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EVALUATION OF MOLECULAR WEIGHT FROM EQUILIBRIUM SEDIMENTATION

PART III. MOLECULAR WEIGHT DISTRIBUTIONS FROM EQUILIBRIUM SEDIMENTATION-DIFFUSION DATA VIA LINEAR PROGRAMMING

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena." Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules," with Dr. M. T. Gehatia acting as task scientist. Coauthors are Mr. R. R. Jurick, ASD Computer Science Center (ASVC), and Dr. D. R. Wiff, Research Institute, University of Dayton. The work was administered under the direction of the Air Force Materials Laboratory, Directorate of Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

The report covers research conducted from September 1968 to August 1969. The manuscript was released by the authors in October 1969 for publication as a technical report.

This technical report has been reviewed and is approved.

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ABSTRACT

Within the past decade easy access to high speed digital computers has renewed interest in deriving molecular weight distributions from sedimentation-diffusion equilibrium data. One of the computational schemes which appears most promising is the Simplex Method of linear programming. The purpose of this work was to investigate the advantages and limitations of this approach.

It was found that, even though inferring a molecular weight distribution from sedimentation-diffusion equilibrium data is mathematically an ill-posed problem, the method of linear programming yields qualitatively a good molecular weight distribution. Also, the method proved satisfactory for the case when sedimentation equilibrium data was acquired from only a single angular velocity.

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INTRODUCTION

The relationship describing sedimentation-diffusion equilibrium of an ideal polydisperse solution in an ultracentrifuge can be given by a Fredholm integral equation of the first kind (Reference 1). Since no rigorous solution of this integral is known, there have been many attempts to solve it by approximation (References 2, 3). These efforts mainly involved use of Fourier transforms or Laplace transforms by assuming an approximate functional expression for the experimental concentration gradient along the ultracentrifugal cell, or by expanding the molecular weight distribution (MWD) into a polynomial of assumed functions.

The main weakness has been that some parts of the calculated distribution would be negative. Physically, of course, we know that the MWD for any molecular weight must always be positive or zero. Recently Lee (Reference 4) carried out an investigation of the Fredholm integral equation and found that mathematically it is an "ill-posed" problem. In trying to infer a MWD from experimental measurements of concentration gradients small errors can lead to an unacceptable MWD. Therefore, we compromised in trying to determine only an "overall" shape of the MWD without being specific to individual points, i. e., we allowed certain fluctuations of the curve to be present and ignored fine structure.

To generalize a theoretical analysis, let us accept that the MWD can be slightly negative for some molecular weight values. Since we chose to ignore the point-by-point functional form of the MWD, the next logical step would be to subdivide the MWD into narrow (not infinitesimal) but finite molecular weight strips. This would result in approximations of MWD by rectangles of finite width and would lead naturally to the use of matrices. This has been done (Reference 5) but unfortunately the matrices are "ill-conditioned" or nearly singular.

Scholte (Reference 6 and 7) in 1968, still using matrices, applied the scheme of linear programming to infer a MWD from experimental measurements of concentration gradients at various angular velocities. The main advantage to this approach is that values of the MWD are forced to be greater than or equal to zero and "slack variables" are introduced to account for experimental error. Scholte evaluated the MWD at ten molecular weights, then shifted to ten other molecular weights in a prescribed manner, continuing until, finally, there were four such sets. Since each set represented an individual solution, one quarter of the sum of the four sets also represented a solution. By doing this, Scholte obtained good agreement between his assumed and calculated molecular weight distributions.

There are, however, three reasons why Scholte's scheme cannot be blindly applied to other systems. These are: (1) Scholte dealt with a molecular weight range of 5×10^4 to 10^6; by comparison, in many cases of synthetic polymers the range is much narrower, e.g., 0 to 10^5. (2) Scholte used five or more angular velocities, each requiring several days for equilibrium. There are, however, cases when equilibrium at each velocity requires a much longer time (Reference 8). Therefore, it is important to have a scheme which would produce a MWD from data taken at one velocity. (3) Since our interest was in a different molecular weight range and we were using experimental data from only one angular velocity, the effects of experimental error on the calculated MWD had to be investigated.

A computer program using Scholte's ideas was independently coded and a different linear programming (LP) solving routine was employed. The new program reliability was verified by reproducing Scholte's published results. Then application of the new program to new specific needs stated above were investigated. A brief description of linear programming theory follows.

SECTION II

THEORY

In the brief discussion which follows, all theorems and definitions are given without proof or examples. All material on linear programming was taken from other works (References 9, 10, and 11).

Definition 1. A simplex is an n-dimensional convex polyhedron having exactly n+1 vertices. The boundary of the simplex contains simplical faces of dimension i where i < n. The number of such faces of dimension i is $\binom{n+1}{i+1}$ where $\binom{n}{m} = n!/m!(n-m)!$. A simplex in zero dimension is a point, in 1-dimension a line, in 2-dimension a triangle, in 3-dimension a tetrahedron, etc. The equation of a simplex with unit intercept is $X_i \geq 0$ and $\sum_i X_i = 1$.

Definition 2. A subset C of E_n (n-dimensional Euclidean Space) is a convex set if and only if for all pairs of points $\underline{V}_1$ and $\underline{V}_2$ in C any convex combination

$$\underline{V} = \beta_1 V_1 + \beta_2 V_2 \tag{1}$$

is also in C, where β_i are scalars, $\beta_i \geq 0$, and $\sum_i \beta_i = 1$.

Definition 3. A point $\underline{V}$ in a convex set C is called an extreme point if $\underline{V}$ cannot be expressed as a convex combination of any other two distinct points in C. That is, if we denote the convex set of solutions to the linear programming problem by K and if K is a convex polygon, then K is the convex hull of the extreme points of K. Therefore, every feasible solution in K can be represented as a convex combination of the extreme feasible solutions in K.

Theorem 1. The set of all feasible solutions to the linear programming problem is a convex set.

In general, the linear programming problem can be described as follows: Given is a convex set defined by a set of linear constraints in E_n. From all the points belonging to the convex set, we wish to determine a subset of points (which will contain either one or many points) for which a linear objective function is optimized.

Usually we are confronted with a set of simultaneous equations

$$\begin{matrix} a_{11}x_1 + a_{12}x_2 + a_{13}x_3 + \cdots + a_{1m}x_m = b_1 \\ \vdots \qquad\qquad\qquad \ddots \qquad\qquad\qquad \vdots \\ a_{n1}x_1 + a_{n2}x_2 + a_{n3}x_3 + \cdots + a_{nm}x_m = b_n \end{matrix} \tag{2}$$

where n > m. For simplicity let m equal n; let A be the matrix, $\left\{a_{ij}\right\}$, (i = 1, 2, 3, --- m and j = 1, 2, 3---m); $\underline{X}$ the vector $\left[X_j\right]$, j = 1, 2, 3---m and $\underline{b}$ the vector $\left\{b_i\right\}$, i = 1 , 2, 3---, m. Then Equation 2 can be written in the form

$$A\underline{x} = \underline{b} \tag{3}$$

Since A is a square matrix and assumed nonsingular, the solution vector is expressed as

$$\underline{x} = A^{-1}\,\underline{b} \tag{4}$$

A simple computational scheme is the complete elimination method of Jordan and Gauss which has a finite number of steps or iterations. In just m iterations the procedure multiplies the system (Equation 2) by A^{-1} to obtain Equation 4. This is the standard matrix problem which is assumed familiar to the reader.

Now, in linear programming the problem is reversed. Instead of having an "over-determined" system as indicated by Equation 2, we have an "under-determined" system (i. e., n < m) subject to other constraints. That is, we wish to find a vector $\left\{x_i\right\}$, i = 1, 2, 3, ---m which minimizes the linear form (i. e., the objective function)

$$C_1x_1 + C_2x_2 + C_3x_3 + - - - + C_mx_m \tag{5}$$

subject to linear constraints

$$x_j \geq o, \quad j = 1, 2, 3, ---, m \tag{6}$$

and the set of equations given by Equation 2 but with n < m.

For large n and m it would be an impossible task to evaluate all possible solutions and select one that minimizes the objective function. A computational scheme is desired which converges to a minimum solution. The Simplex Method, devised by Dantzig (Reference 11) is such a scheme. In Reference 11 the equation $\sum X_i$ is used as a constraint. The procedure finds an extreme point and determines whether it is the minimum. If it is not, the procedure finds a neighboring extreme point whose corresponding value of the objective function is less than or equal to the preceding value. In a finite number of such steps (usually between n and 2n), a minimizing feasible solution is found. The Simplex Method makes it possible to discover whether the problem has any finite minimizing solutions or no feasible solutions at all.

Consideration is now given to how this can be related to the problem at hand, namely, molecular weight determination via sedimentation-diffusion equilibrium. The equation describing sedimentation-diffusion equilibrium for a heterogeneous system is given (from Reference 1) by

$$-\frac{1}{C^0}\frac{dC}{d\xi} = \int_0^\infty \frac{\lambda^2 M^2 e^{-\lambda M} F(M)}{1 - e^{-\lambda M}}\, dM \tag{7}$$

where,

$$\int_0^\infty F(M)\, dM = 1 \tag{8}$$

In the above equations C° is the concentration of the original solution, C is the equilibrium concentration at radial distance r, M is the molecular weight, F(M) is the frequency function of molecular weight, $\xi = (r_b^2 - r^2)/(r_b^2 - r_m^2)$ with r_m the radial distance from the center of rotation to the meniscus, and r_b the radial distance from the center of rotation to the bottom of the cell. Also, $\lambda = (1-v\rho)\,\omega^2\,(r_b^2 - r_m^2)/2RT$, where v is the partial specific volume of the dissolved substance, ρ is the density of the solution, ω is the angular velocity in radian per second, R is the gas constant, and T the absolute temperature.

Rewriting Equations 7 and 8 for the discrete case (Dirac δ-functions) one obtains

$$U(\lambda_i \xi_n) = \sum_m \frac{\lambda_i^2 M_m^2 e^{-\lambda_i M_m \xi_n}}{1 - e^{-\lambda_i M_m}}\, f_m \tag{9}$$

and,

$$\sum_m f_m = 1 \tag{10}$$

where

$$U(\lambda_i, \xi_n) = -\frac{1}{C^\circ}\left(\frac{dC}{d\xi_n}\right)_{\lambda_i} \quad \text{and} \quad f_m$$

is the weight fraction of molecules of a given molecular weight M_m in the original sample. Recall that the $U(\lambda_i, \xi_n)$ and ξ_n are the experimentally measured quantities with λ_i being the product of a constant (determined from auxiliary measurements) and the square of the angular speed of the rotor.

For convenience of notation let

$$K_{\ell n} = \frac{\lambda_i^2 M_m^2 e^{-\lambda_i M_m \xi_n}}{1 - e^{-\lambda_i M_m}} \tag{11}$$

and

$$U_\ell = U(\lambda_i, \xi_n) \tag{12}$$

where for each i, n = 1, 2, ---N; i = 1, 2, ---, I; m = 1, 2, ---M; and ℓ = 1, 2, ---, L with L = IN and L > M.

Thus Equation 9 becomes

$$U_\ell = \sum_m K_{\ell m} f_m \tag{13}$$

Since the quantities of U_ℓ are experimentally measured, they will in all probability be greater than or less than their true precise value (i.e., there exists experimental error). Although this physical fact is accepted, experimentally Equation 13 does not hold true. This is especially apparent when we investigate the matrix $\{K_{\ell m}\}$ and find it ill-conditioned. In essence, the matrix $\{K_{\ell m}\}^{-1}$ acts as an "amplifier" for any error which might exist in the set $\{U_\ell\}$.

If we grant that an error in U_ℓ exists, Equation 13 becomes

$$U_\ell = \sum_m K_{\ell m} f_m + \epsilon_\ell \tag{14}$$

where ϵ_ℓ is the experimental error in U_ℓ. Since the application of linear programming necessitates that all x_i (see Equation 1) are positive or zero, we must account for error's being positive or negative. It is the inclusion of error that now enables us to go from an "over determined" system to an "under determined" system. The linear programming procedure is now applicable. In particular, you will recall that a modified Simplex Method can be used.

Recapitulating, we now obtain the formulation of the linear programming scheme as used to determine the MWD from sedimentation-diffusion equilibrium. We wish to find the set $\{f_m\}$, m = 1, 2, ---Q, which minimizes the linear form (i. e., the objective function)

$$\sum_{\ell=1}^{L} (\delta_\ell + \beta_\ell) \tag{15}$$

subject to the linear constraints

$$\begin{array}{l} f_m \geq 0, \quad m = 1,2,3, \cdots Q \\ \left.\begin{array}{l}\delta_\ell \geq 0 \\ \beta_\ell \geq 0\end{array}\right\}, \ell = 1,2,3, \cdots L \end{array} \tag{16}$$

and

$$\begin{array}{l} K_{11}f_1 + K_{12}f_2 + \cdots + K_{1Q}f_Q + \delta_1 - \beta_1 + 0 + 0 + \cdots + 0 + 0 = U_1 \\ K_{21}f_1 + K_{22}f_2 + \cdots + K_{2Q}f_Q + 0 + 0 + \delta_2 - \beta_2 + \cdots + 0 + 0 = U_2 \\ \vdots \\ K_{L1}f_1 + K_{L2}f_2 + \cdots + K_{LQ}f_Q + 0 + 0 + 0 + 0 + \cdots + \delta_L - \beta_L = U_L \end{array} \tag{17}$$

where L > Q**. Let the set $\{x_i\}$, i = 1, 2, 3, ..., Q + 2L be composed of f_m values for i = 1, 2, 3, ---Q, and alternately δ_ℓ and β_ℓ for i = Q + 1, Q + 2, ----, Q + 2L; where all $X_i \geq 0$. Also let the L x(Q + 2L) matrix P be represented by

**This is not an absolutely necessary condition. When one velocity was used the situation arose where L < Q.

$$P = \begin{pmatrix} K_{11} & K_{12} & \cdots & K_{1Q} & 1 & -1 & 0 & 0 & \cdots & 0 & 0 \\ K_{21} & K_{22} & \cdots & K_{2Q} & 0 & 0 & 1 & -1 & \cdots & 0 & 0 \\ \vdots & & \ddots & & \vdots & & & \ddots & & & \vdots \\ K_{L1} & K_{L2} & \cdots & K_{LQ} & 0 & 0 & 0 & 0 & \cdots & 1 & -1 \end{pmatrix} \tag{18}$$

Then, in matrix notation the problem is formulated by

$$P\underline{X} = \underline{U} \tag{19}$$

The next section will describe the application of this method.

SECTION III

VARIABLE FACTORS IN COMPUTATION AND THEIR INFLUENCE ON RESULTING MWD

A. FORMULATION OF COMPUTER PROBLEM

The objective of this section is to present the results which three variable factors investigated have on a MWD. Since the actual programming involved a slight modification of Equation 9, a listing and discussion of the variable factors investigated will be preceded by a discussion of the actual equation programmed.

The programmed equation is given by

$$U(\lambda_k, \xi_i) = \sum_n \frac{\lambda_k^2 M_n^2 e^{-\lambda_k M_n \xi_i} F(M_n) \Delta M_n}{1 - e^{-\lambda_k M_n}} \tag{20}$$

Here all quantities have the same meaning as in Equation 7 and 9. However, we must remember that, since λ is proportional to the square of the angular velocity, the index k indicates the various velocities at which equilibrium was achieved. For each velocity there exists a set of ξ-values, i.e., for each λ_k there is a corresponding set $\{\xi_i\}$. If there are data from five velocities and for each velocity there corresponds five ξ- values, this would imply twenty-five U-values. It is imperative that the molecular weight range being investigated incorporate all molecular weights present in the solution sample being centrifugated. Since Equation 9 and 20 deal with discrete molecular weights, some procedure must be employed to span the entire molecular weight range (MWR). Following the idea of Scholte (References 6 and 7), a multiplicative factor (g-factor) has been introduced. Therefore, starting with the first molecular weight M_1, the other molecular weights in a given sampled set could be generated. Knowing, a priori, the MWR we can now calculate the g-factor and the number (N_Q) of molecular weights needed to span the MWR. (The g-factor is later used as a variable parameter related to the error in the experimental concentration gradients. However, the value of g must be at least large enough to ensure the actual MWR present in a given experiment is spanned. A convenient technique for finding the MWR is given in Reference 8). The molecular weights sampled will be

$$M_n = M_1 g^{n-1} \tag{21}$$

where $n = 1, 2, 3, ---, N_Q$. This enables one to divide the MWR into non-overlapping subranges. Each subrange span is denoted by

$$\Delta M_n = M_n - M_{n-1} \tag{22}$$

where M_o is assumed zero. By employing the averaging technique of Scholte (Reference 7), after solving Equation 20 for one set of molecular weights, a new set of molecular weights is selected in a prescribed manner. The new set is shifted relative to the previous set by a multiplicative factor $g^{1/N}$, where N is the number of desired molecular weight sets. That is, if the number of the set is labeled by the index n and the molecular weights within a set by j, then

$$M_{j,n} = M_{1n} g^{j-1} \tag{23}$$

and

$$\Delta M_{jn} = (g^{1/2} - g^{-1/2}) M_{jn} \tag{24}$$

where $j = 1, 2, 3, ---, NQ$; $n = 1, 2, 3, ---, N$; and $M_{o,n} = 0$.

