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CHARACTERIZATION OF POROSITY VIA SECONDARY REACTIONS

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SUMMARY

In this quarterly technical progress report, we summarize the progress which has been achieved with the new experimental apparatus currently under development, as well as the continued development of software to analyze small angle scattering (SAS) data.

In particular, the following was accomplished during the reporting period:

- The new TPD-MS/TGA system continues to be tested and improved.
 - Problems with air leaks under subatmospheric operation, and buoyancy and convective effects on the performance of the microbalance have been resolved. Characteristic data are given.
 - The control and data logging software has been developed and implemented for the most part.
- The small angle scattering (SAS) data analysis software has been tested with small angle neutron scattering (SANS) data obtained for solvent-swollen coal samples.

Plans for the next reporting period include:

- Continued work along the two-pronged mode of attack involving the TPD-MS/TGA experimental system, and the analysis of scattering data to obtain porosity characteristics of coal chars:
 - (1) Problems with random mass signal fluctuations from the TGA at high temperatures (e.g., $> 800^{\circ}\text{C}$) will be addressed. Also, the complete control and data logging software package will be integrated and finalized.
 - (2) The other primary task is concerned with the continued development and application of the small angle scattering data analysis software described in this report. A nonlinear, multiparameter estimation program, employing a Marquardt technique, will be added to the modeling program SCATTER to optimize the model parameters used to describe the porosity.

1.0. PROJECT BACKGROUND

1.1. Overview.

Specific surface area, as well as its accessibility to gaseous reactants, are of paramount importance for all heterogeneous interactions occurring at coal char surfaces. Accessibility of this surface area is governed by the pore structure morphology of the char; i.e., pore size distribution, tortuosity, intersections, shape, etc. The porosity morphology of coal chars varies over a considerable range and is determined by a large number of factors including the nature of the porosity of the precursor material prior to carbonization, the carbonization process, and extent and method of any subsequent activation or gasification. A persistent problem in this area has been the reliable, quantitative measurement and characterization of the resultant porosity, especially the micropores. For example, electron microscopy tends to be qualitative; small angle X-ray or small angle neutron scattering (SAXS/SANS) can suffer from sensitivity to interpretive models, and the inability to distinguish porosity that communicates with the surface from that which does not; and gas adsorption techniques also have several well known drawbacks. The latter, however, are perhaps the most reliable in general, but yield pore size distributions indirectly *via* surface area and pore volume measurements, and can also be laborious and time-consuming. Therefore, there is still a critical need for practical and facile techniques to characterize the porosity of coal chars.

1.2. The Current Project.

The current project is directed at the development of a new approach to this very old problem. During the course of recent work applying temperature programmed desorption (TPD) to the determination of energetic distributions of oxygen complexes on the surfaces of oxidized coal chars (Calo *et al.*, DE-AC21-MC23284), we discovered that secondary interactions occurring within the char

structure during TPD produce characteristic features in the resultant spectra that appear to be quite sensitive to char porosity. The relative and absolute extents of these secondary interactions form the basis of a potential characterization technique. The use of such a method to characterize coal char porosity is potentially attractive because the requisite spectra can be obtained in a single TPD experiment -- a very facile experimental procedure. However, the unambiguous and quantitative interpretation of such data in terms of parameters that can be used to characterize coal char porosity still requires development and an improved understanding of the controlling phenomena. These issues define the primary focus of the current work.

The background and general approach of the secondary interaction method for the characterization of porosity was outlined in the first quarterly technical progress report on this grant (DE-FG22-91PC91305-1), and, therefore, it will not be repeated here. Here we report on the progress that has been made in the construction, development and testing of a new TPD-MS/TGA system being developed in our laboratory for the purpose of conducting the temperature programmed desorption experiments for obtaining the secondary interaction data.

The project plan also includes the use of other techniques to characterize porosity in addition to the secondary interaction approach for the purposes of comparison, quantification, and validation. It is noted that at least two other more well established methods will be used in such a manner. Specifically, gas adsorption techniques in our own laboratory, and small angle scattering (SAS) (X-ray (SAXS) and, possibly, neutron (SANS)). The latter will be accomplished in conjunction with Dr. Peter J. Hall of the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, Scotland. It is planned to obtain small angle X-ray scattering data on the coal chars that will be used in our project *via* access to a small angle X-ray scattering system available in his department. As currently envisioned, Dr. Hall and his co-workers will obtain the X-ray scattering data, and we will analyze these data using models and computational techniques being developed in our laboratory. Here we report on the progress that has been made on this front as well.

