 4 (b) and 4 (d),

$$\sum_{i=1}^r \frac{n_i}{N} \approx H(d) = \int_{-\infty}^{d_{r+1}^*} h(d) dd \text{ for the cumulative data.}$$

The function $h(d)$ has the property, $\int_{-\infty}^{\infty} h(d) dd = 1$.

If the form of the distribution function $h(d)$ is unknown (finite interval model), a measure of mean "size", dispersion about the mean, and a measure of asymmetry of the sample distribution are computed⁽¹⁾ as:

$$\text{Mean: } \bar{d} = \sum_{i=1}^I \frac{n_i}{N} d_i, \quad (6)$$

$$\text{Variance: } s_d^2 = \sum_{i=1}^I \frac{n_i}{N} \frac{(d_i - \bar{d})^2}{N-1}, \quad (7)$$

Fig. 4. Relationships between pore "size" sample data and distribution functions.

$$\text{Skewness: } g_d = \sum_{i=1}^I \frac{n_i}{N} (d_i - \bar{d})^3. \quad (8)$$

These three statistics provide a basic definition of the sample distribution of d , and are the minimum number required to provide a definition of an asymmetric or skewed distribution.

If $h(d)$ is known (functional model) the mean, variance, and skewness of the function can be expressed as:

$$\mu_d = \int_{-\infty}^{\infty} d h(d) dd, \quad (9)$$

$$\sigma_d^2 = \int_{-\infty}^{\infty} (d - \mu_d)^2 h(d) dd, \quad (10)$$

$$\gamma_d = \int_{-\infty}^{\infty} (d - \mu_d)^3 h(d) dd. \quad (11)$$

In some instances pore "size" data can be represented by the log normal function.

Consider sample data of the type shown in Fig. 5. If the variable d were transformed to $x = \ln d$ such that a function,

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma_x} \exp \left[\frac{-(x - \mu_x)^2}{2\sigma_x^2} \right], \quad (12)$$

represented the sample distribution, the approximation

Fig. 5. Illustrating the results of transforming d to $x = \ln d$.

$$\frac{n_i}{N} \approx \int_{x_i}^{x_{i+1}^*} p(x) dx \quad (13)$$

would be valid. The distribution of d would be log normal in d and its transform normal in x , since Eq. (12) is the normal or Gaussian distribution function.^(5, 6) The effect of transforming d to x is illustrated in Fig. 5 for the case $h(d)$ log normal. The distribution of x is symmetrical about the most probable value. The function (12) has mean μ_x and variance σ_x^2 and is uniquely defined by these two parameters. The mean, median, and mode or most probable value of x for $p(x)$ have the same value of x . However, the mean, median, and mode of the log normal function, $h(d)$, do not have the same value of d , but are related to the parameters defining $p(x)$ in the following manner:⁽¹⁾

$$\text{Mean} = \mu_d = \int_{-\infty}^{\infty} d p(x) dx = \exp [\mu_x + 0.5 \sigma_x^2], \quad (14)$$

$$\text{Median} = d_{0.5} = e^{x_{0.5}} = e^{\mu_x}, \quad (15)$$

where $d_{0.5}$ and $x_{0.5}$ are the 0.5 decile values of d and x obtained from cumulative plots of $h(d)$ and $p(x)$ respectively, and

$$\text{Mode} = M_d = \exp [\mu_x - \sigma_x^2]. \quad (16)$$

Note that the antilog of μ_x = median of d , but that

$$e^{\mu_x} \neq \mu_d.$$

If the log normal sample data were obtained in the cumulative form illustrated in Fig. 4(b), a log-probability plot of such data would give a straight line, and first estimates of sample statistics $\hat{\mu}_x$ and $\hat{\sigma}_x^2$ would be obtained from the slope and 0.5 decile value as shown in Fig. 6.

The properties of log-probability paper are discussed in Ref. 7. It is sufficient for our purpose to realize

Fig. 6. Log-probability plot of relative frequency data.

that a plot of $P(x) = \int_{-\infty}^{x_{r+1}^*} p(x) dx$ vs $x = \ln d$ on such paper gives a straight line. The sample statistics $\hat{\mu}_x \approx \mu_x$, and $\hat{\sigma}_x^2 \approx \sigma_x^2$ (where $\approx$ is read, "is an estimator of"); i.e., $\hat{\mu}_x$ is an estimator of the distribution parameter μ_x , and $\hat{\sigma}_x^2$ is an estimator of the distribution parameter σ_x^2 . Although the function $P(x)$ can be roughly fitted to the data by graphical methods, a technique such as probit analysis⁽⁸⁾ should be used to obtain a "best" fit.