The concentration of molecular weights in a given subrange is simply the weight fraction (f_m) multiplied by the initial solution concentration ($C°_m = C°f_m$). When Scholte (Reference 7) presents his final results they are in the form MF(M) versus M. In this work a modified system F(M) versus M has been calculated (Equation 20), since one usually has less qualitative feeling for MF(M) than for F(M).

Now, it is possible to list the variable parameters investigated in this work. They are as follows:

1. The effect that varying the g-factor (i. e., the span of the molecular weight subrange) has on the resulting MWD; and also the effect when the number of sets of molecular weights sampled was varied.

2. How the resulting MWD is affected by varying the number of elements in the sets $\{\xi_i\}$ and $\{\lambda_k\}$.

3. Whether the introduction of error into idealized U-values affects the resulting MWD. This includes normal random error and weighted random error.

The results of each will be discussed successively in the following section.

B. DISTRIBUTIONS STUDIED

The g-factor is related to the experimental error in the U-values (Reference 7). Figures 1 through 4 show the effect of varying the g-factor and the number of sets of molecular weights. In each case the solid-line curve is the assumed distribution from which U-values were calculated. For all curves, seven velocities were used and with each velocity five ξ-values. The squared angular velocities were 4.1693 x 10^5, 5.8370 x 10^5, 8.1718 x 10^5, 11.4406 x 10^5, 16.0168 x 10^5, 22.4235 x 10^5, and 31.3929 x 10^5 rad^2/sec^2 with ξ = O, 1/4, 12, 3/4, and 1 for each case. Therefore, thirty-five U-values were used for these calculations.

As previously mentioned, we must always be sure that the MWR is wide enough to incorporate all molecular weights present in the sample. To study the effect of range size on the MWD, all parameters in Figure 4 were held constant except the value for MWR, which was brought closer to the MWR of the assumed distribution. As shown in Figure 5, structure begins to appear when the highest molecular weight sampled was not far beyond the actual highest molecular weight present. Figure 5 represents a calculation involving twenty molecular weight sets. When the number of molecular weight sets was decreased from twenty to ten (Figure 6) then five (Figure 7), there was no appreciable change except that, naturally, the calculated points were spaced farther apart.

What would be the effect if the number of ξ-values associated with each velocity was increased? As previously mentioned, five ξ-values have been used per velocity for Figures 1 through 7. Figure 8 shows the results with all parameters of Figure 6 held constant except that, now, nine ξ-values were used. The nine ξ-values were so chosen that $\xi = 0$ to 1 with $\Delta\xi = 1/8$. From the study of this assumed distribution it appears that using five ξ-values, sampling twenty sets of molecular weights, and using a g-factor ≈ 2.0 seemed to have produced the optimum desired results, i.e., the calculated MWD agreeing best with the assumed MWD. If the g-factor became too small the result was noise, that is, the accuracy of the U-values did not warrant such precision, or the matrix in the LP solver routine became singular.

At this stage a normal Gaussian distribution with a MWR of 0 to 120,000 was investigated. Once again the g-factor was varied. The lowest g-value used was 1.15 and the highest 4.0. The former resulted in an erratic MWD and the latter resulted in a curve which went exponentially to zero at high molecular weights. The best g-value for this specific case was g = 1.8. In general, a satisfactory technique was to start with a low value of g. Then as the value of g was increased the erratic behavior of the MWD disappeared. At the g-value where the erratic results seemed to disappear, that value was established as the appropriate one. Then the maximum reliable "fine structure" for a given set of experimental U-values was attained.

Using this assumed normal distribution (its functional form) the MWR was shifted to investigate the reliability of the method for various molecular weight ranges. One range tried was from 0 to 12,000 and another from 10^5 to 10^6. In each case the results were satisfactory, considering that in all cases g was kept constant (g = 1.8).

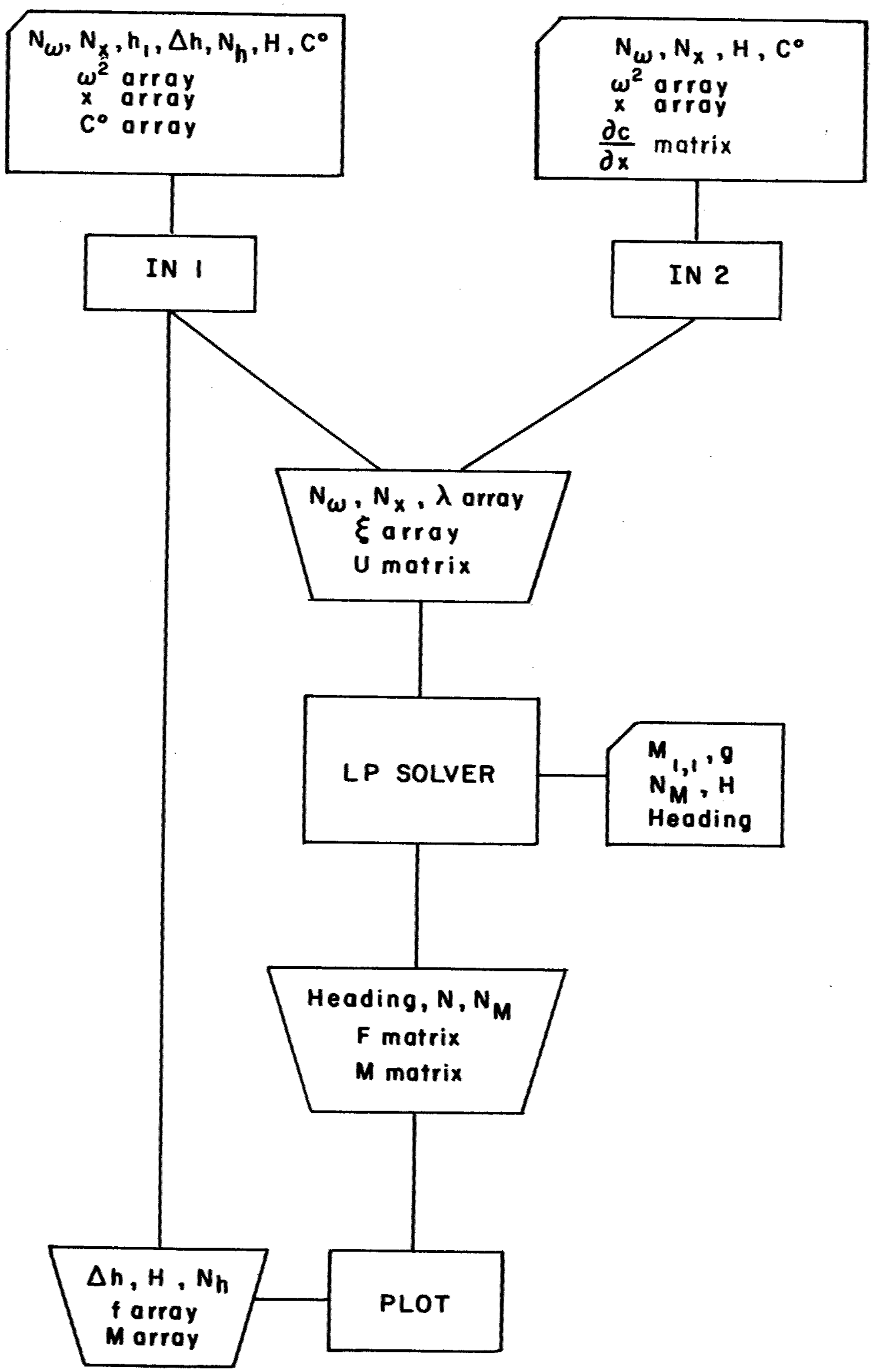
As previously mentioned, the U-values used resulted from seven assumed velocities ranging from about 6,000 to 50,000 RPM. It would be advantageous if the experimental U's were obtained from an equilibrium sedimentation-diffusion experiment at only one angular velocity. To check this, the normal Gaussian distribution, MWR from 0 to 120,000, was approximated (holding all other variables constant) by deleting all U-values associated with various angular velocities. All combinations of the velocities were tried. By using only the lowest angular velocity (6,166 RPM), the computer program produced a MWD which "fit" the assumed MWD as well as the case where all seven angular velocities were used. In fact, all single velocity cases resulted in a reasonable MWD. Therefore, we would conclude that an acceptable MWD could be obtained from an equilibrium sedimentation-diffusion experiment at one angular velocity, at least with a MWR of 0 to 120,000.

The third area of investigation involved use of the normal Gaussian MWD ($0 < M < 120,000$) U-values from one angular velocity (6,166 RPM) and at $\xi = 0$, 1/4, 1/2, 3/4, and 1 to find the effect that error in the U-values would have on the calculated MWD. Error (1, 2, 5, 10, and 20%, respectively) was introduced by aid of a random error generator. For each magnitude of error, five calculations were employed to vitiate any wrong conclusions that one error distribution might have on the final MWD. For each case (1 to 20%) when the error was normally distributed (dotted line Figure 9) the calculated MWD agreed with the assumed MWD. Naturally the 1% error case gave the best "fit" to the assumed MWD, but even for the 20% error case the calculated MWD was not unacceptable. When the error introduced in the U-values was such as to be weighted (dashed curves Figure 9), the calculated MWD was entirely different from the expected normal MWD. This phenomenon substantiates the findings of Lee (Reference 5) and Tikhonov and Glasko (Reference 12).

SECTION IV

DESCRIPTION OF COMPUTER PROGRAM

FLOW DIAGRAM



DESCRIPTION OF VARIABLES

a_{i_j}	-	entry in matrix for LP problem
b	-	largest x value
b_i	-	right-hand side of LP problem
C°	-	initial concentration of solution
C°_m	-	initial concentration of solution whose molecular weight is $\frac{h_n}{H}$
f_n	-	weight fraction of molecular weight M_n
$F_{j,n}$	-	results of LP solution, frequency list for mol. wt. of $M_{j,n}$
g	-	M multiplier
h_n	-	input test array which is a function of molecular weight (References 5 and 8)
H	=	$\frac{2RT}{1-v\rho}$
m	-	smallest x value
M_n	-	molecular weight array associated with input test array
$M_{j,n}$	-	molecular weight matrix of values used in LP solution
N	-	number of LP sets to try
N_h	-	number of input h values
N	-	number of M values to use for use LP solution
N_ω	-	number of input ω^2 values
N_x	-	number of input x values
$U_{k,\ell}$	=	$-\frac{1}{C^\circ}\frac{dc}{d\xi}$
x_ℓ	-	array of distances squared from center of rotation
λk	-	function of $\omega^2 k$
Δh	-	constant difference between values of h_n array
$\Delta M_{j,n}$	-	difference between successive j values of $M_{j,n}$ matrix
ξ_ℓ	-	function of x_ℓ
ω^2	-	square of the angular velocity

IN 1 ROUTINE

Input: N_ω N_x, h_1, Δh, N_n, H, C°, ω_k^2 array, where $k = 1, ---, N_\omega$

x_j array, where $\ell = 1, ---, N_x$

$C°_n$ array, where $n = 1, ---, N_h$

1. $h_{n+1} = h_n + \Delta h$ for $n = 1, ---, (N_h - 1)$

2. $m = x_1$

$b = x_{N_x}$

$\lambda k = (b-m) \cdot H \cdot \omega_k^2$ for $k = 1, ---, N_\omega$

3. $\xi_\ell = \frac{b - x_1}{b-m}$ for $\ell = 1, ---, N_x$

4. $M_n = \frac{h_n}{H}$ for $n = 1, ---, N_h$

$f_n = \frac{C°_n}{C°}$

5. $$U_{k,\ell} = \sum_{n=1}^{N_h} \frac{(\lambda_k M_n)^2 \, e^{-\lambda_k M_n \xi_\ell}}{1 - e^{-\lambda_k M_n}} f_n$$

for $k = 1, ---, N_\omega$ and $\ell = 1, ---, N_x$

6. Write out ω^2 array, ξ array, and U matrix

7. Call LP SOLVER

IN 2 ROUTINE

Input: N_ω, N_x, H, C°, ω_k^2 array where k = 1,---,N_ω

x_ℓ array where ℓ = 1,---,N_x

$(\frac{dC}{dx})_{k\ell}$ matrix where k - 1,---,N_ω and ℓ = 1,---,N_x

1. $m = x_1$

   $b = x_{n_x}$

2. $\lambda k = (b-m)\ H\ \omega_k^2$ for k = 1,---,N_ω

3. $\xi_\ell = \frac{b-x_\ell}{b-m}$ for ℓ = 1,---,N_x

4. $U_{k,\ell} = \frac{b-m}{C°} (\frac{dc}{dx})_{k,\ell}$ for k = 1,---,N_ω

   and ℓ = 1,---,N_x

5. Write out ω^2 array, ξ array, and U matrix

6. Call LP SOLVER

LP SOLVER

1. Input from IN 1: N_ω, N_x, λ array, ξ array, and U matrix

2. Input from cards: $M_{1,1}$, g, N_M, N, HEADING

3. Write out input from cards

4. N_{row} $N_\omega : N_x$

   $N_{col} = N_M + 2\, N_{row}$

   $n = 1$

5. Calculate the following matrix entries

   $a_{i_j} = 1$ for $i = 1, ---, N_{row}$ and $j = N_M + 1$, N_{col-1}, 2

   $a_{i_j} = 1$ for $i = 1, ---, N_{row}$ and $j = N_M + 1$, $N_{col, 2}$

   $$a_{i_j} = \frac{(\lambda_k M_{j,n})^2 \; e^{-\lambda_k M_{j,n} \xi_\ell}}{1 - e^{-\lambda_k M_{j,n}}} \Delta M_{j,n}$$

   for $i = 1, ---, N_{row}$ and $j = 1, ---, N_M$

   where $k = \left[\frac{i-1}{N_x} \right] + 1$

   $$\ell = i\,(k-1) \cdot N_x$$

   $$M_{j,n} = M_{1,n} \cdot g^{j-1}$$

   and

   $$\Delta M_{j,n} = (g^{1/2} - g^{-1/2})\, M_{j,n}$$

6. Calculate the following right-hand sides $b_i = U_{k,\ell}$ where i, k, and ℓ are defined as in step 5.

7. Calculate the following objective coeffcients

   $C_j = O$ for $j = 1, ---, N_M$

   $C_j = 1$ for $j = N_M + 1, ---, N_{col}$

LP SOLVER

8. Write out the determinants of:

$\left[a_{i_j}\right]$ for $i = 1, ---, N_M$ and $j = 1, ---, N_M$

$\left[a_{i_j}\right]$ for $i = N_M + 1, ---, 2 \cdot N_M$

$\left[a_{i_j}\right]$ for all sets of N_M rows less than N_{row}

9. Write out matrix $\left[a_{i_j}\right]$ for $i = 1, ---, N_{row}$ and $j = 1, ---, N_M$ in exponent form.

10. Call LP solver and store solutions in $F_{j,n}$ array.

11. Write out input RHS
    computer RHS using solution
    difference of RHS'S
    absolute value of relative differences of RHS
    average absolute relative difference

12. $n \leftarrow n + 1$

    $M_{1,n} \leftarrow (M_{1,n-1}) g^{1/N}$

13. Return to step 5 until n exceeds N

14. Write out $F_{j,n}$ matrix

15. Call PLOT routine

PLOT ROUTINE

1. Input from LP SOLVER: HEADING, N, N_m, F, and M matrices

2. Input from IN 1 (if used): Δh, H, N_n f, and M arrays

3. $\Delta M = \frac{\Delta h}{H}$

4. Write out heading

5. Label vertical axis F(M)

6. Label horizontal axis M

7. Plot $\frac{f_n}{\Delta M}$ versus M_n for n = 1, ---N_h

8. Plot $F_{j,n}$ versus $M_{j,n}$ for n = 1, ---N and j = 1, ---, N_M

9. STOP

SECTION V

CONCLUSION

To date, the linear programming method seems to be one of the most promising schemes for obtaining the molecular weight distribution from sedimentation-diffusion equilibrium data. There are five main features of this investigation which are worthy of mention.

1. The linear programming method has been found to give acceptable results for the case of experimental data obtained at one angular velocity.

2. It was found that if a normal random error of the experimental gradient curve was about 20% the linear programming method produced a MWD with satisfactory precision. However, if the experimental error was weighted, i.e., the concentration gradient curve was distorted from the true curve, a 1 or 2% error led to an absurd molecular weight distribution. This agrees with the findings of Lee (Reference 5), Tikhonov and Glasko (Reference 12), and Tikhonov (References 13 and 14).