2.0. PROJECT WORK

2.1. *The New TPD-MS/TGA System.*

2.1-1. *Overview.*

All our past work on thermal desorption of oxygen surface complexes from coal chars was conducted in a TPD reactor apparatus separate from the TGA system (Cahn Model 113) in which the chars were prepared (e.g., see Calo *et al.*, 1989). This procedure was found to work quite well for most of the types of studies that were previously conducted. However, in the current project it is essential to obtain quantitative data of a higher precision than previously in order to develop and validate the *secondary interaction* approach. This requirement necessitates a system wherein the coal char sample is never exposed to the atmosphere between preparation and thermal desorption. In addition, in order to improve the sensitivity of the technique, the bulk of the desorbed gases must be sampled directly into the mass spectrometer, rather than simply sampling a small fraction from the one atmosphere mixture of carrier gas and desorbed gases, as was done in the predecessor system. This necessitates thermal desorption at subatmospheric pressures.

In order to meet these more stringent requirements, a new TPD-MS/TGA system was designed. A schematic of this system, which has now been constructed, is presented in Figure 1. As shown, this system is built around a new Cahn D-200 digital recording microbalance, which was purchased for this purpose. The TPD reactor is the "hangdown" tube for the microbalance. The system can operate under vacuum conditions to atmospheric pressure, and, most importantly, the coal char sample need never be handled and exposed to undesirable conditions, such as the ambient atmosphere.

A new "clamshell-type" furnace with low "thermal capacitance" was constructed in our laboratory for this system which allows linear heating rates to 1100°C, at rates as high as 200K/min. The "clamshell" outer enclosure permits facile access to the hangdown tube for sample loading and removal.

Control and data logging of this experimental system are performed using a Macintosh II microcomputer with a GW Instruments 625 Jr. interface. All the control software has been written in QuickBASIC™.

As of this report, the entire system is operational and has undergone extensive testing. However, some "bugs" still remain, which are being addressed. These are discussed below.

2.1-2. Work on the TPD-MS/TGA System.

2.1-2.1 Air Leaks.

Initially, the principal problem during testing of the new apparatus was a persistent air leak under subatmospheric conditions. This was a critical problem since the sample must be oxidized under tightly controlled conditions of oxidant partial pressures, temperature and time, and thermal desorption must be carried out under the complete absence of oxygen. Several steps were taken which seem to have eliminated this problem.

First of all, the factory-supplied, hollow, hemispherical cover of the microbalance mechanism (depicted in the Figure 1 schematic) was replaced by the machined aluminum cap shown in Figure 2. This new cap was designed to reduce the gas volume as much as possible from the headspace in order to eliminate these sources of trapped and residual air. Next, the O-rings of the 3/4" Cajon fitting connecting the hangdown tube and the microbalance mechanism housing were changed to the next larger size. It was found that due to the slightly "off-size" quartz hangdown tube (19 mm O.D.), this fitting tended to leak slightly at ambient temperatures. At high temperatures, however, this leak seemed to disappear, apparently due to thermal expansion effects.

Finally, the oxidant and helium carrier gas supply lines were run to a common, two-way valve so that the gas supplies could be independently evacuated, purged and maintained at elevated pressure in order to eliminate the possibility of air infiltration during gas changeover. The sum total of all these measures has rendered the system

essentially free of air leaks.

2.1-2.2. Convective and Buoyancy Problems.

In order to have a large dynamic range in heating rate, the thermal capacitance of the hangdown tube must be kept as low as possible. For this reason, it was decided to use a small diameter quartz hangdown tube; i.e., 19 mm O.D., 17 mm I.D. However, the relatively large cross sectional area of the original quartz sample bucket (approximately 14 mm in diameter) suspended within it from the microbalance hangdown wire, gave rise to some serious problems. First of all, movement of the sample bucket in the helium carrier gas flow caused it to touch the sides of the hangdown tube with considerable frequency, resulting in unacceptably high noise levels in the mass signal. In addition, due to buoyancy effects, the apparent mass of the large empty bucket increased approximately 0.3 - 0.4 mg from 150°C to 750°C.

In order to minimize these problems, a smaller diameter quartz sample bucket (approximately 7 mm in diameter) was adopted. This eliminated the unacceptably high noise level problems, caused by collisions with the tube walls, and reduced the magnitude of the apparent variation in mass with temperature due to buoyancy effects. However, the latter problems were not completely eliminated. As shown in Figure 3, the apparent mass of the smaller empty sample bucket still decreased with increasing temperature for the case of no helium carrier gas flow. This behavior is opposite to the effect with flow (also shown in Figure 3). Moreover, both the flow rate and the type of gas have effects on the magnitude of this effect (cf. Figure 3).