Pore "size" data are obtained, however, in the form volume fraction vs d . If it is decided that a plot of

$\sum_{i=1}^r \frac{v_i}{V}$ vs $x = \ln d$ is log normal, the statistics defin-

ing the sample distribution are developed using Eqs. (4) and (13), as follows:

$$\frac{v_i}{V} = \frac{n_i C_3 d_i^3}{\sum_{i=1}^I n_i C_3 d_i^3} \approx \frac{\int_{x_i^*}^{x_{i+1}^*} e^{3x} p(x) dx}{\int_{-\infty}^{\infty} e^{3x} p(x) dx} \quad (17)$$

The approximation given by Eq. (17) can be written,

$$\frac{v_i}{V} \approx \int_{x_i^*}^{x_{i+1}^*} f_3(x) dx, \quad (18)$$

where

$$f_3(x) = \frac{e^{3x} p(x)}{\exp[3\mu_x + 4.5\sigma_x^2]},$$

so that

$$f_3(x) = \frac{1}{\sqrt{2\pi}\sigma_{x3}} \exp\left[-\frac{(x - \mu_{x3})^2}{2\sigma_{x3}^2}\right] \quad (19)$$

$F_3(x)$ is then defined as,

$$F_3(x) = \int_{-\infty}^{x_{i+1}^*} f_3(x) dx = \frac{1}{\sqrt{2\pi}\sigma_{x3}} \int_{-\infty}^{x_{i+1}^*} \exp\left[-\frac{(x - \mu_{x3})^2}{2\sigma_{x3}^2}\right] dx \quad (20)$$

The mean of the normal function $f_3(x)$ is then

$$\mu_{x3} = \mu_x + 3\sigma_x^2 \quad (21)$$

and the variance is

$$\sigma_{x3}^2 = \sigma_x^2. \quad (22)$$

The values of $\hat{\mu}_{x3}$ and $\hat{\sigma}_{x3}^2$ can be obtained from a log normal fit as illustrated in Fig. 7.

The mean, variance, and skewness for the volume fraction vs d data are written:

$$\bar{d}_3 = \exp[\hat{\mu}_{x3} + 0.5\hat{\sigma}_{x3}^2], \quad (23)$$

Fig. 7. Log-probability plot of volume fraction data for hot worked AGOT graphite.

$$s_{d_3}^2 = \exp [2\hat{\mu}_{x3} + 2\hat{\sigma}_{x3}^2] - (\bar{d}_3)^2, \quad (24)$$

$$g_{d_3} = \exp [3\hat{\mu}_{x3} + 4.5\hat{\sigma}_{x3}^2] - 3 \exp [3\hat{\mu}_{x3} + 2.5\hat{\sigma}_{x3}^2] + 2(\bar{d}_3)^3. \quad (25)$$

The mean, variance, and skewness of the sample distribution of d are calculated by substituting $\hat{\mu}_x$, $\hat{\sigma}_x^2$, and $\bar{d}$ for $\hat{\mu}_{x3}$, $\hat{\sigma}_{x3}^2$, and $\bar{d}_3$, respectively, in these expressions. Then $\bar{d} \neq \bar{d}_3$, $s_d^2 \neq s_{d_3}^2$ and $g_d \neq g_{d_3}$.

A detailed development of the log normal transforms applicable to particle "size" or pore "size" data is given in Refs. (1) and (2).

It should be obvious that the statistics $\hat{\mu}_{x3}$ and $\hat{\sigma}_{x3}^2$ obtained from the fit of $F_3(x)$ do not define a sample distribution but do define the volume fraction data or cumulative volume fraction diagram, and definitely can be used for comparison of sets of volume fraction data.