3. This investigation did not involve any modification of the LP solver routine. The LP solver limitations were manifested by spurious points sometimes appearing in the determined molecular weight distribution. In general, the linear programming method presents only an overall molecular weight structure. Therefore, when twenty sets of molecular weights were sampled, it was obvious when one point was completely illogical.

4. A great improvement was achieved by solving for F(M) directly (Equation 20), rather than via f_m (Equation 9). In the former case the matrix presented to the LP solver routine was not so ill-conditioned (Tables I and II).

5. The following test was made after each call of the LP solver routine. By having the calculated MWD, the computer program could calculate new U-values (U_{calc}). The difference between U_{exp} and U_{calc} was then printed. Also, the absolute relative differences, the averaged absolute relative error for one set of molecular weights, and the averaged absolute relative error averaged over all molecular weight sets were printed. In general, a good "fit" between the assumed MWD and the derived MWD showed low values for

all the above error analyses; however, the converse was not always found to hold true. At present much effort is being focused on determination of a procedure for obtaining a one-to-one correspondence between the error analysis criteria and the "fit" of the derived MWD.

TABLE I

EXPONENTS OF ELEMENTS IN THE MATRIX PRESENTED TO LP SOLVER ROUTINE USING EQUATION 9 *

-2	-1	-1	-1	0	0	0	0	0	0
-2	-1	-1	-1	0	0	0	0	0	0
-2	-1	-1	-1	0	0	0	0	0	0
-2	-1	-1	-1	0	0	0	0	0	0
-2	-1	-1	-1	0	0	0	0	0	1
-1	-1	0	0	0	0	0	0	-2	-5
-1	-1	0	0	0	0	0	0	-1	-3
-1	-1	0	0	0	0	0	0	0	-1
-1	-1	0	0	0	0	0	0	0	0
-1	-1	0	0	0	0	0	1	1	2

* Value of determinant = - 0.3932972 E-31

TABLE II

EXPONENTS OF ELEMENTS IN THE MATRIX PRESENTED TO LP SOLVER ROUTINE USING EQUATION 20 *

1	1	2	3	3	4	4	5	5	5
1	1	2	3	3	4	4	5	5	5
1	1	2	3	3	4	4	5	6	6
1	1	2	3	3	4	5	5	6	6
1	1	2	3	3	4	5	5	6	7
1	2	3	3	4	4	4	4	3	0
1	2	3	3	4	4	5	5	4	2
1	2	3	3	4	4	5	5	5	4
1	2	3	3	4	5	5	6	6	6
1	2	3	3	4	5	5	6	7	8