In order to solve these problems, a procedure was adopted whereby a "buoyancy correction" was determined under a particular set of operating conditions, and then applied to the mass data for the corresponding experiment. Since the mass loss due to thermal desorption of surface species is a small fraction of the total sample mass (≈ 20 mg) during the TPD process, accurate correction for the effects of varying buoyancy with temperature is important. The results of this approach are discussed below for some specific examples.

2.1-3. System Performance.

As discussed previously, thermal desorption experiments are conducted at subatmospheric pressures in order to optimize sensitivity to the desorbed gases. Since the thermocouple is not physically attached to the sample bucket, only enough carrier gas (e.g., helium) pressure is needed to provide sufficient thermal conductivity to obtain accurate temperature measurements. For the system and flow rates used, 30 torr of helium appears to suffice.

In comparison to its predecessor, one major advantage of the new system is the capability to record sample mass and thermal desorption spectra simultaneously. This makes it possible to correlate TPD spectra with mass loss, thereby providing the necessary data to improve our understanding of the behavior of surface complexes.

Figure 4 presents the results of a sample experimental run for Wyodak coal char prepared at 1100°C in helium for 2 hours and gasified in CO₂ at 800°C to 5% burn off. As shown, both the CO signal and the total mass loss were obtained as a function of temperature during TPD. Due to an overshoot of temperature during the heating process, the temperature profile was not linear with time, especially in the low temperature region. This produced the noise which is evident in both the mass output and CO signals. Although this problem requires further attention, the data in Figure 4 demonstrate the type of capability we are striving for with this apparatus.

2.2. Porosity Characterization Via Small Angle Scattering (SAS).

2.2-1. Overview.

As indicated above, one of the techniques we are considering for the characterization of coal char porosity is small angle scattering. Although it is well known that these methods are inherently model dependent, they are still quite useful in assessing whether experimental observations are consistent with a given model. In addition, a robust analysis that yields realistic values for the model parameters can be used to infer other properties of the porous structure that can be invaluable in assessing

other data, such as that provided by gas adsorption techniques, as well as, in the present case, secondary interaction data.

To date, the preliminary work that we have conducted concerning the analysis of such data has been done in conjunction with Dr. Peter J. Hall of the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, U.K. In addition to this analytical work, it is anticipated that we will be able to obtain small angle X-ray scattering data on the coal chars that will be used in our project *via* access to a small angle X-ray scattering system available in his department.

2.2-2. Modeling Porosity From SAS Data.

At least two criteria should be met when selecting a suitable porous structure model. The first is that the model incorporate as much of the essential characteristics of the real structure as possible. In the case of the types of porous structures under consideration, *connectedness* of the porosity is of particular concern, since small angle scattering is only sensitive to the local structure and is thus insensitive to *connectedness*, which is a global property. The other important criterion in model selection is mathematical tractability. If the model is too complex, the interpretation of model results may become difficult and the correspondence with other techniques may be difficult or impossible to draw.

One such model that seems to fulfill these two criteria in some sense is known as the Fully Penetrable Polydisperse Spheres (FPPS) model, as proposed by Foster and Jensen (1990), for example. Essentially, this model approximates porosity by randomly distributing spheres (e.g., voids) within a material (e.g., the solid phase). The interpenetration of these spheres imparts connectedness to the resultant pore structure. The size of these spheres can be distributed over a finite or infinite size range. When the porosity is multimodal, as it is in many coal chars for example, more than one mode or distribution of spheres may be needed to describe the porosity.

As a necessary first step in attempting to develop a robust procedure for

analyzing the scattering data to be obtained for the coal chars to be used in the current project, we have implemented the software necessary to analyze these data using the FPPS model. Initially the model was fully developed on the spreadsheet program EXCEL using function MACROS. Although this was relatively straightforward, the final complete model for a bimodal sphere size distribution proved to be quite slow to solve using the spreadsheet.. Therefore, the model was translated into FORTRAN and currently runs on a Macintosh IICI microcomputer as the program SCATTER. A complete listing of the this program is included in Appendix A.

Initial work has been done in attempting to fit some SANS data on coals to a bimodal model. These efforts are described below. But first, an outline of the analysis approach follows.

2.2-3. The Procedure.