If the log-probability plot of sample data is obviously not log normal, the finite interval model can be used to compute the statistics $\bar{d}_3$, $s_{d_3}^2$, and g_{d_3} or $\bar{x}_3$, s_{x3}^2 , and g_{x3} to describe the volume fraction sample data. These statistics are computed using the following expressions:

$$\bar{d}_3 = \sum_{i=1}^I \frac{v_i}{V} d_i, \quad (26)$$

$$s_{d_3}^2 = \sum_{i=1}^I \frac{v_i}{V} (d_i - \bar{d}_3)^2, \quad (27)$$

$$g_{d_3} = \sum_{i=1}^I \frac{v_i}{V} (d_i - \bar{d}_3)^3, \quad (28)$$

$$\bar{x}_3 = \sum_{i=1}^I \frac{v_i}{V} x_i, \quad (29)$$

$$s_{x3}^2 = \sum_{i=1}^I \frac{v_i}{V} (x_i - \bar{x}_3)^2, \quad (30)$$

$$g_{x3} = \sum_{i=1}^I \frac{v_i}{V} (x_i - \bar{x}_3)^3. \quad (31)$$

It is emphasized that these expressions do not define the mean, variance, and skewness of d or x , respectively, but can be considered analogous statistics for volume fraction data. This is indicated by the notation 3 or x_3 . It should be clear that the finite interval model does not provide functional relationships between $\bar{d}_3$ and $\bar{x}_3$, $s_{d_3}^2$ and s_{x3}^2 , and g_{d_3} and g_{x3} . Computation of these statistics is based on proper definition of interval endpoint and midpoint values as illustrated in Fig. 8.

$$\text{Since } x_i^* = \ln d_i^*,$$

$$x_i = \frac{\ln d_i^* + \ln d_{i+1}^*}{2} = \ln \left[(d_i^*) (d_{i+1}^*) \right]^{\frac{1}{2}}, \text{ and it is}$$

apparent that $x_i \neq \ln d_i$.

The statistics computed from volume fraction data, for either the functional or finite interval models, are numbers which provide quantitative comparisons among sets of sample data. The calculation of statistics representing the sample distribution of d or the volume fraction vs d data must involve a simplified pore shape assumption.

SAMPLE CALCULATIONS

Even though the theory behind the calculations of porosity data may seem complex, the procedures used in making the actual calculations are quite simple. The

TABLE I
SAMPLE CALCULATION FOR AGOT (HOT-WORKED GRAPHITE)

1	2	3	4	5	6	7	8
p_i^*	d_i^*	x_i^*	x_i	$\sum_1^r \frac{v_i'}{v_i'}$	$\sum_1^r \frac{v_i'}{V}$	$\sum_1^r \frac{v_i'}{V}$	$\frac{v_i'}{V}$
1.56	137.	4.9		0	0	1.0	
			4.725				0
2.37	90.	4.5		0	0	1.0	
			4.25				0
3.87	55.	4.0		0	0	1.0	
			3.75				0
6.24	34.	3.5		0	0	1.0	
			3.25				0
10.1	21.	3.0		0	0	1.0	
			2.75				0.006
17.7	12.	2.5		0.0005	0.0056	0.994	
			2.25				0.005
26.6	8.	2.0		0.001	0.011	0.989	
			1.75				0.006
47.3	4.5	1.5		0.0015	0.017	0.983	
			1.25				0.005
78.9	2.7	1.0		0.002	0.022	0.978	
			0.75				0.067
129.	1.6	0.5		0.008	0.089	0.911	
			0.25				0.089
213.	1.0	0.0		0.016	0.178	0.822	
			-0.25				0.144
349.	0.61	-0.5		0.029	0.322	0.678	
			-0.75				0.200
576.	0.37	-1.0		0.047	0.522	0.478	
			-1.25				0.234
968.	0.22	-1.5		0.068	0.756	0.244	
			-1.75				0.133
1580.	0.14	-2.0		0.080	0.889	0.111	
			-2.25				0.111
2600.	0.08	-2.5		0.090	1.000	0	

1. Pressure in psi

2. Pore "diam" in microns, from $d = 213/p$

$$3. x_i^* = \frac{\ln d_i^*}{(\ln d_i^* + \ln d_{i+1}^*)}$$

$$4. x_i = \frac{2}{2}$$

5. Cumulative volume of intruded mercury in pores having diameter larger than the corresponding d

6. Cumulative volume fraction of mercury in pores having diameter larger than the corresponding d

7. Cumulative volume fraction of mercury in pores having diameter less than the corresponding d

8. Volume fraction of pores in interval from x_i^* to x_{i+1}^* whose midpoint is x_i

Fig. 8. Relationships between midpoint and endpoints of x and d "size" intervals.