* Value of determinant = -0.1500715 E 17

APPENDIX

LISTING OF COMPUTER PROGRAM

```
$IBFTC EXEC.    DECK
C
C     MAIN PROGRAM EXECUTIVE CONTROL
C        INITIALIZE PLOTTING ROUTINES
C        INITIALIZE PLOT COUNT
C        DETERMINE SEQUENCE OF SUBROUTINES CALLED
C        TERMINATE PLOTTING BEFORE EXITING
C        WRITE HEADING AND PLOT COUNT
C
      COMMON /PLTR/ PDATA(438), IPLTS, HEAD(12)
      COMMON  /PRTCTL/  WRITE
C
      LOGICAL WRITE
C
      IPLTS = 0
      CALL PLOTS ( PDATA, 438 )
    1 READ (5,500) HEAD
      WRITE (6,600) HEAD
      CALL INI ( $900 )
      IF ( WRITE )  WRITE (6,600) HEAD
      CALL LPS ( $900 )
      CALL PLOTR
      GO TO 1
  900 WRITE (6,601) IPLTS
      CALL PLOTE
      STOP
  500 FORMAT ( 12A6 )
  600 FORMAT ( 1H1, 12A6   / ( 1X, 12A6 ) )
  601 FORMAT ( 1H0, I2, 17H PLOT(S) COMPLETE )
      END
```

```
$IBFTC BIN1.    DECK
C
C     BLOCK DATA SUBPROGRAM TO SUPPLY INPUT DATA WHEN INP1. IS BY-PASSED
C
      BLOCK DATA
C
      COMMON /BIN1/ NW, NX, XL(20), Z(20), U(20,20)
C
      DATA NW /5/
      DATA NX /5/
      DATA XL / 2.5E-6, 10.E-6, 40.E-6, 160.E-6, 640.E-6, 15*0. /
      DATA  Z /1.0,    .75,    .5,    .25,    0.,   15*0. /
      DATA  U / .187, .405, .372, .144, .005,           15*0.,
     X          .208, .554, .639, .337, .026,           15*0.,
     X          .232, .799,1.346, .959, .164,           15*0.,
     X          .260,1.237, 0.  , 0.  , 0.   ,          15*0.,
     X          .294,2.121, 0.,   0.,     0.,           15*0. ,
     X 300*0. /
      END
```

```
$IBFTC BDR.                                                      BDR.0001
      BLOCK DATA                                                 BDR.0002
C     X IS R**2                                                  BDR.0003
C                                                                BDR.0004
      COMMON /BLOCKR/ X(20)                                      BDR.0005
      DATA  X / 36.548312,                                       BDR.0006
     X          39.358308,                                       BDR.0007
     X          42.272363,                                       BDR.0008
     X          46.838556,                                       BDR.0009
     X          48.412651,                                       BDR.0010
     X          50.012759,                                       BDR.0011
     X          14*0.    /                                       BDR.0012
      END                                                        BDR.0013
```

```
$IBFTC BD.      DECK
C
C     BLOCK DATA SUBPROGRAM FOR 122 CO VALUES AND 7 W2 VALUES
C
      BLOCK DATA
C
      COMMON /BLOCKW/ W2(20)
      COMMON /BLOCKC/ CO(160)
C
      DATA W2
     1/416930.0, 583702.0, 817182.8, 1144056., 1601678., 2242349.,
     2 3139289., 13*0.     /
C
      DATA  CO
     1/.170E-5, .350E-5, .530E-4, .115E-3, .850E-4, .550E-4, .310E-4,
     2 .750E-5, .700E-5, .650E-5, .820E-5, .100E-4, .135E-4, .170E-4,
     3 .260E-4, .340E-4, .360E-4, .370E-4, .300E-4, .225E-4, .215E-4,
     4 .205E-4, .301E-4, .400E-4, .435E-4, .470E-4, .410E-4, .350E-4,
     5 .280E-4, .210E-4, .225E-4, .235E-4, .245E-4, .260E-4, .258E-4,
     6 .255E-4, .245E-4, .235E-4, .225E-4, .210E-4, .205E-4, .200E-4,
     7 .310E-4, .420E-4, .440E-4, .420E-4, .380E-4, .340E-4, .300E-4,
     8 .260E-4, .255E-4, .250E-4, .245E-4, .240E-4, .232E-4, .225E-4,
     9 .215E-4, .205E-4, .190E-4, .170E-4, .163E-4, .155E-4, .175E-4,
     X .190E-4, .225E-4, .260E-4, .240E-4, .220E-4, .195E-4, .190E-4,
     1 .182E-4, .175E-4, .170E-4, .165E-4, .160E-4, .150E-4, .140E-4,
     2 .130E-4, .110E-4, .900E-5, .650E-5, .450E-5, .500E-5, .550E-5,
     3 .820E-5, .110E-4, .113E-4, .115E-4, .920E-5, .700E-5, .600E-5,
     4 .500E-5, .400E-5, .300E-5, .230E-5, .150E-5, .100E-5, .150E-5,
     5 .220E-5, .300E-5, .400E-5, .500E-5, .470E-5, .450E-5, .420E-5,
     6 .400E-5, .500E-5, .600E-5, .680E-5, .750E-5, .700E-5, .650E-5,
     7 .580E-5, .500E-5, .420E-5, .350E-5, .300E-5, .200E-5, .150E-5,
     8 .100E-5, .500E-6, .0, 0., 0., 36*0.                           /
      END
```

```
$IBFTC BD.      DECK
C
C      BLOCK DATA SUBPROGRAM FOR 160 CO VALUES AND 7 W2 VALUES
C
       BLOCK DATA
C
       COMMON /BLOCKW/ W2(20)
       COMMON /BLOCKC/ CO(160)
C
       DATA W2
     1/416930.0, 583702.0, 817182.8, 1144056., 1601678., 2242349.,
     23139289., 13*0.     /
C
       DATA (CO(I),I=1,114)
     1/.65000E-5,.90000E-5,.11000E-4,.13250E-4,.16000E-4,.19250E-4,
     2 .23250E-4,.28000E-4,.33500E-4,.40000E-4,.47750E-4,.56750E-4,
     3 .67250E-4,.79500E-4,.93750E-4,.11025E-3,.12925E-3,.15150E-3,
     4 .17700E-3,.20600E-3,.23925E-3,.27725E-3,.32050E-3,.36975E-3,
     5 .42525E-3,.48775E-3,.55825E-3,.63725E-3,.72575E-3,.82450E-3,
     6 .93425E-3,.105575E-2,.119025E-2,.133875E-2,.150175E-2,.168025E-2,
     7 .18755E-2,.208825E-2,.231925E-2,.256950E-2,.283950E-2,.313025E-2,
     8 .34420E-2,.377525E-2,.413075E-2,.450825E-2,.490775E-2,.532950E-2,
     9.577325E-2,.623825E-2,.672375E-2,.722900E-2,.775275E-2,.829375E-2,
     X.885050E-2,.942100E-2,.01000325 ,.01059475 ,.01119325 ,.01179625 ,
     1.01240075 ,.01300375 ,.01360175 ,.01419175 ,.01477075 ,.01533475 ,
     2.01588050 ,.01640475 ,.01690400 ,.01737525 ,.01781500 ,.01822000 ,
     3.01858775 ,.01891575 ,.01920150 ,.01944275 ,.01963800 ,.01978575 ,
     4.01988475 ,.01993450 ,.01993450 ,.01988475 ,.01978575 ,.01963800 ,
     5.01944275 ,.01920150 ,.01891575 ,.01858775 ,.01822000 ,.01781500 ,
     6.01737525 ,.01690400 ,.01640475 ,.01588050 ,.01533475 ,.01477075 ,
     7.01419175 ,.01360175 ,.01300375 ,.01240075 ,.01179625 ,.01119325 ,
     8.01059475 ,.01000325 ,.00942010 ,.00885050 ,.00829375 ,.00775275 ,
     9.00722900 ,.00672375 ,.00623825 ,.00577325 ,.00532950 ,.00490775 /
       DATA (CO(I),I=115,160)
     1/.00450825,.00413075 ,.00377525 ,.00344200 ,.00313025 ,.00283950 ,
     2.002569500,.00231925 ,.00208825 ,.00187550 ,.00168025 ,.00150175 ,
     3.001338750,.00119025 ,.00105575 ,.934250E-3,.824500E-3,.725750E-3,
     4.637250E-3,.558250E-3,.487750E-3,.425250E-3,.369750E-3,.320050E-3,
     5.277250E-3,.239250E-3,.206000E-3,.177000E-3,.151500E-3,.129250E-3,
     6.110250E-3,.937500E-4,.795000E-4,.672500E-4,.567500E-4,.477500E-4,
     7.400000E-4,.335000E-4,.280000E-4,.232500E-4,.192500E-4,.160000E-4,
     8.132500E-4,.110000E-4,.900000E-5,.650000E-5 /
       END
```

```
$IBFTC BD.      DECK
C
C     BLOCK DATA SUBPROGRAM FOR 32 CO VALUES AND 7 W2 VALUES
C
      BLOCK DATA
C
      COMMON /BLOCKW/ W2(20)
      COMMON /BLOCKC/ CO(160)
C
      DATA W2
     1/416930.0, 583702.0, 817182.8, 1144056., 1601678., 2242349.,
     23139289., 13*0.    /
C
      DATA CO
     1/.9132400E-3, .3044140E-2, .6392700E-2, .1053272E-1, .1497716E-1
     2,.2051750E-1, .2538812E-1, .3031964E-1, .3494672E-1, .3975646E-1
     3,.4383562E-1, .4706240E-1, .4968036E-1, .5144596E-1, .5296804E-1
     4,.5382040E-1, .5461188E-1, .5467276E-1, .5418570E-1, .5333334E-1
     5,.5144596E-1, .4858448E-1, .4407914E-1, .3835616E-1, .3117200E-1
     6,.2496194E-1, .1960426E-1, .1503806E-1, .1120244E-1, .7427700E-2
     7,.4322599E-2, .8140020E-4, 128*0. /
      END
```

```
$IBMAP RAND.    100,DECK                                               RAND.001
*               GENERATES UNIFORM RANDOM NUMBERS                       RAND.002
*               R=FLRAN(Y), Y DUMMY GIVES REAL NUMBER                  RAND.003
*               CALL SAVE(Z) GIVES LAST OCTAL VALUE                    RAND.004
*               CALL VALUE(Z) GIVES STARTING OCTAL VALUE               RAND.005
       ENTRY    FLRAN                                                  RAND.006
       ENTRY    SAVE                                                   RAND.007
       ENTRY    VALUE                                                  RAND.008
 FLRAN LDQ      RANDOM                                                 RAND.009
       MPY      GENERA                                                 RAND.010
       STQ      RANDOM                                                 RAND.011
       CLA      AAA                                                    RAND.012
       LGL      28                                                     RAND.013
       FAD      AAA                                                    RAND.014
       TRA      1,4                                                    RAND.015
 VALUE CLA*     3,4                                                    RAND.016
       STO      RANDOM                                                 RAND.017
       TRA      1,4                                                    RAND.018
 SAVE  CLA      RANDOM                                                 RAND.019
       STO*     3,4                                                    RAND.020
       TRA      1,4                                                    RAND.021
RANDOM OCT      343277244615                                           RAND.022
AAA    OCT      172000000100                                           RAND.023
GENERA OCT      343277244615                                           RAND.024
       END                                                             RAND.025
```

```
$IBFTC PLOTR.   DECK                                                    PLOTR.01
      SUBROUTINE PLOTR                                                  PLOTR.02
      COMMON  SCH(4), SCF(4)                                            PLOTR.03
      COMMON /PLTR/ PDATA(438), IPLTS, HEAD(12)                         PLOTR.04
      COMMON /BINP1/ DH, H, NC, F(162), CM(162) , SKIP2                 PLOTR.05
      COMMON /BLPS/ N, NM, BF(1000), BM(1000), K                        PLOTR.06
      COMMON /BIN2/ USEIN2                                              PLOTR.07
      DATA HTITLE /1HM/, FTITLE /4HF(M)/                                PLOTR.08
      LOGICAL SKIP2                                                     PLOTR.09
      LOGICAL  USEIN2                                                   PLOTR.10
      IF ( SKIP2 )  RETURN                                              PLOTR.11
      IF ( .NOT. USEIN2 )  GO TO 7                                      PLOTR.12
      SCH(1) = BM(1)                                                    PLOTR.13
      SCH(2) = BM(K)                                                    PLOTR.14
      GO TO 8                                                           PLOTR.15
    7 DM = DH/H                                                         PLOTR.16
      DO 5 I = 1,NC                                                     PLOTR.17
    5 F(I) = F(I) / DM                                                  PLOTR.18
      SCH(1) = AMIN1( CM(1), BM(1) )                                    PLOTR.19
      SCH(2) = AMAX1( CM(NC), BM(K) )                                   PLOTR.20
    8 SCF(1) = 0.                                                       PLOTR.21
      SCF(2) = 0.                                                       PLOTR.22
      IF ( USEIN2 )  GO TO 15                                           PLOTR.23
      DO 10 I = 1,NC                                                    PLOTR.24
   10 SCF(2) = AMAX1( SCF(2), F(I) )                                    PLOTR.25
   15 DO 20 I = 1,K                                                     PLOTR.26
   20 SCF(2) = AMAX1( SCF(2), BF(I) )                                   PLOTR.27
      CALL SCALE (SCH, 15., 2, 1, 10. )                                 PLOTR.28
      CALL SCALE (SCF, 10., 2, 1, 10. )                                 PLOTR.29
      IF ( USEIN2 )  GO TO 25                                           PLOTR.30
      CM(NC+1) = SCH(3)                                                 PLOTR.31
      CM(NC+2) = SCH(4)                                                 PLOTR.32
      F(NC+1)  = SCF(3)                                                 PLOTR.33
      F(NC+2)  = SCF(4)                                                 PLOTR.34
   25 BM(K+1) = SCH(3)                                                  PLOTR.35
      BM(K+2) = SCH(4)                                                  PLOTR.36
      BF(K+1) = SCF(3)                                                  PLOTR.37
      BF(K+2) = SCF(4)                                                  PLOTR.38
      CALL PLOT ( 5., -11., -3 )                                        PLOTR.39
      CALL PLOT ( 0.,  .5 , -3 )                                        PLOTR.40
      CALL AXIS ( 0., 0., HTITLE, -1, 16., 0., SCH(3), SCH(4), 10. )    PLOTR.41
      CALL AXIS ( 0., 0., FTITLE,  4, 10.,90., SCF(3), SCF(4), 10. )    PLOTR.42
      CALL SYMBOL ( 1., 9.5, .25, HEAD, 0., 72 )                        PLOTR.43
      IF ( .NOT. USEIN2 )  CALL LINE ( CM, F, NC, 1, 0, 0 )             PLOTR.44
      CALL LINE ( BM, BF, K, 1, 1, 1 )                                  PLOTR.45
      CALL PLOT ( 15., 0., -3 )                                         PLOTR.46
      IPLTS = IPLTS + 1                                                 PLOTR.47
      RETURN                                                            PLOTR.48
      END                                                               PLOTR.49
```

```
$IBFTC ORDER.  DECK                                                ORDER.01
      SUBROUTINE ORDER ( X, Y, NM, N, K )                          ORDER.02
      COMMON  /PRTCTL/ WRITE                                       ORDER.03
      DIMENSION X(1), Y(1)                                         ORDER.04
      LOGICAL  WRITE                                               ORDER.05
      J = 0                                                        ORDER.06
      DO 10 LN = 1,N                                               ORDER.07
      N20 = (LN-1) * 20                                            ORDER.08
      L = N20 + 1                                                  ORDER.09
      J = J + 1                                                    ORDER.10
      X(J) = X(L)                                                  ORDER.11
      Y(J) = Y(L)                                                  ORDER.12
      DO 10 I = 2,NM                                               ORDER.13
      L = N20 + I                                                  ORDER.14
      J = J + 1                                                    ORDER.15
      X(J) = X(L)                                                  ORDER.16
   10 Y(J) = Y(L)                                                  ORDER.17
      K = J                                                        ORDER.18
   20 TEST = 0.                                                    ORDER.19
      DO 30 I =2,J                                                 ORDER.20
      IF ( X(I-1) .LE. X(I) )  GO TO 30                            ORDER.21
      XS = X(I-1)                                                  ORDER.22
      YS = Y(I-1)                                                  ORDER.23
      X(I-1) = X(I)                                                ORDER.24
      Y(I-1) = Y(I)                                                ORDER.25
      X(I) = XS                                                    ORDER.26
      Y(I) = YS                                                    ORDER.27
      TEST = 1.                                                    ORDER.28
   30 CONTINUE                                                     ORDER.29
      IF ( (TEST .EQ. 0.) .OR. ( J .EQ. 2 ) )  GO TO 40            ORDER.30
      J = J - 1                                                    ORDER.31
      GO TO 20                                                     ORDER.32
   40 IF ( WRITE ) WRITE (6,600) (I, X(I), Y(I), I=1,K )           ORDER.33
      RETURN                                                       ORDER.34
  600 FORMAT        ( 1H1, 15X, 1HM, 19X, 1HF / 1H /               ORDER.35
     X                                       ( 1X, I3, 2E20.7 ) )  ORDER.36
      END                                                          ORDER.37
```

```
$IBFTC DETA.    DECK
      SUBROUTINE DETA ( A, B, NM, NROW )
      COMMON  /PRTCTL/ WRITE
      DIMENSION A(51,120), B(NM,NM)
      LOGICAL  WRITE
      IF ( WRITE )  WRITE (6,600)
      J = 1
   10 DO 20 I = 1,NM
      DO 20 K = 1,NM
      JI = J + I
   20 B(I,K) = A(JI,K)
      D = DET ( B, NM )
      IF ( WRITE )  WRITE (6,601) J, D
      J = J + NM
      IF ( (J+NM-1) .GT. NROW )  RETURN
      GO TO 10
  600 FORMAT ( 13HODETERMINANTS )
  601 FORMAT ( 3X, I4, E19.7 )
      END
```

```
$IBFTC DLETE.  DECK
      SUBROUTINE DLETE ( IRHS, NROW, NRP1, NCOL, NM, * )
      COMMON  JRHS(100)
      COMMON /BIN1/ NW, NX, XL(20), Z(20), U(20,20)
      COMMON /DLT/  NWW, NXX
      COMMON  /PRTCTL/ WRITE
      LOGICAL WRITE
      KRHS = 2 * IRHS
      IF ( KRHS .GT. 100 )  GO TO 900
      READ (5,500) (JRHS(I),I=1,KRHS)
      IF ( WRITE )  WRITE (6,601) IRHS, (JRHS(I),I=1,KRHS)
      DO 10 I = 1,KRHS,2
      K = JRHS(I)
      L = JRHS(I+1)
   10 U(K,L) = 0.
      NWW = NW
      I = 0
      DO 30 K = 1,NW
      USUM = 0.
      DO 20 L = 1,NX
   20 USUM = USUM + U(K,L)
      IF ( USUM .EQ. 0. )  GO TO 28
      I = I + 1
      DO 25 J = 1,NX
   25 U(I,J) = U(K,J)
      XL(I) = XL(K)
      GO TO 30
   28 NWW = NWW- 1
   30 CONTINUE
      NXX = NX
      J = 0
      DO 50 L = 1,NX
      USUM = 0.
      DO 40 K = 1,NWW
   40 USUM = USUM + U(K,L)
      IF ( USUM .EQ. 0. )  GO TO 48
      J = J + 1
      DO 45 I = 1,NWW
   45 U(I,J) = U(I,L)
      Z(J) = Z(L)
      GO TO 50
   48 NXX = NXX - 1
   50 CONTINUE
      NROW = NXX * NWW
      NRP1 = NROW + 1
      NCOL = NM + (2*NROW)
      IF ( .NOT. WRITE )  RETURN
      WRITE (6,602)  NWW, NXX
      DO 60 I = 1,NWW
   60 WRITE (6,603) I, (U(I,J),J=1,NXX)
      RETURN
  900 WRITE (6,600) IRHS
      RETURN 1
  500 FORMAT ( 27( 2I1,1X) )
  600 FORMAT ( 45H0NUMBER OF U MATRIX DELETIONS GREATER THAN 50 /
     X           7H0IRHS = I4 )
  601 FORMAT ( 1H0, I3, 41H ELEMENTS OF MATRIX -U- HAVE BEEN DELETED /
     X           33(2X,2I1) )
  602 FORMAT ( 20H0U MATRIX (ADJUSTED), I10, 5H ROWS, I6, 8H COLUMNS )
  603 FORMAT ( 4H0ROW, I4, 1X, 6E20.7 / (9X, 6E20.7) )
      END
```

```
$IBFTC LPS.     DECK
      SUBROUTINE LPS ( * )
      COMMON  IE(20), E(51,51), X(51), P(51), Y(51), JH(51),
     X          KB(120), KOUT(7), ERR(8)
      COMMON /BIN1/  NW, NX, XL(20), Z(20), U(20,20)
      COMMON /BLPS/ N, NM, BF(20,50), BM(20,50), K
      COMMON /DLT/  NWW, NXX
      COMMON  /PRTCTL/ WRITE
      DIMENSION A(51,120), B(51), INFIX(8), TOL(4), BA(400)
      DIMENSION ABR(50), BS(51)
      LOGICAL  WRITE
      DATA NMAX/50/, NMMAX/20/, NCOLMX/120/, NROWMX/50/
      NAME LIST  /LP/ XM11, G, NM, N, IRHS,PERT
      PERT = 0.
      IRHS = 0
      READ (5,LP)
      IF ( WRITE )  WRITE (6,600)  XM11, G, NM, N
      IF ( N .GT. NMAX )  GO TO 900
      IF ( NM .GT. NMMAX )  GO TO 904
      NROW = NW * NX
      IF ( NROW .GT. NROWMX )  GO TO 902
      NCOL = NM + (2*NROW)
      IF ( NCOL .GT. NCOLMX )  GO TO 901
      NRP1 = NROW + 1
      NWW = NW
      NXX = NX
      IF ( IRHS .GT. 0 )
     X   CALL DLETE ( IRHS, NROW, NRP1, NCOL, NM, $903 )
   20 DO 30 I = 1,NRP1
      DO 30 J = 1,NCOL
   30 A(I,J) = 0.
      DO 35 I = 1,NMMAX
      DO 35 J = 1,NMAX
   35 BF(I,J) = 0.
      INFIX(1) = 4
      INFIX(2) = NCOL
      INFIX(3) = 51
      INFIX(4) = NRP1
      INFIX(5) = 2
      INFIX(6) = 1
      INFIX(7) = 500
      INFIX(8) = 20
      TOL(1)   = 1.E-7
      TOL(2)   = 1.E-7
      TOL(3) = 1.E-6
      TOL(4) = 1.E-10
      PRM = 0.
      B(1) = 0.
      DO 50 I = 1,NROW
      IN = (I-1) / NXX
      K  = IN + 1
      L =  I- (IN*NXX)
      B(I+1) = U(K,L)
      IF ( PERT .GT. 0. )  B(I+1) = B(I+1)*(1.+2.*PERT*(FLRAN(X)-.5))
   50 BS(I+1) = B(I+1)
      LN = 1
      SQRTG = SQRT( G )
      GMG = SQRTG - (1. / SQRTG)
      XN = 1. / FLOAT(N)
      BM(1,1) = XM11
      NROWS = NROW
```

```
   55 IF ( WRITE )  WRITE (6,612)  LN, N
      NROW = NROWS
      NRP1 = NROW + 1
      DO 60 J = 1,NM
      BM(J,LN) = BM(1,LN)* G**(J-1)
      DBM = GMG * BM(J,LN)
      DO 60 I = 1,NROW
      IN = (I-1) / NXX
      K  = IN +1
      L =  I- (IN*NXX)
      XLKM = XL(K) * BM(J,LN)
      XNUM = XLKM**2 * EXP( -XLKM * Z(L) )
      DENOM= 1. - EXP( -XLKM )
   60 A(I+1,J) = (XNUM / DENOM) * DBM
      II = 1
      DO 64 I = 2,NRP1
      B(I) = BS(I)
      IF ( B(I) .EQ. 0. )  GO TO 64
      II = II + 1
      B(II) = B(I)
      DO 62 J = 1,NM
   62 A(II,J) = A(I,J)
   64 CONTINUE
      NRP1 = II
      NROW = NRP1 - 1
      INFIX(4) = NRP1
      J = NM
      DO 68 I = 2,NRP1
      J = J + 1
      A(1,J) = 1.0
      A(I,J) = 1.0
      J = J + 1
      A(1,J) = 1.0
   68 A(I,J) = -1.0
      CALL DETA ( A, BA, NM, NROW )
      IF ( WRITE )  WRITE (6,601) (M,M=1,30)
      DO 80 I = 2,NRP1
      DO 70 J = 1,NM
      IF(J) = -99
   70 IF ( A(I,J) .NE. 0. )  IF(J) = ALOG10( A(I,J) )
      IM1 = I - 1
   80 IF ( WRITE )  WRITE (6,602)  IM1, (IF(J),J=1,NM)
      CALL SIMPLX ( INFIX, A, B, TOL, PRM, KOUT, ERR, JH, X, P, Y,KB,E )
      IF ( WRITE )  WRITE (6,603)
      DO 90 J = 1,NRP1
      MX = JH(J)
   90 IF ( (MX .GT. 0) .AND. (MX .LE. NM) )  BF(MX,LN) = X(J)
      ABR(LN) = 0.
      DO 110 I = 2,NRP1
      BC = 0.
      DO 100 J = 1,NM
  100 BC = BC + BF(J,LN) * A(I,J)
      BD = B(I) - BC
      AB = ABS( BD ) / B(I)
      IF ( WRITE )  WRITE (6,604)  B(I), BC, BD, AB
  110 ABR(LN) = ABR(LN) + AB
      ABR(LN) = ABR(LN) / FLOAT( NROW )
      IF ( .NOT. WRITE )  GO TO 115
      WRITE (6,605) ABR(LN)
      WRITE (6,606) LN, (BF(M,LN),M=1,NM)
      WRITE (6,610)
```

```
115 LN = LN + 1
    IF ( LN .GT. N ) GO TO 120
    BM(1,LN) = BM(1,LN-1) * G**XN
    GO TO 55
120 IF ( WRITE )  WRITE (6,610)
    WRITE (6,615)
    ARBAVG = 0.
    DO 130 I = 1,N
    ARBAVG = ARBAVG + ABR(I)
130 WRITE (6,614)  I, ABR(I), (BF(M,I),M=1,NM)
    ARBAVG = ARBAVG / FLOAT( N )
    WRITE (6,613) ARBAVG
    CALL ORDER ( BM, BF, NM, N, K )
    RETURN
900 WRITE (6,607) N
    RETURN 1
901 WRITE (6,608) NCOL
    RETURN 1
902 WRITE (6,609) NROW
903 RETURN 1
904 WRITE (6,611) NM
    RETURN 1
600 FORMAT ( 33HAFIRST MOLECULAR WEIGHT          = E16.7  /
   X         33H MOLECULAR WEIGHT MULTIPLIER     = E16.7  /
   X         33H NUMBER OF MOLECULAR WT. VALUES = I8     /
   X         33H NUMBER OF LP SETS FOR SOLUTION = I8     )