SAS data are typically obtained as the scattered signal intensity, I , as a function of the scattering vector, h . For a random, isotropic structure with two phases of uniform density, $I(h)$ may be expressed in terms of the correlation function $\gamma(r, \mathbf{p})$:

$$I(h) = I_e(h) V(\Delta\rho_e^2) \phi_s (1 - \phi_s) \int_0^\infty \gamma(r, \mathbf{p}) (\sin(h r)/h r) 4 \pi r^2 dr, \quad [1]$$

where $I_e(h)$ is the intensity scattered by a single electron, V the scattering volume, $\Delta\rho_e$ the electron density difference between phases, and ϕ_s the volume fraction of the phase s . The scattering vector h is defined as:

$$h = 4 \pi \sin \theta/\lambda, \quad [2]$$

for scattering angle 2θ and wavelength λ . The correlation function, $\gamma(r, \mathbf{p})$ for a model with parameter values $\mathbf{p}$ represents the probability that a point at distance r in an arbitrary direction from a point in a given phase will also be in that phase.

The number of parameters $\mathbf{p}$ required to specify the correlation function depends on the form chosen for the frequency distribution of the sphere sizes, $f(a)$, as well as the solid volume fraction, ϕ_s . The correlation function is closely related to the two-point conditional probability function $S_2(r; f(a), \phi_s)$; viz.,

$$\gamma(r; f(a), \phi_s) = [S_2(r; f(a), \phi_s) - \phi_s^2]/[\phi_s(1 - \phi_s)]. \quad [3]$$

$S_2(r; f(a), \phi_s)$ has been derived for a general, single mode distribution, $f(a)$, by Foster and Jenkins (1990). The resultant expression can be found in that paper. For the current purposes, suffice it to say that evaluation of $S_2(r; f(a), \phi_s)$ involves integrations over the frequency distribution $f(a)$. Hence, the application of Eq. [1] to calculate the scattering intensity requires a double integration over r .

One convenient frequency distribution for the sphere sizes, examined by Foster and Jenkins (1990), is the Schulz distribution:

$$f(a) = (1/\Gamma(b))(b/a_0)^b a^{b-1} \exp(-b a/a_0) \quad [4]$$

In this distribution, a is the sphere radius, a_0 is the mean sphere radius and b is a breadth or variance parameter that increases with sharpness of the distribution.

We have simplified the requisite integration for the evaluation of $S_2(r; f(a), \phi_s)$ by making use of the fact that the integrals in the two-point conditional probability function for the Schulz distribution can be simply represented by incomplete gamma functions, $P(c, x)$:

$$P(c, x) = \int_0^x t^{c-1} e^{-t} dt \quad [5]$$

In this form, the expression for $S_2(r; f(a), \phi_s)$ for the Schulz distribution simplifies to:

$$S_2(r; f(a), \phi_s) = \exp[-\ln \phi_s (I_1 + I_2 - I_3)] \quad [6]$$

where:

$$I_1 = 1 + P(b+3, x) \quad [7a]$$

$$I_2 = (3/4) r (1 - P(b+2, x)) / [(b+2)^2 (a_0/b)^2] \quad [7b]$$

$$I_3 = (r^3/16) (1 - P(b, x)) / \mu_3 \quad [7c]$$

where,

$$x = b r / 2 a_0 \quad [7d]$$

Moreover, the incomplete gamma functions are related to one another by simple recursion relationships; i.e.,

$$P(b+1, x) = P(b, x) - A \quad [8a]$$

$$P(b+2, x) = P(b+1) - x A / (b+1) \quad [8b]$$

$$P(b+3, x) = P(b+2) - x^2 A / [(b+2)(b+1)] \quad [8c]$$

where,

$$A = x^b e^{-x} / (b \Gamma(b)), \quad [8d]$$

such that only one incomplete gamma function, $P(b,x)$, and $\Gamma(b)$ need be evaluated for each value of x . This ultimately represents a considerable savings in computation time, since it essentially eliminates the inner integrations. The gamma function, $\Gamma(b)$, and the incomplete gamma functions, $P(b,x)$, are evaluated using series approximations obtained from *Numerical Recipes* (Press *et al.*, 1987).

In order to use the preceding approach to calculate the scattering function $I(h)$ for a char with a bimodal porosity distribution, at least two modes must be incorporated into the distribution function of spheres. It has been shown (Brumberger and Goodisman, 1983) that the resultant correlation function is simply a linear combination of that for each of the n modes; *viz.*

$$\gamma(r; f(a), \phi_s) = \sum_{i=1}^n \epsilon_i \gamma_i(r; f_i(a), \phi_s), \quad [9]$$

where the ϵ_i are the relative weights, and $\sum \epsilon_i = 1$. Thus, for example, for a bimodal model,

$$\gamma(r; f(a), \phi_s) = \epsilon_1 \gamma_1(r; f_1(a), \phi_s) + (1 - \epsilon_1) \gamma_2(r; f_2(a), \phi_s) \quad [10]$$

In Figure 5 we present scattering intensities as a function of the scattering vector, h , calculated for an arbitrary bimodal Schulz distribution model.