procedures for converting the raw data to a form suitable for use in the porosity calculations are illustrated with the use of Table I. In general, a set of intrusion pressures, p , can be plotted against a cumulative volume,

$\sum_1^r v_i'$, as shown in Fig. 1 to give a typical graph of

porosity data. If finite interval data are to be calculated, it has been found convenient to determine pressures p_i^* such that the interval between successive x_i^* values remains the same. It should be pointed out that the results of the finite interval calculations can be meaningfully compared only with results calculated over the same intervals. In practice, then, the values of x_i are selected such that

the interval widths (x_i^*, x_{i+1}^*) are constant, (0.5 for this example). Then the intervals (d_i^*, d_{i+1}^*) and (p_i^*, p_{i+1}^*) are determined from (x_i^*, x_{i+1}^*) . These values are shown in the first 4 columns of Table I and need be calculated only once for a series of experiments. At the

indicated values of p_i^* , the values of $\sum_1^r v_i'$ are

determined from the graph in Fig. 1 and are tabulated in column 5. As illustrated in Fig. 1, the values of p_i^* do not necessarily correspond to the experimental values of p . These cumulative volumes are then divided by the total volume to give the volume fractions larger than the indicated pore "sizes", column 6, and these values can be subtracted from unity to give the volume fractions less than the indicated pore "sizes", column 7. This conver-

sion of $\sum_1^r \frac{v_i'}{V}$ to $\sum_1^r \frac{v_i}{V}$ was made to facilitate

calculations based on the log normal model. The differences between successive volume fractions in columns 6 or 7 then give the volume fraction of pores, column 8, in the size interval (x_i^*, x_{i+1}^*) whose midpoint is represented by x_i . The values in columns 4 and 8 can be used to calculate the sample statistics using Eqs. (29), (30) and (31).

When the log normal model is used to calculate sam-

ple statistics, the values d_i , x_i and $\sum_1^r \frac{v_i'}{V}$ should be

calculated directly from the experimental values of p and

$\sum_1^r v_i'$ using the procedure just discussed for the finite

interval model. The log-probability plot of the converted experimental data of Fig. 1 is shown in Fig. 7. The fit of the straight line to the sample data indicates the log normal model is a good approximation. The straight line shown in Fig. 7 was actually fit to the data using probit analysis. The mean and variance of the volume fraction sample data can then be calculated as shown in Fig. 7.

For the AGOT hot-worked graphite sample, these values were determined as:

$$\hat{\mu}_{x3} = x_{.5} = \ln 0.42 = -0.868,$$

$$\hat{\sigma}_{x3}^2 = (x_{.8413} - x_{.5})^2 = (\ln d_{.8413} - \ln d_{.5})^2 =$$

$$\hat{\sigma}_{x3}^2 = (\ln 1.265 - \ln 0.42)^2,$$

$$\hat{\sigma}_{x3}^2 = 1.217.$$

Calculations based on either model are greatly facilitated by use of a computer program.

DISCUSSION

The usefulness of these methods of porosity data treatment can be best shown using some examples. The effects of hot-working on the porosity of AGOT graphite can be dramatically shown using these statistical methods of data treatment.

A specimen of AGOT graphite was hot-worked by compressing it with a pressure of 5000 psi at 3050°C. Using mercury porosimetry, the pore "size distributions" were measured before and after the hot-working operation.

The results, which are shown in Tables II and III along with some other pore "size" statistics, tell a great deal about the effect of hot-working on the pore "size distributions". The statistics calculated using the log normal model, Table II, show a substantial decrease in the mean of the sample data as a result of the hot-working operation. If this is converted to median pore "diameter" in microns the change was from 2.5 to 0.4 microns pore "diameter". Accompanying this change in pore "diameter", the sample variance, $\hat{\sigma}_{x3}^2$, decreased from 2.2 to 1.2, indicating that the fraction of pores having entrance "diameters" larger than the mean "size" decreased more than the decrease in "size" of the smaller pores. This is emphasized by the finite interval statistics given in Table III. In addition to the sample mean and variance, which show the same behavior as those calculated by the log normal model, the skewness, g_{x3} , changed considerably because of the hot-working operation. The change from -1.47 before, to +0.57 after hot-working indicated that a greater number of large pores than small pores tended to be eliminated by the hot-working operation.