601 FORMAT ( 1HA, 57X, 14HA MATRIX (LOG) / 1H0, 60X, 7HCOLUMNS /
   X         5H ROWS, 30I4 / 1H )
602 FORMAT ( 1X, I3, 1X, 30I4 / ( 5X, 30I4 ) )
603 FORMAT ( 1H1, 7X, 9HINPUT RHS, 7X, 12HCOMPUTED RHS, 6X,
   X                 14HRHS DIFFERENCE, 4X, 16HABS REL DIFF RHS / 1H )
604 FORMAT ( 1X, 4E18.7 )
605 FORMAT ( 34H0AVERAGE RELATIVE DIFFERENCE RHS = E16.7 )
606 FORMAT ( 9H0SOLUTION, I4, 7X, 7E16.7 / (20X, 7E16.7) )
607 FORMAT ( 4H0N = I4, 42H IS GREATER THAN DIMENSION FOR NO. OF SETS)
608 FORMAT ( 56H0NUMBER OF COLUMNS FOR -A- MATRIX GREATER THAN DIMENSI
   XON   /  7H0NROW = I4 )
609 FORMAT ( 53H0NUMBER OF ROWS FOR -A- MATRIX GREATER THAN DIMENSION
   X         / 7H0ROW = I4 )
610 FORMAT ( 1H1 )
611 FORMAT ( 5H0NM = I4, 59H IS GREATER THAN DIMENSION FOR NUMBER OF S
   XOLUTIONS PER SET )
612 FORMAT ( 1H0, 57X, 3HSET I3, 3H OF I3 )
613 FORMAT ( 1H0 / 20X, 38HTHE AVERAGE REL. DIFF. FOR ALL SETS IS
   X         E16.7 )
614 FORMAT (  1H0, I4, E22.7, 9X, 6E16.7 / (36X, 6E16.7) )
615 FORMAT (6H0  SET,6X,15HAVG. REL. ERROR,12X,11HSOLUTIONS  ,82(1H*)
   X      / 1H )
    END
```

```
$IBFTC IN1.     DECK
      SUBROUTINE IN1 ( * )
      COMMON  /BLOCKR/ X(20)
      COMMON /BLOCKC/ CO(160)
      COMMON /BLOCKW/ W2(20)
      COMMON /BIN1/  NW, NX, XL(20), Z(20), U(20,20)
      COMMON /BIN2/ USEIN2
      COMMON /BINP1/ DH, H, NC, F(162), HO(162), SKIP2
      COMMON  /PRTCTL/ WRITE
C
      DATA  NXMAX/20/, NHMAX/160/, NWMAX/20/
C
      LOGICAL  WRITE, SKIP1, SKIP2
      LOGICAL USEIN2
C
      NAME LIST  /INP1/ NW, NX, H1, DH, NH, H, CZ, X1, DX,
     X              IST, LST, LAST, WRITE, SKIP1, SKIP2, USEIN2
C
      WRITE =.FALSE.
      SKIP1 = .FALSE.
      SKIP2 = .FALSE.
      USEIN2 = .FALSE.
      LAST = 1
      READ (5,INP1)
      IF ( LAST .EQ. 0 )  RETURN 1
      IF ( SKIP1 )  GO TO 75
      IF ( NX .GT. NXMAX )  GO TO 900
      IF ( NH .GT. NHMAX )  GO TO 901
      IF ( NW .GT. NWMAX )  GO TO 902
      IF ( USEIN2 )  CALL IN2 ( $85 )
      NC = LST - IST + 1
      IF ( NC .GT. NHMAX )  GO TO 903
      IF ( X1 .LE. 0. )  GO TO 5
      X(1) = X1
      DO 10 L = 2,NX
   10 X(L) = X1 + FLOAT(L-1) * DX
    5 HO(1) = H1
      HO(1) = H1
      DO 20 N = 2,NH
   20 HO(N) = H1 + FLOAT(N-1) * DH
      DO 30 I = 1,NC
      IC = I + IST - 1
      F(I)  = CO(IC) / CZ
   30 HO(I) = HO(IC) / H
      B = X(NX)
      BMM = B - X1
      DO 40 K = 1,NW
   40 XL(K) = BMM * H * W2(K)
      DO 50 L = 1,NX
   50 Z(L) = (B - X(L)) / BMM
      DO 70 K = 1,NW
      DO 70 L = 1,NX
      U(K,L) = 0.
      DO 70 N = 1,NC
      XLM = XL(K) * HO(N)
      XNUM = XLM**2 * EXP( -XLM*Z(L) )
      DENOM= 1. - EXP( -XLM )
   70 U(K,L) = U(K,L) + ( XNUM / DENOM ) * F(N)
   75 IF ( .NOT. WRITE )  GO TO 85
      WRITE (6,601) NW, (W2(K),K=1,NW)
      WRITE (6,602) NX, (Z(L),L=1,NX)
```

```
      WRITE (6,603) NW, NX
      DO 80 K = 1,NW
   80 WRITE (6,604) K, (U(K,L),L=1,NX)
   85 RETURN
  900 WRITE (6,605) NX
      STOP
  901 WRITE (6,606) NH
      STOP
  902 WRITE (6,607) NW
      STOP
  903 WRITE (6,608) NC
      STOP
  601 FORMAT ( 1HA, I4, 40H VALUES OF ANGULAR VELOCITY SQUARED - W2 /
     X          1H / ( 9X, 6E20.7 ) )
  602 FORMAT ( 1H0, I4, 71H VALUES OF THE FUNCTION OF DISTANCE SQUARED F
     XROM CENTER OF ROTATION - Z  / 1H / ( 9X, 6E20.7 ) )
  603 FORMAT ( 9H0U MATRIX, I10, 5H ROWS, I6, 8H COLUMNS )
  604 FORMAT ( 4H0ROW, I4, 1X, 6E20.7, / ( 9X, 6E20.7 ) )
  605 FORMAT ( 5H0NX = I4, 33H IS GREATER THAN DIMENSION FOR X. )
  606 FORMAT ( 5H0NH = I4, 33H IS GREATER THAN DIMENSION FOR H. )
  607 FORMAT ( 5H0NW = I4, 37H IS GREATER THAN DIMENSION FOR OMEGA. )
  608 FORMAT ( 5H0NC = I4, 41H IS GREATER THAN DIMENSION FOR SELECTED H)
      END
```

```
$IBFTC IN2.     DECK
      SUBROUTINE IN2 ( * )
C          SCRATCH STORAGE
      COMMON DCDX(20,20)
C
      DIMENSION DNDR(20,20)
C
      LOGICAL  WRITE
C
      COMMON  /BIN1 / NW, NR, XL(20), Z(20), U(20,20)
      COMMON /BLOCKW/  W2(20)
      COMMON  /BLOCKR/ X(20)
      COMMON  /PRTCTL/ WRITE
C
      DATA  NRMAX/20/, NWMAX/20/
C
      NAME LIST  /INP2/ NW, NR, H, CO, R1, DR, DCDN, DNDR, W2
C
      READ (5,INP2)
C
      IF ( NR .GT. NRMAX )  GO TO 900
      IF ( NW .GT. NWMAX )  GO TO 901
C
      DO 10 L = 1,NR
      IF ( R1 .LE. 0. )  GO TO 5
      X(L) = ( R1 + FLOAT(L-1) * DR )**2
C
    5 DO 10 K = 1,NW
   10 DCDX(K,L) = 1.0 / SQRT(X(L)) * DCDN * DNDR(K,L)
C
      XM = X(1)
      B  = X(NR)
C
      DO 20 K = 1, NW
   20 XL(K) = (B-XM) * H * W2(K)
C
      DO 30 L = 1, NR
   30 Z(L) = (B-X(L)) / (B-XM)
C
      DO 40 L = 1,NR
      DO 40 K = 1,NW
   40 U(K,L) =((B-XM) / CO) *  DCDX(K,L)
C
      IF ( .NOT. WRITE )  GO TO 60
C
      WRITE (6,601)  NW, (W2(K),K=1,NW)
      WRITE (6,602)  NR, ( Z(L),L=1,NR)
      WRITE (6,603)  NW, NR
      DO 50 K = 1,NW
   50 WRITE (6,604)  K, (U(K,L),L=1,NR)
C
   60 RETURN 1
  900 WRITE (6,605) NR, NRMAX
      STOP
  901 WRITE (6,606) NW, NWMAX
      STOP
C
  601 FORMAT ( 1HA, I4, 40H VALUES OF ANGULAR VELOCITY SQUARED - W2 /
     X         1H / ( 9X, 6E20.7 ) )
  602 FORMAT ( 1H0, I4, 71H VALUES OF THE FUNCTION OF DISTANCE SQUARED F
     XROM CENTER OF ROTATION - Z  / 1H / ( 9X, 6E20.7 ) )
```

```
603 FORMAT ( 9H0U MATRIX, I10, 5H ROWS, I6, 8H COLUMNS )                IN2.0062
604 FORMAT ( 4H0ROW, I4, 1X, 6E20.7 / ( 9X, 6E20.7 ) )                 IN2.0063
605 FORMAT ( 5H0NR = I4, 33H IS GREATER THAN DIMENSION FOR X(,I2,2H).)IN2.0064
606 FORMAT ( 5H0NW = I4, 33H IS GREATER THAN DIMENSION FOR W(,I2,2H).)IN2.0065
C                                                                       IN2.0066
    END                                                                 IN2.0067
```

```
$IBFTC DET.     DECK                                               L. B. FALL
      FUNCTION DET(A,N)
C
C          DETERMINANT EVALUATING FUNCTION
C
C          FUNCTION DET(A,N) COMPUTES THE DETERMINANT
C     OF THE N-TH ORDER MATRIX A, WHICH MUST BE
C     DIMENSIONED A(N,N).  THE ORIGINAL MATRIX A
C     IS NOT ALTERED.
C
C     612 CELLS OF BLANK COMMON ARE USED
C
C     TO CHANGE DIMENSIONS, CHANGE DIMENSIONS OF ARRAYS B AND PIV,
C     AND ALSO CHANGE VALUE OF NMAX IN THE DATA STATEMENT.
C
      DIMENSION   A(N,N)
      COMMON   D, I, II, J, K, KCT, KFROM, KTO, NN, NPR, RLE, TPE
      COMMON   B(24,24), PIV(24)
      DATA     NMAX/ 24/
C
C     TEST ARGUMENT N TO PREVENT OVERFLOWING BLANK COMMON
C
      NN=N
      IF ( NN .GT. NMAX .OR. NN .LE. 0 )     GO TO 100
C
C     MOVE INPUT MATRIX A TO SCRATCH MATRIX B
C
      DO 10 I=1,NN
      DO 10 J=1,NN
 10   B(I,J)=A(I,J)
C
C     INITIALIZE DETERMINANT VALUE AND ROW INTERCHANGE COUNT
C
      D=1.0
      KCT=0
C
C     PERFORM ELIMINATION ON N COLUMNS
C
      DO 90 I=1,NN
C
C     SEARCH I-TH SUB-COLUMN FOR I-TH PIVOT ELEMENT
C
      TPE=0.
      DO 30 II=I,NN
      IF (ABS(B(II,I))-TPE) 30,20,20
 20   NPR=II
      TPE=ABS(B(II,I))
 30   CONTINUE
C
C     IF PIVOT ELEMENT IS ZERO, THEN DET(A,N)=0.0
C
      IF (B(NPR,I)) 35,32,35
 32   D=0.
      GO TO 95
C
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
 35   DO 40 J=I,NN
 40   PIV(J)=B(NPR,J)/B(NPR,I)
C
C     UPDATE THE PRODUCT OF PIVOT ELEMENTS AND SUM OF ROW INTERCHANGES
```

```
C
      D=D*B(NPR,I)
      KCT=KCT+(NPR-I)
C
C     ELIMINATE REMAINING ELEMENTS IN I-TH SUB-COLUMN
C
      KTO=NN
      KFROM=NN
      DO 90 K=I,NN
      IF (KFROM-NPR) 70,80,70
 70   RLE=-B(KFROM,I)
      DO 75 J=I,NN
 75   B(KTO,J)=B(KFROM,J)+RLE*PIV(J)
      KTO=KTO-1
 80   KFROM=KFROM-1
 90   CONTINUE
C
C     IF TOTAL NO. OF ROW INTERCHANGES WAS ODD, THEN
C     NEGATE THE PRODUCT OF THE PIVOT ELEMENTS
C
 95   IF ( KCT .NE. 2*(KCT/2) )      D=-D
      DET=D
      RETURN
C
C     GIVE ERROR MESSAGE FOR INCORRECT VALUE OF N
C     AND RETURN TO SYSTEM VIA FXEM
C
 100  WRITE (6,1000) NN
      CALL FXEM
      RETURN
C
 1000 FORMAT (3HON=,I12,30H IS INCORRECT FOR FUNCTION DET)
      END
```

```
$IBFTC MSUB    DECK
CMSUBJ        VERSION 1 OF  RS MSUB
      SUBROUTINE SIMPLX (INFIX,A,B,TOL,PRM,KOUT,ERR,JH,X,P,Y,KB,E)
C
      DIMENSION INFIX(8),A(1),B(1),TOL(4),KOUT(7),ERR(8),JH(1),X(1),
     1 P(1),Y(1),KB(1),E(1),ZZ(3), IOFIX(16) , TERR(8)
C
      EQUIVALENCE  (INFLAG,IOFIX(1) ), (N , IOFIX(2) ) ,
     1            (ME,IOFIX(3) ),  (M,IOFIX(4)), (MF,IOFIX(5)),
     2  (MC, IOFIX(6) ),  ( NCUI, IOFIX(7) ) , ( NVER, IOFIX(8) ),
     3 ( K, IOFIX(9) ), (IIER, IOFIX(10) ), (INVC , IOFIX(11) ) ,
     4 (NUMVR, IOFIX(12) ), ( NUMPV, IOFIX(13) ) ,
     5  (INFS, IOFIX(14)  ) , ( JT,  IOFIX(15) ) ,( LA  , IOFIX(16) ),
     6 (ZZ(1),TPIV), (ZZ(2),TZERO),(ZZ(3),TCOST)
C
C                        MOVE INPUTS  ...  ZERO OUTPUTS
      DO 1340  I= 1, 8
       TERR(I) = 0.0
      IOFIX(I+8)  =  0
 1340  IOFIX(I)  =  INFIX(I)
      LA   =   0
      DO 1308  I = 1 , 3
 1308 ZZ(I)  =  TOL(I)
      TCOST  =  -  ABS  (TCOST)
      PMIX = PRM
      M2 = M**2
      INFS = 1
C                   CHECK FOR ILLEGAL INPUT
      IF (N)  1304, 1304, 1371
 1371  IF (M - MF ) 1304, 1304, 1372
 1372  IF (MF - MC)  1304, 1304, 1373
 1373  IF ( MC ) 1304 , 1304,  1374
 1374  IF (ME - M ) 1304, 1375, 1375
 1375 IF(  MOD (INFLAG, 4 )  - 1 )  1400,  1320,  100
C
C
C  NEW 1            STARTS PHASE ONE
C*****SUBROUTINE NEW (M,N, JH, KB, A, B, MF, ME )
C
C                             INITIATE
 1400   DO 1401 I = 1, M
 1401 JH(I) = 0
C                 INSTALL SINGLETONS
       KT  =  0
        DO 1402  J = 1, N
      KB(J) = 0
      MM  =  KT + MF
      LL  =  KT + M
C                              TALLY ENTRIES IN CONSTRAINTS
      KQ  = 0
      DO  1403 L = MM , LL
      IF (A(L)) 1404, 1403, 1404
 1404 KQ = KQ+1
      LQ = L
 1403   CONTINUE
C                              CHECK WHETHER J IS CANDIDATE
            IF (KQ - 1) 1402, 1405, 1402
 1405 IA = LQ- KT
          IF ( JH(IA) ) 1402, 1406, 1402
 1406 IF (A(LQ)*B(IA)) 1402, 1407, 1407
C                              J IS CANDIDATE. INSTALL
```

```
 1407 JH(IA) = J
      KB(J)  = IA
 1402 KT = KT + ME
C
C**END OF NEW
C
C
 1320 CONTINUE
C
C  VER 1           FORMS INVERSE FROM  KB
C*****SUBROUTINE VER ( A, B, JH, X, E, KB, Y, IOFIX, TPIV, M2  )
C
C                  INITIATE
 1100 ASSIGN  1102  TO KPIV
      ASSIGN  1114  TO KJMY
      IF (LA)  1121, 1121, 1122
 1121 INVC = 0
 1122 NUMVR    =   NUMVR  +1
       DO 1101  I = 1, M2
 1101 E(I)=0.
      MM=1
       DO 1113  I = 1, M
      E(MM) =1.0
      X(I) = B(I)
 1113 MM = MM + M + 1
        DO 1110  I = MF, M
      IF (JH(I)) 1111, 1110, 1111
 1111 JH(I) = 12345
 1110 CONTINUE
      INFS = 1
C                  FORM INVERSE
        DO 1102  JT= 1, N
      IF ( KB(JT))  600 , 1102 , 600
C 600 CALL  JMY  (JT, A, E, M, Y )
C                        CHOOSE PIVOT
 1114 TY = 0.
        DO 1104  I = MF, M
      IF (JH(I)  - 12345 )  1104, 1105, 1104
 1105 IF ( ABS ( Y(I) ) -  TY )  1104, 1104, 1106
 1106 IR   = I
      TY =  ABS  ( Y(I) )
 1104   CONTINUE
C                        TEST PIVOT
      IF  (TY - TPIV )    1107, 1108, 1108
C        BAD  PIVOT,  ROW IR,  COLUMN JT
 1107 KB(JT)= 0
      GO TO 1102
C                        PIVOT
 1108 JH(IR) = JT
      KB(JT) = IR
      GO TO 900
C 900 CALL PIV    (IR, Y, M, E, Z, X)
 1102      CONTINUE
C                  RESET ARTIFICIALS
        DO 1109  I = 1, M
      IF ( JH(I) - 12345  )  1109, 1112, 1109
 1112 JH(I) = 0
 1109   CONTINUE
C**END OF VER
C
C
```

```
  100 ASSIGN   705  TO  NDEL
      ASSIGN  1000  TO  KJMY
      ASSIGN   221  TO  KPIV
C
C                              PERFORM ONE ITERATION
C
C  XCK 1    X CHECKER
C*****SUBROUTINE XCK ( M, MF, JH, X, TZERO, JIN )
C
C            RESET X AND CHECK FOR INFEASIBILITIES
 1200   JIN  =  0
      NEG = 0
      DO 1201 I = MF, M
      IF ( ABS  ( X(I) )   - TZERO)  1202, 1203, 1203
 1202 X(I) = 0.0
      GO TO 1201
 1203 IF ( X(I) )  1208, 1201, 1205
 1205 IF ( JH(I) )  1201, 1206, 1201
 1208 NEG = 1
 1206   JIN = 1
 1201   CONTINUE
C**END OF XCK
C
C
C            CHECK CHANGE OF PHASE.. GO BACK TO INVERT IF GONE INFEAS.
      IF (INFS - JIN ) 1320,  500,  200
C                  BECOME FEASIBLE
  200 INFS = 0
  201 PMIX  =  0.0
C
C  GET 1    GET PRICES
C*****SUBROUTINE GET ( M, MC, MF, JH, X, P, E, INFS, PMIX )
C
  500 MM  = MC
C                       PRIMAL PRICES
  502 DO 503 J = 1, M
      P(J) = E(MM )
  503 MM  =MM  + M
      IF ( INFS )  501, 599, 501
C                       COMPOSITE PRICES
  501 DO 504  J = 1, M
  504 P(J) = P(J)* PMIX
      DO 505  I = MF, M
      MM  =I
      IF  ( X(I) )  506, 507, 507
  506 DO 508  J = 1, M
      P(J) =  P(J) + E(MM )
  508 MM  = MM  + M
      GO TO 505
  507 IF (JH(I))  505, 509, 505
  509 DO 510  J = 1, M
      P(J) = P(J) - E(MM )
  510 MM  =  MM  +M
  505   CONTINUE
C
  599 CONTINUE
C**END OF GET
C
C
C
C    MIN         MIN D-J.  SELECTS COLUMN TO ENIER BASIS
```

```
C*****SUBROUTINE MIN ( JT, N, M, A, P, KB, ME, ICOST )
C
  700 JT = 0
      BB = TCOST
C
  701 DO  702  JM = 1, N
C                                    SKIP COLUMNS IN BASIS
  703 IF ( KB(JM) )  702, 300, 702
C 300 CALL DEL ( JM, DT, M, A, P)
  705 IF  ( DT - BB )  708, 702, 702
  708 BB = DT
      JT = JM
  702    CONTINUE
C
C**END OF MIN
C
          IF  (JT)    203, 203, 600
C            ALL COSTS NON-NEGATIVE...  K = 3 OR 4
  203 K = 3 + INFS
      GO TO 257
C                                    NORMAL CYCLE
C
C  JMY 1          J MULTIPLY.  BASIS INVERSE * COLUMN JT
C*****SUBROUTINE JMY (JT, A, E, M, Y, ME )
C
  600 DO 610  I= 1,M
  610 Y(I) =0.
      LP  =  JT*ME - ME
      LL = 0
      DO 605   I= 1,M
      LP = LP + 1
      IF  (A(LP))   601, 602, 601
  601 DO 606  J  =  1,M
      LL = LL + 1
  606 Y(J) = Y(J) + A(LP) * E(LL)
      GO TO 605
  602 LL = LL + M
  605 CONTINUE
C
  699 GO TO KJMY , ( 1000 , 1114 ,  1392  )
C**END OF JMY
C
C
C  ROW 1    ROW SELECTION--COMPOSITE
C*****SUBROUTINE  ROW  ( IR, M, MF, JH, X, Y, IPIV )
C
C AMONG EQS. WITH X=0, FIND MAX ABS(Y) AMONG ARTIFICIALS, OR, IF NONE,
C  GET MAX POSITIVE Y(I) AMONG REALS.
 1000 IR = 0
      AA = 0.0
      IA  =  0
      DO 1050  I = MF,  M
      IF ( X(I) )  1050, 1041, 1050
 1041 YI  =  ABS  ( Y(I) )
      IF  (  YI  -  TPIV   )   1050, 1050, 1042
 1042 IF  ( JH(I) )  1043, 1044, 1043
 1043 IF  (IA)   1050, 1048, 1050
 1048  IF  ( Y(I) )  1050, 1050, 1045
 1044 IF   (IA)   1045, 1046, 1045
 1045 IF   (  YI    -  AA   )   1050, 1050, 1047
 1046    IA = 1
```

```
 1047 AA   =   YI
      IR   =   I
 1050 CONTINUE
      IF (IR)1099,1001,1099
 1001 AA = 1.0E+20
C                   FIND MIN. PIVOT AMONG POSITIVE EQUATIONS
      DO 1010 IT = MF  , M
      IF   ( Y(IT)   -   TPIV )   1010, 1010, 1002
 1002 IF   ( X(IT) ) 1010, 1010, 1003
 1003 XY = X(IT) / Y(IT)
      IF ( XY - AA )   1004, 1005, 1010
 1005 IF ( JH(IT))   1010, 1004, 1010
 1004 AA = XY
      IR = IT
 1010 CONTINUE
      IF (NEG)    1016, 1099, 1016
C  FIND PIVOT AMONG NEGATIVE EQUATIONS, IN WHICH X/Y IS LESS THAN THE
C MINIMUM X/Y IN THE POSITIVE EQUATIONS, THAT HAS THE LARGEST ABSF(Y)
 1016 BB = - TPIV
      DO 1030 I   = MF  , M
      IF (X(I))    1012, 1030, 1030
 1012  IF   ( Y(I)     -   BB   )    1022, 1030, 1030
 1022 IF   (   Y(I) * AA   -   X(I)     )    1024, 1024, 1030
 1024 BB   =   Y(I)
      IR   =   I
 1030 CONTINUE
 1099 CONTINUE
C**END OF ROW
C
C                                      TEST PIVOT
  206    IF( IR )    207, 207, 210
C                                      NO PIVOT
  207 K = 5
  257 IF (PMIX)    201, 400, 201
C                              ITERATION LIMIT FOR CUT OFF
  210 IF (ITER -NCUT )      900,  160,  160
C                                      PIVOT FOUND
C
C  PIV 1             PIVOT.  PIVOTS ON GIVEN ROW
C*****SUBROUTINE PIV   ( IR, Y, M, E, X, NUMPV, TECOL )
C                              LEAVE TRANSFORMED COLUMN IN Y(I)
C
  900 NUMPV   =   NUMPV   +   1
      YI = -Y(IR)
      Y(IR) = -1.
      LL = 0
C                                      TRANSFORM INVERSE
  903 DO 904  L =   IR, M2, M
      IF   ( E(L) )   905, 914, 905
  914 LL = LL + M
      GO TO 904
  905 XY =   E(L) / YI
      E(L) =0.
      DO 906   I   = 1, M
      LL= LL +1
  906 E(LL) = E(LL) +XY* Y(I)
  904 CONTINUE
C                                      TRANSFORM X
       XY = X(IR) / YI
      X(IR) = 0.
      DO 908   I   = 1, M
```

```
  908 X(I) = X(I) +XY* Y(I)                                                     MSUB.306
C                                RESTORE Y(IR)                                  MSUB.307
      Y(IR) = -YI                                                               MSUB.308
C                                                                               MSUB.309
  999  GO TO KPIV , ( 221, 1102 )                                               MSUB.310
C**END OF PIV                                                                    MSUB.311
C                                                                               MSUB.312
  221  IA    = JH(IR)                                                           MSUB.313
      IF ( IA ) 213, 213, 214                                                   MSUB.314
  214 KB( IA ) = 0                                                              MSUB.315
  213 KB(JT)    = IR                                                            MSUB.316
      JH(IR)    = JT                                                            MSUB.317
      LA   =   0                                                                MSUB.318
      ITER    = ITER    +1                                                      MSUB.319
      INVC    = INVC    +1                                                      MSUB.320
C                                INVERSION FREQUENCY                            MSUB.321
      IF (INVC - NVER   ) 1200, 1320,1200                                       MSUB.322
C                                            CUT OFF ... TOO MANY ITERATIONS    MSUB.323
  160 K = 6                                                                     MSUB.324
C                                                                               MSUB.325
C                                                                               MSUB.326
C  ERR 1          ERROR CHECK.  COMPARES AX WITH B, PA WITH ZERO                MSUB.327
C*****SUBROUTINE ERR ( M, A, B, TERR, JH, X, P, Y, ME, LA )                     MSUB.328
C                                                                               MSUB.329
C                                      STORE AX-B AT Y                          MSUB.330
  400  ASSIGN 410 TO NDEL                                                       MSUB.331
      DO 401 I = 1, M                                                           MSUB.332
  401 Y(I) =-B(I)                                                               MSUB.333
      DO 402 I = 1, M                                                           MSUB.334
      JA = JH(I)                                                                MSUB.335
      IF (JA) 403, 402, 403                                                     MSUB.336
  403 IA =ME* (JA-1)                                                            MSUB.337
      DO 405 IT = 1, M                                                          MSUB.338
      IA = IA + 1                                                               MSUB.339
      IF(A(IA) )  415, 405, 415                                                 MSUB.340
  415 Y(IT) =Y(IT) +X(I) * A(IA)                                                MSUB.341
  405 CONTINUE                                                                  MSUB.342
  402 CONTINUE                                                                  MSUB.343
C                                      FIND SUM AND MAXIMUM OF ERRORS           MSUB.344
      DO 481   I = 1, M                                                         MSUB.345
      YI   = Y(I)                                                               MSUB.346
      IF ( JH(I) )   472, 471, 472                                              MSUB.347
  471  YI = YI + X(I)                                                           MSUB.348
  472 TERR(LA+1) = TERR(LA+1) + ABS (YI)                                        MSUB.349
      IF   ( ABS  (TERR(LA+2))- ABS    (   YI   )   )    482, 481, 481          MSUB.350
  482 TERR(LA+2) = YI                                                           MSUB.351
  481   CONTINUE                                                                MSUB.352
C                                      STORE P TIMES BASIS AT DT                MSUB.353
      DO 411   I = 1, M                                                         MSUB.354
      JM = JH(I)                                                                MSUB.355
      IF ( JM     )  300 , 411 , 300                                            MSUB.356
C 300 CALL DEL ( JM, DT, M, A, P)                                               MSUB.357
  410 TERR(LA+3)   =    TERR(LA +3)   +   ABS (DT)                              MSUB.358
      IF (ABS (TERR(LA+4))    -     ABS (DT)   )  413, 411, 411                 MSUB.359
  413  TERR(LA+4)   =   DT                                                      MSUB.360
  411 CONTINUE                                                                  MSUB.361
C**END OF ERR                                                                    MSUB.362
C                                                                               MSUB.363
C                                                                               MSUB.364
      IF (LA)    193, 191,   193                                                MSUB.365
  191 LA   =   4                                                                MSUB.366
```

```
      IF (INFLAG  -  4  )  1320,  193,  193
  193 IF  (K-5)    1392,  194,  1392
  194 ASSIGN 1392 TO KJMY
      GO TO 600
C 600 CALL JMY ( . . . . . . )
C     GO TO 1392
 1304 K  =  7
C                SET EXIT VALUES
 1392   DO  1309  I=  1, 8
 1309 ERR(I)          =   TERR(I)
       DO 1329  I = 1, 7
 1329 KOUT(I)  =  IOFIX(I+8)
      RETURN
C
C    DEL          DELTA-JAY.  PRICES OUT ONE MATRIX COLUMN
C*****SUBROUTINE DEL (  JM, DT, M, A, P, ME )
C
C
  300 DT = 0.
       LL  = (JM - 1) * ME
  301 DO  303   MM  = 1, M
      LL   =  LL  + 1
      IF ( A( LL ))304, 303, 304
  304 DT = DT + P( MM ) * A ( LL )
  303 CONTINUE
C
  399   GO TO NDEL , ( 410 , 705 )
C**END OF DEL
C
       END
```