The final step in fitting small angle scattering data is to obtain the model parameters which provide a best fit to the experimental data. For a bimodal Schulz distribution model, this becomes a nonlinear, six-parameter fit; i.e., the parameter set is $a_{0,1}$, b_1 , $a_{0,2}$, b_2 , ϵ_1 , ϕ_s . In general, the model prediction of $I(h)$ must be determined numerically and the reconciliation of the experimental and calculated scattering intensities then requires nonlinear regression. Although various objective functions can be formulated, in order to more equally weight evenly spaced data (in h), Foster and Jensen (1990) suggested an objective function based on the logarithms of the intensities:

$$\Phi = \sum_{i=1}^N [\ln(I^*(h)) - \ln(I(h))]^2, \quad [11]$$

where the $I^*(h)$ and the $I(h)$ are the experimental and calculated scattering intensities, respectively. A nonlinear least squares fitting algorithm can then be used to evaluate the model parameter set which minimizes the objective function, Φ .

2.2-4. SANS Data Analysis Results.

The first tests of the data analysis software involved SANS data obtained on certain solvent-swollen Argonne Premium Coal Sample Bank coals at the Argonne National Laboratory by Dr. P.J. Hall of the University of Strathclyde, and co-workers. A typical neutron scattering intensity curve is presented in Figure 6 for Pittsburgh #8 coal swollen by d-NMP solvent. In the same figure, a curve produced by fitting these data is also presented. As shown, the neutron scattering data exhibits a gradual flattening out at the higher wave numbers. This characteristic has made it difficult to fit these data to a bimodal model. It appears that the bimodal model typically exhibits a plateau and sharp drop-off in the high wave number region. This is clearly evident in the curve fit to the data presented in Figure 6, as well as in the synthesized data shown in Figure 5. In this region, the scattering is controlled by the smaller pores. Thus, it may very well be that another type of distribution function may have to be assumed for these smaller pores, and/ or that a trimodal model may provide a better fit. These issues will be explored, as well as the development of an automated parameter estimation technique using a Marquardt-type routine.

3.0. PLANS FOR NEXT REPORTING PERIOD

Plans for the next reporting period include continued work along the two-pronged mode of attack involving the TPD-MS/TGA system and the analysis of scattering data to obtain porosity characteristics of coal chars.

Concerning the new system, at least one problem remains to be solved with respect to unacceptably high noise levels in the thermal desorption spectra at high temperatures. Random signal fluctuations at high temperatures (e.g., $> 800^{\circ}\text{C}$) by as much as a factor of two have been recorded. At this point, the source of this problem is unclear. It may be simply an electronics or data logging problem, or an actual physical problem with the new apparatus that we have not yet identified, or a combination of both. Tests to narrow down the possibilities are underway.

The complete control and data logging software package remains to be finalized. This software controls the mass spectrometer and the furnace, and also logs the data and prepares it for plotting and archiving. We have made extensive use of existing software within the laboratory developed for a similar interface system (G.W. Instruments Model 411 MacADIOS). Practically all the software has now been tested. Only the final integration of the package remains to be done.

The other primary task is concerned with the continued development and application of the small angle scattering data analysis software described in this report. A nonlinear, multiparameter estimation program using a Marquardt technique will be adapted to optimizing the model parameters using the modeling program described in this report.

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Figure 1. Schematic of new TPD-MS/TGA apparatus.

Side View

Bottom View

Figure 2. Schematic of new aluminum cap for microbalance headspace.

Figure 3. Apparent mass variation of the small (7 mm) empty quartz sample bucket under various conditions. The total pressure in each case is 30 torr.

Figure 4. Simultaneous record of mass loss and CO desorption spectrum following gasification of Wyodak coal char (prepared at 1100°C for 2h) to 5% burn-off in one atmosphere of CO_2 at 800°C

Figure 5. Small angle scattering curve calculated from Eq. [1] for a bimodal Schulz distribution for the parameter values: $a_{0,1} = 10\text{\AA}$, $b_1 = 20$, $a_{0,2} = 60\text{\AA}$, $b_2 = 20$, $\epsilon_1 = 0.9091$, $\phi_s = 0.99999$.