TABLE II
LOG NORMAL VOLUME FRACTION POROSITY
STATISTICS FOR GRAPHITES

Graphite	$\hat{\mu}_{x3}$	$\hat{\sigma}_{x3}^2$	$\bar{d}_3$ microns	Median d_3 microns
AAA	-0.290	1.131		
AAC2	-0.131	1.158		
608	0.221	1.211	2.285	1.246
721	-0.270	0.750	1.111	0.763
AGOT ⁽¹⁾	0.910	2.177	7.38	2.490
AGOT ⁽²⁾	-0.870	1.217	0.770	0.419

(1) As Received

(2) Hot Worked 5000 psi at 3050°C

TABLE III
FINITE INTERVAL VOLUME FRACTION POROSITY
STATISTICS FOR GRAPHITES

Graphite	$\bar{x}_3$	s_{x3}^2	g_{x3}
AAA-7	-0.444	0.657	0.507
AAC-2	-0.363	0.650	0.107
608	0.097	0.839	-0.854
721	-0.293	0.566	-0.451
H4LM	2.021	3.796	7.476
ATJ	1.323	1.019	-2.160
ZTA	-0.863	1.203	2.865
AGOT ⁽¹⁾	0.931	1.924	-1.473
AGOT ⁽²⁾	-0.844	0.844	0.572
POCO	-0.003	0.299	0.345
SX-5	2.158	1.502	-2.324

(1) As Received

(2) Hot Worked 5000 psi at 3050°C

This change from negative to positive skewness indicates a change in the most probable pore "size" from a value greater than the mean "size" to a value smaller than the mean "size".

Another example of how pore "size" statistics indicate the effect of hot-working is shown by the statistics for ATJ and ZTA given in Table III. The ZTA graphite is made by hot-working ATJ. The decrease in $\bar{x}_3$ and the change from negative to positive skewness indicates a relatively large decrease in the most probable pore "size". This data treatment method then can be used to follow the effect of hot working on the porosity of graphites.

Another interesting example was provided by the examination of two supposedly identical graphites which had different permeabilities. It was found that the graphites were made using as filler material different lots of graphite flour that had small but real differences in particle "size" distributions and acicularity ratios. These differences are shown in Table IV. The flour used to make the less permeable graphite had a smaller mean particle diameter, a larger variance in x , $\hat{\sigma}_x^2$, a larger coefficient of variation in d , CV_d , and a smaller acicularity ratio.⁽¹⁾ The effect of $\bar{d}$, $\hat{\sigma}_x^2$ and CV_d on packing density of particles is discussed in Ref. (9).

The sample statistics of Table II indicate that the less permeable graphite, 721, had a smaller pore "size" and smaller variance in pore "size" than the more permeable graphite, 608. The pore "size" statistics of Table III indicate that graphite 721 had the smaller pore "size" and variance. The skewness values indicate a smaller most probable value of pore diameter for 721 than for 608. The data from the pore "size" evaluation from both the log normal and the finite interval pore "size" models then lead to the same conclusions. Use of the graphite powder which should have given the higher packing density resulted in an extruded graphite which had the smaller interconnected pore "size". This tends to explain the differences in permeability of the two graphites.

Pore "size" statistics for several other graphites are listed in Tables II and III. Some of the graphites listed in Table III, H4LM, ATJ, ZTA, and SX-5, have absolute values of skewness considerably larger than zero. The log normal model was therefore not used in these pore "size" analyses.

TABLE IV
PARTICLE SIZE STATISTICS
FOR TWO GRAPHITE FLOURS

Sample Statistics	Flour to make graphite having	
	Low permeability	High permeability
Mean, $\hat{\mu}_x$	-0.57	-0.26
Mean, $\bar{d}$	1.261	1.593
Variance $\hat{\sigma}_x^2$	1.59	1.46
Variance s_d^2	6.25	8.407
Acicularity Ratio,		
$\bar{R}_a$	2.73	3.18
Coefficient of Variation,		
$CV_d^{(+)}$	1.98	1.82
$(+) CV_d = \frac{s_d}{\bar{d}}$		

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