REFERENCES

1. H. Fujita, "Mathematical Theory of Sedimentation Analysis, Academic Press, New York, 1962.

2. T. H. Donnelly, J. Phys. Chem., 70, 1862 (1966).

3. E. T. Adams, Jr., "Molecular Weights and Molecular-Weight Distributions from Sedimentation-Equilibrium Experiments," p. 84, "Characterization of Macromolecular Structure," Publication 1573 National Academy of Sciences, Washington, D. C., 1968.

4. D. A. Lee, (private communication), to be published.

5. M. Gehatia, AFML-TR-67-121, Pt. I.

6. Th. G. Scholte, J. of Polymer Sci., A-2, 6, 91-109 (1968).

7. Th. G. Scholte, J. of Polymer Sci., A-2, 6, 111-127 (1968).

8. M. Gehatia and D. R. Wiff, AFML-TR-67-121, Pt. II.

9. S. I. Gass, "Linear Programming Methods and Applications," 2nd Ed., McGraw-Hill Company, New York, 1964.

10. A. Charnes, W. W. Cooper, and A. Henderson, "Introduction to Linear Programming," John Wiley & Sons, Inc., New York, 1953.

11. G. B. Dantzig, "Maximization of a Linear Function of Variables Subject to Linear Inequalities," Chap. XXI, T. C. Koopman (ed.), "Activity Analysis of Production and Allocation," Cowles Commission Monograph 13, John Wiley & Sons, Inc., New York, 1951.

12. A. N. Tikhonov and V. B. Glasko, USSR Computational Mathematics and Mathematical Physics, 4, 1 (1964).

13. A. N. Tikhonov, Dokl. Akad. Nauk SSSR, 151, 3, 501-504 (1963).

14. A. N. Tikhonov, Dokl. Akad. Nauk. SSSR, 153, 1, 49-52 (1963).

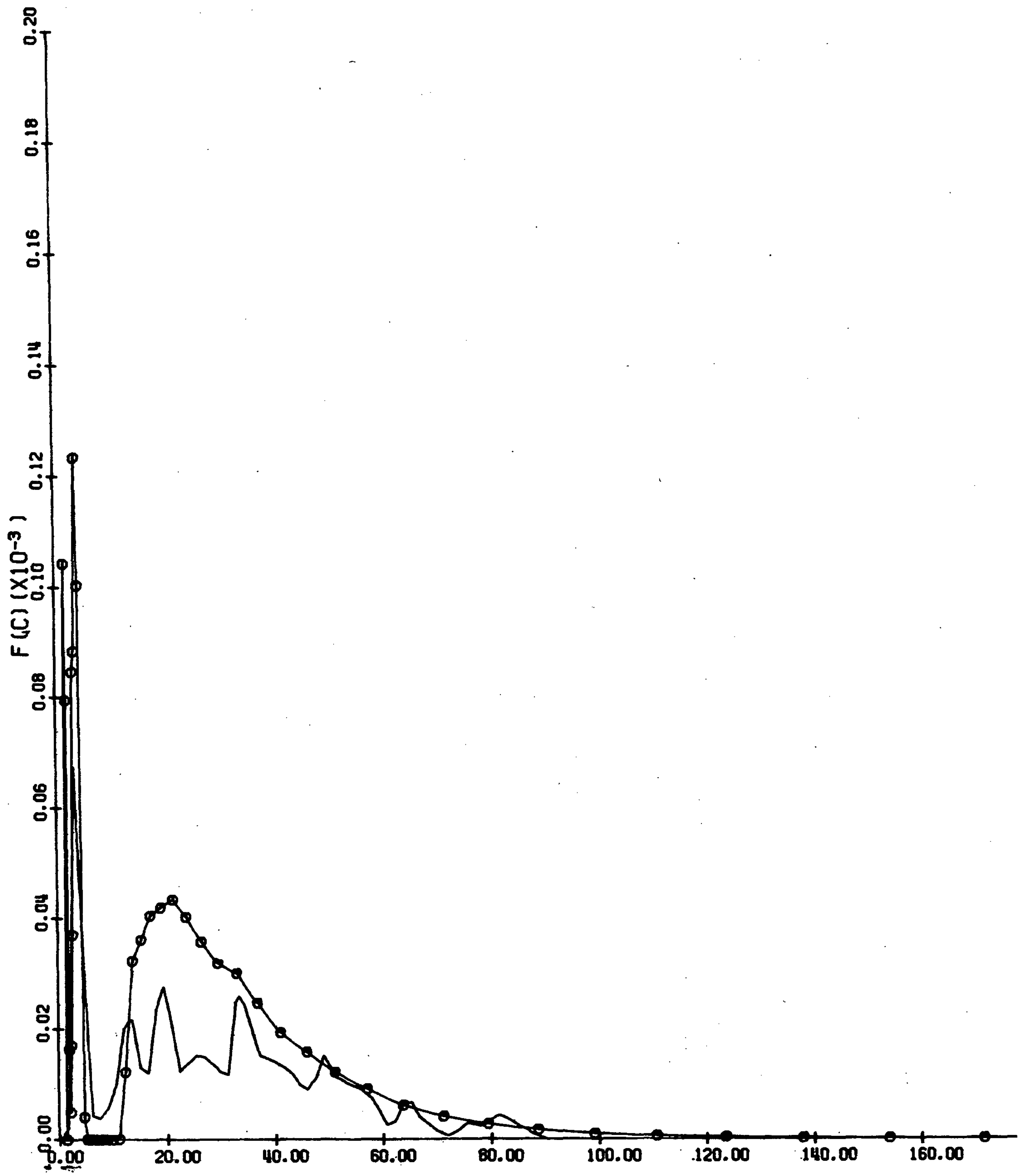
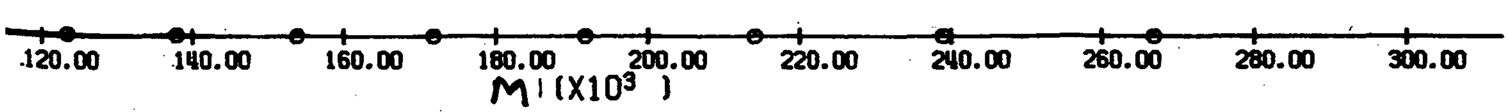


Figure 1. Resulting MWD Using Ten Sets of Molecular Weights a



Ten Sets of Molecular Weights and g = 3. 0, (Compare with Figures 2-4)