Figure 6. Four-parameter fit of small angle neutron scattering (SANS) data obtained for Pittsburgh #8 coal swollen with deuterated 1-methyl, 2-pyrrolidinone. The parameter set is: $a_{0,1} = 0.7\text{\AA}$, $b_1 = 0.5$, $a_{0,2} = 100\text{\AA}$, $b_2 = 1$, $\epsilon_1 = 0.91$, $\phi_s = 0.995$.

Appendix A. Source Code Listing for Program SCATTER

```
PROGRAM SCATTER
INCLUDE SCATTER.INC
DIMENSION HX(200),TEN(200),TENCAL(200)
DIMENSION XA(200),YA(200),YACAL(200)
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 HX,TEN,TENCAL,EPS1
CHARACTER*30 filename1
CHARACTER*30 filename2
COMMON A01,B1,PC1,A02,B2,PC2,EPS1,PHI,PP
C PRINT *, 'Data File Name:'
C READ *, filename1
  filename1='S1635'
  PRINT *, 'Output File Name:'
  READ *, filename2
  open (UNIT=10,FILE=filename1,ERR=500,
+ STATUS='OLD',ACTION='READ')
11 format(I3)
12 format(F8.5,F10.6)
  READ(10,11) NUM
  DO 13 K=1,NUM
    READ(10,12) HX(K),TEN(K)
13 CONTINUE
  goto 501
500 CONTINUE
  PRINT *, 'Error Opening File '
501 CONTINUE
  close (10)
  PRINT *, 'A01 ='
  READ *, A01
  PRINT *, 'B1 ='
  READ *, B1
  PRINT *, 'A02 ='
  READ *, A02
  PRINT *, 'B2 ='
  READ *, B2
  PRINT *, 'PHI ='
  READ *, PHI
  PRINT *, 'EPS1 ='
  READ *, EPS1
  PP=3.141592653589793D0
  T1 =(A01/B1)**3
  T2=GAMMLN(B1+3.0D0)
  T3 = GAMMLN(B1)
  TM1=T1*DEXP(T2-T3)
  PC1=-DLOG(PHI)/TM1
  T4 = (A02/B2)**3
  T5 = GAMMLN(B2+3.0D0)
  T6 = GAMMLN(B2)
  TM2 = T4*DEXP(T5-T6)
  PC2=-DLOG(PHI)/TM2
```

```

C      INTEGRATION ROUTINE
      PRINT *, 'Calculating h loop'
      SSUM = 0.0D0
      DO 200 J=1, NUM
      H=HX(J)
      SUM=0.0D0
      DEX=6.0D0
      BEGIN=0.0D0
100    ROOT=DEX*PP/H
      FINISH=ROOT
      CALL QGAUSS(BEGIN, FINISH, H, GRAL)
      SUM = SUM + GRAL
      BEGIN = FINISH
      DEX = DEX + 6.0D0
      IF(DABS(GRAL/SUM).GT.1.0D-4) GO TO 100
      IF(SUM.LT.0.0D0) GO TO 100
      TENCAL(J)=SUM
      IF(J.NE.1) GO TO 150
      SCALE=TEN(1)/TENCAL(1)
150    TENCAL(J)=SCALE*SUM
      SSUM = SSUM + (DLOG(TENCAL(J))-DLOG(TEN(J)))*2
200    CONTINUE
C Write to Output Data File: filename2
      open (UNIT=10, FILE=filename2, STATUS='UNKNOWN',
+      ERR=700, ACTION='WRITE')
      write(10,34) A01,B1
      write(10,34) A02,B2
      write(10,34) PHI, EPS1
      write(10,35) SSUM
35    format(F8.3)
      DO 600 J=1, NUM
      write(10,33) HX(J), TEN(J), TENCAL(J)
33    format (E20.8, 1H,, E20.8, 1H,, E20.8)
34    format(F8.2, 1H,, F8.2, 1H,)
600    CONTINUE
      goto 701
700    CONTINUE
      type *, 'Error Opening File '
      print *, filename2
701    CONTINUE
      close (10)
C      Convert to Single Precision for Plotting
      DO 300 I=1, NUM
      XA(I)=REAL(HX(I))
      YA(I)=REAL(TEN(I))
      YACAL(I)=REAL(TENCAL(I))
300    CONTINUE
      CALL GRAPH(XA, YA, YACAL, NUM)
      PRINT *, A01, B1, PC1
      PRINT *, A02, B2, PC2
      PRINT *, SSUM, SCALE
      PAUSE
      STOP

```

```

      END
C*****
      SUBROUTINE QGAUSS(A,B,H,SS)
C*****
      DIMENSION X(5),W(5)
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A01,B1,PC1,A02,B2,PC2,EPS1,PHI,PP
      DATA X/.1488743389,.4333953941,.6794095682,.8650633666,.9739065285/
      DATA W/.2955242247,.2692667193,.2190863625,.1494513491,.0666713443/
      XM=0.5D0*(B+A)
      XR=0.5D0*(B-A)
      SS=0
      DO 11 J=1,5
      DX=XR*X(J)
      SS=SS+W(J)*(FUNC(XM+DX,H)+FUNC(XM-DX,H))
11    CONTINUE
      SS=XR*SS
C    PRINT *,SS
      RETURN
      END
C*****
      SUBROUTINE GCF(GAMMCF,A,X)
C*****
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER (ITMAX=100,EPS=3.D-7)
C    PRINT *,A,X
      GLN=GAMMLN(A)
      GOLD=0.0D0
      A0=1.0D0
      A1=X
      B0=0.0D0
      B1=1.0D0
      FAC=1.0D0
      DO 11 N=1,ITMAX
      AN=DBLE(N)
      ANA=AN-A
      A0=(A1+A0*ANA)*FAC
      B0=(B1+B0*ANA)*FAC
      ANF=AN*FAC
      A1=X*A0+ANF*A1
      B1=X*B0+ANF*B1
      IF(A1.NE.0.0D0)THEN
      FAC=1.0D0/A1
      G=B1*FAC
      IF(DABS((G-GOLD)/G).LT.EPS)GO TO 1
      GOLD=G
      ENDIF
11    CONTINUE
C    PRINT *,'GCF',A,X
      PAUSE 'A too large, ITMAX too small'
1    GAMMCF=DEXP(-X+A*DLOG(X)-GLN)*G
      RETURN

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      END
C*****
      SUBROUTINE GSER(GAMSER,A,X)
C*****
      IMPLICIT REAL*8 (A-H,O-Z)
      PARAMETER (ITMAX=100,EPS=3.D-7)
      GLN=GAMMLN(A)
      IF(X.LE.0.0D0)THEN
      IF(X.LT.0.0D0)PAUSE
      GAMSER=0.0D0
      RETURN
      ENDIF
      AP=A
      SUM=1.0D0/A
      DEL=SUM
      DO 11 N=1,ITMAX
      AP=AP+1.0D0
      DEL=DEL*X/AP
      SUM=SUM+DEL
      IF(DABS(DEL).LT.DABS(SUM)*EPS)GO TO 1
11    CONTINUE
C    PRINT *,'GSER',A,X
      PAUSE 'A too large, ITMAX too small'
1    GAMSER=SUM*DEXP(-X+A*DLOG(X)-GLN)
      RETURN
      END
C*****
      FUNCTION FUNC(R,H)
C*****
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A01,B1,PC1,A02,B2,PC2,EPS1,PHI,PP
C    PRINT *,'FUNC',A01
      CALL S2R(R,A01,B1,PC1,GAM1)
      CALL S2R(R,A02,B2,PC2,GAM2)
      GAM1=GAM1-PHI**2
      GAM2=GAM2-PHI**2
      IF(R.EQ.0.0D0) GO TO 10
      FUNC=(GAM1*EPS1+(1.0D0-EPS1)*GAM2)*DSIN(H*R)*4*PP*R**2/H/R
      GO TO 20
10    FUNC=0.0D0
20    CONTINUE
      RETURN
      END
C*****
      SUBROUTINE S2R(R,A0,B,PC,GAM)
C*****
      IMPLICIT REAL*8 (A-H,O-Z)
      IF(R.EQ.0.0D0) GOTO 10
      XX = B*R/A0/2.0D0
C    PRINT *,'S2R',R,A0,B,PC,XX
      T1 = GAMMP(B+3.0D0,XX)
      GRAL1=2*(A0/B)**3*T1*(B+2.0D0)*(B+1.0D0)*B
      GRAL2 = GRAL1*(1.0D0-T1)/T1/2.0D0

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T2 = GAMMP(B+2.0D0,XX)
GRAL3 = (1-T2)*(B+1.0D0)*B*(A0/B)**2*3.0D0*R/4.0D0
T3 = GAMMP(B,XX)