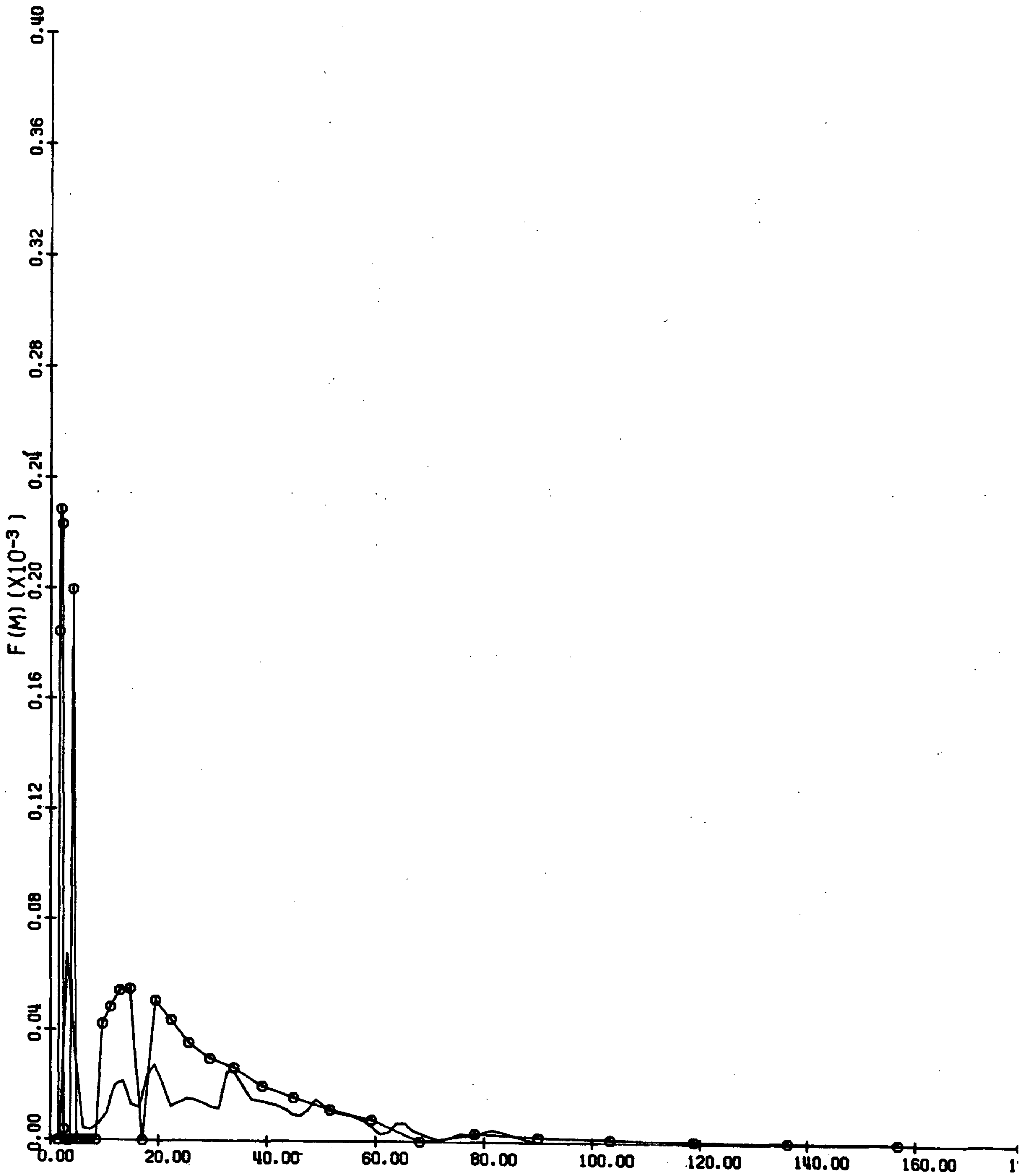
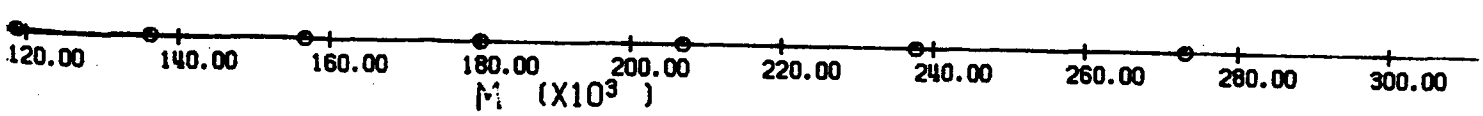


Figure 2. Resulting MWD Using Ten Sets of Molecular Weights and g =



ets of Molecular Weights and g = 4. 0, (Compare with Figures 1, 3, and 4)

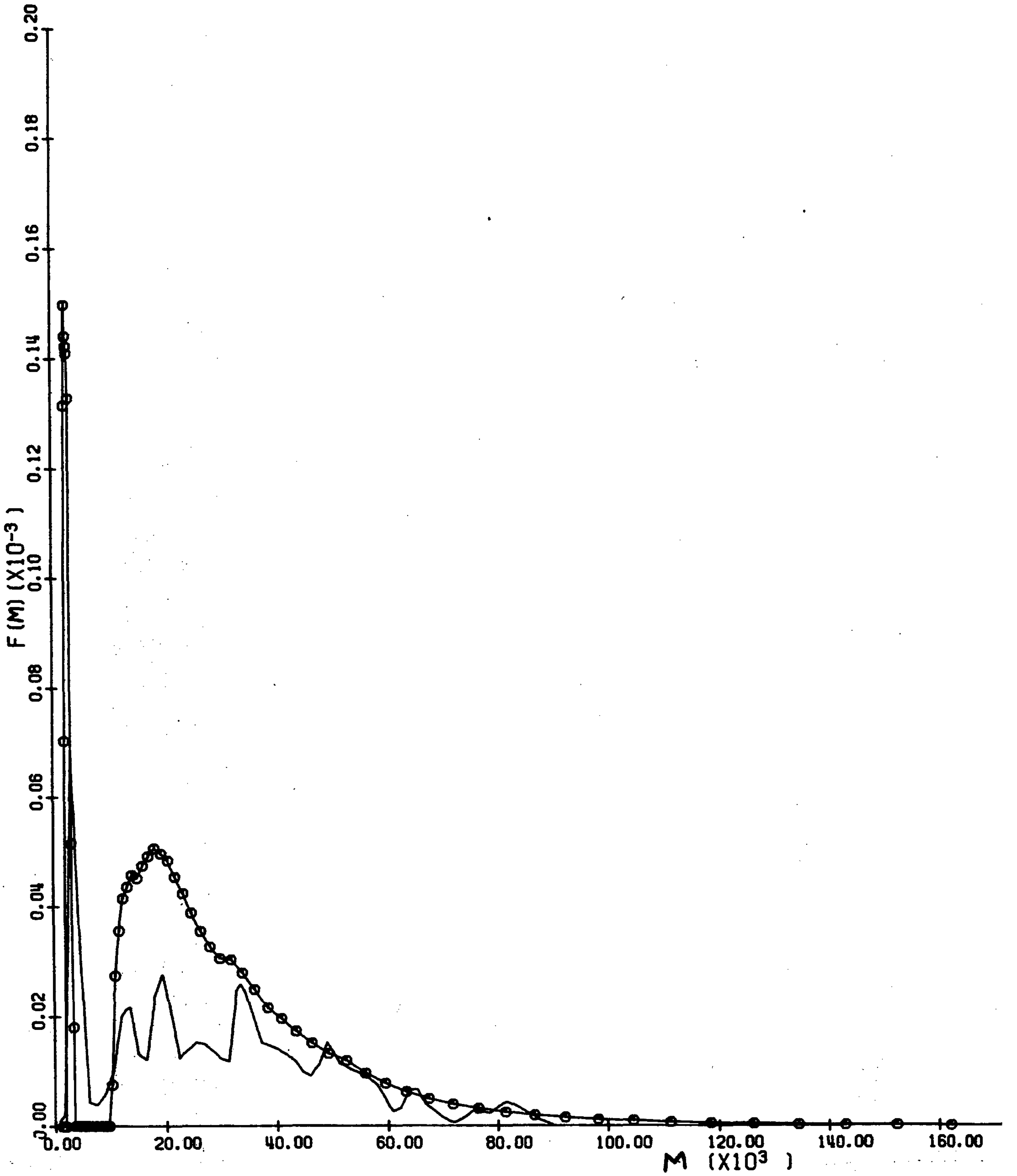
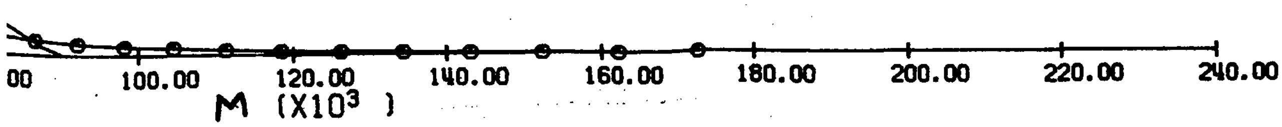


Figure 3. Resulting MWD Using Twenty Sets of Molecular Weights and g = 3.5, (Co



ənty Sets of Molecular Weights and g = 3.5, (Compare with Figures 1, 2, and 4)

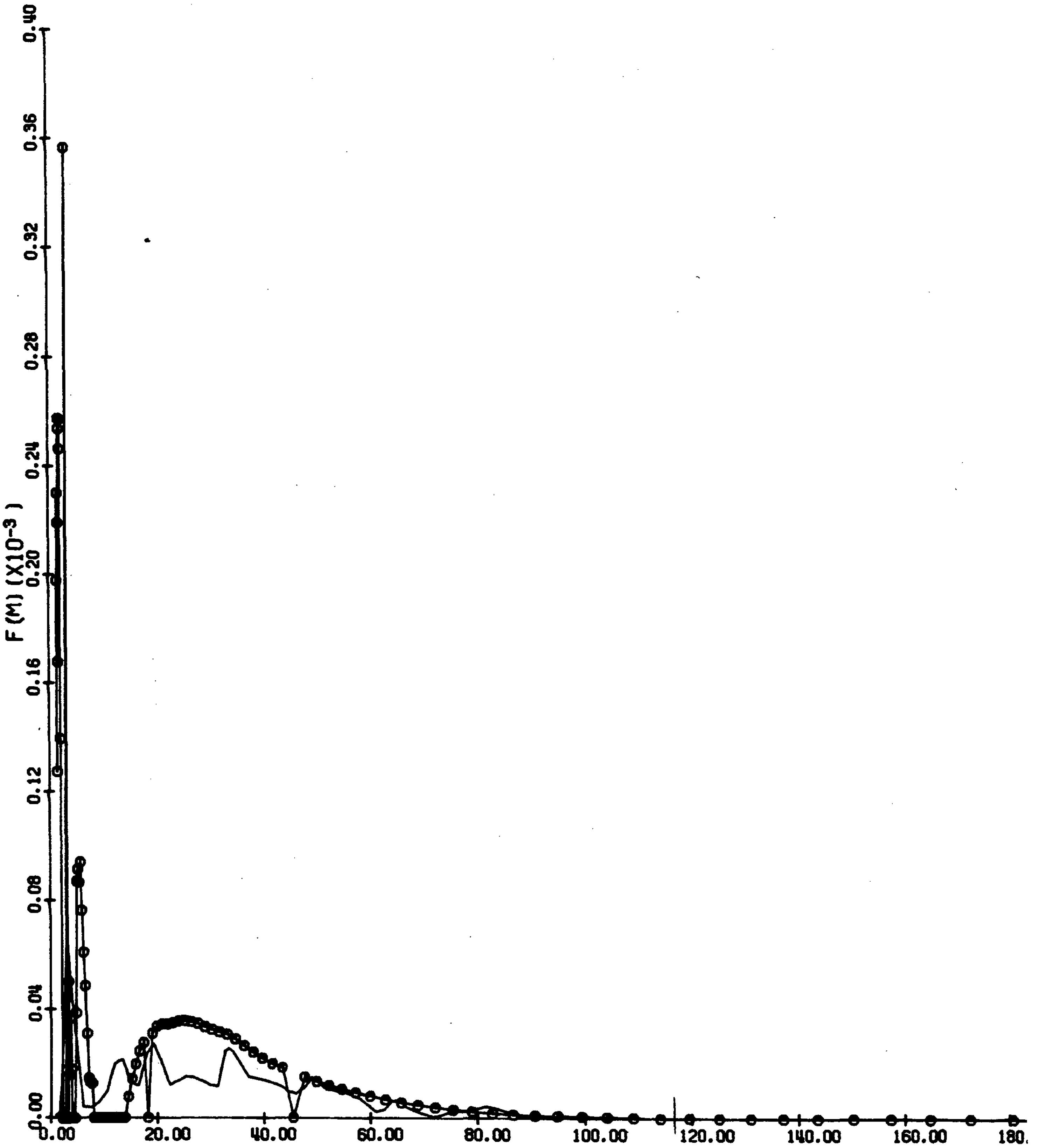
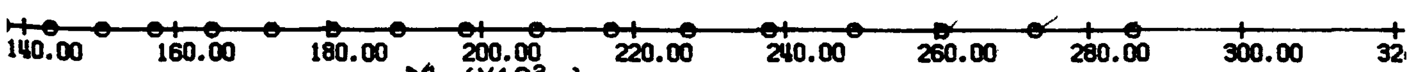


Figure 4. Resulting MWD Using Twenty Sets of Molecular W



enty Sets of Molecular Weights and g = 2.5, (Compare with Figures 1-3)