GRAL4 = (1-T3)*3.0D0*R**3/48.0D0
GAM=DEXP(-PC*(GRAL1+GRAL2+GRAL3-GRAL4))
GO TO 20
10  GAM = DEXP(-PC*(A0/B)**3*(B+2.0D0)*(B+1.0D0)*B)
20  CONTINUE
C   PRINT *,R,GAM
    RETURN
    END
C*****
FUNCTION GAMMLN(XX)
C*****
  DIMENSION COF(6)
  IMPLICIT REAL*8 (A-H,O-Z)
  REAL*8 COF(6),STP,HALF,ONE,FPF,X,TMP,SER
  DATA COF,STP/76.18009173D0,-86.50532033D0,24.01409822D0,
* -1.231739516D0,.120858003D-2,-.536382D-5,2.50662827465D0/
  DATA HALF,ONE,FPF/0.5D0,1.0D0,5.5D0/
  X=XX-ONE
  TMP=X+FPF
  TMP=(X+HALF)*DLOG(TMP)-TMP
  SER=ONE
  DO 11 J=1,6
    X=X+ONE
    SER=SER+COF(J)/X
11  CONTINUE
  GAMMLN=TMP+DLOG(STP*SER)
  RETURN
  END
C*****
FUNCTION GAMMP(A,X)
C*****
  IMPLICIT REAL*8 (A-H,O-Z)
  IF(X.LT.0.0D0.OR.A.LE.0.0D0)PAUSE
  IF(X.LT.A+1.0D0)THEN
    CALL GSER(GAMMP,A,X)
  ELSE
    CALL GCF(GAMMCF,A,X)
    GAMMP=1.0D0-GAMMCF
  ENDIF
  RETURN
  END
C*****
SUBROUTINE GRAPH(XA,YA,YACAL,NUM)
C*****
C   General Purpose MacGraphics Routine
  DIMENSION XA(200),YA(200),YACAL(200)
  INTEGER MTMINX,MTMINY,MTMAXX,MTMAXY,MTSIZE
  COMMON MTMINX,MTMINY,MTMAXX,MTMAXY,MTSIZE
* PROCEDURE Moveto (H,V: Integer);

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      INTEGER MOVETO
      PARAMETER (MOVETO=Z'89309000')
* PROCEDURE Lineto (H,V: Integer);
      INTEGER LINETO
      PARAMETER (LINETO=Z'89109000')
* PROCEDURE Move (Dh,Dv: Integer);
      INTEGER MOVE
      PARAMETER(MOVE=Z'89409000')
* PROCEDURE Line (Dh,Dv: Integer);
      INTEGER LINE
      PARAMETER (LINE=Z'89209000')
C  FUNCTIONS FOR GKAPH ROUTINES -- TRANSLATION OF COORDINATES
      REAL OLDX,OLDY,OLDR
      REAL VX,VY,VXS,VYS
      INTEGER TRANSX,TRANSY,TRANSR
      TRANSX(OLDX)=NINT(MTMAXX+70*OLDX)
      TRANSY(OLDY)=NINT(150-20*OLDY)
      TRANSR(OLDR)=NINT(MTSIZE*OLDR)
C  Make space for graphics
      DO 889 L=1,30
      PRINT *,''
889  CONTINUE
C  INITIALIZE VARIABLES
      MTMINX=10
      MTMINY=10
      MTMAXX=490
      MTMAXY=290
      MTSIZE=250
C  DRAW PLOT
      CALL TOOLBX(MOVETO,MTMINX,MTMINY)
      CALL TOOLBX(LINETO,MTMAXX,MTMINY)
      CALL TOOLBX(LINETO,MTMAXX,MTMAXY)
      CALL TOOLBX(LINETO,MTMINX,MTMAXY)
      CALL TOOLBX(LINETO,MTMINX,MTMINY)
C  DRAW PLOTS
      VXS=LOG(XA(1))
      VYS=LOG(YA(1))
      CALL TOOLBX(MOVETO,TRANSX(VXS),TRANSY(VYS))
      IND=NUM-1
      DO 100 I=1,IND
      VX=LOG(XA(I))
      VY=LOG(YA(I))
      CALL TOOLBX(LINETO,TRANSX(VX),TRANSY(VY))
100  CONTINUE
      CALL TOOLBX(MOVETO,TRANSX(VXS),TRANSY(VYS))
      DO 200 I=1,IND
      VX=LOG(XA(I))
      VY=LOG(YACAL(I))
      CALL TOOLBX(LINETO,TRANSX(VX),TRANSY(VY))
200  CONTINUE
      CALL TOOLBX(MOVETO,400,20)
      RETURN
      END

```

END

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