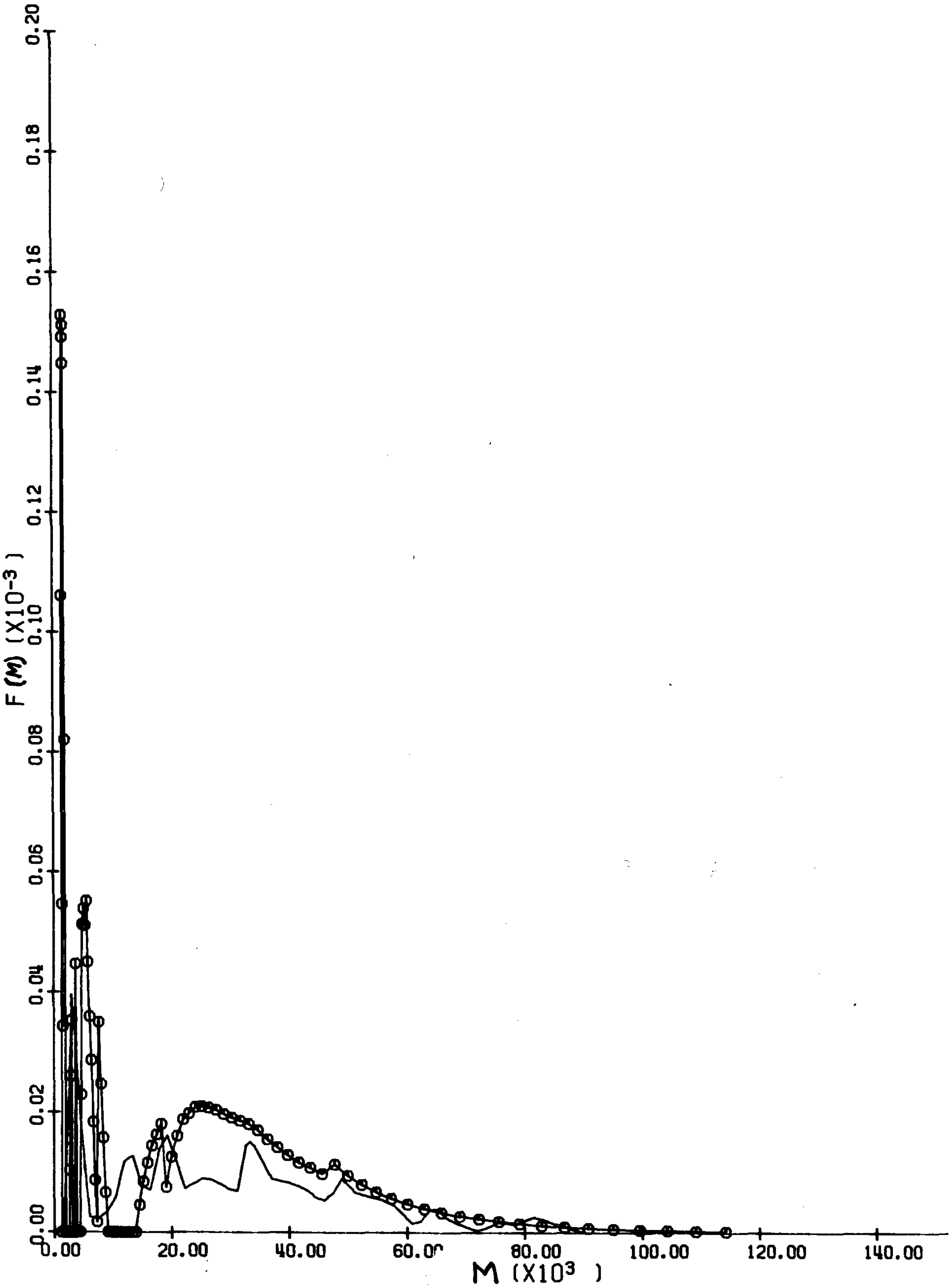


Figure 5. The Effect of Decreasing the MWR on the MWD

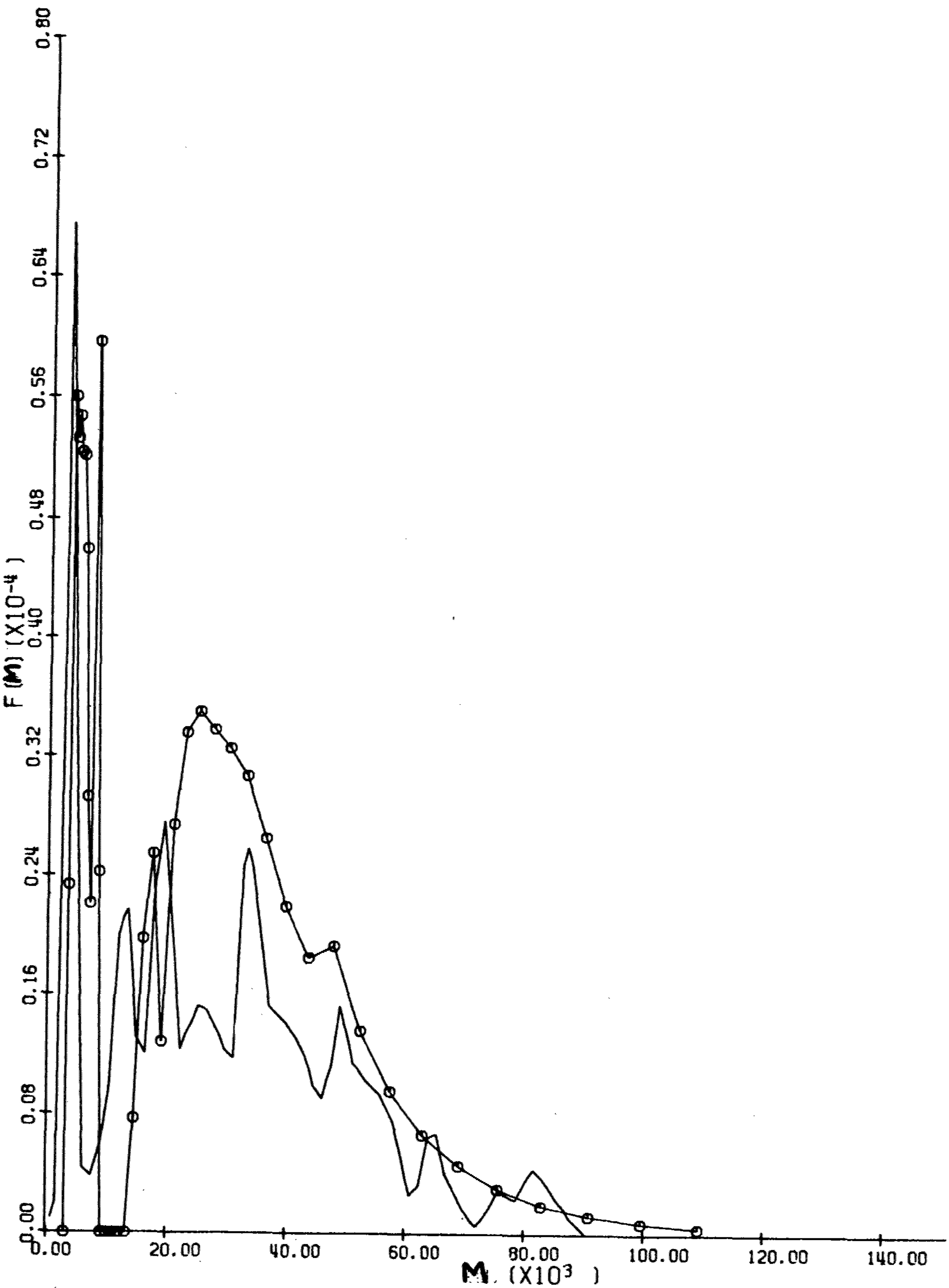


Figure 6. The Effect of Decreasing the MWR and the Number of Molecular Weight Sets on the MWD

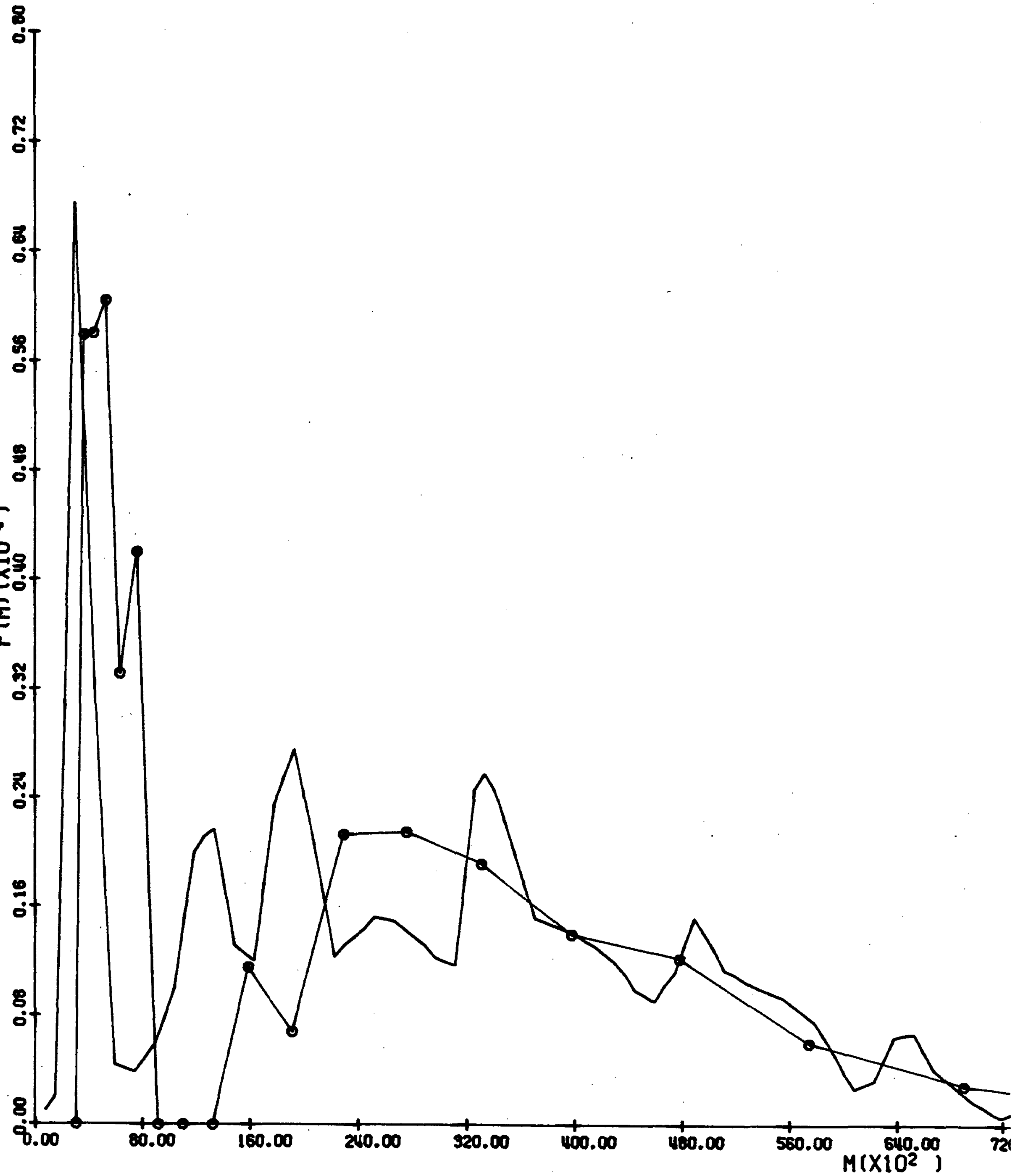
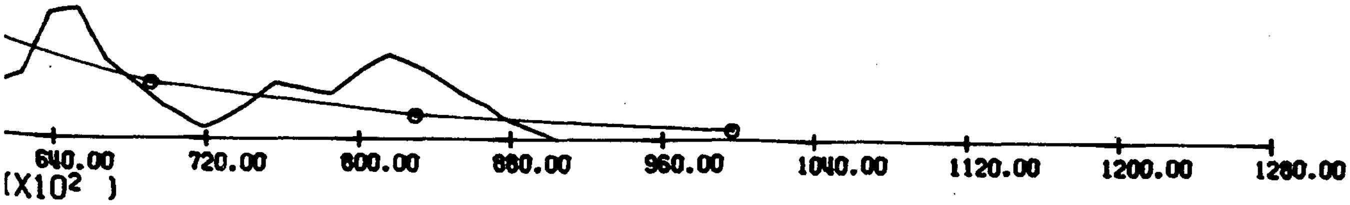


Figure 7. The Effect of Further Decreasing t



ɜr Decreasing the Number of Molecular Weight Sets

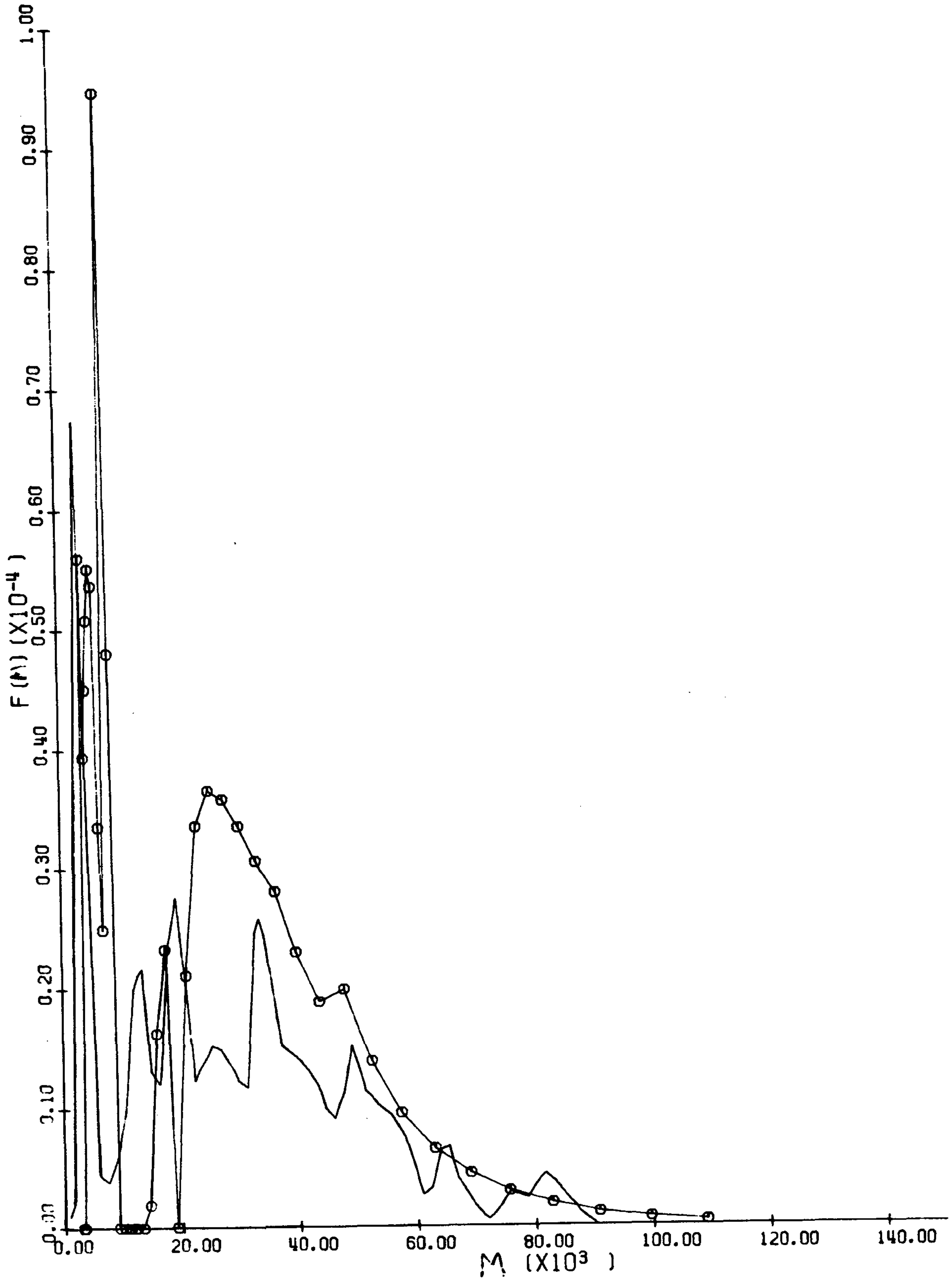


Figure 8. The Effect of Using More Experimental Data on the MWD

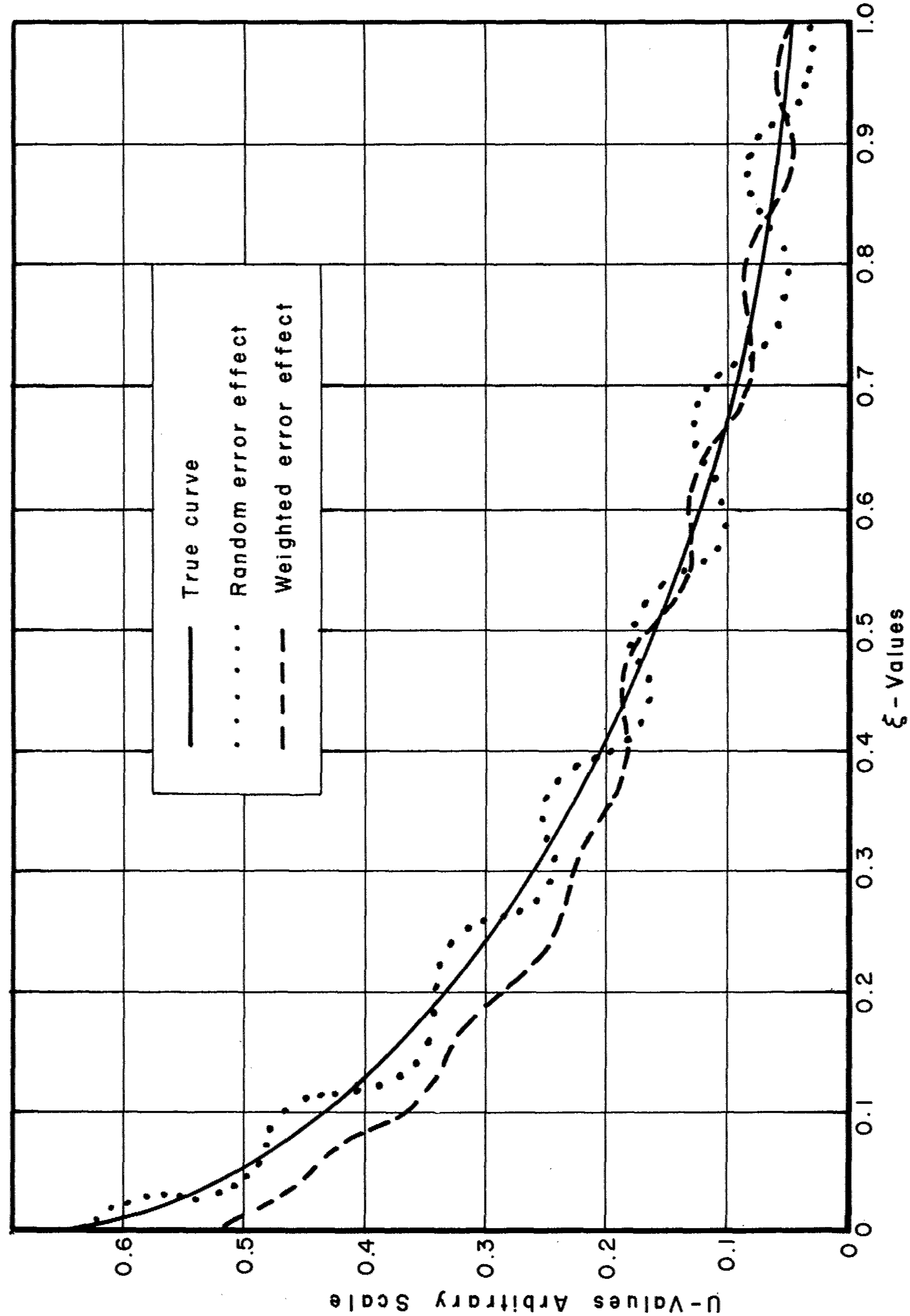


Figure 9. A Typical Curve of Concentration Gradient from One Angular Velocity

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13. ABSTRACT

Within the past decade easy access to high speed digital computers has renewed interest in deriving a molecular weight distribution from equilibrium sedimentation-diffusion data. One of the computational schemes which appears most promising is the Simplex Method of linear programming. The purpose of this work was to investigate the advantages and limitations of this approach.

It was found that even though inferring a molecular weight distribution from equilibrium sedimentation-diffusion data is mathematically an ill-posed problem, the method of linear programming yields qualitatively a good molecular weight distribution. Also, the method is applicable to the case of one angular velocity.

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Simplex Method						

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